In Situ Remediation of Chlorinated Solvent Plumes

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In Situ Remediation of Chlorinated Solvent Plumes

SERDP and ESTCP Remediation Technology Monograph Series

Series Editor: C. Herb Ward, Rice University

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Cover design: The image that appears on the cover of this volume is a synthesis of possible scenarios and locations where *in situ* remediation of chlorinated solvents in groundwater has been implemented.

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SERDP/ESTCP Remediation Technology Monograph Series
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SERDP and ESTCP have joined to facilitate the development of a series of monographs on remediation technology written by leading experts in each subject area. This volume provides a review of the state-of-the-art on *in situ* remediation of chlorinated solvent plumes. Additional volumes planned for publication in the near future include:

- Delivery and Mixing in the Subsurface: Processes and Design Principles for *In Situ* Remediation
- Bioaugmentation for Groundwater Remediation
- *In Situ* Chemical Oxidation for Groundwater Remediation
- Chlorinated Solvent Source Zone Remediation
- Characterization and Remediation of Contaminated Sediments
- Remediation of Munition Constituents in Soil and Groundwater

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Preface

In the late 1970s and early 1980s, our nation began to grapple with the legacy of past disposal practices for toxic chemicals. With the passage in 1980 of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), commonly known as Superfund, it became the law of the land to remediate these sites. The U.S. Department of Defense (DoD), the nation's largest industrial organization, also recognized that it too had a legacy of contaminated sites. Historic operations at Army, Navy, Air Force, and Marine Corps facilities, ranges, manufacturing sites, shipyards, and depots had resulted in widespread contamination of soil, groundwater, and sediment. While Superfund began in 1980 to focus on remediation of heavily contaminated sites largely abandoned or neglected by the private sector, the DoD had already initiated its Installation Restoration Program in the mid-1970s. In 1984, the DoD began the Defense Environmental Restoration Program (DERP) for contaminated site assessment and remediation. Two years later, the U.S. Congress codified the DERP and directed the Secretary of Defense to carry out a concurrent program of research, development, and demonstration of innovative remediation technologies.

As chronicled in the 1994 National Research Council report, "Ranking Hazardous-Waste Sites for Remedial Action," our early estimates on the cost and suitability of existing technologies for cleaning up contaminated sites were wildly optimistic. Original estimates, in 1980, projected an average Superfund cleanup cost of a mere \$3.6 million per site and assumed only around 400 sites would require remediation. The DoD's early estimates of the cost to clean up its contaminated sites were also optimistic. In 1985, the DoD estimated the cleanup of its contaminated sites would cost from \$5 billion to \$10 billion, assuming 400 to 800 potential sites. A decade later, after an investment of over \$12 billion on environmental restoration, the cost-to-complete estimates had grown to over \$20 billion and the number of sites had increased to over 20,000. By 2007, after spending over \$20 billion in the previous decade, the estimated cost to address the DoD's known liability for traditional cleanup (not including the munitions response program for unexploded ordnance) was still over \$13 billion. Why did we underestimate the costs of cleaning up contaminated sites? All of these estimates were made with the tacit assumption that existing, off-the-shelf remedial technology was adequate to accomplish the task, that we had the scientific and engineering knowledge and tools to remediate these sites, and that we knew the full scope of chemicals of concern.

However, it was soon and painfully realized that the technology needed to address the more recalcitrant environmental contamination problems, such as fuels and chlorinated solvents in groundwater and dense nonaqueous phase liquids (DNAPLs) in the subsurface, was seriously lacking. In 1994, in the "Alternatives for Ground Water Cleanup" document, the National Research Council clearly showed that as a nation we had been conducting a failed 15-year experiment to clean up our nation's groundwater and that the default technology, pump-and-treat, was often ineffective at remediating contaminated aquifers. The answer for the DoD was clear. The DoD needed better technologies to clean up its contaminated sites and better technologies could only arise through a better scientific and engineering understanding of the subsurface and the associated chemical, physical, and biological processes. Two DoD organizations were given responsibility for initiating new research, development, and demonstrations to obtain the technologies needed for cost-effective remediation of facilities across the DoD: the Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP).

SERDP was established by the Defense Authorization Act of 1991, as a partnership of the DoD, the U.S. Department of Energy, and the U.S. Environmental Protection Agency. Its mission is “to address environmental matters of concern to the Department of Defense and the Department of Energy through support of basic and applied research and development of technologies that can enhance the capabilities of the departments to meet their environmental obligations.” SERDP was created with a vision of bringing the capabilities and assets of the nation to bear on the environmental challenges faced by the DoD. As such, SERDP is the DoD’s environmental research and development program. To address the highest-priority issues confronting the Army, Navy, Air Force, and Marine Corps, SERDP focuses on cross-service requirements and pursues high-risk and high-payoff solutions to the DoD’s most intractable environmental problems. SERDP’s charter permits investment across the broad spectrum of research and development, from basic research through applied research and exploratory development. SERDP invests with a philosophy that all research, whether basic or applied, when focused on the critical technical issues, can impact environmental operations in the near term.

A DoD partner organization, ESTCP, was established in 1995 as the DoD’s environmental technology demonstration and validation program. ESTCP’s goal is to identify, demonstrate, and transfer technologies that address the DoD’s highest priority environmental requirements. The program promotes innovative, cost-effective environmental technologies through demonstrations at DoD facilities and sites. These technologies provide a large return on investment through improved efficiency, reduced liability, and direct cost savings. The current cost and impact on DoD operations of environmental compliance is significant. Innovative technologies are reducing both the cost of environmental remediation and compliance and the impact of DoD operations on the environment, while enhancing military readiness. ESTCP’s strategy is to select laboratory-proven technologies with potential broad DoD application and use DoD facilities as test beds. By supporting rigorous test and evaluation of innovative environmental technologies, ESTCP provides validated cost and performance information. Through these tests, new technologies gain end-user and regulatory acceptance.

In the 14 to 18 years since SERDP and ESTCP were formed, much progress has been made in the development of innovative and more cost-effective environmental remediation technology. Since then, recalcitrant environmental contamination problems for which little or no effective technology had been available are now tractable. However, we understand that newly developed technologies will not be broadly used in government or industry unless the consulting engineering community has the knowledge and experience needed to design, cost, market and apply them.

To help accomplish the needed technology transfer, SERDP and ESTCP have facilitated the development of a series of monographs on remediation technology written by leading experts in each subject area. Each volume will be designed to provide the background in process design and engineering needed by professionals who have advanced training and five or more years of experience. The first volume in this series, *In Situ Bioremediation of Perchlorate in Groundwater*, met a critical need for state-of-the-technology guidance on perchlorate remediation. This second volume, *In Situ Remediation of Chlorinated Solvent Plumes*, addresses the diverse physical, chemical, and biological technologies currently in use to treat what has become one of the most recalcitrant contamination problems in the developed world. Other volumes will follow on such topics as the remediation of DNAPL chlorinated solvents source zones, bioaugmentation to enhance bioremediation processes, delivery and mixing strategies and technologies to enhance subsurface remediation, chemical oxidation technologies to treat groundwater contamination, and remediation of contaminated sediments. Additional volumes will be written as new remediation technologies are developed and proven to be effective.

This volume provides a review of the past 10 to 15 years of intensive research, development and demonstrations on the *in situ* remediation of chlorinated solvent plumes. The intended audience includes the decision makers and practicing engineers and hydrogeologists who will select, design and operate these remedial systems, as well as researchers seeking to improve the current state of the art. Our hope is that this volume will serve as a useful resource to assist remediation professionals in applying and developing the technology as effectively as possible. Topics addressed in this volume include:

- A brief history and technology overview of groundwater contamination by chlorinated solvents (Chapter 1).
- A detailed review of the chemistry of chlorinated solvents that underlies remediation technology development (Chapter 2).
- The state of the science for key microbial processes involved in the biodegradation of chlorinated solvents (Chapter 3).
- A summary of the abiotic processes responsible for chlorinated solvent degradation (Chapter 4).
- An analysis of the challenges associated with remediating chlorinated solvent sites and recommendations for overcoming some of these challenges (Chapter 5).
- The evolution and current state of the art of groundwater modeling applicable to chlorinated solvent remediation, with emphasis on the modeling tools available to practitioners (Chapter 6).
- An assessment of how source zone architecture impacts the characterization and remediation of chlorinated solvent plumes and the effects of source treatment on source strength, mass flux and plume longevity (Chapters 7 and 8).
- An introduction to the technology-specific chapters, including a summary of the advantages and limitations of the major *in situ* groundwater remediation technologies to help the reader through the technology selection process (Chapter 9).
- A thorough review of the diverse physical, chemical and biological technologies currently in use for remediating chlorinated solvent plumes, including: biological processes such as monitored natural attenuation, biostimulation and bioaugmentation (Chapters 10-13); physical-chemical technologies such as air sparging; chemical oxidation and reduction; and barrier walls, including the use of zero-valent iron, and the less well known use of electrolytic reactive barriers (Chapters 14-17); in-well treatment technologies (Chapter 18); and phytoremediation (Chapter 19).

The final chapters provide insight into the factors that most influence technology costing and a view of the research needed to more cost-effectively address what remains of a multi-billion dollar legacy environmental contamination problem. Chapter 20 provides cost information needed to evaluate the applicability of the most frequently used technologies for the treatment of dissolved chlorinated aliphatic compounds in groundwater. Cost information for each technology has been derived for several template sites in order to objectively compare the relative economics of applying select technologies at other sites. Chapter 21 considers important unknowns and uncertainties that impact the state-of-the-science that underpins remediation technology development, including the potential role of rapidly developing molecular biological tools. This chapter, written in consultation with a broad range of experts in the remediation field, should help guide the research agenda on remediation of chlorinated solvents.

Each chapter in this volume has been thoroughly reviewed for technical content by one or more experts in each subject area covered. The editors and chapter authors have produced a well-written and up-to-date treatise that we hope will prove to be a useful reference for those making decisions on remediation of chlorinated solvents, for remediation practitioners, and for those involved in development of advanced technology for the *in situ* remediation of dissolved chlorinated solvents in groundwater.

SERDP and ESTCP are committed to the development of new and innovative technologies to reduce the cost of remediation of soil, groundwater and sediment contamination as a result of past operational and industrial practices. We are also firmly committed to the widest dissemination of these technologies to ensure that our investments continue to yield savings for not only the DoD, but also the nation. In facilitating this monograph series, we hope to provide the broader remediation community with the most current knowledge and tools available in order to bring these technologies to bear on the remediation of chlorinated solvents.

Jeffrey A. Marqusee, Ph.D., Executive Director, SERDP and ESTCP
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About the Editors

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Dr. Stroo is a Principal Technical Advisor with HydroGeoLogic, Inc. He provides technical support on large remediation projects for private- and public-sector clients and has served as a technical advisor to the SERDP and ESTCP programs for over 10 years.

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Dr. Stroo has served on several Expert Review Panels for SERDP, other government agencies and private companies. Recently, he served as Co-Chair of the SERDP workshops on Remediation of Chlorinated Solvents in Groundwater and Remediation of DNAPL Source Zones. He is coeditor of the SERDP-facilitated monograph on *In Situ* Bioremediation of Perchlorate in Groundwater.

C. Herb Ward

Dr. Ward holds the Foyt Family Chair of Engineering in the George R. Brown School of Engineering at Rice University. He is also Professor of Civil and Environmental Engineering and Ecology and Evolutionary Biology.

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He has been a faculty member at Rice University for 43 years where he has served as Chair of the Department of Environmental Science and Engineering and the Department of Civil and Environmental Engineering, and as the founding Director of the University's Energy and Environmental Systems Institute. He has also served as Director of the U.S. Environmental Protection Agency (ESEPA)-sponsored National Center for Ground Water Research and the DoD-sponsored Advanced Applied (Environmental) Technology Development Facility (AATDF).

Dr. Ward has been a member of the USEPA Science Advisory Board and served as Chair of the SERDP Scientific Advisory Board. He is the founding and current Editor-in-Chief of the international scientific journal *Environmental Toxicology and Chemistry*.

Dr. Ward received the Frederick George Pohland Medal for Outstanding Contributions to Bridging Environmental Research, Education, and Practice and the Brown and Caldwell Lifetime Achievement Award in 2006 and the Water Environment Federation Jack Edward McKee Medal for Achievement in Groundwater Restoration in 2007.

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He received his BA (Chemistry) from Harvard and MS (Inorganic and Analytical Chemistry) and PhD (Organometallic Chemistry) degrees from Cornell University. Dr Brown has worked on new technologies for the investigation and treatment of complex, contaminated sites including wood treating, coal gasification, mining and Superfund sites. He currently holds 20 U.S. patents and has two additional patent applications on the *in situ* ozonation of recalcitrant organics and two on the use of sodium persulfate for ISCO. Dr. Brown has authored over 100 technical papers.

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Mr. Duchene is co-author of several PRB-related publications, including the Interstate Technology & Regulatory Council (ITRC) guidance document, *Permeable Reactive Barriers: Lessons Learned/New Directions* in 2005, and served as an instructor on the related ITRC training sessions.

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Dr. Gilbert was a Research Scientist in the Department of Civil and Environmental Engineering at Colorado State University from 2002 through 2008. Areas of expertise included electrically induced redox barriers for *in situ* treatment of contaminated groundwater and chemical thermodynamics of contaminant release from anoxic reservoir sediments. His educational background included a BS degree in Geology, an MS degree in Environmental Engineering and a PhD in Hydrology. In addition, Dr. Gilbert had ten years of industry experience in groundwater and surface water. Unexpectedly, Dr. Gilbert passed away in 2008.

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Dr. Gossett received all of his university degrees from Stanford University—a BS in Chemical Engineering and an MS and PhD in Civil and Environmental Engineering. He joined the Cornell faculty in 1976. He was a North Atlantic Treaty Organization (NATO) fellow (1987–92), participating in a pilot study on remedial-action technologies for contaminated land and groundwater, and a Pacific Northwest National Laboratory (PNNL) Affiliate Staff Scientist (1996–1999).

Dr. Gossett's research has been featured frequently in the media including in *The Washington Post*, *The New York Times, News Day, Le Figaro, Scientific American Explorations, Chemical and Engineering News,* and *Civil Engineering*. He has also appeared in numerous broadcast-media reports, including interviews with BBCWorldService, RTL (a German TV network) and CNN, as well as a segment on CNN's weekly magazine show, *Science & Technology Week.*

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Mr. Harkness received his BS and MS degrees in Chemical Engineering from Rensselaer Polytechnic Institute. In 21 years at GE Global Research, his work has focused on development of novel remedial solutions for polychlorinated biphenyls (PCBs), petroleum hydrocarbon oils, and chlorinated solvents. His current specialty is the design of passive bioremediation systems for chlorinated solvents in groundwater. He has served as the GE representative on the steering committee of the Remediation Technologies Development Forum (RTDF) Bioremediation Consortium and has published numerous journal articles and book chapters in the field of bioremediation.

Bruce M. Henry

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Mr. Henry provides project management and technical direction for the *in situ* remediation of fuel hydrocarbons and chlorinated solvents in groundwater. He has worked with the U.S. Air Force to develop technical protocols for enhanced *in situ* bioremediation of chlorinated solvents and is the primary author of the Air Force *Principles and Practices of Enhanced Bioremediation of Chlorinated Solvents* and the *Technical Protocol for Enhanced Anaerobic Bioremediation using Permeable Mulch Biowalls and Bioreactors*. Mr. Henry provides technical support on remediation projects for private- and public-sector clients.

Paul C. Johnson

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For over 20 years he has been active in the development and evaluation of technologies and strategies for the management and cleanup of contaminated soil and groundwater sites. He has also developed approaches for assessing the risks of chemicals posed in the subsurface. His work in the areas of soil vapor extraction, *in situ* air sparging, aerobic biobarriers, thermal treatment, vapor intrusion to buildings, and risk-based corrective action is reflected today in practice and in many guidance documents related to these topics.

Dr. Johnson is the editor of the Nation Ground Water Association journal *Ground Water Monitoring and Remediation* and serves as a consultant to regulatory agencies, government agencies and industry.

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Dr. Johnson received his BS degree in Chemistry from the University of Washington and his MS and PhD degrees from the Oregon Graduate Institute (now part of OHSU).

He teaches in the areas of groundwater flow and transport and more broadly in all aspects of chemical mass transport in the environment. His research includes laboratory and field studies of chemical transport and fate, *in situ* remediation using chemical oxidation and reduction, and heat to facilitate remediation, and the application of molecular tools to demonstrate microbiological activity.

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Space Hall of Fame® in 2007 and received a Science's Alumni of Honor Award from the University of Waterloo.

He also served as a member for the U.S. Environmental Protection Agency (USEPA) RTDF, the USEPA Expert Panel to address the benefits of partial source treatment of dense nonaqueous phase liquids (DNAPLs), and the U.S. National Research Council Committee on Geological and Geotechnical Engineering in the New Millennium. Dr. Major has been an active member of the ITRC since 1996 and co-developed and taught ITRC courses on MNA, accelerated anaerobic bioremediation of chlorinated solvents, and bioremediation of DNAPLs. Dr. Major is also on the Steering Committee of the Sustainable Remediation Forum (SuRF).

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His research focus has been on biological processes for the control of environmental contaminants. He was elected to the National Academy of Engineering in 1977, the American Academy of Arts and Sciences in 1996, and to Honorary Membership in the American Academy of Environmental Engineers in 2009. He received the John and Alice Tyler Prize for Environmental Achievement in 1992, the Athalie Richardson Irvine Clarke Prize for Outstanding Achievements in Water Science and Technology in 1997, the Stockholm Water Prize in 2007, and was inducted into the Water Industry Hall of Fame in 2009. Dr. McCarty has over 350 publications, and is coauthor of the textbooks, *Chemistry for Environmental Engineering and Science,* and *Environmental Biotechnology–Principles and Applications*.

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Dr. Mercer is a hydrogeologist with GeoTrans, Inc. He received his BS degree from Florida State University and MS and PhD degrees from the University of Illinois; all of his degrees are in Geology. He spent eight years with the U.S. Geological Survey in the Northeastern Research Group working on contaminant and heat transport issues, including multiphase flow. He co-founded GeoTrans in 1979, and in 1980 began working on DNAPL issues at Love Canal. In 1985, Dr. Mercer received the Wesley W. Horner Award of the American Society of Civil Engineers for the work performed at Love Canal. Dr. Mercer continued to work on DNAPL issues and co-authored a book on *DNAPL Site Evaluation* in 1993. In 1994, he received the American Institute of Hydrology Theis Award for contributions to groundwater hydrology. Dr. Mercer has served on the National Research Council's Water Science and Technology Board and was a member of the USEPA's Science Advisory Board. He is currently a member of the SERDP Scientific Advisory Board.

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CHAPTER 1

GROUNDWATER CONTAMINATION BY CHLORINATED SOLVENTS: HISTORY, REMEDIATION TECHNOLOGIES AND STRATEGIES

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1.1 INTRODUCTION

Chlorinated solvents have seen broad usage for a wide variety of purposes, from cleaning of machinery, clothes and electronic parts to use in chemical manufacturing. However, through general dispersal, during normal usage and also as a result of indiscriminate disposal, chlorinated solvents have caused a variety of environmental problems. One such problem of great concern is the contamination of soil and groundwater. This problem became most evident following the passage in the United States of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), or Superfund legislation, in 1980 and the subsequent evaluation of chemical contamination of groundwater. It is now recognized that there are thousands of public and private sites with chlorinated solvent related groundwater contamination problems. Remediation of such sites has been found to be especially difficult and costly. Many potential technical solutions have been developed and applied, often with limited success. Time frames for remediation tend to be long, often measured in decades. It is incumbent upon those responsible for planning, designing and overseeing the remediation of soil and groundwater contamination with chlorinated solvents to fully understand the difficulties and high costs that are likely to be involved, and to have sufficient knowledge of the uses and limitations of the many available technologies that may be applied to a solution. It is highly likely that several technical approaches will be needed together to reach a satisfactory solution that will effectively reduce risks to human health and the environment.

The purpose of this introductory chapter is to provide an overview of the chlorinated solvent problem. This includes a history of chlorinated solvent usage together with the physical, chemical, and biological properties of chlorinated solvents that affect their movement and fate in the environment. A brief discussion of various chemical, physical, and biological processes that have been developed and used for site remediation is then presented. This is followed by a discussion of goals and strategies for remediation of chlorinated solvent contaminated sites.

1.2 CHLORINATED SOLVENT USAGE

Chlorinated solvents, including carbon tetrachloride (CT), perchloroethene (also termed tetrachloroethene or PCE), trichloroethene (TCE) and 1,1,1-trichloroethane (TCA) have been among the most widely used cleaning and degreasing solvents in the United States (Doherty, 2000a). They also have been used in a wide variety of other applications such as adhesives, and in pharmaceuticals, textile processing, coating solvents and as feed stocks for other chemicals. Prior to World War I, virtually no manufacturing of synthetic chemicals, except for coal tar derivates, occurred in the United States. Most chemicals came from Europe, but after exports

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to the United States were halted during the war, the U.S. chemical industry expanded rapidly, such that by the end of the war in 1918, the United States had developed the capacity to satisfy all of its own synthetic chemical needs. Between 1921 and 1929, the U.S. production of synthetic organic chemicals increased from 21 million to over 633 million pounds. The trends in the U.S. manufacture of the four solvents over the years are indicated in Figure 1.1 (Doherty, 2000a; 2000b).

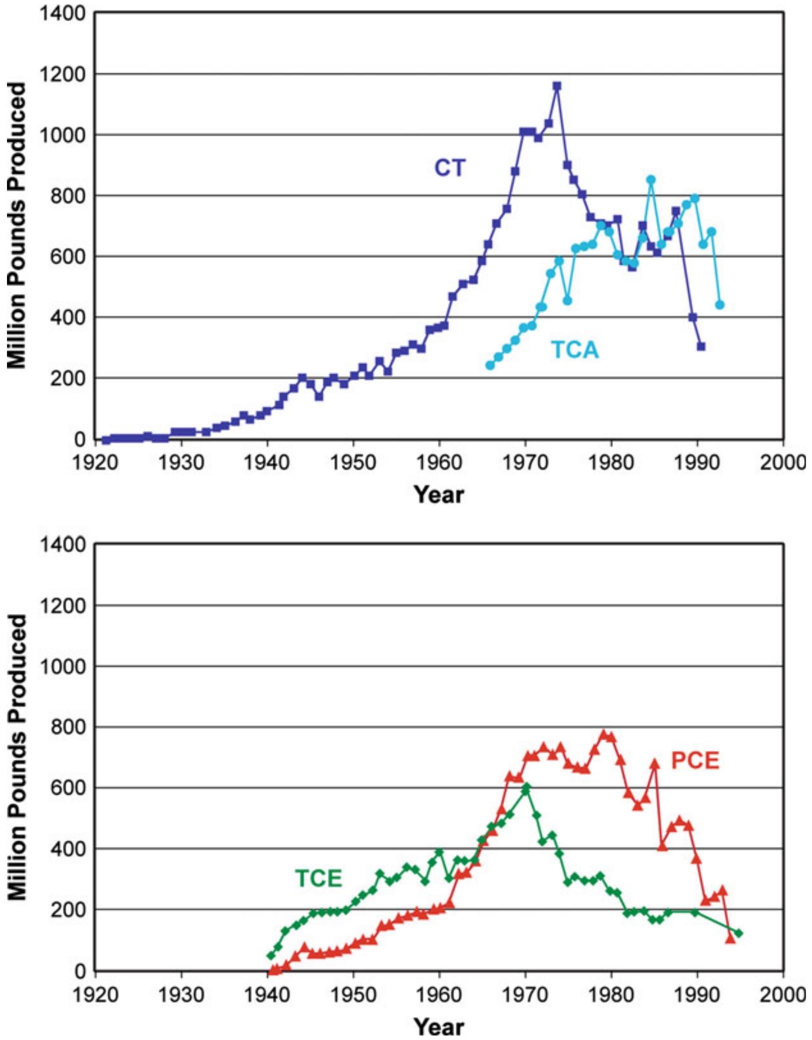

Figure 1.1. United States yearly production of chlorinated solvents (after Doherty, 2000a; 2000b).

Dry cleaning fluids in the early 1900s consisted almost entirely of gasoline (Doherty, 2000a). Because of gasoline's explosion hazard, chlorinated solvents slowly replaced hydrocarbons, and by 1962 exceeded hydrocarbon consumption for this purpose. In the early part of the twentieth century, CT was the first of the four chlorinated solvents to come into wide usage for dry cleaning, but many other uses were soon found for it. Examples are use as a fire extinguisher; to render petroleum fractions nonflammable; as a delousing agent; to extract oils from flowers and seeds, and grease from bones and hides; in petroleum refining and pharmaceutical manufacturing; and as a component of floor waxes, furniture polishes, paints and varnishes. As a solvent, CT was used in liquid chromatography, for de-inking of paper, and in the manufacture of rubber. However, its use for metal degreasing was limited because it increased metal corrosion.

By the 1930s, concern grew over the use of CT as a fire extinguisher because of its ability to form phosgene gas when heated in the presence of moisture (Doherty, 2000a). By the early 1940s, CT began being replaced as a dry-cleaning and degreasing agent by TCE and PCE because of CT toxicity, better recovery methods for TCE and PCE, and the reduced corrosion of metal containers by the latter. However, its use continued to grow for other purposes, especially for the manufacture of chlorofluorocarbons (CFCs), which consumed 95% of the CT produced in 1974. With the ban on the use of CFCs for aerosol products in 1978, and then further required reductions in line with the Montreal Protocol because of stratospheric ozone depletion, CT manufacturing declined precipitously.

PCE has been widely used in the dry-cleaning industry, which was its highest volume usage until about 1996, with a peak usage for that purpose of about 90% in 1962 (Doherty, 2000a). Other uses, while small by comparison, have been for aluminum cleaning, sulfur recovery, rubber dissolution, paint removal, printing ink bleeding, soot removal, catalyst regeneration, treatment of hookworm and some trematodes, various purposes in the textile industry, and as a replacement for polychlorinated biphenyls (PCBs) in electrical transformers and for an intermediate in CFC manufacturing. Small quantities have been used for many purposes such as in typewriter correction fluid and shoe polish. The decline in U.S. PCE production after 1980 resulted from various factors, including improvements in dry-cleaning equipment, growing popularity of washable fabrics, PCE imports, reduction in CFC manufacture and new environmental regulations. PCE is still the solvent of choice for dry-cleaning, but efficient recovery systems and development of alternative technologies to PCE dry cleaning have greatly reduced demand for this chemical. It is the fourth most frequently found organic contaminant at Superfund sites, being reported present at 924 of 1689 National Priorities List (NPL) sites in 2007 (ATSDR, 2007).

TCE has been one of the best solvents for cleaning and degreasing because of its effectiveness, noncorrosivity, nonflammability and ease of recycling (Doherty, 2000b). It has been used for this purpose by a wide variety of entities, including the electronics, defense, chemical, automotive, boat, food processing, textile and dry-cleaning industries. It has also found use as a refrigerant, a low-temperature heat transfer medium, a freezing-point depressant in some fire extinguishers, an extraction agent in decaffeination of coffee, a general human and animal anesthetic, and as an ingredient in printing inks, industrial paints, paint strippers, lacquers, varnishes, lubricants, pesticides and adhesives. It has been contained in many household products such as shoe polish, household cleaners, spot removers, disinfectants, paint removers, upholstery cleaners, deodorizers, mildew preventives, typewriter correction fluid and septic tank cleaners. However, by the 1940s the largest use of TCE was for vapor degreasing of metals, and by 1952 about 92% of the TCE produced was used for this purpose. In 1966, Los Angeles County, California, adopted Rule 66, which limited the emission of TCE and several other solvents–but not PCE, CT or TCA–from industrial facilities. This state regulation was followed by the 1970 Clean Air Act (CAA), which further controlled TCE emissions. In 1975, the National Cancer Institute found that TCE caused cancerous tumor growth in mice. TCE is the most frequently found organic contaminant at Superfund sites, being reported present at 1,022 of 1,689 NPL sites in 2007 (ATSDR, 2007). The uncertain future for TCE led to TCE-manufacturing plant closings and price increases for TCE. For these various reasons, the usage of TCE plummeted after 1970.

TCA became a widely used replacement for CT, TCE and PCE as each ran into environmental difficulties, since it is an excellent solvent and is significantly less toxic than the solvents used previously (Doherty, 2000b). Its primary uses were in cold-cleaning, vapor degreasing and ultrasonic cleaning, with 65% used for those purposes in 1984. It was used in the aircraft, automotive, electronic and missile industries. TCA was used in spray and solid pesticides, drain cleaners and carpet glue. It also had many smaller usages similar to that for TCE and PCE. It became important also as a feed stock for the manufacture of hydrochlorofluorocarbons (HCFCs) following the phase-out of CFCs. A disadvantage of TCA is its vigorous reaction with aluminum; stabilizers such as 1,4-dioxane are generally added at about 4% to reduce this problem. Groundwater contamination with such stabilizers as well as with TCA is now of considerable environmental concern. TCA's 6% use in aerosol propellants was banned in 1978 as an early effort to protect the stratospheric ozone layer, and its use in septic tank and cesspool cleaners was withdrawn in New York in 1979. In 1990, various regulations came into effect, particularly the 1990 CAA Amendments, which classified TCA as a hazardous air pollutant. The Montreal Protocol called for the complete phase-out of TCA by 2002 because of its ozone-depleting potential. TCA usage in the 1990s decreased rapidly.

Environmental concerns were thus major factors leading to control of chlorinated solvents and their decline in usage. By the late 1960s, the public became more aware of the environmental effects of industrial chemicals and pressures for regulation on their disposal increased (Doherty, 2000a). The 1970 CAA Amendments began federal regulation of emissions of TCE and PCE due to their suspected role in ground-level ozone and smog formation. As a result, many users turned to TCA, which was not so regulated, but it was then later banned because it caused ozone depletion in the upper atmosphere. The priority pollutant list generated by the U.S. Environmental Protection Agency (USEPA) as a result of the 1977 Clean Water Act specifically included CT, PCE, TCE and TCA. Proposed drinking water quality criteria for these chemicals were published in 1979 and 1980. Wastes containing these four solvents were also classified as hazardous in 1980 under the 1976 Resource Conservation and Recovery Act. The 1984 Hazardous and Solid Waste Amendments required the USEPA to restrict the land disposal of untreated solvent wastes. CERCLA, passed in 1980, established reportable quantities of spills for a variety of chemicals, including the four chlorinated solvents. The four solvents became the most widely detected contaminants at Superfund sites.

1.3 EARLY HISTORY AND CLEANUP TECHNOLOGIES

1.3.1 Discovery of Contamination

In an extensive 1960 literature survey of groundwater contamination (Stanley and Eliassen, 1960), many organic contaminants such as petroleum hydrocarbons, coal tar derivatives, synthetic detergents and pesticides were noted, but there was no mention of the four chlorinated solvents. An early note of chlorinated solvent contamination of groundwater is found in the Proceedings of a 1961 Symposium on "Ground Water Contamination" sponsored by the U.S. Public Health Service (PHS, 1961). The only mention of chlorinated solvents in those extensive proceedings was in a summary report of groundwater contamination in the United States by Middleton and Walton (1961). There in a brief table of organic chemical contaminants that were responsible for one or more incidents of groundwater contamination was the name, trichloroethylene (also termed trichloroethene or TCE). It was not mentioned further. Most of the discussion concerned contamination from petroleum products, phenolic compounds and detergents, compounds easily detected visually or by taste or odor. Gas chromatography for organic analysis was just emerging, and so procedures for measuring specific contaminants were very limited.

Nevertheless, in describing the objectives of the Symposium, Rear Admiral Harry G. Hanson, the Director of the Sanitary Engineering Center, noted in a prophetic statement that "[t]he pollution of ground water is insidious. It appears belatedly and often is not recognized until a considerable area has been affected. Once an aquifer is polluted, a very long time may be required to clean it up, even after the source of pollution is removed." He further stated that "[a] great deal has been learned, but at the same time the vastness of our ignorance has become even more apparent." Middleton and Walton (1961) noted that "[a] wide variety of organic contaminants are reaching groundwaters from leaky tanks, lagoons and septic tanks or by accidental means. The problem is nationwide, and the reported incidents probably represent a small fraction of actual occurrences.. . .Knowledge of time of travel and geological and biological and other effects, of saturated and unsaturated aquifers, and of soil types, as related to organic contamination of ground waters, is limited. Concerted effort is needed to extend this knowledge." Unfortunately, the nation did not heed the warnings and recommendations of this Symposium and as a result has paid a high price when the extensive contamination, especially from chlorinated solvents, became recognized about two decades later.

By the early 1970s, gas chromatographic methods to detect and quantify specific organic chemicals at very low concentrations in water improved greatly, the major advance being the development of computerized gas chromatography/mass spectrometry (GC/MS), which permitted the rapid and positive identification of compounds. Prior to that time, pesticides were the halogenated compounds of most concern, but now a broader range of short-chain chlorinated aliphatic compounds that were overlooked previously came into focus. Using this technique, Robert Harris, a scientist with the Environmental Defense Fund, reported on the finding of chloroform among other chemicals in New Orleans' water supply (Marx, 1974). The high concentration present could not be explained as coming from chemical sources. Fortunately, a Dutch chemist, Rook (1974), had already identified the source to be from the reaction between chlorine, generally used as a disinfectant for water supplies, and humic materials commonly present in natural waters. When bromide is present in small quantities, not only chloroform is formed, but also other trihalomethanes. This finding led to a broad survey of drinking water supplies with the finding that trihalomethane formation could be expected in essentially any water treated with chlorine or hypochlorite. This finding brought on perhaps the first general concerns with short-chain halogenated molecules in water supplies.

In California and other water-short areas, reclamation of domestic wastewater as a source of drinking water grew, but concern over health effects of unknown chemicals that may be present had prevented widespread use for this purpose. The development of GC/MS permitted much more detailed investigation of this issue. In studies on water produced by advanced treatment of domestic wastewater in the late 1970s and early 1980s for the Orange County Water District (Water Factory 21), California (Reinhard et al., 1979), and at pilot facilities in the Palo Alto Baylands for the Santa Clara Valley Water District, California (Roberts et al., 1978b), TCA, TCE and PCE were clearly present in low microgram per liter (μg/L) concentrations in biologically treated wastewater, and in measurable concentrations even after advanced physical and chemical processes that followed biological treatment. In the studies conducted on the removal of these contaminants by aboveground advanced wastewater treatment processes, two removal processes stood out, activated carbon adsorption (granular activated carbon [GAC]) and air stripping.

1.3.2 Development of Cleanup Technologies

The purpose of using air stripping at Water Factory 21 was ammonia removal following lime treatment, and carbon dioxide removal following acidification and reverse osmosis treatment. However, in analyzing for trace organic compounds, the major benefit of air stripping for chlorinated solvent removal became evident (McCarty et al., 1977; McCarty et al., 1979b; Reinhard et al., 1979). More than 80% removals were obtained. In subsequent years following the finding of widespread contamination of groundwater with chlorinated solvents, air stripping became the favored *ex situ* treatment process for their removal. It later also became used for *in situ* removal, as will be discussed in more detail in Section 1.6.2.2.

GAC treatment was the other effective aboveground removal process for chlorinated solvents at these sites (McCarty et al., 1979a). While more expensive than air stripping for removal from water, GAC later became employed to remove chlorinated solvents from contaminated air following air stripping in order to avoid an air pollution problem. GAC is more effective when used in this manner as air stripping separates the volatile organics from other water contaminants, especially humic substances, that tend to rapidly consume GAC's adsorptive capacity.

1.3.3 Movement and Fate

The major purpose of the wastewater reclamation studies in the Palo Alto Baylands was to determine the movement and fate of remaining organic contaminants in groundwater. The relative importance of advection, diffusion, sorption and degradation were evaluated (Roberts et al., 1978a; Roberts et al., 1980). These initial studies led to a much broader evaluation of the movement and fate of organics in groundwater (Roberts et al., 1986). From these studies, sorption was demonstrated to be an important process not only causing retardation in the movement of the trace organics, but also resulting in transfer of a significant fraction of the organics to aquifer solid material. Subsequently, this was found to be one of the factors that increased the difficulty and time span for groundwater cleanup by pump-and-treat processes.

A surprising observation from the Palo Alto Baylands studies was the disappearance of some trace organics by some unknown degradation process (Bouwer et al., 1981). The single carbon trihalomethanes disappeared much more rapidly than TCA, TCE or PCE, but nevertheless, there was a decline in these compounds with time as well. This was highly unexpected since a 1978 report by the National Research Council (NRC) of the National Academy of Sciences (NRC, 1978) indicated these compounds were refractory to natural processes, other than to photolysis which would not be active in dark groundwaters. The finding of chlorinated solvent disappearance in groundwater led to studies concerning the hypothesis that biodegradation may be involved.

Subsequent studies indicated that the chlorinated solvents could indeed be transformed by both abiotic and biotic processes at normal groundwater temperatures, leading to the production of many intermediate chlorinated compounds in groundwater that were also of health concern (Vogel et al., 1987). PCE was first reported to be biologically reduced under anaerobic conditions to form TCE (Bouwer et al., 1981), and later TCE was also found to be biologically reduced to form *cis*-1,2-dichloroethene (*cis*-DCE) and vinyl chloride (VC) (Parsons and Lage, 1985; Vogel and McCarty, 1985). VC was of even greater concern than the parent compounds as it was a known human carcinogen. However, in 1989 VC was also found to be capable of biological reduction, forming ethene (Freedman and Gossett, 1989). This good news led to further research to take advantage of biological reduction as a remediation technology for both PCE– and TCE–contaminated groundwater. In order for biological reduction to occur, other organic compounds must be present to serve as electron donors for the bacteria. When this occurs, transformation of PCE or TCE to intermediate and end products is frequently found, leading to "natural attenuation."

Transformations of TCA have been found to be even more complex as both abiotic and biotic processes are operable in its transformation (Vogel and McCarty, 1987). Abiotically, TCA can be transformed into 1,1-dichloroethene (1,1-DCE) by removal of one chlorine atom and one hydrogen atom (dehydrohalogenation), or into acetic acid through hydrolysis reactions. The rate of transformation to acetic acid is about 4 times that to 1,1-DCE. Formation of 1,1-DCE is harmful as this compound is much more toxic than TCA itself, while formation of acetic acid is beneficial as this is a normal compound in the human diet and readily degraded biologically. The half life for TCA transformation to the two different products is on the order of two years, a relatively short time when compared to the residence time of groundwater contaminants. Thus, 1,1-DCE is generally found in groundwater contaminated with TCA. TCA can also be transformed biologically by reductive dehalogenation to form 1,1-dichloroethane (1,1-DCA), which can be further reduced to chloroethane. Chloroethane can be further reduced biologically to form ethane, although chemical hydrolysis to form ethanol is generally faster.

CT also can be transformed by both abiotic and biotic processes, primarily through free radical processes that lead to a variety of possible end products (Criddle and McCarty, 1991). The abiotic processes, however, generally require the presence of a reducing agent of some type, and thus abiotic transformations do not often occur spontaneously as with TCA. Many of the CT transformation intermediates are unstable and do not last long. The main compound of concern found present from CT transformation, either abiotic or biotic, is chloroform. This too can be transformed by both abiotic and biotic processes, although generally much slower than CT.

A consequence of the many different abiotic and biotic transformation processes that chlorinated solvents undergo in groundwater is that many different chlorinated aliphatic compounds besides the chlorinated solvents themselves are often found at contamination sites. Such intermediates are often toxic, and in some cases, such as with VC and 1,1-DCE, the intermediates are more hazardous than the parent compounds themselves. It is evident that cleanup technologies must be capable of addressing the intermediates as well as the parent compounds. Sometimes alternative technologies are required to do this satisfactorily. For example, *ex situ* treatment by air stripping and activated carbon sorption works well for removing PCE and TCE from groundwater, but VC does not sorb as well, making removal by activated carbon not very effective. To satisfy the need for an alternative for VC, catalytic oxidation of off gases from air stripping can be used.

1.3.4 Superfund

The broad general concern with organic chemical contamination in groundwater began with the report in 1978 of soil contamination in a schoolyard and neighborhood in Niagara Falls, New York. This highly publicized contamination resulted from leaking drums of hazardous chemicals that were dumped about 25 years previously into Love Canal, which was then covered over and the contaminated property was sold to the city for one dollar for community use. The outrage that resulted from discovery of such contamination led to the passage in 1980 of CERCLA or Superfund, the federal program to clean up uncontrolled hazardous waste sites. The extensive studies that followed led to the finding of widespread groundwater contamination, with chlorinated solvents and related compounds being the contaminants most commonly found (Westerick et al., 1984). These findings led to the search for methods for groundwater remediation, as well as research to better understand contaminant movement and fate as well as to find new methods for treatment and removal.

1.4 PHYSICAL AND CHEMICAL PROPERTIES

The physical and chemical properties of chlorinated solvents affect their movement and fate in the environment and the potential technologies for dealing with them. Key properties are listed in Table 1.1. They are all liquids at room temperature. The chlorinated solvents and many of their transformation products have densities greater than 1.0 gram per cubic centimeter (g/cm^3). That means that they are heavier than water and thus can penetrate deeply into an aquifer. Henry's Law constant (K_H) is a measure of the strength of partitioning from water into air. Generally when K_H for a compound exceeds 0.2 atmosphere/mole fraction (atm/M), which is true of all compounds in Table 1.1, it can readily be removed from water by air stripping. Water solubility indicates the degree to which a chemical can dissolve in water. Most of the compounds, except PCE and CT, have solubilities greater than 1,000 milligrams per liter (mg/L). This concentration might seem to be high, but the compounds are nevertheless considered to be sparingly soluble. With the general slow movement of groundwater, loss of liquid chlorinated solvents by dissolving in water is a slow process because of their relatively low solubilities. The octanol-water partition coefficient (K_{ow}) is a measure of the hydrophobicity of the chemical, that is its tendency to partition out of water onto an aquifer solid or onto activated carbon during treatment. Log K_{ow} values less than 3 indicate that the compound does not sorb strongly to aquifer solids, but nevertheless it would be sufficiently hydrophobic so that it can be removed readily by activated carbon, a much better sorber than aquifer solids. On the other hand, compounds with log K_{ow} less than 2, such as VC, generally are not removed well by activated carbon. Thus, one can learn much by reviewing the chemical properties of compounds.

Table 1.1. Physical and Chemical Properties of Chlorinated Solvents and Their Transformation Products at 25 Degrees Celsius (°C) (after Yaws, 1999)

Chlorinated Compound	Density (g/cm^3)	Henry's Law Constant, K_H (atm/M)	Water Solubility (mg/L)	Octanol/Water Partition Coefficient (log K_{ow})
Methanes				
Carbon Tetrachloride	1.59	29	790	2.83
Trichloromethane	1.48	4.1	7,500	1.97
Dichloromethane	1.33	2.5	19,400	1.25
Chloromethane	0.92	8.2	5,900	0.91
Ethanes				
1,1,1-Trichloroethane	1.34	22	1,000	2.49
1,1-Dichloroethane	1.18	5.8	5,000	1.79
1,2-Dichloroethane	1.24	1.2	8,700	1.48
Chloroethane	0.90	6.9	9,000	1.43
Ethenes				
Tetrachloroethene	1.62	27	150	3.4
Trichloroethene	1.46	12	1,100	2.42
cis-1,2-Dichloroethene	1.28	7.4	3,500	1.85
trans-1,2-Dichloroethene	1.26	6.7	6,300	2.09
1,1-Dichloroethene	1.22	23	3,400	2.13
Vinyl Chloride	0.91	22	2,700	1.62

1.5 NATURE OF THE PROBLEM

When chlorinated solvents are discharged onto soil, their movement and fate are determined by their physical, chemical and biological properties and by site hydrogeological characteristics. Figure 1.2 provides a simplified picture of the situation. In simple terms, the site itself may be characterized by having a permeable surface soil layer through which the solvent will be pulled downward through the force of gravity. Just below the surface soil may be an unsaturated (vadose) zone containing little moisture and primarily containing air or other gases in between the subsurface solids. The solvent will continue its migration down through the vadose zone, probably leaving some residual solvent behind as it follows the path of least resistance, which may take many turns through a complex subsurface structure. Eventually, if sufficient solvent has been released, it may encounter groundwater that forms the aquifer of a potential groundwater supply.

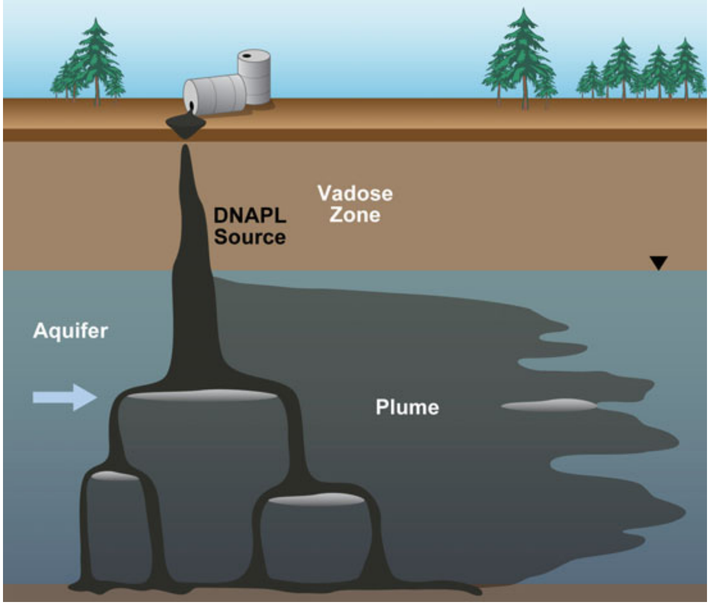

Figure 1.2. Formation of dense nonaqueous phase liquid (DNAPL) source and contamination plume following spill of chlorinated solvents.

Since the chlorinated solvents are denser than water, the downward movement will continue, perhaps again following a circuitous route of least resistance. Soils and aquifer solids contain different materials. Some such as sand and gravel represent particles that are relatively large in diameter and thus are relatively porous, allowing good passage of both water and chlorinated solvent liquids through them. Others, such as clays, are very fine and may be relatively impervious to water and solvents. When chlorinated solvents meet clay layers in their downward passage, they may pool on top of the clay, or seek a downward passage around the clay layer. Even when chlorinated solvents in their downward movement meet sand and gravel layers that contain different diameter particles, they may be diverted into one or the other because of different capillary forces in the different media or because of chemical properties, such as high organic carbon content, that may be more attractive to solvents with higher octanol-water coefficients. Thus, knowing the particular surface location where a chlorinated solvent spill occurred is insufficient information to know where it will be found several meters below the surface because of the many erratic paths it may follow.

The liquid solvent present in soil, subsurface solids and groundwater is termed the “source” of the contamination. Such dense nonaqueous phase liquids are termed DNAPLs. They generally represent the source of groundwater contamination. As groundwater moves through the permeable (sand and gravel) layers in the subsurface environment and encounters the DNAPL, the chlorinated solvents dissolve into the groundwater up to the solubility limits noted in Table 1.1. As the groundwater moves horizontally in response to a downward gradient in the groundwater, the contaminated water moves with it forming a contaminated groundwater plume, a plume which may eventually reach and contaminate a well that supplies groundwater to surface users or may emerge into a stream or other open water source, thus contaminating it. The two different problems that must be faced in the remediation of a chlorinated solvent contaminated site are what to do with the DNAPL source, and how to control or remediate the plume of contamination. Technologies have been developed to address either or both of these problems and are briefly described in the following section.

1.6 TREATMENT TECHNOLOGIES

The initial remediation efforts applied commonly available approaches such as removal of contaminated soil and subsurface solids and pumping of groundwater with treatment at the surface (pump-and-treat). Aboveground treatment systems initially applied GAC, but the newly discovered efficiency of removal by air stripping rapidly led to this being the most widely used approach. Concern over the discharge of chlorinated organic compounds to the atmosphere soon led to removal of air-stripped volatile compounds by GAC, which was found to be more economical than using GAC for treatment of water itself because of interference with other water-based organics such as humic materials. Early studies also began to indicate the difficulty and expense of contaminated soil and subsurface solids removal, and so containment of the contaminant source with physical barriers such as slurry walls was also used in the early 1980s (NRC, 1994).

There was a fairly rapid development of other technologies to address the remediation of contaminated groundwater following the implementation of CERCLA, as listed in Table 1.2. These included both *ex situ* and *in situ* processes. Many of these processes are covered in detail elsewhere in this volume, and thus are only briefly described here.

Table 1.2. Possible Treatment Technologies for Chlorinated Solvent Contamination of Soil and Groundwater

Conventional Pump-and-Treat	Flushing
Ex situ Air Stripping	Cosolvent Flushing
Ex situ Activated Carbon Adsorption	Surfactant Flushing
Ex situ Catalytic Oxidation	
Air Injection	***In Situ* Thermal Technologies**
Vapor Extraction	Hot Fluid Injection–Air, Water, Steam
Bioventing	Electrical Resistive Heating
Air Sparging	Thermal Conductive Heating
Biodegradation	***In Situ* Chemical Processes**
Aerobic Cometabolism	Oxidative Chemical Processes
Anaerobic Reductive Dehalogenation	Reductive Chemical Processes

1.6.1 Conventional Pump-and-Treat

Conventional pump-and-treat systems were the first and probably still represent the most widely used method of remediation for contaminated groundwater, being represented in 73%

of the cleanup agreements between 1982 and 1992 (NRC, 1994). Conventional pump-and-treat involves extracting contaminated water from an aquifer and replacing it with clean water either from areas immediately adjacent to the contaminated zone or by injection of clean water. The extracted water may be discharged to a surface water body, discharged to a sewer or spread on the soil, either before or after some form of *ex situ* treatment. For chlorinated solvents, the most common method of *ex situ* treatment has been air stripping, generally followed by adsorption from the air stream on GAC as already mentioned. Catalytic combustion of air stripping off gases also may be used in some cases, such as when VC is present. In other approaches, the air-borne solvents may be condensed and disposed in liquid form. Treated groundwater also may be reinjected into the aquifer, and if done properly, can result in more rapid cleanup of groundwater contamination, a reduction in the amount of water needed for remediation, and preservation of the water resource.

Pump-and-treat may be used to meet different objectives in plume management, plume migration control or complete plume remediation. However, complete plume remediation through the use of pump-and-treat has proven difficult to achieve. Of the 77 sites reviewed by an NRC panel (NRC, 1994), 69 had not yet met cleanup goals. Because of the complexity of geological settings and slow rates of contaminant desorption from the aquifer solids matrix, many pore volumes of water must often be removed in order to flush out the contaminants from a given area, and long time frames, on the order of decades, may be involved. An objective of many of the alternative treatment approaches is to surmount some of these difficulties.

1.6.2 Air-Injection Systems

Since chlorinated solvents and their intermediate degradation products are readily removed from water by air stripping, alternative air-injection approaches to *ex situ* air stripping have been developed and are in use. These include vacuum extraction, bioventing and air sparging.

1.6.2.1 Vapor Extraction and Bioventing

Soil vapor extraction (SVE) was one of the earlier *in situ* technologies used for volatile contaminants, and has the primary purpose of removing such contaminants as chlorinated solvents from the vadose zone (Johnson et al., 1994). Here, air movement through the soil and vadose zone is induced by applying a vacuum at a sealed wellhead or with the aid of blowers. This removes contaminated air from the vadose zone, and such air movement over chlorinated solvent DNAPL residing in the vadose zone also causes vaporization of the DNAPL and its removal as well. The system consists of one or more extraction wells, vacuum pumps or air blowers, and an *ex situ* treatment system to remove contaminants from the contaminated air. An impermeable cap may be placed over the soil to improve performance and wells also may be placed to serve as air inlets to the aquifer. Sometimes SVE is used in conjunction with groundwater extraction. The purpose of groundwater extraction here is to lower the groundwater surface so that more DNAPL or sorbed contaminants are exposed to air passing through the vadose zone, and thus become removable by the SVE system. Other terms used for this technology are soil venting, subsurface venting, *in situ* soil air stripping and vacuum extraction.

Bioventing is similar to SVE except that its purpose is to induce biodegradation in the vadose zone by supplying atmospheric oxygen. Hinchee and Alleman (1997) indicated the effectiveness of this process was discovered in the early 1980s in experiments designed to evaluate surfactant treatment for removing spilled gasoline. Column studies indicated, however, that the addition of air enhanced hydrocarbon biodegradation. Wilson and Ward (1987) appear to be the first to propose this process as a technology for remediation of hydrocarbons in the vadose zone. Subsequently, bioventing was fully developed and widely tested by the U.S. Air Force and is now considered a "presumptive remedy" by the U.S. Air Force (Stanin et al., 1996).

While most subsequent applications of bioventing have been for treatment of compounds that are readily biodegradable aerobically, such as hydrocarbons, it has been used for biodegradation of TCE as well, as a method to stimulate aerobic cometabolism. Here an electron donor such as methane is added to serve as a food for organisms that carry out TCE cometabolism (Brockman et al., 1995) as discussed later. Generally, however, chlorinated solvent cometabolism is carried out in association with air sparging or *in situ* biodegradation.

1.6.2.2 Air Sparging

Air sparging is an *in situ* method of removing chlorinated solvents from groundwater that also takes advantage of the volatility of these compounds (Brown, 1997). Here, air is injected directly into an aquifer formation or into specially designed wells. With injection directly into an aquifer, sparging wells are used through which pressurized air is injected. The rising air displaces the water in the aquifer forming a rising cone pattern, removing sorbed contaminant and DNAPL residual to the vadose zone, where it can be captured by SVE for *ex situ* treatment. In an alternative scheme, parallel horizontal wells have been used, one located in the groundwater and another above in the vadose zone (Brockman et al., 1995). Here, air is injected into the aquifer through the lower horizontal well, moves through the aquifer to remove sorbed contaminant and residual DNAPL, and then is collected in the upper horizontal well.

In-well air sparging (also referred to as in-well vapor stripping) is generally carried out in specially designed recirculation wells with a lower screen located in the aquifer and an upper screen located in the vadose zone. In an earlier design (Herrling, 1991), a pump was used to draw water through the lower screen into the well to be transported upward to a zone where air was drawn through the water with a vacuum pump, removing contaminants by air stripping. The treated water then passed through the upper screen and into the vadose zone, where it trickled back down to the groundwater. Later designs used air in the manner of an air-lift pump (Gonen and Gvirtzman, 1997), which causes water to circulate through the well in an upward movement and at the same time achieves air-stripping of contaminants from the upward moving water. In both systems, the contaminated air is cleaned at the surface, generally with GAC.

1.6.3 Biodegradation

In the early 1980s when the abiotic and biological transformations of chlorinated solvents were first discovered, the interest was primarily in use of this information to help explain the variety of chlorinated products often found in groundwater, products that were unrelated to known chemical spills in the area. The knowledge gained helped in the determination of potentially responsible parties. However, since transformation products known at that time were generally also hazardous, with some such as VC being even more hazardous than the original contaminants, there was little to favor the use of bioremediation for chlorinated solvent spills.

1.6.3.1 Aerobic Cometabolism

However, in 1985, John and Barbara Wilson reported from laboratory studies that TCE could be degraded aerobically through the process of cometabolism (Wilson and Wilson, 1985).

In their studies, methane and oxygen were mixed with TCE and cultures naturally present on aquifer solids. Methane monooxygenase, an enzyme known to initiate methane oxidation as part of the organism's normal energy metabolism, fortuitously oxidized TCE as well, forming TCE epoxide, an unstable chemical that degraded to other smaller chemicals that were either further degraded abiotically, or could be used as an energy source by other microorganisms present. Since aerobic cometabolism could destroy TCE, rather than simply transforming it into other hazardous compounds, the process received a great deal of interest, and much research was pursued to obtain a better fundamental understanding of the process and to evaluate its potential for groundwater remediation.

Field pilot studies were conducted to evaluate the feasibility of using cometabolism for groundwater bioremediation (Hopkins and McCarty, 1995; Semprini et al., 1991). A full-scale evaluation was conducted at Edwards Air Force Base (AFB), California, using dual recirculation wells for plume migration control and the more efficient toluene instead of methane as the substrate for cometabolism (McCarty et al., 1998). The field studies were successful in removing 97% of the TCE, with an upgradient concentration of 1,000 to 1,200 μg/L. Higher concentrations proved to be difficult to treat by *in situ* cometabolism, primarily because of the limited solubility of oxygen, which in turn limits the concentration of toluene substrate that can be added to effect cometabolism. Additionally, only TCE of the chlorinated solvents and some of the lesser-chlorinated intermediate degradation products were effectively biodegraded through cometabolism.

1.6.3.2 Anaerobic Reductive Dehalogenation

The finding by Freedman and Gossett (1989) that VC also could be reductively dechlorinated, forming non-hazardous ethene, renewed interest in the anaerobic process as a possible alternative to aerobic cometabolism. Other reports also indicated that VC could be degraded aerobically, both through cometabolism and even better, through use as a source of energy for organism growth (Hartmans et al., 1985). One important consequence of these findings was that natural attenuation of chlorinated solvents through anaerobic biological processes became of interest as an alternative remediation approach. All chlorinated solvents and their intermediate biodegradation products could be transformed anaerobically, and concentration limits were much higher than for aerobic cometabolism (i.e., concentrations even higher than 100 mg/L could readily be biodegraded). Because high concentrations of chlorinated solvents are not as inhibitory to the process as once thought, there is interest recently in using reductive dehalogenation to enhance the dissolution and hence to reduce the longevity of DNAPL sources of plume contamination.

Initially, anaerobic transformation was thought to be a cometabolic process, but Holliger and Zehnder in 1993 demonstrated that reductive dehalogenation of PCE was coupled with organism growth (Holliger et al., 1993). Subsequently, many organisms were isolated that could reductively transform PCE, TCE and TCA with coupling to growth, although often without transformation completely to ethene. In 1997, an organism called *Dehalococcoides ethenogenes* was isolated that could convert PCE and TCE to ethene, coupling each step of the reduction to growth, except for the last step of VC transformation to ethene, which was carried out by cometabolism (Maymó-Gatell et al., 1997). Subsequently, other closely related organisms were found to couple the last step with growth as well (Cupples et al., 2003; He et al., 2003). While the necessary *Dehalococcoides* organisms were not always present at a site, this deficiency could be remedied through bioaugmentation with mixed laboratory cultures containing *Dehalococcoides* species, the subject of another volume in this series (Stroo et al., 2010).

In reductive dehalogenation, the chlorinated compounds are used as electron acceptors, and as such require an electron donor or food source to support coupling of the organism with the chlorinated compounds. Generally hydrogen is used for this purpose, but some organisms, at least in PCE to *cis*-DCE conversion, can use organic substrates such as lactate or acetate. Most organic substrates are converted anaerobically to acetate and hydrogen, and a great variety of substrates have been added to aquifers to achieve reductive dehalogenation. Included are acetate, lactate, methanol, molasses and vegetable oils, which have been formulated into a variety of proprietary materials for use in the remediation industry. Natural attenuation of chlorinated solvents in aquifers by reductive dehalogenation also requires the presence of fermentable organic material. Insufficient electron donor is generally why the desired extent of reductive dehalogenation of the chlorinated solvents does not occur.

CT appears to be the only chlorinated solvent for which anaerobic transformation is not coupled with energy production. Its transformation appears primarily to be a cometabolic process that generally leads to chloroform formation. However, one organism, *Pseudomonas* sp. strain KC, can reductively transform CT under denitrifying conditions without forming chloroform, and field bioaugmentation and bioremediation with this organism has been successful (Dybas et al., 2002). Thus, in recent years much progress has been made in understanding chlorinated solvent biodegradation and in applying this process for remediation of chlorinated solvent contaminated sites.

1.6.4 Cosolvent and Surfactant Flushing

Groundwater is often contaminated by a mixture of chemicals, and an early question was what effect one chemical would have on the solubility and sorption characteristics of another. Among the findings was that the presence in groundwater of highly soluble, water-miscible solvents (hydrophilic) such as ethanol resulted in an increased solubility and decreased sorption for more hydrophobic chemicals (Nkedi-Kizza et al., 1985). With the growing concern about the longevity of DNAPL sources, this finding suggested one possibility in the search for new technologies with potential for DNAPL removal, and led to what is termed cosolvent flushing (Augustijn et al., 1994). Cosolvents such as methanol, ethanol and acetone are highly soluble in water, and chlorinated solvents are much more soluble in such cosolvent mixtures than in water itself. Thus, when a cosolvent mixture containing perhaps 20% or more of the cosolvent is passed through the vadose zone or injected into the groundwater near a source area, the DNAPL dissolves much more readily and can be rapidly cleansed by this process if the cosolvent solution can find its way to come into contact with DNAPL. The cosolvent/DNAPL mixture is then pumped to the surface for reuse or disposal.

1.6.4.1 Cosolvent Flushing

Perhaps the first application of cosolvent flushing was a field demonstration on a mixed petroleum/chlorinated solvent source area at Hill AFB, Utah, in a hydraulically isolated test cell (Rao et al., 1997). Here, a cosolvent mixture consisting of 70% ethanol, 12% n-pentanol and 18% water was pumped through the test cell over a period of 10 days, and was followed by flushing with water for 20 days. Greater than 85% of the mass of the target contaminants was removed. A pilot-scale field test of the process was later conducted for PCE removal from a site contaminated by a dry cleaner (Jawitz et al., 2000). Here, an 85% ethanol/15% water solution was pumped into the aquifer over a three-day period, with an estimated removal of 65% of the PCE.

One concern has been with the impact of the ethanol left behind with this approach, as well as with the cost of treating or disposing of the contaminated solvent removed from the aquifer.

However, studies conducted three years after the cosolvent flushing was completed found that the residual ethanol left behind had served as an effective electron donor for reductive dehalogenation with a significant conversion of residual PCE primarily to *cis*-DCE, but VC and ethene formation were also taking place (Mravik et al., 2003). Thus, cosolvent flushing combined with use of residual cosolvent for bioremediation emerged as a combined treatment approach for DNAPL removal.

1.6.4.2 Surfactant Flushing

Surfactant flushing emerged as another possible method for increasing the solubility of DNAPLs so that they could more readily be extracted from groundwater (Abdul et al., 1990; Fountain et al., 1991; Vigon and Rubin, 1989). Surfactants are organic molecules that contain a hydrophilic end with affinity for water and a hydrophobic end with an affinity for organic materials, such as chlorinated solvents. At a sufficiently high concentration of a surfactant (the critical micelle concentration), several surfactant molecules can come together to form a micelle, with the hydrophobic ends gathered together in the center and the hydrophilic ends facing out into water. Hydrophobic compounds, such as the chlorinated solvents, then can migrate into the hydrophobic center and hence become “solubilized.” Surfactants can also lower the interfacial tension of DNAPLs, causing them to migrate downward more readily, a problem that was early recognized (Fountain et al., 1991) and one that must be prevented from occurring (Pennell et al., 1996).

One of the first field demonstrations of surfactant flushing was in a controlled test cell at Hill AFB, where two aquifer floods were made of the petroleum/chlorinated solvent source area (Londergan et al., 2001). The reported removal of the estimated 1,300 L (340 gallons [gal]) of residual DNAPL was 98.5%. In a subsequent demonstration of surfactant flushing for removal of a defined release of PCE DNAPL into a confined cell at Dover AFB, Delaware, a smaller 68% removal was obtained (Childs et al., 2006) through 10 pore volumes of flushing. Here, a surfactant formulation consisting of sodium dihexyl sulfosuccinate, isopropanol and calcium chloride was used.

In a pilot field-scale demonstration of surfactant flushing of PCE DNAPL under a dry cleaning facility (Abriola et al., 2005), removal of 19 L (5 gal) of PCE was obtained with PCE solution concentrations decreasing by two orders of magnitude at some locations (Ramsburg et al., 2005). Here, 68 cubic meters (m^3) of an aqueous solution containing 6% by weight of Tween 80, a non-ionic food-grade surfactant, were injected, with 95% recovery of the injected surfactant during extraction. An interesting observation here, as in the case with solvent flushing with ethanol, was that the residual surfactant in the aquifer stimulated the growth of PCE-reducing microorganisms, leading to the formation of TCE and *cis*-DCE (Ramsburg et al., 2004). This finding once again demonstrated the potential for combining a chemical process for removal with a biological process for transformation of residual chlorinated solvent.

1.6.5 *In Situ* Thermal Technologies

While chlorinated solvents and their degradation products are all quite volatile, *in situ* air stripping processes for their removal tend to be relatively slow, especially for sorbed materials where rates may be limited by diffusion processes. Since partitioning both from DNAPL and sorbed contaminants to air increases with increase in temperature, as do the kinetics of transfer between phases, ways to add heat to an aquifer were sought following the passage of CERCLA. The use of thermal technologies for recovery of volatile organic materials from the subsurface environment was not new; they had been widely explored and were in use in the petroleum industry for enhanced oil recovery (Udell, 1997). Possible *in situ* thermal techniques include hot fluid injection (air, water or steam), electrical resistive heating and thermal conductive heating.

One of the first proposals for use of steam injection for groundwater cleanup came in 1988 (Hunt et al., 1988a), and was supported by experimental laboratory studies (Hunt et al., 1988b). With this process, steam is injected through vertical wells with screens located at appropriate depths (NRC, 1994). Three separate zones result. In the first, where temperature exceeds 100°C, all compounds with vapor pressure greater than 1 atm at 100°C, such as chlorinated solvents, are completely evaporated. In a second zone further out, heat transfer to aquifer solids and fluids occurs, causing steam and organic vapors moving out from the first zone to condense out. Thus, a zone of condensed organic compounds proceeds in front of the first zone. Further out, in the third zone, compounds and fluids remain in their original state and concentration, awaiting the arrival of the second zone as it spreads out. The practical problem becomes one of recovering the mobilized contaminants. For this, extraction wells or trenches or vacuum extraction techniques might be used.

The first field pilot study of steam injection for removal of solvents was conducted at a solvent recycling facility where a mixture of six principal volatile organic chemicals with concentrations greater than 500 mg/L, including TCA, TCE and PCE, had contaminated the subsurface (Udell, 1997). The steam injection system consisted of six injection wells surrounding a central recovery well. After 140 hours of steam injection and vacuum extraction, 400 kilograms (kg) of contaminants were recovered, representing a reported 90% of the original contaminant mass. Subsequent to this 1980s study, several applications of steam injection for remediation of chlorinated solvent sites have been conducted.

Electrical resistive heating (ERH) involves the generation of heat in the subsurface through the application of electrical current (USEPA, 2004). As electrical current is applied to electrodes placed in the ground, the natural resistance within the subsurface to the flowing current results in electrical energy dissipation in the form of heat. When the subsurface temperature reaches the boiling point, steam is generated, stripping contaminants from the subsurface matrix, allowing them to be extracted to the surface. Applied voltages range from 100 to 1,500 volts. Since about 1997 there have been many pilot and full-scale applications of ERH (USEPA, 2004).

Thermal conductive heating (TCH) involves the use of electrical subsurface heaters to generate high temperatures in the subsurface. Increased temperature radiates outward from the heaters, boiling water in the aquifer to produce steam and high temperatures that volatilize chlorinated solvent contaminants. Temperatures are highest near the heaters and may reach 500°C. A vapor extraction system is used to capture volatilized water and contaminants. There have been several full-scale applications of this approach as well (USEPA, 2004).

1.6.6 *In Situ* Chemical Processes

An advantage of biological processes is that they can result in the destruction as well as removal of chlorinated solvents. The same can be said of applicable chemical processes. As with biological processes, the chemical processes can be divided into oxidative and reductive processes. Oxidative processes would logically result in the oxidation of organic carbon in the chlorinated solvents to carbon dioxide, while releasing organic chlorine as chloride. Reductive processes on the other hand, reduce the organic carbon in chlorinated solvents to a lower oxidation state such as ethane, while again releasing the organic chlorine as chloride. As previously discussed, some chemical processes for chlorinated solvent transformation occur under ambient environmental conditions associated with aquifer conditions (Reinhard et al., 1997). Often natural chemical transformations do not result in complete conversion to harmless end products. Nevertheless, an understanding of these natural processes is important for assessing the source of contaminants that may be found at a site and in selecting processes and strategies for remediation. Engineered remediation using chemical processes for *in situ* contaminant destruction have been broadly studied, and some have been frequently applied.

1.6.6.1 Oxidative Chemical Processes

Chemical oxidants have been used in the water treatment industry for decades for the destruction of unwanted organic chemicals in water. Most frequently used have been ozone, permanganate and Fenton's reagent. However, possible use of chemical oxidants for *in situ* destruction of chlorinated solvents has been explored in detail only in recent years, and that has been for addressing the difficult problem of DNAPL destruction. This has become known as *in situ* chemical oxidation (ISCO). Perhaps the first to explore the use of permanganate for this purpose was Schnarr et al. (1998). They reported on both laboratory and field experiments for PCE and TCE destruction in which 10 g/L permanganate was found to completely oxidize the compounds to carbon dioxide and chloride. Two field experiments were conducted. In the first, 1 L of PCE that was added to a confined area was completely removed within 120 days by flushing through 100 L per day of the 10 g/L potassium permanganate ($KMnO_4$) solution. For the second, 8 L of a mixed PCE/TCE DNAPL was added to a test cell, and after 290 days of flushing with 10 g/L permanganate (MnO_4^-), 62% of the initial source had been oxidized. In this oxidation process, the MnO_4^- oxidant is reduced to form the insoluble manganese dioxide (MnO_2). Subsequently, many studies by a wide range of researchers have been conducted to further evaluate the use of permanganate; the process is currently used at numerous commercial sites.

Fenton's reagent is a mixture of hydrogen peroxide (H_2O_2) and ferrous iron, which serves as a catalyst, forming hydroxyl radicals, the main oxidizing species in Fenton's reagent. An earlier experiment using Fenton's reagent for oxidation of PCE was conducted by Leung et al. (1992), who reported mineralization of 1 g PCE per kg soil within 3 hours with a solution containing 2.1 molar (M) H_2O_2 and 5 millimolar (mM) ferrous sulfate ($FeSO_4$). TCE appears to be oxidized somewhat more slowly than PCE (Teel et al., 2001). Interestingly, CT, in which the carbon is already in the oxidized form, is also degraded by Fenton's reagent (Teel and Watts, 2002), apparently by a reduction mechanism in which a superoxide radical anion is involved (Smith et al., 2006). Many studies using Fenton's reagent for destruction of chlorinated solvents have now been conducted.

1.6.6.2 Reductive Chemical Processes

Perhaps the first to recognize the potential for abiotic reduction of chlorinated solvents for *in situ* destruction was Gillham and O'Hannesin (1994), who found that 100-mesh zero-valent iron (Fe(0)) was capable of removing chloride from 14 different chlorinated methanes, ethenes and ethanes, and replacing the chlorides with hydrogen. In the process, Fe(0) is converted to Fe (II). The rates of transformation were sufficiently fast for field application, except perhaps for dichloromethane. Gillham and O'Hannesin proposed that zero-valent iron might be used for either *in situ* or aboveground application for remediation of contaminated groundwater. A field demonstration of the technology was initiated in 1991 at Canadian Forces Base, Borden, Ontario, to treat a plume containing 268 mg/L TCE and 58 mg/L PCE (O'Hannesin and Gillham, 1998). Here, a mixture of 22% granular iron and 78% sand installed as a permeable "wall" across the path of the plume removed approximately 90% of the TCE and 86% of the PCE. The first full-scale application of granular zero-valent iron was a reactive wall installed in 1996 in North Carolina to treat overlapping plumes of chromate and chlorinated solvents (Puls et al., 1998). This passive approach to the control of plume migration, while involving a relatively high capital expenditure, has been an attractive alternative to those wishing to avoid an active program of control, which has lower capital but higher maintenance costs.

Experiments with zero-valent iron have been conducted for other than plume migration control. For example, a demonstration was conducted in which zero-valent iron was mixed with soil contaminated with TCE DNAPL using a large-diameter mixing blade (Wadley and Gillham, 2003). Here, bentonite was added as well to serve as a lubricant to facilitate injection of the iron and to isolate the contaminated zone. PCE was reported to decrease to non-detectable levels within the 13-month monitoring period. Alternatively, Cantrell and Kaplan (1997) proposed using colloidal-size suspensions of zero-valent iron that could be injected directly into an aquifer without the need to build a reactive wall. This has been carried further by Zhang et al. (1998), who have suggested use of nanoscale bimetallic particles in which one metal (Fe or zinc [Zn]) serves as the reductant, while palladium or platinum serves as a catalyst to speed up the reaction. Much research and several field studies have been conducted on this alterative approach. In a further alternative which also uses a palladium catalyst, Schreier and Reinhard (1995) demonstrated that molecular hydrogen could be used instead of iron as the reductant. Here, the reaction is much faster, sufficiently so that the system lends itself to a down-well or surface reactor. Thus, many alternatives for treatment of chlorinated solvent contaminated plumes as well as DNAPL source areas using reductive chemical processes have emerged in recent years.

1.7 REMEDIATION STRATEGIES

Those faced with the remediation of chlorinated solvent contamination of soil, subsurface solids and groundwater face two basic problems: (1) how to address the DNAPL solvent source, if found, that remains near the original site of the contamination and (2) how to clean up the groundwater that has passed through the DNAPL source, emanating from it to form a chlorinated solvent contaminated plume that may reach distant water supply wells or surface waters. The subject of this book is the remediation of the contaminated plume, but that cannot be addressed alone as groundwater contamination from the source can continue for centuries if the source itself is not controlled in some manner. Thus, source control is a vital part of plume control. Possible goals for remediation of a site contaminated with chlorinated solvents are listed in Table 1.3. The first two address the source and the last two the plume. There are different strategies for meeting each goal, and under each strategy there may be several different treatment technologies that apply. The task then is to select treatment technologies that best meet the goals and strategies for a given site.

There may be a single goal, but most commonly used is a combination of goals. If there is a known source of the contamination, the containment or remediation of the source, or both, is generally called for. The source, generally in the form of a DNAPL, will continue to contaminate groundwater moving through it for decades, if not centuries, if containment and/or removal are not practiced. Thus, source control is likely to be a major goal in overall site remediation.

The goal to address a contaminant plume may be remediation or simply to control its migration to a downgradient receptor, such as a water-supply well. Complete plume remediation may be called for, or a combination of migration control with remediation only of contaminants present downgradient from the point of migration control. For example, the location of migration control may be an industrial site boundary, in order to prevent contamination from reaching neighboring property.

Different strategies may be used to meet one or a combination of the goals. For example, to contain a source, a physical barrier may be built (Mitchell and van Court, 1997) or some form of hydraulic control may be used that prevents upgradient groundwater from passing through the source of contamination. Either strategy, if properly designed, built and maintained, is capable of accomplishing this objective. Different strategies have different capital and operating costs. For example, a physical barrier for source containment would have a much higher capital cost for construction than use of hydraulic containment, but would have a much lower maintenance cost. Technologies that require little intervention after initial construction, such as a physical barrier, are often termed a "passive" approach, while a hydraulic barrier, which requires continual pumping, may be termed an "active" approach. Often a passive approach is sought for sites remediated by governmental bodies, which tend to favor high-capital low-maintenance approaches, while industry often favors just the opposite since capital can be used for other investments.

Table 1.3. Possible Goals in the Remediation of Chlorinated Solvent Contamination Together with Strategies and Applicable Treatment Technologies for Meeting Goals

Goal	Strategy	Possible Treatment Technologies
Source Containment	Physical barrier	Slurry wall
		Sheet piling
	Hydraulic barrier	Groundwater extraction and reinjection
Source Remediation	Contaminant removal	Soil removal
		Cosolvent or surfactant flushing
		Steam stripping
		In situ thermal desorption
	Contaminant *in situ* destruction	*In situ* chemical oxidation or reduction
		In situ bioremediation
Plume Migration Control	Reactive wall	Chemical reduction
		Bioremediation
	Hydraulic control	*Ex situ* treatment
		In situ air sparging
		In situ chemical oxidation
		In situ bioremediation
Plume Removal	Physical	Pump-and-treat
		Air sparging (vertical or horizontal wells)
	Chemical	Chemical oxidation
	Biological	*In situ* bioremediation
		Intrinsic bioremediation (monitored natural attenuation)

Initial approaches to source control involved contaminated subsurface solids removal, removal of DNAPL through pumping, and SVE. Removal of DNAPL through these approaches is generally only partially complete because chlorinated solvents are denser than water and often penetrate deep below a groundwater table, too deep to make subsurface solids removal cost effective. Also, movement of chlorinated solvents downward through the vadose zone and groundwater through the forces of gravity is a very complex phenomenon because of the general heterogeneity of the subsurface environment, causing DNAPLs to move in directions that are difficult to discern from the surface. Finding the location of DNAPL residuals is a challenging problem that is being addressed with some good progress being made. However, it is still a highly uncertain science. Physical, chemical and biological methods for removal of residual DNAPL have been proposed as noted in Section 1.6, and there have been several pilot- and full-scale evaluations of these technologies. All of the technologies tend to be quite expensive and are generally not 100% effective. Thus, while offering promise for reducing the severity and longevity of the problem, approaches that reduce contact between the remaining source contamination and groundwater are most often still needed. Common approaches for reducing water contact with residual contaminants are construction of solid impermeable walls, such as slurry walls, or permeable reactive walls around the DNAPL source, both passive approaches, or use of hydraulic control, an active approach.

Along with source control, remediation of the contaminated plume needs to be addressed. The earliest approach was simply to pump contaminated water to the surface with treatment there to remove the chlorinated solvents (pump-and-treat technology). As already indicated, air stripping followed by activated carbon sorption was the earliest approach used here, and still is quite commonly used today. Treated water was then often discharged to surface waters or disposed onto the soil, frequently resulting in the loss of water as a resource, which is a particular problem in water-limited areas. Today, direct recharge of treated water to the groundwater is often practiced, and can result in better hydraulic control of a groundwater plume, as well as preservation of the resource.

The term "pump-and-treat" generally is thought to represent pumping groundwater to the surface and surface treatment, often with discharge of treated water to a surface source, such as to a river or through spreading over surface soil. This can be a very costly approach as uncontaminated as well as contaminated water may be brought into an extraction well for treatment and disposal at the surface. However, if treated water is reinjected into the aquifer in a well-planned manner, the system can be designed so that only contaminated water is treated, which greatly reduces the cost and the loss of the water resource. Treatment (chemical or biological) may be conducted at the surface (*ex situ*) or may be conducted within the aquifer itself (*in situ*). All such approaches might be termed "pump-and-treat," but because each approach is quite different, this generally inclusive label might best be avoided. It is perhaps best to use the term "pump-and-treat" to refer primarily to surface treatment and discharge processes, and to use more specific terms such a biological treatment, chemical treatment, *in situ* vapor extraction or hydraulic control for other remediation schemes. Most use some form of pumping, but generally for hydraulic control.

Plume management can have different goals as summarized in Table 1.3. One goal may be to remediate the entire plume (plume removal). Another is to simply prevent plume migration beyond a certain point, such as at the boundary of an industrial facility. Some treatment technologies can be used to meet either of the two objectives, while others may be appropriate for only one. For example, pump-and-treat can be applied to any of the objectives, while permeable reactive barriers (PRBs) primarily address plume migration. When comparing the cost and effectiveness of alternative technologies, they should be evaluated for the same objective. For example, if one is comparing the cost and effectiveness of PRBs with a pump-and-treat alternative, then both should be compared on their ability to prevent plume migration. Too often, comparisons are made between pump-and-treat for the whole plume, which can be very expensive, with use of PRBs. However, pump-and-treat or similar technologies that use some form of hydraulic control would obviously be much less costly when used simply for plume migration control, rather than for complete plume treatment.

For example, consider a groundwater table lying 8 m below the surface underlain by a plume that is 10 m deep and 60 m wide in an aquifer with a permeability of 0.3 and flowing at a typical Darcy velocity of 0.3 m/day. Alternative active and passive approaches for preventing plume migration in such situations are illustrated in Figure 1.3.

The volume of contaminated water flowing through the aquifer in this case is 10 x 60 x 0.3 x 0.3 or 54 m^3/day (10 gallons per minute [gpm]). Thus, a groundwater extraction, treatment and reinjection system would only need to pump and treat 10 gpm, which may include just a few wells and a relatively small treatment system for migration control. Either an aboveground or an *in situ* treatment system could be used. A PRB to prevent contamination migration by comparison would need to be 18 m deep and 60 m long, which could represent a sizeable capital investment. Additionally, if the PRB were not placed correctly because of inaccurate hydrogeology, then considerable cost is likely to result for making needed changes. Changing the pumping location of a few wells would be relatively inexpensive by comparison. The passive approach of a PRB certainly has advantages in preventing the need for continual operation and maintenance, but this convenience does come at a price. The important point is to not mix objectives in making cost and effectiveness comparisons, and also to consider the relative advantages and disadvantages of passive and active systems.

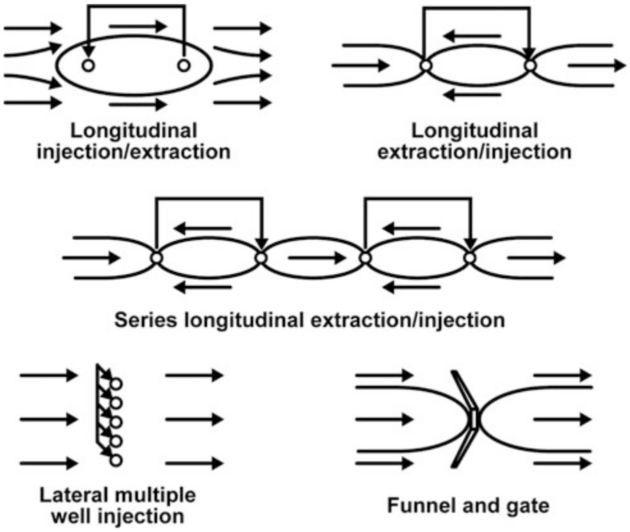

Figure 1.3. Possible schemes for control of plume migration.

1.8 EFFECTIVENESS OF TREATMENT TECHNOLOGIES

As suggested in Table 1.3, not all treatment technologies are capable of satisfying all strategies or goals. In addition, some technologies are more successful than others in meeting a given strategy, and this may depend greatly upon site hydrogeology and contaminant mass and distribution. The NRC addressed the relative effectiveness of different technologies in a 1994 report (NRC, 1994) for the range of contaminants found at sites throughout the country. Tables 1.4, 1.5 and 1.6 represent their judgments at that time for technologies that address chlorinated solvent plumes. Table 1.4 addresses the relative effectiveness of different technologies as a function of the physical phase of the contaminant, that is whether it is dissolved or sorbed to the aquifer matrix material (generally related to the plume), or occurs as a separate phase or DNAPL (the source). Table 1.5 considers the relative performance of different technologies for remediation of the soluble and the sorbed materials in a plume, and the typical cleanup time that can be expected for each. Table 1.6 is similar to Table 1.5, but applied to the DNAPL source area. These are judgments that were made several years ago, and since then much progress has been made in fundamental studies and field applications. Thus, it is likely that some of the estimates made then would be found different by a more current committee of experts. Nevertheless, the tables do serve to indicate somewhat in more detail the relative differences between technologies and their capabilities.

Table 1.4. Relative Effectiveness[a] of Alternative Treatment Technologies for Chlorinated Solvents and Related Compounds as a Function of the Physical Phase of Contaminant (after NRC, 1994)

Alternative Technology	Dissolved	Sorbed	Separate Phase DNAPL
Conventional pump-and-treat	1	2	4
Vacuum extraction and bioventing	NA[b]	2	3
Air sparging (vertical or horizontal wells)	2	2	3
In situ bioremediation	1–2	3	3–4
Cosolvent or surfactant flushing	NA	NA	2–3
Steam stripping	NA	2	3
In situ thermal desorption	NA	2	3
In situ chemical oxidation	3	3	3
In situ reactive barrier	2	NA	NA
Intrinsic bioremediation	2	NA	NA

[a] Relative effectiveness, where 1 is highly effective and 4 is least effective.
[b] "NA" denotes that the technology is not applicable for this type of situation.

Table 1.5. Relative Performance of Alternative Technologies for Plume Remediation (after NRC, 1994)

Alternative Technology	Residual Groundwater Concentration	Residual Sorbed Concentration in Aquifer	Cleanup Time[a]
Conventional pump-and-treat	Low	Medium to high	Long
Vacuum extraction and bioventing	NA	NA	NA
Air sparging (vertical or horizontal wells)	Low to medium	Low to medium	Medium to long
In situ bioremediation	Low to medium	Low to high	Medium to long
Cosolvent or surfactant flushing	NA	NA	NA
Steam stripping	NA	NA	NA
In situ thermal desorption	NA	NA	NA
In situ chemical oxidation	NA	NA	NA
In situ reactive barrier	Low	NA	Long
Intrinsic bioremediation	Low to medium	Low to medium	Long

Note: A "low" residual concentration and a "short" cleanup time reflect relatively good performance, while a "high" residual concentration and a "long" cleanup time reflect much less effective performance. "NA" denotes that the technology is not applicable to this situation.
[a] Because few cases of achieving cleanup goals have been reported, these qualitative assessments reflect the judgment of the NRC committee members.

Table 1.6. Relative Performance of Alternative Technologies for Source Remediation (after NRC, 1994)

Alternative Technology	Residual Groundwater Concentration	Residual Sorbed Concentration in Source Area	Cleanup Time[a]
Conventional pump-and-treat	Low to medium	Medium to high	Long
Vacuum extraction and bioventing	NA	Low to medium	Short
Air sparging (vertical or horizontal wells)	Low to medium	Low to medium	Short to medium
In situ bioremediation	Low to medium	Low to high	Medium to long
Cosolvent or surfactant flushing	Low to medium	Low to medium	Short to medium
Steam stripping	Low to medium	Low to medium	Short
In situ thermal desorption	Low to medium	Low to medium	Short
In situ chemical oxidation	Medium (?)	Medium (?)	Medium (?)
In situ reactive barrier	Low to medium	Low to high	Medium to high
Intrinsic bioremediation	Low to medium	Low to high	Long

Note: A "low" residual concentration and a "short" cleanup time reflect relatively good performance, while a "high" residual concentration and a "long" cleanup time reflect much less effective performance. "NA" denotes that the technology is not applicable to this situation. (?) denotes a high degree of uncertainty regarding the performance of this technology.

[a] Because few cases of achieving cleanup goals have been reported, these qualitative assessments reflect the judgment of the NRC committee members.

1.9 SUMMARY

Chlorinated solvents have been highly useful for many commercial purposes, especially for cleaning of clothes, machine parts and electronic circuits. However, because of the many environmental problems they have caused, their use has come under strict regulatory control, and this has led to seeking more environmentally benign replacements for chlorinated solvents, and closer control of their usage coupled with recycling used solvents. These changes have resulted in a drastic reduction in chlorinated solvent production and a greatly minimized problem with environmental contamination. Nevertheless, the legacy of soil and groundwater contamination from past use and disposal practices constitutes one of the most difficult and costly environmental problems yet being faced, a problem that is not likely to be resolved satisfactorily for decades to come.

Since 1980, when the widespread contamination with chlorinated solvents became apparent, much has been learned about their movement and fate in the environment, and many different technical approaches to addressing their contamination of soil, air and groundwater have been developed. Because of the cost, magnitude and difficulty of remediation of sites contaminated with chlorinated solvents, the seeking and applying of new physical, chemical and biological approaches has not yet ended. There is no silver bullet technology that is appropriate for every site, each requires a detailed characterization of hydrogeology and contaminant history, setting of realistic goals for remediation, and selection of the most appropriate technologies for reaching that goal. Because of the great expense involved, engineers and regulators addressing this complex problem must be familiar not only with past approaches and technologies, but also with those that are evolving. The advantages and limitations of each, along with their relative costs and effectiveness, need to be well understood. Only then can cost-effective solutions be developed that satisfy both the short- and long-term needs at a given site.

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CHAPTER 2

CHLORINATED SOLVENT CHEMISTRY: STRUCTURES, NOMENCLATURE AND PROPERTIES

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2.1 INTRODUCTION

This chapter summarizes the principles of chlorinated solvent remediation, provides overviews of the biotic and abiotic reactions that can transform and detoxify these compounds, and discusses the remediation challenges posed by the properties and behavior of these compounds in the subsurface environment.

2.2 STRUCTURE AND NOMENCLATURE

Chlorinated solvents are organic compounds generally constructed of a simple hydrocarbon chain (typically one to three carbon atoms in length) to which at least one chlorine atom is covalently bonded. For the current discussion, chlorinated solvents will be further divided into three categories based upon common structural characteristics: chlorinated methanes, chlorinated ethanes and chlorinated ethenes. Examples from each solvent class are shown in Figure 2.1. Additional information pertaining to the nomenclature of these chemical species is provided in Table 2.1.

Chlorinated methanes represent the most structurally simple solvent class and consist of a single carbon center (known as a methyl carbon) to which as many as four chlorine atoms are covalently bonded. From the perspective of groundwater contamination, perhaps the most well known chlorinated methane is carbon tetrachloride (CT). Also known by its International Union of Pure and Applied Chemistry (IUPAC) name of tetrachloromethane, CT consists of a fully chlorinated methyl carbon. By IUPAC conventions, the modifier of "tetra" serves as an indicator of the number of chlorine atoms bound to the carbon center. For chlorinated methanes other than CT, hydrogen atoms usually make up the remainder of the substituents necessary to satisfy the methyl carbon's bonding requirements. Named in a similar fashion by IUPAC, the chlorinated methanes with a lower degree of halogenation are trichloromethane (commonly referred to as chloroform [CF]), dichloromethane (DCM, more commonly called methylene chloride [MC]) and chloromethane (CM, also referred to as methyl chloride).

Chlorinated ethanes consist of two carbon centers joined by a single covalent bond. Common groundwater pollutants from this class include 1,1,1-trichloroethane (1,1,1-TCA) and 1,2-dichloroethane. In regards to the nomenclature associated with chlorinated ethanes, a similar convention to that used for chlorinated methanes is employed in which the prefix attached to "chloroethane" indicates the total number of chlorine atoms on the solvent molecule. Common acronyms for this class follow the pattern in which the first letter (or series of letters) refers to the number of total halogen substituents (e.g., "T" for trichloro- or "Te" for

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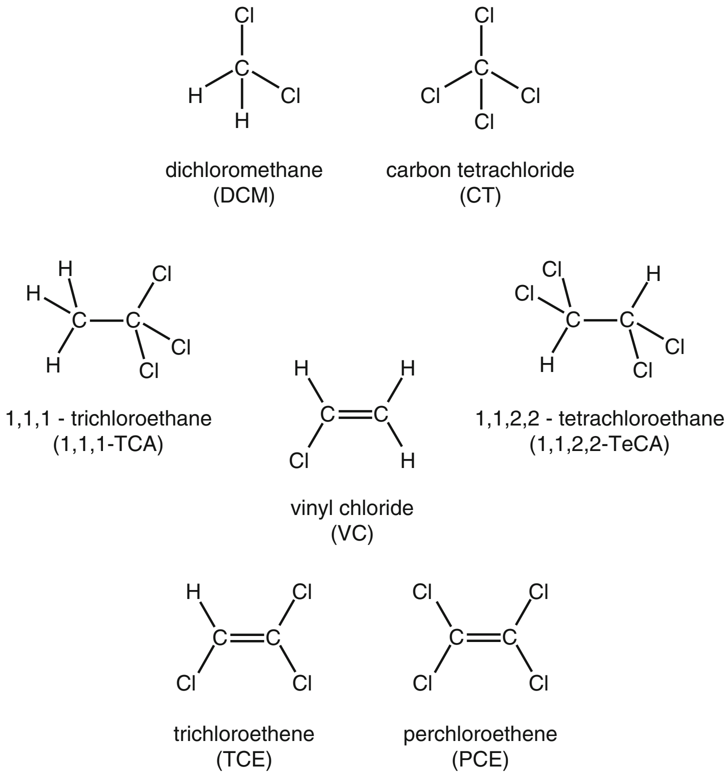
dichloromethane (DCM)

carbon tetrachloride (CT)

1,1,1 - trichloroethane (1,1,1-TCA)

vinyl chloride (VC)

1,1,2,2 - tetrachloroethane (1,1,2,2-TeCA)

trichloroethene (TCE)

perchloroethene (PCE)

Figure 2.1. Chemical structures of some common chlorinated solvents.

tetrachloro-), the second letter refers to the halogen identity (e.g., “C” for chlorine) and the last letter, in all cases “A”, refers to ethane.

In addition, the numbers preceding the name or abbreviation indicate the location of the chlorine substituents on the two possible carbon centers. For example, 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA) possesses two chlorine atoms on each of its carbon centers, whereas the three chlorine atoms of 1,1,1-TCA are all located on the same carbon. In certain instances, there can be more than one way in which the same number of chlorine atoms distribute themselves on the carbon centers, as is the case for 1,1,2-TCA and 1,1,1-TCA. These compounds, which share the same chemical formula ($C_2H_3Cl_3$) yet differ in the sequence in which their atoms are connected, are referred to as structural isomers (Vollhardt and Schore, 1994).

Chlorinated ethenes (sometimes referred to as chlorinated ethylenes) also possess two carbon centers, but unlike chlorinated ethanes, these carbon atoms are joined by a carbon-carbon double bond known as a π-bond (pi-bond) system. Another important difference between chlorinated ethanes and chlorinated ethenes is the maximum number of atoms bound to the carbon centers in each case. The double-bonded carbon centers in chlorinated ethenes can accommodate at most two halogen (or hydrogen) substituents, whereas the single-bonded ethanes can accommodate three halogen (or hydrogen) substituents.

Examples of chlorinated ethenes that are important groundwater pollutants include tetrachloroethene, commonly referred to as perchloroethene (PCE), and trichloroethene (TCE). Another chlorinated ethene of note is the monochlorinated species that is most commonly referred to as vinyl chloride (VC). The nomenclature associated with the chlorinated ethenes follows a similar convention to that used with the chlorinated methanes and ethanes (e.g., tetrachloroethene contains four chlorine substituents). The same is true for the acronyms commonly applied to this solvent class, only this time the last letter in all cases is "E", which represents "ethenes". The lone exception to this convention for acronyms is vinyl chloride, which is typically abbreviated as VC.

Table 2.1. Nomenclature for Selected Chlorinated Solvents

IUPAC Name	Common Name	Abbreviation/Acronym	Molecular Formula
Chlorinated Methanes			
tetrachloromethane	carbon tetrachloride	CT	CCl_4
trichloromethane	chloroform	CF	$CHCl_3$
dichloromethane	methylene chloride	DCM	CH_2Cl_2
chloromethane	methyl chloride	CM	CH_3Cl
Chlorinated Ethanes			
hexachloroethane	perchloroethane	HCA	C_2Cl_6
pentachloroethane	—	PCA	C_2HCl_5
1,1,1,2-tetrachloroethane	—	1,1,1,2-TeCA	$C_2H_2Cl_4$
1,1,2,2-tetrachloroethane	—	1,1,2,2-TeCA	$C_2H_2Cl_4$
1,1,2-trichloroethane	—	1,1,2-TCA	$C_2H_3Cl_3$
1,1,1-trichloroethane	methyl chloroform	1,1,1-TCA	$C_2H_3Cl_3$
1,2-dichloroethane	—	1,2-DCA	$C_2H_4Cl_2$
1,1-dichloroethane	—	1,1-DCA	$C_2H_4Cl_2$
chloroethane	—	CA	C_2H_5Cl
Chlorinated Ethenes			
tetrachloroethene	perchloroethene	PCE	C_2Cl_4
trichloroethene	—	TCE	C_2HCl_3
cis-1,2-dichloroethene	*cis*-dichloroethene	*cis*-DCE	$C_2H_2Cl_2$
trans-1,2-dichloroethene	*trans*-dichloroethene	*trans*-DCE	$C_2H_2Cl_2$
1,1-dichloroethene	vinylidene chloride	1,1-DCE	$C_2H_2Cl_2$
chloroethene	vinyl chloride	VC	C_2H_3Cl

Additional nomenclature is necessary in order to distinguish the possible isomers of dichloroethene. As with 1,1,1-TCA and 1,1,2-TCA, dichloroethene (DCE) can exist as either of two structural isomers (1,1-DCE and 1,2-DCE). In addition, the π-bond system in chlorinated ethenes differs from the single carbon-carbon bond in chlorinated ethanes because it does not allow the halogen substituents to rotate freely in the plane perpendicular to the direction of the π-bond. Consequently, there are multiple spatial orientations for the two chloride substituents in 1,2-dichloroethene (Figure 2.2). One possibility is for the chlorine atoms to arrange themselves on the same side of the carbon-carbon double bond in a configuration known as *cis*. Alternatively, the chlorine atoms can be located on the opposite side of the π-bond system in a configuration known as *trans*. These two dichloroethenes, which are structurally identical but differ in the spatial arrangement of their chlorine substituents, are called conformational isomers (or simply conformers) (Vollhardt and Schore, 1994).

Figure 2.2. Conformational isomers of 1,2-dichloroethene.

Chlorinated methanes, ethanes and ethenes clearly do not encompass all types of chlorinated solvents that may be encountered at hazardous waste sites. For instance, chlorinated propanes, which possess three carbon atoms joined by single bonds, can represent important groundwater pollutants. Some examples of chlorinated propanes include 1,2-dichloropropane, which is regulated in drinking water by the U.S. Environmental Protection Agency (USEPA) (2003). Another example is 1,2,3-trichloropropane, which has been detected at more than 20 National Priorities List sites identified by the USEPA (ATSDR, 1992). Although such species are not the focus of subsequent portions of this chapter, the physical and chemical principles developed for chlorinated methanes, ethanes and ethenes can easily be extended to include these additional chlorinated solvents.

Although this chapter is devoted to treatment strategies for chlorinated solvents, solvents with other halogen substituents (such as bromine or fluorine) are also frequently encountered in contaminated groundwater. A common example is 1,2-dibromoethane (also known as ethylene dibromide [EDB]), which was used as an additive in leaded gasoline (Baird and Cann, 2005). Methanes, ethanes and ethenes with mixed halogen substituents can represent important environmental pollutants as well, as is the case for common disinfection byproducts bromodichloromethane ($CHBrCl_2$) and dibromochloromethane ($CHBr_2Cl$). When necessary, key differences in the behavior and environmental fate of halogenated solvents with chlorine, bromine and fluorine substituents will be noted.

2.3 PROPERTIES

The behavior of chlorinated solvents in the subsurface is controlled to a large extent by their physical and chemical properties. The properties considered most relevant to chlorinated solvent fate and transport in the subsurface are summarized in Table 2.2. In order to maintain some consistency among the values presented, the majority of the values were obtained from Mackay et al. (1993), one of the very few sources that contain data for all of the chlorinated methanes, ethanes and ethenes. In general, there is reasonable agreement between these values and several other summary tables available (e.g., Pankow and Cherry, 1996; Fetter, 1999; Schwarzenbach et al., 2003; Chapter 1 of this volume). Table 2.2 is provided for purposes of discussion with regards to relevant trends in behavior and properties and is not intended as a set of values selected from a critical review of the literature. For a review of the primary literature, Pankow and Cherry (1996) is recommended because it provides a detailed review of the chlorinated solvent properties discussed herein as well as an excellent discussion of the history of production and industrial uses of chlorinated solvents.

The following discussion of chemical and physical properties is organized around the major processes that impact the fate and transport of chlorinated solvents in the subsurface, starting with the process by which pure phase chlorinated solvents dissolve into groundwater, followed by their partitioning between the three phases present in the subsurface: aquifer solids, water and air. An overview linking these partitioning processes to the relevant chlorinated solvent properties is provided in Figure 2.3. The discussion concludes with an introduction to transformation reactions, which are discussed in greater detail in Chapters 3 and 4.

Table 2.2. Summary of Some Physical and Chemical Properties of Chlorinated Organic Solvents at 25 Degrees Celsius (°C). Unless otherwise noted, all values have been taken from Mackay et al. (1993).

Species	Formula Weight (g/mol)	Carbon Oxidation State[a]	Density (ρ) (g/mL)	Solubility (S) (mg/L)	Vapor Pressure ($p°$) (torr)	Henry's Law Constant (K_H) (× 10^{-3} atm·m^3/mol)	Log (K_{ow})	Log (K_{oc})[b]	MCL[c] (mg/L)
Chlorinated Methanes									
CT	153.8	+IV	1.59	800	153.8	28.9	2.64	1.9	0.005
CF	119.4	+III	1.49	8,200	196.8	3.8	1.97	1.52	0.10[d]
DCM	84.9	+II	1.33	13,200	415	1.7	1.25	—	0.005
CM	50.5	+I	0.92	5,235	4,275	9.6	0.91	—	NR[e]
Chlorinated Ethanes									
HCA	236.7	+III	2.09	50	0.38[f]	—	3.93	—	NR
PCA	202.3	+II	1.68	500	4.7	2.5	2.89	—	NR
1122-TeCA	167.9	+I	1.60	2,962	5.9	0.44	2.39	1.9	NR
1112-TeCA	167.9	+I	1.54	1,100	11.9	2.4	—	—	NR
111-TCA	133.4	0	1.35	1,495	123.8	14.5	2.49	2.25	0.2
112-TCA	133.4	0	1.44	4,394	24.2	0.96	2.38	—	0.005
12-DCA	99.0	-I	1.25	8,606	79.0	1.2	1.48	1.52	0.005
11-DCA	99.0	-I	1.17	4,676	227	6.2	1.79	—	NR
CA	64.5	-II	0.90	5,700	120	1.8	1.43	—	NR
Chlorinated Ethenes									
PCE	165.8	+II	1.63	150	18.1	26.3	2.88	2.29	0.005
TCE	131.4	+I	1.46	1,100	74.2	11.7	2.53	1.53	0.005
cis-DCE	96.9	0	1.28	3,500	203	7.4	1.86	—	0.07
trans-DCE	96.9	0	1.26	6,260	333	6.8	1.93	—	0.1
11-DCE	96.9	0	1.22	3,344	604	23.0	2.13	—	0.007
VC	62.5	-I	0.91	2,763	2,660	79.2	1.38	—	0.002

[a] Average value calculated using oxidation states for H = +I and Cl = −I.
[b] When available, log(K_{oc}) values were obtained from Nguyen et al. (2005).
[c] Source: USEPA (2003).
[d] MCL for total trihalomethanes, which is defined as the summed concentration of chloroform, bromoform ($CHBr_3$), bromodichloromethane ($CHBrCl_2$), and dibromochloromethane ($CHBr_2Cl$).
[e] NR = Not regulated.
[f] Reported vapor pressure for solid-phase hexachloroethane.
Notes: atm – atmosphere; g – gram; K_{ow} – octanol/water partitioning coefficient; K_{oc} – soil organic carbon/water partitioning coefficient; L – liter; MCL – maximum contaminant level; mg – milligram; mL – milliliter; mol – mole.

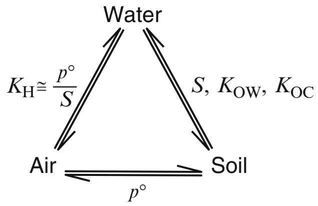

Figure 2.3. The three major phases present in the subsurface and the properties of chlorinated solvents that govern the partitioning between these phases.

2.3.1 Dissolution

At room temperature (25 degrees Celsius [°C]), most chlorinated solvents are colorless liquids with densities (ρ) greater than that of water ($\rho_{\text{solvent}} > 1$ gram per liter [g/L]).

Chlorinated solvents are typically discharged into the environment as pure organic liquids or as mixtures of several organic liquids. The process through which these organic phases are gradually released into groundwater is referred to as dissolution.

For a chlorinated solvent, the extent of dissolution is controlled by the solvent's aqueous solubility (S), defined as the maximum amount of a chlorinated solvent that will partition into water at a given temperature (Lyman, 1982). Also referred to as saturation concentrations (Schwarzenbach et al., 2003), aqueous solubilities are typically reported with units of moles of chlorinated solvent per liter of water (molarity or M) or milligrams of chlorinated solvent per liter of water (mg/L, which is equivalent to parts per million [ppm]). Most chlorinated solvents can be classified as sparingly soluble in water, with aqueous solubilities generally on the order of several tens to hundreds of mg/L (Table 2.2). However, their aqueous solubilities are high relative to their established USEPA MCLs (Pankow and Cherry, 1996), which contributes to their prominence as groundwater pollutants. Another consequence of their limited solubility is their tendency to occur in the subsurface as a separate liquid phase at the base of an aquifer commonly referred to as dense nonaqueous phase liquid (DNAPL).

Table 2.2 reveals the general solubility trend among chlorinated solvents- as the number of chlorine atoms on a compound increases, the aqueous solubility of that species decreases. This inverse relationship illustrates the influence that molecular size (specifically molar volume [Horvath et al., 1999]) exerts on the miscibility of a chlorinated solvent in water. Environmental variables also can influence chlorinated solvent solubility. One such variable is temperature, although changes in the solubility of most chlorinated solvents are relatively minor over environmentally relevant temperature ranges (Horvath, 1982). Another important variable is salinity; an increased concentration of dissolved salts results in a moderate decrease in chlorinated solvent solubility (Lyman, 1982). The presence of other organic chemicals (referred to as co-solutes) also can increase the saturation concentration of chlorinated solvents in water, behavior that is utilized for the treatment of chlorinated solvents during surfactant-enhanced aquifer remediation (SEAR) (e.g., Pennell et al., 1994; Fountain et al., 1996).

2.3.2 Solid-Water Partitioning

Partitioning of chlorinated solvents between aquifer solids and water plays an important role in contaminant fate and treatability because it affects the rate of transport in the subsurface. As a class, chlorinated solvents can be considered moderately hydrophobic; although they partition (or sorb) onto aquifer solids, their affinity for such processes is not as great as that for other organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) or polychlorinated biphenyls (PCBs).

A practical measure of a compound's hydrophobicity is the octanol-water partitioning coefficient (K_{ow}). For a two-phase system containing octanol and water, values of K_{ow} are defined as the equilibrium concentration of the chlorinated solvent in octanol relative to its equilibrium concentration in water (Equation 2.1).

$$\left(K_{\mathrm{ow}} = \frac{C_{\mathrm{octanol}}}{C_{\mathrm{water}}}\right) \qquad \text{(Eq. 2.1)}$$

For laboratory investigations of hydrophobicity, octanol is chosen as a convenient reference solvent because it is immiscible with water. By definition, large values of K_{ow} correspond to hydrophobic chemicals that are expected to sorb to soils and sediments more readily.

More pertinent for describing processes in the subsurface are values of K_{oc}, which represent a measure of a chemical's equilibrium partitioning between water and the organic carbon fraction of aquifer solids (Equation 2.2).

$$\left(K_{\text{oc}} = \frac{C_{\text{organic carbon}}}{C_{\text{water}}}\right) \quad \text{(Eq. 2.2)}$$

Accordingly, a key factor controlling the extent of chlorinated solvent sorption is the organic carbon content of the subsurface material and the dissolved organic matter. Often times, values of K_{oc} can be estimated using linear correlations developed between $\log(K_{ow})$ and $\log(K_{oc})$ for a given pollutant class.

In Table 2.2, values of both K_{ow} and K_{oc} generally increase as the number of chlorine substituents on a compound increases. These larger values of solid-water partitioning coefficients will result in slower rates of subsurface transport. An inverse relationship between aqueous solubility and K_{ow} (or K_{oc}) values is also observed in Table 2.2; chemicals with limited aqueous solubilities generally prefer to partition into a phase such as octanol or soil organic matter rather than associate with water.

2.3.3 Air-Water Partitioning

Chlorinated solvents are relatively volatile compounds. Accordingly, air-water partitioning is expected to take place when contaminated groundwater comes into contact with air, as is the case in unsaturated subsurface zones (e.g., the vadose zone). In such instances, the equilibrium partitioning between air and water is typically described by Henry's Law, which is applicable to dilute solutions of a chlorinated solvent in water. The Henry's Law constant, K_H, relates the equilibrium concentration of the chlorinated solvent in air to its equilibrium concentration in water (Equation 2.3).

$$\left(K_{\text{H}} = \frac{C_{\text{air}}}{C_{\text{water}}}\right) \quad \text{(Eq. 2.3)}$$

By definition, large K_H values indicate a chemical's preference to partition from water into air, although additional chemical properties and several environmental factors will also influence the volatility of a species (Thomas, 1982a).

In Table 2.2, K_H values are reported with units of atm·m^3/mol, but K_H values also are commonly reported with alternative units that depend upon the conventions used to report the chlorinated solvent's concentrations in air and water. Unlike reported values of S, K_{ow} and K_{oc}, the K_H values presented in Table 2.2 do not reveal any significant trends within or across the different classes of chlorinated solvents.

2.3.4 Solid-Air Partitioning

The last chlorinated solvent partitioning process to consider is that between aquifer solids and air, a topic covered in detail by Thomas (1982b). As with volatilization between air and water, several chemical and environmental factors are at play in solid-air partitioning processes (Thomas, 1982b), but our mechanistic understanding of this process is rather limited. One noteworthy variable is the vapor pressure ($p°$) of a chlorinated solvent, which represents the maximum attainable concentration of a chlorinated solvent in air (Schwarzenbach et al., 2003). Compounds with high values of $p°$ (which has units of torr or atm) tend to partition more readily between air and sediments (and similarly, between air and water), and empirical relationships have been developed to estimate the rates at which such partitioning processes occur (Thomas, 1982b). Values of $p°$ tend to decrease with increasing chlorination, although exceptions to this generalization are frequently observed (e.g., compare the $p°$ values for chloroethane and 1,1,2-trichloroethane in Table 2.2).

2.3.5 Transformation Reactions

Not included in Figure 2.3 is an additional critical pathway that impacts chlorinated solvent fate in groundwater, that of transformation reactions. Rates and products of transformation reactions will depend upon many of the chemical and physical properties discussed above, as well as the average oxidation state of carbon in the chlorinated solvent (Table 2.2). The carbon oxidation state is a measure of the number of electrons associated with the carbon atoms in a chlorinated solvent; this value ranges from −I to +IV for the chlorinated solvents listed in Table 2.2. The more negative the oxidation state, the more electrons associated with the carbon atom. A positive oxidation state (e.g., carbon tetrachloride with a +IV) corresponds to a species in a highly oxidized form that is prone to reduction (gaining electrons). On the other hand, chlorinated solvents with more reduced carbon centers, such as vinyl chloride (C oxidation state of −I), are more susceptible to being oxidized (losing electrons).

From a practical sense, transformation reactions are often classified as either biotic or abiotic. Biotic reactions are typically those that involve microbial processes associated with bacterial metabolism, whereas abiotic reactions are defined as those processes that involve another chemical species. The distinction, however, can become blurred when discussing chemicals such as biological exudates or minerals formed as a direct result of microbial activity or as an indirect result of biological modification of a chemical environment.

The classification does, however, provide a convenient organizational structure for discussing the principles of chlorinated solvent remediation, and it has been adopted for use by the authors in Chapter 4. Chapter 3 discusses microbially driven processes, including cometabolic reductive reactions, oxidative metabolism, and dehalorespiration. Chapter 4 describes the important abiotic processes for chlorinated solvents, including sorption, volatilization and transformation reactions such as substitution, elimination, oxidation and reduction. Chapter 5 examines the practical challenges for site remediation that result from the properties and behavior of chlorinated solvents.

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CHAPTER 3

BIODEGRADATION OF CHLORINATED ETHENES

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3.1 INTRODUCTION

Biodegradation of chlorinated ethenes by naturally occurring or artificially enhanced processes is an important component of current site remediation strategies. At this writing, several microbial mechanisms for chlorinated ethene transformation and degradation have been identified. The purpose of this chapter is to briefly summarize the current understanding of those processes that lead to the biodegradation of chlorinated ethenes.

3.2 OPERATIONAL DEFINITION OF BIODEGRADATION

In a relatively strict theoretical sense, "biodegradation" is the chemical breakdown of contaminant compounds by organisms, often microorganisms, and their associated metabolic processes. This definition of biodegradation is usually expanded, for practical reasons, to include "biologically-driven" degradation: any degradation process which, while not directly involving a biochemical reaction, only occurs to any significant extent under environmental conditions that are created by biological activity. An example is the abiotic reduction of the fuel oxygenate compound, methyl tertiary butyl ether (MTBE), to *tert*-butyl alcohol (TBA) by molecular hydrogen (Bradley et al., 2006). While current evidence suggests that this reduction step occurs abiotically, the significance of this process under environmental conditions will largely depend on the production of hydrogen (H_2) by fermentative microorganisms and, thus, would be a "biologically-driven" reaction (Bradley et al., 2006). Likewise, any geochemical reaction that can occur abiotically, but is opportunistically catalyzed by microorganisms in order to meet metabolic and/or energetic requirements, would fall under this definition of biodegradation if a net transformation or breakdown of a contaminant compound results. Thus, for this discussion, the theoretical definition of biodegradation includes those degradative processes that depend on biological activity, either directly or indirectly, or that are opportunistically catalyzed by microorganisms under environmental conditions.

However, practical methods of assessing contaminant biodegradation provide an imperfect approximation of this theoretical definition. In fact, biodegradation activity is rarely measured directly. Rather, the contaminant degradation activity that is attributed to biodegradation is often inferred from the difference in the activity observed under viable conditions and the activity observed under nominally "non-viable" conditions. For example, the most common method employed by microbiologists to establish sterile-control treatments for sediment or soil biodegradation studies involves heat-sterilization under high pressure (autoclaving). This method, a direct inheritance of medical sterilization practices, very effectively suppresses but may not completely inhibit biological activity in sediments. Incomplete sterilization may lead to a significant underestimation of contaminant biodegradation. Moreover, exposure to high temperature and pressure can also significantly alter the geochemical and physical characteristics of the sediment environment and, consequently, may inhibit any number of potentially

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important abiotic degradation mechanisms. The net effect of this possible “sterilization” artifact would be an overestimation of biodegradation and an underestimation of abiotic degradation processes. Thus, while comparison with sterile control treatments continues to be a powerful and eminently practical tool for roughly estimating the contribution of biological processes to contaminant degradation, the approach is not perfect and the potential artifacts must be considered.

3.3 HISTORICAL OVERVIEW OF CHLORINATED ETHENE BIODEGRADATION

Prior to 1980, chlorinated ethene compounds were widely considered to be recalcitrant to biodegradation based, in large part, on the presumption that they were not natural components of the biosphere (Asplund, 1995; Gribble, 1992, 1994). Fewer than 30 naturally-occurring organochlorine compounds were recognized in the scientific literature before 1970 (Gribble, 1994). Consequently, when the environmental threat posed by chlorinated ethene contaminants was demonstrated in the early 1980s by highly publicized cases of contamination like Woburn, Massachusetts (Harr, 1995), the perception was that the natural capacity for chlorinated ethene biodegradation was negligible.

In the early 1980s, however, evidence for the accumulation of perchloroethene (PCE: also termed tetrachloroethene) and trichloroethene (TCE) transformation products in anoxic groundwater systems was increasingly observed and attributed to reductive dechlorination (Vogel and McCarty, 1985; Barrio-Lage et al., 1987, 1990; Bouwer, 1994; McCarty and Semprini, 1994; Vogel, 1994; Odum et al., 1995). Initially the mechanism underlying reductive dechlorination was presumed to be cometabolic, because the first laboratory pure cultures shown to be capable of reductive dechlorination were methanogens (*Methanosarcina* sp.) which did not grow on chlorinated ethenes and apparently did not gain energy from the reaction (Fathepure et al., 1987; Fathepure and Boyd, 1988a, 1988b; Jablonski and Ferry, 1992; El Fantroussi et al., 1998). Subsequent investigation demonstrated that reductive dechlorination of PCE to TCE and dichloroethene (DCE) also could be mediated by sulfate (SO_4)-reducing bacteria (Fathepure et al., 1987; Freedman and Gossett, 1989; Cole et al., 1995; Townsend and Suflita, 1997) and homoacetogens (Terzenbach and Blaut, 1994). Each of these organisms mediated slow and partial reductive dechlorination of PCE and TCE to yield primarily *cis*-DCE in a non-specific process attributed to the presence of cellular corrinoids or other reduced cellular compounds (for review see El Fantroussi et al., 1998; Mohn and Tiedje, 1992). Based on these observations, *in situ* reductive dechlorination was originally assumed to result from cometabolism, brought about by the fortuitous interaction of chlorinated ethenes with the enzymes and reduced cofactors produced by the microorganisms for other metabolic purposes (McCarty and Semprini, 1994). Today, cometabolic dechlorination is considered a ubiquitous but inefficient mechanism of chlorinated ethene biodegradation in anoxic environments (Bouwer, 1994; Chapelle, 1996; Gossett and Zinder, 1996; McCarty, 1996; McCarty and Semprini, 1994; Vogel, 1994).

By the end of the 1980s, researchers started to recognize that reductive dechlorination was not solely due to cometabolic processes, and that direct use of these compounds as electron acceptors was an important mechanism for biodegradation in anoxic systems. Although the energetic potential of chlorinated ethene compounds had long suggested a possible role as metabolic substrates for anaerobic microorganisms (Vogel et al., 1987), the key element in the shift from a predominantly “cometabolic” view of reductive dechlorination to the concept of chlorinated ethenes as primary substrates was the discovery of microorganisms which conserve energy during reductive dechlorination (e.g., Holliger et al., 1993; Krumholz et al., 1996;

Maymó-Gatell et al., 1997; Sharma and McCarty, 1996). Such microorganisms are able to grow using chlorinated ethenes as respiratory terminal electron acceptors, a process termed chlororespiration (or dechlororespiration), and are capable of much higher rates of reductive dechlorination than were previously attributed to cometabolic reductive dechlorination processes (e.g., Gerritse et al., 1996; Gerritse et al., 1999; He et al., 2002; Holliger et al., 1993; Holliger et al., 1998; Krumholz et al., 1996; Krumholz, 1997; Magnuson et al., 1998; Maymó-Gatell et al., 1997; Mohn and Tiedje, 1992; Scholz-Muramatsu et al., 1995; Sharma and McCarty, 1996; Wild et al., 1996).

Ironically, chlororespiration was not the first process by which microorganisms were shown to utilize chlorinated ethenes for growth and energy production. A decade earlier, Hartmans et al. (1985) reported oxidative microbial degradation of vinyl chloride (VC) as carbon and energy source under oxic conditions (Hartmans et al., 1985; Hartmans and deBont, 1992). However, because the presence of DCE and VC in groundwater is generally associated with the reductive dechlorination of PCE and TCE under anoxic conditions, the potential importance of oxidative microbial degradation of chlorinated ethenes was not appreciated until microbial mineralization of VC under iron(III) (Fe[III])-reducing conditions was suggested in 1996 (Bradley and Chapelle, 1996) and anoxic microbial oxidation of VC as a primary substrate was reported in 1998 (Bradley et al., 1998a). Identification of these reductive and oxidative processes demonstrated that several mechanisms for microbial degradation of chlorinated ethene contaminants can occur in groundwater and surface water systems (Figure 3.1).

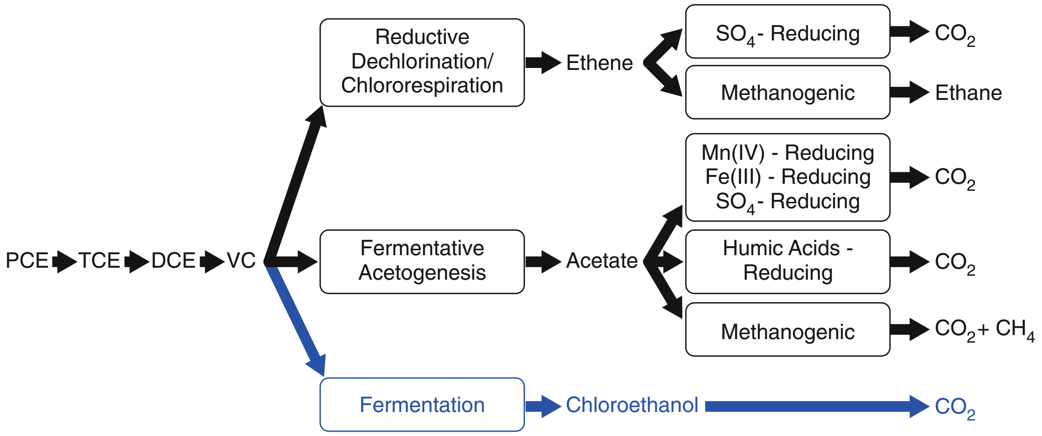


Figure 3.1. Demonstrated (black) and hypothesized (blue) pathways of anoxic VC biodegradation. The sequential biotransformation of PCE to TCE to DCE to VC results from cometabolic reductive dechlorination and/or chlororespiration. Adapted from Bradley, 2003.

3.4 CHLORINATED ETHENE BIODEGRADATION AND REDOX CONDITIONS

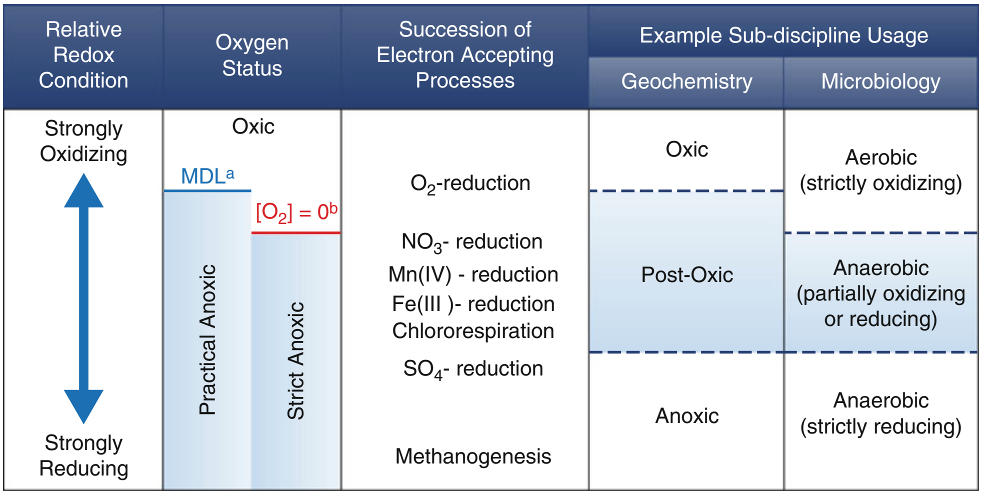
3.4.1 Role of Redox in Chlorinated Ethene Biodegradation

For many environmental contaminants, biodegradation is the result of microbiologically catalyzed redox reactions in which the contaminant compound is transformed while serving either as an electron donor or as an electron acceptor in a biochemical reaction. Thus, it is not surprising that *in situ* redox conditions are a primary determinant of the efficiency of biodegradation for many environmental contaminants. Relatively reduced contaminants, like petroleum hydrocarbon compounds, can serve as microbial electron donors and thus, efficient biodegradation is generally observed when energetic microbial terminal electron acceptors like oxygen are available *in situ*. Highly oxidized contaminants, like perchlorate (e.g., Logan et al., 2001), can also serve as microbial terminal electron acceptors and, consequently, efficient biodegradation is generally observed when electron donor compounds are readily available *in situ* (i.e., under strongly reducing conditions).

The *in situ* redox environment is a particularly important control on chlorinated ethene biodegradation because chlorinated ethene compounds can serve as either microbial electron donors or microbial terminal electron acceptors, depending on ambient redox conditions. Consequently, for chlorinated ethenes, both the redox role of the contaminant compound and the efficiency of the redox-based degradation reaction are influenced by *in situ* redox conditions. In light of the impact of *in situ* redox conditions on chlorinated ethene biodegradation, and particularly the importance of accurately assessing the oxic/anoxic status of the *in situ* environment, the redox conditions that favor a specific degradation pathway will be considered throughout this chapter in conjunction with the discussions of the respective chlorinated ethene biodegradation processes.

3.4.2 A Brief Overview of Redox Terminology

Several terms are employed by different scientific sub-disciplines to describe redox conditions, in general, and oxygen-limited and oxygen-free environmental conditions in particular (see Bradley et al., 2008 for a complete discussion of this issue). The fact that many of these terms have well established but markedly different meanings for individual sub-disciplines is a fundamental concern. To illustrate this ambiguity, some of the terms that are frequently employed to describe the *in situ* redox environment are discussed along with their common usages. It should be noted that each term has, at some point, been employed in the scientific literature as a synonym for “oxygen-free.” Figure 3.2 depicts the relationship between the different terms and usages.



[a] MDL: Minimum detection limit as defined by the analytical method.

[b] $[O_2] = 0$: Theoretical point at which the dissolved oxygen concentration falls to zero.

Figure 3.2. Schematic presentation of the various terms used to describe environmental oxygen and redox conditions in subsurface environments. Dashed lines indicate imprecisely defined boundaries between categories. From Bradley et al., 2008.

ANOXIC – is a Greek-derived term composed of the prefix "*an*" which means "not" or "without" and the root "*oxic*" which, in a scientific context, refers to "oxygen." Anoxic is conceptually the most straightforward of the many terms used to describe "oxygen-free" environments and, theoretically, indicates the complete absence of oxygen. In light of the difficulty in assessing low oxygen concentrations while inhabiting a 21% by volume oxygen atmosphere, however, groundwater has been considered anoxic at dissolved oxygen concentrations below 0.1–0.5 milligrams per liter (mg/L). Although meticulous sampling technique can improve the field detection limit for dissolved oxygen, the fact remains that in the environmental sciences, anoxia is operationally defined by practical limitations on field oxygen measurements.

The term "anoxic" does not identify the alternative terminal electron accepting processes that may be occurring in the absence of oxygen. Nevertheless, certain environmental sub-disciplines (e.g., geochemistry) have reserved this term for those highly reducing conditions under which sulfidogenesis and methanogenesis provide tacit evidence for the absence of oxygen. For these sub-disciplines, a variety of additional terms [e.g., post-oxic ("after" oxygen), dysoxic ("bad" oxygen), sub-oxic ("below" oxygen), and hypoxic ("low" or "deficient" oxygen)] have been coined to refer to the poorly defined range between verifiably "oxic" conditions and detectably sulfidogenic/methanogenic conditions.

Throughout this chapter, "anoxic" and its related terms are used in accordance with the practical definition and specifically refer to *in situ* conditions under which the dissolved oxygen concentrations are below the field detection limit of 0.1 mg/L. It should be noted that this field standard for nominal anoxic conditions may include environments with sub-detection concentrations of dissolved oxygen. In the section on mineralization of chlorinated ethene contaminants under nominally anoxic conditions, precise experimental detection limits for oxygen are provided when available.

ANAEROBIC – is also a Greek-derived term composed of the prefix "*an*" meaning "without" and the prefix "*aero*" meaning "air." The root, "bic" is an adjective form of "bios" and refers to "life" or "living." In a strict sense, anaerobic refers to life or activity in the "absence of air." However, this literal interpretation is misleading, because the term anaerobic is used almost exclusively to refer to an absence of free oxygen but not to an absence of nitrogen, despite the fact that air is 78% nitrogen by volume.

The potential for confusion is exacerbated by the fact that "anaerobic" and particularly the combined term, "strictly anaerobic," are used by many microbiologists to refer exclusively to highly-reducing homoacetogenic, sulfidogenic (sulfate-reducing) and/or methanogenic conditions, but not to the more oxidized nitrate-reducing, manganese-reducing or iron-reducing conditions, which also occur in the "absence of air."

Throughout this chapter, "anaerobic" and its related terms are also used in accordance with practical oxygen detection limits and specifically refer to microbial processes that are relevant at dissolved oxygen concentrations below the field detection limit of 0.1 mg/L. The term aerobic is used to refer to microorganisms that utilize oxygen as a respiratory terminal electron acceptor.

MICROAEROPHILIC – is a Greek-based term composed of the prefix "*micro*" meaning "little," the prefix "*aero*" which means "air," and the root "*philic*" which means "loving." Microaerophilic is an adjective describing those microorganisms that require some oxygen for growth and metabolic activity but that do not function well, or at all, at ambient (i.e., 21% by volume) oxygen concentrations. Thus, "microaerophilic" is an imprecise term indicating that the oxygen concentration is below 21% but not zero.

REDUCING – refers to environmental conditions that favor a decrease in the oxidation state of reactive chemical species. For the succession of terminal electron accepting processes (Figure 3.2), those conditions on the oxygen-reducing end would be considered strongly oxidizing while conditions on the methanogenic end would be considered strongly reducing. Reducing is a relative term that is meaningful only in contrast to the term oxidizing. For example, methanogenic conditions are substantially more reducing than are iron-reducing conditions, even though both occur in the absence of oxygen.

3.5 MICROBIAL REDUCTIVE DECHLORINATION OF CHLORINATED ETHENES

3.5.1 Reductive Dechlorination and *In Situ* Redox Conditions

It was apparent by the early 1980s that reductive dechlorination of chlorinated ethene contaminants is a common occurrence in groundwater systems where dissolved oxygen concentrations are below field-based detection limits for oxic conditions (0.1–0.5 mg/L). However, the efficiency of the process is also highly variable under field conditions (Table 3.1). Specifically, the rate and extent of reduction is dependent on the number of chlorine substituents attached to the ethene backbone and on the *in situ* redox conditions (Bouwer, 1994; McCarty and Semprini, 1994; Vogel, 1994; Vogel et al., 1987; Chapelle, 1996; Wiedemeier et al., 1998). PCE, with its four chlorine atoms, is a stronger oxidant than the naturally occurring electron accepting species found in groundwater systems, with the exception of oxygen (O_2) (Vogel et al., 1987). Thus, PCE commonly undergoes reductive dechlorination to TCE in the absence of detectable dissolved oxygen.

Reductive dechlorination of TCE to *cis*-DCE can occur under Fe(III)-reducing conditions and in more strongly reducing environments (Chapelle, 1996). Reductive dechlorination of *cis*-DCE to yield VC appears to be favored under SO_4-reducing and methanogenic conditions (Chapelle, 1996; Vogel et al., 1987). Reductive dechlorination of VC to the non-chlorinated product, ethene, appears to be slow *in situ* and generally associated with highly reducing, methanogenic conditions (Ballapragada et al., 1995; Barrio-Lage et al., 1987, 1990; Bouwer, 1994; Carter and Jewell, 1993; De Bruin et al., 1992; DiStefano et al., 1991; Fennell et al., 1995; Freedman and Gossett, 1989; Maymó-Gatell et al., 1995; Odum et al., 1995; Vogel and McCarty, 1985; Wu et al., 1995). In the field, reductive dechlorination of chlorinated ethene contaminants under non-engineered groundwater conditions often appears incomplete and to lead to the accumulation of *cis*-DCE and VC (Haston et al., 1994; Kitanidis et al., 1993; Major et al., 1991; McCarty and Reinhard, 1993; Weaver et al., 1996; Wilson et al., 1995).

3.5.2 *In Situ* Chlororespiration of Chlorinated Ethenes

In 1984, a SO_4-reducing bacterium, *Desulfomonile tiedjei* DCB-1, was found capable of coupling the reductive dechlorination of 3-chlorobenzoate to growth (Shelton and Tiedje, 1984). *D. tiedjei* was later reported to reduce PCE to TCE and DCE (Fathepure et al., 1987; DeWeerd and Suflita, 1990; Cole et al., 1995) via an energy conserving, respiratory reductive dechlorination process termed chlororespiration (Mohn and Tiedje, 1992). Subsequent investigations have isolated a number of chlororespiring microbial pure cultures capable of reducing various chlorinated ethene compounds (Cupples et al., 2003; Gerritse et al., 1996, 1999; He et al., 2003; Holliger et al., 1993; Löffler et al., 1999, 2000; Krumholz et al., 1996; Krumholz, 1997; Maymó-Gatell et al., 1997, 1999; Scholz-Muramatsu et al., 1995; Sharma and McCarty, 1996). Notable among these, *Dehalococcoides ethenogenes* can catalyze the complete reductive dechlorination of PCE to ethene and is capable of growth on PCE, TCE and *cis*-DCE.

Table 3.1. Relative Efficiency of Chlorinated Ethene Biodegradation Processes Under Environmental Redox Conditions[a]

Compound	Process	Predominant Redox Condition				
			Anoxic			
		Oxic	Mn-reduction	Fe-reduction	SO_4-reduction	Methanogenesis
PCE	Cometabolic Reduction[b]	–	–	–	+	+
	Chlororespiration	–	?	++	++++	++++
	Mineralization	?	–	–	–	–
TCE	Cometabolic Reduction[b]	–	–	–	+	+
	Chlororespiration	–	?	++	++++	++++
	Mineralization	++[c]	–	–	–	–
DCE	Cometabolic Reduction[b]	–	–	–	–	–
	Chlororespiration	–	–	+	+++	++++
	Mineralization	+++[d]	++	+	+	–
VC	Cometabolic Reduction[b]	–	–	–	–	–
	Chlororespiration	–	–	–	++	+++
	Mineralization	++++[d]	+++	+++	++	+

[a] Number of "+" symbols indicates relative efficiency of process under specified redox condition. The "–" symbol indicates process is not generally important under specified redox condition.

[b] Cometabolic reduction may be environmentally relevant for PCE and TCE biodegradation but is not considered to be an effective mechanism for DCE and VC biodegradation. Process requires a co-substrate and anoxic conditions.

[c] Only aerobic cometabolism has been reported for TCE. Process requires co-substrate and oxic conditions.

[d] Aerobic cometabolism and energy-yielding oxidation processes have been described for DCE and VC under oxic conditions.

In addition, a growing number of mixed microbial populations that are capable of efficient reductive dechlorination of DCE and VC have been described (e.g., Rosner et al., 1997; Löffler et al., 1999; Flynn et al., 2000). Rosner et al. (1997) described DCE and VC dechlorinating activity that appeared to be independent of the corrinoid compounds involved in PCE and TCE reductive dechlorination (Magnuson et al., 1998). Löffler et al. (1999) reported three acetogenic mixed cultures capable of reductively dechlorinating VC to ethene and concluded, on the basis of energetic calculations and low H_2 consumption thresholds, that this was a respiratory process.

In a separate study, two mixed subcultures capable of complete dechlorination of DCE and VC were found incapable of PCE dechlorination (Flynn et al., 2000), indicating that the ability of the original cultures to completely dechlorinate PCE to ethene was the result of at least two distinct dechlorinating populations. Consistent with these observations, recent reports indicate the existence of distinct *Dehalococcoides* species that, in contrast to *D. ethenogenes*, are capable of efficient dechlorination of *cis*-DCE and VC but not of PCE and TCE (Cupples et al., 2003; He et al., 2003). *D. ethenogenes* was found capable of reductively dechlorinating DCE and VC (Maymó-Gatell et al., 1997, 1999), although reductive dechlorination of VC to ethene by *D. ethenogenes* was two orders of magnitude slower than reduction of the other chlorinated ethenes (Magnuson et al., 1998), was inhibited by high concentrations of PCE (Maymó-Gatell et al., 2001), and did not appear to support growth (Maymó-Gatell et al., 1999).

Several observations suggest that reductive dechlorination of chlorinated ethene contaminants in groundwater systems is attributable to cooperative microbial consortia rather than to the activity of individual species. The relatively large number of pure cultures identified as being capable of chlororespiration of PCE to TCE or DCE (Mohn and Tiedje, 1992; Holliger et al., 1993; Gerritse et al., 1996, 1999; Löffler et al., 1999; Scholz-Muramatsu et al., 1995; Krumholz et al., 1996; Sharma and McCarty, 1996) and the clear evidence for independent DCE and VC dechlorinating cultures (Rosner et al., 1997; Löffler et al., 1999; Flynn et al., 2000; Cupples et al., 2003; He et al., 2003) are consistent with this hypothesis. Likewise, a number of mixed cultures capable of complete dechlorination of PCE to ethene have been identified (Freedman and Gossett, 1989; DiStefano et al., 1991; DeBruin et al., 1992; Rosner et al., 1997; Flynn et al., 2000), while only one pure culture, *D. ethenogenes,* has demonstrated complete reductive dechlorination of all of the chlorinated ethenes (Maymó-Gatell et al., 1997). A study of three Michigan river enrichment cultures capable of complete reductive dechlorination of PCE to ethene revealed that two of the three cultures contained distinct microbial populations for PCE and VC dechlorination (Flynn et al., 2000). The fact that VC dechlorination does not appear to support growth in *D. ethenogenes* (Maymó-Gatell et al., 1999), but apparently is a specialized, energy conserving process in some mixed microbial cultures (Rosner et al., 1997; Löffler et al., 1999; Flynn et al., 2000; Cupples et al., 2003; He et al., 2003), further suggests the importance of microbial consortia in facilitating complete reductive dechlorination of chlorinated ethene contaminants.

3.5.3 Kinetic Constraints on Chlorinated Ethene Reductive Dechlorination

In general, the tendency of chlorinated ethene compounds to undergo reductive dechlorination appears to decrease with a decrease in the number of chlorine substituents (Vogel, 1994; Vogel et al., 1987). However, the corresponding Gibbs free energy changes for the sequential reductive dechlorinations from PCE to ethene (assuming H_2 is the electron donor) decrease only from approximately -164 kilojoules per mole (kJ/mol) H_2 for PCE to TCE to -141 kJ/mol H_2 and -155 kJ/mol H_2 for *cis*-DCE to VC and VC to ethene, respectively (He et al., 2002; Dolfing and Janssen, 1994; Löffler et al., 1999; Mazur and Jones, 2001; Vogel, 1994; Vogel et al., 1987). Assuming that a suitable electron donor is present in the environment in sufficient concentration to realize these calculated energy potential changes, these thermodynamic considerations indicate that each of the reductive dechlorination steps is potentially exergonic and a possible source of energy for metabolism and growth (Dolfing and Janssen, 1994; Löffler et al., 1999; Mazur and Jones, 2001). Thus, the reported differences in the efficiency of reductive dechlorination of the different chlorinated ethene species under field conditions appear to be related to kinetic rather than energetic constraints.

PCE and TCE reductive dechlorination was characterized as rapid in *D. ethenogenes*, while reductive dechlorination of *cis*-DCE was much slower and reduction of VC was negligible (Maymó-Gatell et al., 1999). Consistent with this trend, reductive dechorination of PCE, TCE and *cis*-DCE supported growth in *D. ethenogenes*. A similar pattern of decreasing rate of reductive dechlorination with decreasing chlorine number was reported for an anaerobic mixed culture derived from a PCE-contaminated aquifer system (Haston and McCarty, 1999; Rosner et al., 1997). Dechlorination rates and 95% confidence intervals were reported as 77 ± 5, 59 ± 11, 14 ± 3 and 13 ± 3 micromoles per day (μM/day) for PCE, TCE, *cis*-DCE and VC, respectively (Haston and McCarty, 1999). It is worth noting, however, that unlike the *D. ethenogenes* results, the apparent rates of VC dechlorination in the mixed culture study were comparable to those for *cis*-DCE and within an order of magnitude of those for PCE and TCE (Haston and McCarty, 1999).

Equally important, from an environmental remediation standpoint, the half-saturation (k_S) coefficient for reductive dechlorination appears to be at least an order of magnitude higher for VC than for PCE (Haston and McCarty, 1999; Maymó-Gatell et al., 1999). These observations suggest that the substrate affinity of the enzymes involved may be comparatively poor for VC, and that the *in situ* rates of VC reductive dechlorination may be well below maximum for a significant portion of the groundwater plume (Haston and McCarty, 1999; Maymó-Gatell et al., 1999).

Thus, both thermodynamic and kinetic evidence suggest that *in situ* microbial reduction of PCE and TCE is favorable under anoxic conditions. Kinetic considerations indicate that the microbial reductive dechlorination of VC may be limited under relatively oxidized field conditions and at low VC concentrations.

3.5.4 Electron Donor Availability

H_2 is generally considered to be the ultimate electron donor for the majority of chlororespiratory microorganisms (DiStefano et al., 1991; Maymó-Gatell et al., 1995; Smatlak et al., 1996; Fennell et al., 1995; Ballapragada et al., 1997; Carr and Hughes, 1998; Yang and McCarty, 1998; Yang and McCarty, 1999; He et al., 2002; Gossett and Zinder, 1996; Chapelle, 1996), with acetate (and perhaps formate) serving as electron donor for a limited number of isolates (Krumholz et al. 1996; Krumholz, 1997; Löffler et al., 2000). Under mixed culture conditions and in environmental samples, complex carbon substrates (e.g., butyrate, lactate, benzoate, proprionate, methanol, ethanol, formate, acetate and glucose) have been shown to support chlororespiration of chloroethene compounds to ethene (Freedman and Gossett, 1989; DiStefano et al., 1991; DeBruin et al., 1992; Maymó-Gatell et al., 1995; Scholz-Muramatsu et al., 1995; Sharma and McCarty, 1996; Smatlak et al., 1996; Ballapragada et al., 1997; Maymó-Gatell et al.,1997; Yang and McCarty, 1998; Gerritse et al., 1999; Holliger et al., 1998; Löffler et al., 1999; He et al., 2002). However, the use of complex carbon substrates requires the presence of a microbial community capable of fermenting that substrate to H_2 or acetate for subsequent use in chlororespiration. Thus, the efficiency of reductive dechlorination, under the mixed culture conditions found in groundwater and surface water systems, depends on the existence of a ready supply of fermentable carbon substrate(s) and the presence of fermentative microorganisms. Because shallow groundwater systems are often oligotrophic, the *in situ* availability of electron donor has long been considered an important factor limiting the efficiency of microbial reductive dechlorination of chloroethenes to ethene in groundwater (Gibson and Sewell, 1992; Bouwer, 1994; McCarty, 1996; McCarty and Semprini, 1994; Gossett and Zinder, 1996; Wiedemeier et al., 1998; Vogel, 1994).

The apparent dependence on H_2 as ultimate electron donor suggests that, under *in situ* conditions, chlororespiring microorganisms must compete with a number of other anaerobic hydrogenotrophs including nitrate (NO_3)-reducers, manganese(IV) (Mn[IV])-reducers, Fe(III)-reducers, SO_4-reducers, autotrophic methanogens and homoacetogens (Yang and McCarty, 1998; Löffler et al., 1999). Laboratory results suggest that chlororespiration of chlorinated ethene compounds is favored at dissolved H_2 concentrations well below the reported H_2 thresholds for methanogens or homoacetogens (Smatlak et al., 1996; Yang and McCarty, 1998; Löffler et al., 1999). Likewise, the fact that the H_2 thresholds for the chlororespiration of chlorinated ethenes, including VC, appear to be at least as low as 1-2 nanomolar (nM), suggests that chlororespiration also can be competitive under SO_4-reducing conditions (Yang and McCarty, 1998; Löffler et al., 1999; Mazur and Jones, 2001), and perhaps under Fe(III)-reducing conditions (Löffler et al., 1999).

Both thermodynamic and kinetic evidence indicate that efficient uptake and utilization of H_2 by chlororespirers is favored under highly reduced (SO_4-reducing, methanogenic or homoacetogenic) conditions and that the competitive advantage of chlororespiration decreases as the alternative terminal electron accepting processes become more oxidizing (Vogel et al., 1987; Ballapragada et al., 1997; Löffler et al., 1999; Smatlak et al., 1996; Yang and McCarty, 1998; Mazur and Jones, 2001). The ability of chlororespiratory microorganisms to compete for H_2 under more oxidized (e.g., Mn-reducing and Fe-reducing) conditions is less clear.

3.5.5 Conclusions for Chlorinated Ethene Reductive Dechlorination

For practitioners, several important conclusions can be inferred from the research on reductive dechlorination.

- Reductive dechlorination is common in groundwater systems in the absence of detectable dissolved oxygen (dissolved oxygen concentration less than 0.1 - 0.5 mg/L). Reductive dechlorination appears to be the primary mechanism for *in situ* biotransformation of the parent compounds, PCE and TCE.
- Microorganisms are capable of completely dechlorinating chlorinated ethenes to ethene under anoxic conditions via an energy-conserving process termed chlororespiration.
- Only a few species of *Dehalococcoides* have been shown to chlororespire DCE and VC.
- The efficiency of chlorinated ethene reductive dechlorination appears to decrease with decreasing chlorine number, such that toxic intermediates (*cis*-DCE and VC) may accumulate.
- Complete dechlorination to innocuous non-chlorinated products (ethene and ethane) can be significant in some groundwater systems, but may be limited under non-engineered conditions.
- The potential causes of incomplete dechlorination include (1) insufficient electron donor supply, (2) interspecies H_2 competition, (3) the presence of alternative terminal electron acceptors (such as nitrate), (4) the absence or low activity of *cis*-DCE and VC dechlorinating microorganisms and (5) the presence of inhibitory substances including more oxidized chlorinated ethene compounds.
- Careful characterization, data analysis and bench-scale testing may be needed to determine which of these causes are responsible for incomplete dechlorination at a particular site and to design an appropriate remediation solution.
- Reductive dechlorination of VC to ethene may be inefficient except under highly reducing methanogenic conditions.
- The *in situ* production of ethene and its reduction product, ethane, within chlorinated ethene plumes represents compelling evidence of complete chlorinated ethene biodegradation. However, the accumulation of these compounds is often insufficient to explain observed decreases in chlorinated ethene concentrations in anoxic groundwater systems.

3.6 MICROBIAL MINERALIZATION OF CHLORINATED ETHENES UNDER OXIC CONDITIONS

3.6.1 Cometabolic Oxidation under Oxic Conditions

Wilson and Wilson (1985) first reported that methanotrophic bacteria were capable of oxidizing TCE to carbon dioxide (CO_2) under oxic conditions. Subsequent investigations have identified a wide variety of aerobic microorganisms that are able to oxidize chlorinated ethene compounds to CO_2. These include methane oxidizers (Baek and Jaffé, 1989; Moore et al., 1989; Tsien et al., 1989; Gerritse et al., 1995; Semprini, 1995), methanol oxidizers (Fitch et al., 1996), ethene oxidizers (Verce et al., 2001), propane oxidizers (Malachlowsky et al., 1994), propene oxidizers (Reij et al., 1995), aromatic compound (e.g., toluene) oxidizers (Nelson et al., 1986; Fan and Scow, 1993; Malachowsky et al., 1994; Fuller et al., 1995; Hopkins and McCarty, 1995; Semprini, 1995; Mars et al., 1996; Ryoo et al., 2000; Shim et al., 2001), ammonium oxidizers (Vannelli et al., 1990), isoprene oxidizers (McCarty and Semprini, 1994) and vinyl chloride oxidizers (Verce et al., 2002). These processes do not appear to yield energy for microbial growth or metabolism and have therefore been characterized as aerobic cometabolism (McCarty and Semprini, 1994).

The microorganisms responsible for this aerobic cometabolism contain non-specific oxygenases which fortuitously oxidize chlorinated ethenes to CO_2. Aerobic cometabolism of chlorinated ethenes requires the presence of oxygen and a primary carbon substrate to induce and maintain the production of a suitable oxygenase (McCarty and Semprini, 1994). Cometabolic oxidation generally is not considered a significant, long-term mechanism for non-engineered bioremediation of chlorinated ethenes, but has been successfully exploited for engineered remediation of chlorinated ethene contaminants in groundwater (Battelle, 2001; McCarty and Semprini, 1994; Semprini, 1995; Fan and Scow, 1993; Fuller et al., 1995; Hopkins and McCarty, 1995; Mars et al., 1996). For example, TCE in oxic aquifers can be biodegraded by methanotrophic microorganisms when methane is supplied to the subsurface in sufficient quantity to stimulate and support methanotrophic activity (McCarty and Semprini, 1994; Semprini, 1995). Because methane and oxygen do not typically occur together in groundwater systems, however, methanotrophic oxidation of chlorinated ethenes is unlikely under non-engineered circumstances.

On the other hand, mixed-waste plumes containing chlorinated ethenes and aromatic compounds are not uncommon and oxidizers of aromatic compounds can effectively cometabolize chlorinated ethenes under oxic conditions (Fan and Scow, 1993; Fuller et al., 1995; Hopkins and McCarty, 1995; Mars et al., 1996). Unfortunately, contaminant plumes which contain cosubstrates at concentrations high enough to support cometabolic oxidation of chlorinated ethenes are typically anoxic as the result of respiratory oxygen consumption. Also, intermediates produced during cometabolic biodegradation of chlorinated ethenes (notably epoxides) can be toxic to the oxidative microbial community and the cometabolic substrates can themselves inhibit cometabolic biodegradation (as a competitive substrate for the oxygenase enzymes) (Battelle, 2001). Hence, cometabolic oxidation of chlorinated ethenes appears to be poorly suited to long-term contaminant remediation under either engineered or natural conditions (Battelle, 2001).

Notable exceptions are the potential for aerobic cometabolism of chlorinated ethene contaminants at the fringe of the chlorinated ethene plume and at the point of plume discharge to surface water systems. The potential for aerobic cometabolic oxidation of chlorinated ethene contaminants exists at the periphery of anoxic chlorinated ethene plumes due to the diffusion of oxygen from the surrounding oxic aquifer system and to the direct infiltration of oxygenated recharge (Dolan and McCarty, 1995). Likewise, the groundwater and surface water interface is a non-engineered environment that supports cometabolic contaminant oxidation. When shallow groundwater is contaminated, plumes may discharge to nearby surface water bodies. The sediments of surface water systems typically are characterized by geochemical heterogeneity and a variety of cometabolic capabilities including methanotrophy. For example, oxidation of

DCE and VC has been reported in stream-bed sediments characterized by mixed aerobic/methanogenic conditions (Bradley and Chapelle, 1997).

3.6.2 Degradation of Chlorinated Ethenes as Primary Substrates under Oxic Conditions

The problematic requirement for both oxic conditions and cosubstrate can be avoided, if the chlorinated ethene contaminant can serve as a primary substrate. The tendency of chlorinated ethene compounds to undergo oxidation increases with decreasing number of chlorine substituents (Vogel et al., 1987). Due to their highly oxidized character, neither PCE nor TCE are considered primary substrates for aerobic microbial degradation, although aerobic cometabolism of these compounds has been demonstrated (McCarty and Semprini, 1994; Ryoo et al., 2000; Shim et al., 2001).

In contrast, aerobic microbial degradation of DCE and VC as primary substrates has been shown (Hartmans et al., 1985; Hartmans and de Bont, 1992; Hartmans, 1995; Verce et al., 2000; Bradley and Chapelle, 2000a; Coleman et al., 2002a; Coleman et al., 2002b; Elango et al., 2006). As the least chlorinated of the chlorinated ethenes, VC has the greatest tendency to undergo oxidation and was the first chlorinated ethene shown to serve as primary substrate for growth and metabolism in the presence of oxygen (Hartmans et al., 1985; Hartmans and de Bont, 1992; Hartmans et al., 1992; Verce et al., 2000). Rapid microbial degradation of vinyl chloride, including mineralization, has been observed in aquifer microcosms under oxic conditions (Bradley and Chapelle, 1996, 1998a, 1998b; Bradley et al., 1998b; Davis and Carpenter, 1990; Hartmans et al., 1985; Phelps et al., 1991).

Hartmans and coworkers (Hartmans et al., 1985; Hartmans and de Bont, 1992; Hartmans et al., 1992) isolated several strains of *Mycobacterium aurum* from soil that are capable of growth on VC as a sole source of carbon and energy. More recently, *Psuedomonas aeruginosa* strain MF1 has been isolated from an activated sludge enrichment culture and shown to use VC as primary growth substrate (Verce et al., 2002). Coleman et al. (2002a) reported aerobic VC biodegradation in more than 60% of environmental microcosms and enrichments collected from 22 locations in the United States and Europe. From these samples, 11 *Mycobacterium* strains and 1 *Nocardioides* strain capable of aerobic growth on VC as sole carbon substrate were isolated (Coleman et al., 2002a). These observations suggest that the potential for non-cometabolic, aerobic biodegradation of VC is widespread in chlorinated ethene-contaminated environments (Coleman et al., 2002a).

Although cometabolic oxidation of DCE under oxic conditions has been demonstrated for a variety of cosubstrates (McCarty and Semprini, 1994), several recent studies indicate that microbial oxidation of DCE can also occur under oxic conditions in the absence of an apparent cosubstrate (Bradley and Chapelle, 1998b; Bradley et al., 1998b, 1998c; Klier et al., 1999). Significant aerobic oxidation of *cis*-DCE was demonstrated for an organic-rich, stream-bed sediment (Bradley and Chapelle, 1998b; Bradley et al., 1998b, 1998c), organic rich surface soils (Klier et al., 1999) and organic-poor aquifer sediments (Bradley and Chapelle, 1998b; Bradley et al., 1998b, 1998c).

Microorganisms collected from the sediments of a high dissolved organic carbon (DOC) stream system utilized *cis*-DCE as a sole carbon substrate for aerobic metabolism (Bradley and Chapelle, 2000a). Coleman et al. (2002b) described an environmental isolate (strain JS666) most closely related to *Polaromonas vacuolata*, which is capable of aerobic growth on *cis*-DCE as sole source of carbon. These reports suggest that DCE can be degraded aerobically, with DCE acting as a primary substrate in microbial metabolism, and that this process may contribute to the natural attenuation of DCE even under circumstances where aerobic cometabolism is not favored.

3.6.3 Importance of Chlorinated Ethene Degradation under Oxic Conditions

In the unusual event that VC is directly released to oxic aquifers, as reported at polyvinyl chloride (PVC) manufacturing sites (Hartmans, 1995), aerobic mineralization of VC by aquifer microorganisms may be significant. For the majority of sites, however, the presence of DCE and VC in groundwater is associated with reductive dechlorination of PCE and TCE under reducing conditions. Thus, under non-engineered conditions, oxygen-based biodegradation of chlorinated ethenes in groundwater may be limited to the periphery of the contaminant plume where dissolved oxygen has not been eliminated by microbial respiration (Bradley et al., 1998b; Erwin et al., 2005; Sorenson et al., 2000). Because existing natural attenuation protocols infer the importance of oxygen-based contaminant biodegradation from *in situ* dissolved oxygen concentrations and not from a quantitative assessment of the flux of dissolved oxygen, however, oxygen-based chlorinated ethene biodegradation under nominally anoxic (i.e., dissolved oxygen concentrations below the field oxygen standard) conditions is poorly understood and, considering the environmental implications of a potentially substantial but unrecognized contaminant degradation mechanism, merits further investigation (Gossett, 2010). Microbial mineralization of DCE and VC under oxic conditions can be substantial at the interface of groundwater and surface water systems (Bradley and Chapelle, 1998a, 1998b).

3.6.4 Conclusions for Chlorinated Ethene Mineralization under Oxic Conditions

For practitioners, several important conclusions can be inferred from the research on microbial degradation of chlorinated ethenes under oxic conditions.

- A number of organisms have been shown to be capable of aerobic cometabolism of chlorinated ethenes, using a variety of cosubstrates.
- These mechanisms may be of value in natural attenuation of some dissolved-phase plumes, particularly those with low contaminant concentrations and low levels of potential metabolites such as aromatic hydrocarbons.
- Unfortunately, the limitations of these organisms (need for biodegradable cometabolites in the presence of oxygen, toxicity from byproducts of cometabolite biodegradation, and competitive inhibition by the cometabolites) undermine the utility of this process at most sites.
- An increasing number of organisms have been shown to be capable of oxic mineralization of some chlorinated ethenes (VC and *cis*-DCE) as primary substrates.
- Oxic mineralization may contribute substantially to natural attenuation of chlorinated ethenes at the oxic periphery of plumes and at the points of discharge to oxic surface waters.

3.7 MICROBIAL MINERALIZATION OF CHLORINATED ETHENES UNDER ANOXIC CONDITIONS

3.7.1 A Practical Definition of Anoxic Field Conditions

Historically, anaerobic microbiology has focused on the microorganisms and associated metabolic pathways that operate in the strict absence of oxygen. Consequently, most investigations in the area of anaerobic microbiology have been conducted under highly reducing conditions to ensure the strict absence of oxygen. From a practical remediation assessment point of view, if a study site is in fact predominated by highly reducing conditions, then laboratory experimental procedures that establish such conditions are appropriate when assessing the potential for *in situ* contaminant biodegradation. However, if the site evaluation indicates that dissolved oxygen concentrations are below the field standard for oxic conditions, but ongoing nitrate-reduction, manganese-reduction, and/or iron-reduction indicate relatively oxidized redox conditions remain, then the biodegradation assessment approach must address the degradation potential associated with these relatively oxidized electron acceptors. In this context, the experimental approach should approximate the *in situ* conditions as closely as possible, in order to accurately assess the full suite of relevant contaminant degradation processes and their associated rates. By ensuring that dissolved oxygen concentrations are below the field detection standard while preserving the indigenous potential for nitrate-, manganese- and iron-reduction, the cumulative effect of reductive dechorination processes, anoxic mineralization processes, as well as the mineralization associated with sub-detection concentrations of dissolved oxygen ("microaerophilic" biodegradation) can be assessed. For this purpose, the definition of anoxic conditions must reflect the operant field standard for anoxic conditions, typically dissolved oxygen concentrations less than 0.1–0.5 mg/L.

3.7.2 Minimizing Experimental Artifacts

The risk associated with oxygen contamination of nominally "oxygen-free" systems is well known and a primary focus of traditional "anaerobic" microbiological methods. For many environmental contaminants, including DCE and VC, rates of biodegradation can be orders of magnitude greater in the presence of oxygen than in its absence. Moreover, oxygen-based processes are more likely to result in complete degradation to innocuous mineralization products like CO_2, whereas biodegradation under highly reducing conditions may lead to accumulation of toxic intermediates. In general, the presence of oxygen under ostensibly "oxygen-free" conditions can lead to an overestimation of the potential for *in situ* bioremediation and an unacceptable underestimation of the environmental risk associated with groundwater and surface-water contaminants.

Because of the well-known biases associated with oxygen contamination, many efforts to assess microbial activity under nominally anoxic field conditions alter the redox character of the experimental environment to the extent that the presence of oxygen is unlikely in the extreme. Common alterations include the preparation of experimental cultures and microcosms in anaerobic chambers that contain a reducing atmosphere (i.e., hydrogen up to 5% by volume), the use of organic and/or inorganic reductants (e.g., sulfide, cysteine, dithiothreitol, titanium citrate) to promote reducing conditions, and the strict use of the Hungate technique for media preparation and culture manipulation. To visually confirm reducing conditions, redox indicators like resazurin (changes color from pink to clear below -110 millivolts [mV]) are often added to the culture medium. The use of such strict anaerobic techniques has been fundamental to the study of reductive dechlorination processes, development of stable dechlorinating consortia and pure cultures, ongoing characterization of *Dehalococcoides* biology, and field applications where native or bioaugmented *Dehalococcoides* bacteria have been used to detoxify chlorinated ethene contamination.

However, such strict anaerobic techniques have impacts beyond the establishment of oxygen-free conditions. Hydrogen that is present in the "anaerobic mixed gases" used in glove boxes, is a powerful reductant and an excellent electron donor for many microbially-mediated terminal electron accepting processes, including respiratory reductive dechlorination (chlororespiration). In addition to the intended elimination of oxygen, incorporation of organic (e.g., cysteine, dithiothreitol or titanium citrate) and/or inorganic (e.g., sulfide) reductants can deplete the pool of relatively oxidized anoxic terminal electron acceptors such as Fe(III). Although the redox indicator resazurin is useful to visualize strongly reducing conditions, it is not an appropriate indicator for relatively oxidized, anoxic redox conditions.

If the potential for contaminant biodegradation under the entire range of anoxic terminal electron accepting conditions is to be investigated, then the use of highly reducing "anaerobic" techniques introduces an unacceptable, but poorly recognized, experimental artifact. Such conditions are likely to inhibit or even prohibit the contribution of a number of terminal electron accepting processes like nitrate-, manganese-, and iron-reduction, which occur in anoxic but relatively oxidizing environments. Indeed, the predominance in anaerobic microbiology of procedures that establish highly reducing conditions introduces enrichment biases against microorganisms that prefer or require more oxidizing redox conditions and may have contributed to the relatively late isolation of Mn(IV)- and Fe(III)-reducing organisms. Thus, when assessing the quantitative importance of microbial mineralization processes that may occur under field conditions where dissolved oxygen concentrations are below the field standard, it is critical that laboratory investigations include relatively oxidizing, anoxic redox conditions.

3.7.3 Evidence for Chlorinated Ethene Mineralization under Anoxic Conditions

The potential for mineralization of chlorinated ethene contaminants in the absence of detectable oxygen was first reported by Vogel and McCarty (1985) for a continuous flow, fixed-film, mixed methanogenic bioreactor amended with [1,2-^{14}C] PCE and acetate (Vogel and McCarty, 1985). Under these conditions, [1,2-^{14}C] PCE was transformed primarily to [1,2-^{14}C] TCE with lesser quantities of [1,2-^{14}C] *cis*-DCE and [1,2-^{14}C] VC. Approximately 24% of the [1,2-^{14}C] PCE radiolabel was recovered as $^{14}CO_2$ after four days under steady state flow conditions. The fact that addition of unlabeled VC lowered the recovery of $^{14}CO_2$ by 50% led the authors to hypothesize that [1,2-^{14}C] PCE degradation involved sequential reduction to [1,2-^{14}C] TCE, [1,2-^{14}C] *cis*-DCE and [1,2-^{14}C] VC followed by oxidation of [1,2-^{14}C] VC to $^{14}CO_2$ (Vogel and McCarty, 1985). Similar results were reported for a lactate-fed, mixed dechlorinating/methanogenic bioreactor (Adamson and Parkin, 2001). Approximately 8% of the initial [1,2-^{14}C] PCE radiolabel was recovered as $^{14}CO_2$, while the remainder was transformed to ^{14}C-TCE, ^{14}C-*cis*-DCE, ^{14}C-VC and ^{14}C-ethene (Adamson and Parkin, 2001).

Bradley and Chapelle (1996) used shallow aquifer sediments characterized by visible iron staining and predominately iron-reducing redox conditions in order to investigate the potential for mineralization of VC in the absence of detectable dissolved oxygen. Initial efforts to prepare nominally anoxic sediment microcosms using chemical reductants resulted in highly-reducing sulfidogenic conditions, termination of iron reduction and immediate concerns that such an approach significantly altered the microbial ecology, pathways and products of contaminant degradation that may be important under field conditions. Subsequently, microcosms were prepared by purging oxygen to below detection (the analytical detection limit for oxygen in these studies was 10 micromolar (μM) in the headspace, less than 0.01 mg/L dissolved oxygen), pre-incubating microcosms for 1-5 days to allow biological and/or chemical oxygen consumption to further deplete residual oxygen prior to the addition of ^{14}C-substrates, but avoiding further changes to the sediment redox environment.

Under these conditions, Fe(III)-reduction predominated and mineralization of [1,2-^{14}C] VC to $^{14}CO_2$ was observed. This observation raised the possibility that anoxic microbial mineralization of VC may be an environmentally relevant mechanism and indicated that the potential for this process should be assessed under relatively oxidized, anoxic conditions (Bradley and Chapelle, 1996; Bradley et al., 1998b). Addition of Fe(III) to these anoxic aquifer microcosms resulted in VC mineralization rates comparable to those observed under oxic conditions. These results indicated that VC could be mineralized under nominally anoxic, demonstrably Fe(III)-reducing conditions and suggested a potential anoxic alternative to the reduction of VC to ethene (Bradley and Chapelle, 1996). Subsequent investigation indicated that DCE also is susceptible to net microbial oxidation under anoxic conditions (Bradley et al., 1998c).

The possibility that environmental microorganisms can mineralize DCE and VC under nominally anoxic conditions has important implications for natural attenuation of chlorinated ethene contaminants in groundwater systems. In anoxic aquifers, highly oxidized chlorinated ethenes like PCE and TCE can be readily transformed to DCE and VC, which are susceptible to microbial mineralization under anoxic redox conditions. Thus, the combination of reductive dechlorination of PCE and TCE under anoxic conditions followed by microbial mineralization of DCE and VC provides a possible microbial pathway for complete degradation of chlorinated ethene contaminants in groundwater systems. Because microbial mineralization of DCE or VC in the absence of detectable dissolved oxygen yields CO_2 rather than a unique product directly attributable to chlorinated ethene degradation (for example, ethene in the case of complete chlorinated ethene reductive dechlorination), the combination of reductive dechlorination of PCE and TCE followed by anoxic mineralization of DCE, VC, ethene or ethane represents an alternative explanation for the common phenomenon of significant DCE and VC production but insignificant accumulation of ethene and ethane in anoxic, chlorinated ethene contaminated groundwater systems.

3.7.4 Mechanisms for Chlorinated Ethene Mineralization under Anoxic Conditions

Identification and clarification of the mechanisms underlying anoxic microbial mineralization of chlorinated ethene compounds have been hindered by the current lack of pure cultures or even defined mixed cultures capable of net mineralization of DCE or VC to CO_2. The evidence gathered thus far suggests that microbial mineralization of chlorinated ethenes in the absence of detectable oxygen generally involves a syntrophic relationship between chlorinated ethene-transforming microorganisms and various respiratory microorganisms capable of mineralizing the transformation products to CO_2 or CO_2 and methane (CH_4) (Bradley and Chapelle, 2000b). A number of mechanisms for the net mineralization of chlorinated ethene compounds by microorganisms under nominally anoxic conditions have been envisioned: (1) net oxidation with chloroethanol as intermediate (Vogel and McCarty, 1985), (2) syntrophic oxidation with acetate as an intermediate (Bradley and Chapelle, 1999a, 1999b, 2000b), (3) syntrophic oxidation with ethene as an intermediate (Bradley and Chapelle, 2002), (4) microaerophilic mineralization at sub-detection dissolved oxygen concentrations (Gossett, 2010) and (5) mineralization associated with abiotic processes that are inhibited by sterilization and erroneously attributed to biological activity.

Vogel and McCarty (1985) hypothesized that microbial oxidation of VC may involve a hydration reaction to yield chloroethanol which would then be oxidized to aldehyde and ultimately mineralized to CO_2 and perhaps CH_4 (Vogel and McCarty, 1985). However, none of the postulated intermediates have been confirmed (Vogel and McCarty, 1985). Direct evidence has been reported for net mineralization of VC to CO_2 via acetate (Bradley and Chapelle, 1999a, 1999b, 2000b) or ethene (Bradley and Chapelle, 2002) under anoxic laboratory conditions. Because the underlying mechanism for acetogenic fermentation of VC has not yet been clarified, the mechanism proposed by Vogel and McCarty (1985), in which VC is hydrated to chloroethanol, cannot be ruled out. Microbial fermentation of simple and substituted alcohols to acetate is well known (Buschhorn et al., 1989; Eichler and Schink, 1984; Emde and Schink, 1987; Schink, 1984; Schink, 1994). Alternatively, VC may be reductively dechlorinated to ethene, followed by mineralization of ethene to CO_2, as has been reported under SO_4-reducing conditions (Bradley and Chapelle, 2002).

The studies that have reported significant mineralization of chlorinated ethenes in the absence of detectable dissolved oxygen have, in general, emphasized the purging of dissolved oxygen below detection limits (0.01 mg/L dissolved oxygen) rather than the establishment of highly reducing (and by implication anoxic) conditions. As a result, the possibility remains that the observed mineralization of DCE and VC is associated with oxygen at concentrations below the analytical detection limit. The primary drawbacks to this interpretation are the facts that (1) for many of these studies the incorporation of container controls in the experimental design verified that ongoing oxygen contamination was not an issue (e.g., Bradley and Chapelle, 2007) and (2) the study sediments typically contained significant concentrations of organic carbon (e.g., Bradley and Chapelle, 2007). Thus, even making the unrealistic assumptions that (1) oxygen was consumed solely by chlorinated ethene mineralization processes and not by metabolism of the 0.2–10% (by dry weight) organic matter associated with the sediment solids, (2) oxygen was present in the microcosms at the analytical limit of detection (0.01 mg/L dissolved oxygen) and (3) only two moles of molecular oxygen were required per mole of [1,2-^{14}C] DCE or VC mineralized, the maximum amount of the [1,2-^{14}C] DCE or VC mineralization to $^{14}CO_2$ that could be attributed to aerobic metabolism was estimated to not exceed 5% of the theoretical requirement. The fact that recoveries of $^{14}CO_2$ from [1,2-^{14}C] VC have been observed repeatedly in the range of 20–100% of theoretical under Mn(IV)- and Fe(III)-reducing conditions suggests that the mineralization of chlorinated ethene observed in these studies in the absence of detectable oxygen was not due solely to sub-detection oxygen. However, because recent evidence (Gossett, 2010) indicates that oxygen-based microbial degradation of VC and, potentially, DCE can be significant at dissolved oxygen concentrations (0.01-0.02 mg/L) that are well below the 0.1-0.5 mg/L field standard for nominally anoxic conditions, the potential for significant oxygen-based mineralization at dissolved oxygen concentrations below 0.01 mg/L cannot be ruled out.

The possible contribution of abiotic processes to the reported mineralization of chlorinated ethenes in the absence of detectable oxygen is less easily evaluated. As noted earlier, for the majority of published biodegradation assessments (and all of the studies by Bradley and others), the activity attributed to biodegradation is inferred from the difference in the activity between viable treatments and autoclaved control treatments. Because exposure to the high temperature and pressure associated with autoclaving can significantly alter the geochemical and physical character of the sediment environment, the possibility remains that potentially important abiotic degradation mechanisms may be inhibited by this “sterilization” procedure. The net effect of this possible “sterilization” artifact would be erroneous attribution of the observed degradation to biodegradation and potentially significant underestimation of the contribution of abiotic degradation processes.

3.7.5 Conclusions for Chlorinated Ethene Mineralization under Anoxic Conditions

For practitioners, several important conclusions can be inferred from the research on microbial mineralization of chlorinated ethenes when dissolved oxygen concentrations are below the field standard for oxic conditions.

- At present, there is no evidence that PCE or TCE are susceptible to microbial mineralization in the absence of detectable oxygen. Thus, reductive dechlorination appears to be the primary mechanism for *in situ* biotransformation of these chlorinated ethene parent compounds under anoxic conditions.
- DCE and VC are susceptible to microbial mineralization in the absence of detectable oxygen. The potential for anoxic mineralization is higher for VC than DCE and increases with increasingly oxidizing groundwater conditions.
- In combination with reductive dechlorination, microbial mineralization in the absence of detectable oxygen provides a mechanism for complete degradation of chlorinated ethene contaminants without the stoichiometric accumulation of reductive dechlorination daughter products.

3.8 PRODUCT ACCUMULATION AS AN INDICATOR OF *IN SITU* BIODEGRADATION

Evaluating chlorinated ethene natural attenuation processes under field conditions usually involves some variation of four lines of evidence (USEPA, 1997; Wiedemeier et al., 1998). The first, and arguably most important, line of evidence for contaminant attenuation is a quantitative decrease in the concentration of the original contaminants over time and/or space. However, contaminant concentration decreases are the sum of many processes and not necessarily indicative of biodegradation. For this reason, production and accumulation of diagnostic, process-specific daughter products has been widely used as evidence of biodegradation (for review see Bradley, 2003). The existence of conditions conducive to chlorinated ethene degradation (e.g., favorable redox conditions, suitable dissolved H_2 concentrations and presence of degradative microbial communities) may help establish the potential for specific degradation processes, but does not demonstrate occurrence. Laboratory assessments of sediment-specific degradation processes are often viewed as optional due to the analytical requirements, the associated costs and the perceived duplication of evidence provided by the *in situ* production and accumulation of process-specific degradation products (Table 3.2).

Table 3.2. Lines of Evidence for Attenuation and Degradation of Chloroethene Contaminants in Groundwater (from Bradley and Chapelle, 2007)

Line of Evidence	Comment
Decrease in the concentration of parent contaminant over time or along the groundwater flowpath	Essential demonstration of contaminant attenuation
Production and accumulation of diagnostic, process-specific degradation products along groundwater flowpath	Evidence of degradation process
In situ existence of conditions conducive to recognized degradation processes	Establishes potential for degradation process, not occurrence
Laboratory microcosm assessment of degradation processes in indigenous groundwater and sediment	Often considered optional due to perceived redundancy

Reliance on daughter product accumulation to document degradation, however, makes two crucial assumptions. First, reductive dechlorination is assumed to be the principal process contributing to degradation. Second, the products of degradation are assumed to be diagnostic and, more importantly, conservative under *in situ* conditions.

The *in situ* occurrence of the chlorinated daughter products (DCE and VC) and accumulation of the nonchlorinated products (ethene and ethane) are diagnostic of microbial reductive dechlorination. However, field and laboratory evidence indicate that these compounds are not conservative and that their degradation products are not necessarily diagnostic (for review see Bradley, 2003; Wiedemeier et al., 1999). Assuming that ethene and ethane are conservative under anoxic conditions would seem particularly untenable, because both compounds are common in the environment (ethene is a ubiquitous plant hormone and ethane is present in the atmosphere at part per billion by volume [ppbv] concentrations) and, thus, the existence of significant environmental degradation mechanisms is reasonable. The well-known reduction of ethene to ethane under methanogenic conditions (Koene-Cottaar and Schraa, 1998) is clear evidence that ethene, at least, is nonconservative under anoxic conditions. Hence, a lack of ethene accumulation under anoxic conditions may reflect (1) insignificant reductive dechlorination of VC, or (2) an environmental degradation mechanism such as anoxic mineralization of ethene to the nondiagnostic product CO_2 (Bradley and Chapelle, 2002; Bradley, 2003).

Among the potential products of chlorinated ethene mineralization (CO_2, CH_4 and chloride (Cl^-) ion) (Bradley and Chapelle, 1996, 1999a; Bradley, 2003; Vogel and McCarty, 1985), only the accumulation of Cl^- ion above background concentrations can be convincingly attributed to chlorinated ethene degradation (Bradley, 2003). CO_2 and CH_4 are common microbial products. In contrast, increasing concentrations of dissolved Cl^- along the flowpath of a chlorinated ethene plume can provide compelling, quantitative evidence of contaminant dechlorination independent of the underlying degradation mechanism (Wiedemeier et al., 1999). However, the practical utility of Cl^- accumulation is often limited by high background Cl^- concentrations that can mask the Cl^- released during dechlorination. Thus, accumulation of ethene, ethane or chlorinated daughter products can provide compelling evidence for *in situ* reductive dechlorination of chlorinated ethenes, but this accumulation does not necessarily reflect total chlorinated ethene degradation.

In fact, field evidence from sites where background Cl^- concentrations are low enough to evaluate in-plume Cl^- accumulation suggests that the apparent extent of chlorinated ethene biodegradation that can be inferred from the accumulation of ethene, ethane and chlorinated daughter products significantly underestimates total chlorinated ethene degradation (Chapelle and Bradley, 1998; Ferrey and Wilson, 2002; Ferrey et al., 2004; Chapelle et al., 2005; Wiedemeier et al., 1999). For example, in a study of 17 chlorinated ethene-contaminated groundwater sites, Wiedemeier et al. (1999) reported that the production and accumulation of Cl^- along the contaminant flowpath greatly exceeded the total accumulation of ethene, ethane and chlorinated daughter products. Based on these observations, Wiedemeier et al. (1999) concluded that: (1) much more chlorinated ethene degradation occurred at these sites than was apparent in the cumulative concentrations of ethene, ethane or chlorinated daughter products, (2) degradation processes other than reductive dechlorination contributed to the disparity between Cl^- ion accumulation and the accumulation of ethene, ethane and chlorinated daughter products and (3) ethene and ethane were not conservative indicators of *in situ* chlorinated ethene degradation.

Laboratory evidence also indicates that the accumulation of ethene, ethane and chlorinated daughter products substantially underestimates total chlorinated ethene biodegradation. Over the last several years, the Toxic Substances Hydrology Program of the U.S. Geological Survey has investigated the anoxic (non-detectable dissolved oxygen) biodegradation of chlorinated ethene contaminants in aquifer and surface water sediment systems throughout the United States (Bradley and Chapelle, 2007). These investigations used ^{14}C-substrates ([1,2-^{14}C] TCE, [1,2-^{14}C] DCE, or [1,2-^{14}C] VC) and radiometric detection gas chromatography to separate and quantify ^{14}C-products (Bradley and Chapelle, 1999a, 1999b, 2000, 2002; Bradley et al., 2001a, 2001b). This approach allowed a quantitative comparison of the accumulation of both diagnostic reductive degradation products (ethene, ethane and chlorinated daughter products) and nondiagnostic mineralization products (CO_2 and CH_4). A total of 27 sediments (12 aquifer sediments and 15 surface water sediments) from 11 sites throughout the United States were examined.

The only ^{14}C-products of chlorinated ethene biodegradation that accumulated were those associated with reductive dechlorination (^{14}C-ethene, ^{14}C-ethane and the ^{14}C-radiolabled, chlorinated daughter products, ^{14}C-DCE and ^{14}C-VC) or with net mineralization ($^{14}CO_2$ and $^{14}CH_4$). The distribution of chlorinated ethene biodegradation products varied between two extremes, with some sediments producing predominantly reductive products and others yielding predominantly mineralization products (Figure 3.3). Results from control microcosms indicated that the chlorinated ethene degradation observed in these studies was due to biological activity. Of the 48 sediment and ^{14}C-substrate combinations examined, 73% (35 of 48) of the treatments demonstrated 10% or greater loss of ^{14}C-substrate during the study periods. Of these, all five of the [1,2-^{14}C] TCE treatments demonstrated only accumulation of ethene, ethane or chlorinated daughter products. In contrast, of the 30 active treatments containing [1,2-^{14}C] DCE (11 treatments) or [1,2-^{14}C] VC (19 treatments), roughly half (seven [1,2-^{14}C] DCE treatments and nine [1,2-^{14}C] VC treatments) showed only net mineralization products ($^{14}CO_2$ and $^{14}CH_4$) and no significant accumulation of ethene, ethane or chlorinated daughter products. These results indicate that, while the accumulation of ethene, ethane and the chlorinated daughter products may provide a relatively accurate indication of chlorinated ethene biodegradation when TCE and, perhaps, PCE are the predominant chlorinated ethene contaminants, the accumulation of these compounds is a poor indicator of total biodegradation when DCE and/or VC predominate (Bradley and Chapelle, 2007).

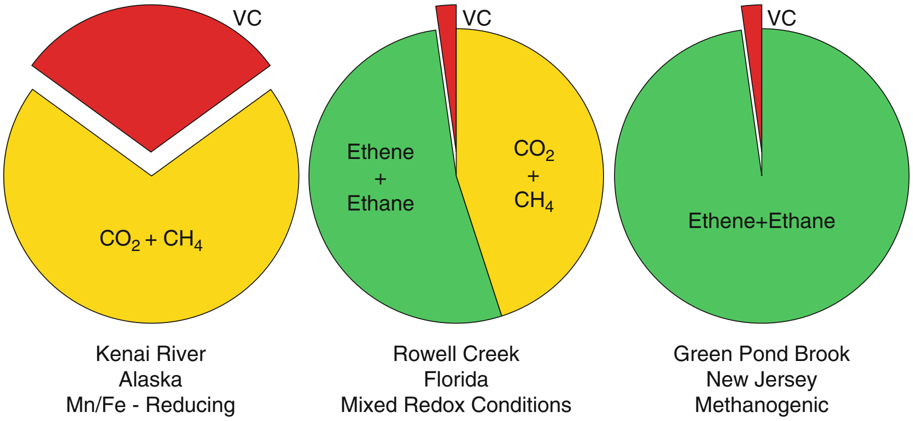


Figure 3.3. Example final distributions of reductive dechlorination (ethene + ethane) and mineralization (CO_2 + CH_4) products observed in microcosms containing surface water and sediment, amended with [1,2-^{14}C] VC. From Bradley and Chapelle, 2007.

These laboratory results are consistent with the survey of field results reported by Wiedemeier et al. (1999) and indicate that the *in situ* accumulation of the diagnostic degradation products (ethene, ethane and the chlorinated daughter compounds) can significantly underestimate the extent of *in situ* reductive dechlorination as well as the total chlorothene biodegradation that occurs in chlorinated ethene contaminated systems. These results (Adamson and

Parkin, 2001; Bradley and Chapelle, 1996, 1998b, 1999a, 2002, 2007; Bradley, 2003; Hata et al., 2003; Vogel and McCarty, 1985; Wiedemeier et al., 1999) argue compellingly that ethene, ethane, DCE and VC are more appropriately viewed as intermediate products with a significant potential to degrade to innocuous final products. The accumulation of intermediate products depends on a balance between production and consumption and is not a reliable indicator of total chlorinated ethene degradation.

3.9 FINAL CONCLUSIONS

Chlorinated ethenes are subject to a variety of microbial degradation processes that include cometabolic reductive dechlorination, chlororespiration, aerobic cometabolism and aerobic oxidation as a primary substrate, as well as fermentation and mineralization under nominally anoxic conditions. Although our present understanding of chlorinated ethene biodegradation is far from complete, several conclusions may reasonably be drawn from the research to date:

- Under demonstrably oxic conditions ($[O_2]_{\text{dissolved}} > 1$ mg/L), highly chlorinated ethenes such as PCE and TCE are relatively stable and will tend to accumulate in the environment. However, the potential for aerobic cometabolism of TCE can be significant if a supply of co-substrate exists *in situ*.
- Under oxic conditions ($[O_2]_{\text{dissolved}} > 1$ mg/L), less chlorinated ethenes such as DCE and VC are susceptible to microbial mineralization to CO_2. Little or no accumulation of reduced intermediates may occur.
- Under highly-reducing, anoxic conditions (e.g., sulfate-reducing or methanogenic environments), reductive dechlorination pathways tend to predominate, leading to the accumulation of ethene, ethane and chlorinated daughter products.
- In environments where dissolved oxygen concentrations are below the practical field detection limit but the relatively oxidized, anoxic terminal electron accepting processes are evident (Mn(IV)-reducing and Fe(III)-reducing environments), net mineralization may be a significant mechanism for *in situ* DCE and VC degradation and may alter the final distribution of degradation products.
- Net mineralization of DCE and VC in environments where dissolved oxygen is below the practical field detection limit may result from: (1) strict anoxic mineralization, (2) oxygen-based mineralization at sub-detection oxygen concentrations and/or (3) abiotic mechanisms that are inhibited by autoclaving and erroneously attributed to biodegradation.
- Because the biodegradation of DCE and VC to non-specific mineralization products such as CO_2 and CH_4 may be substantial, relying on the accumulation of the daughter products associated with reductive dechlorination may greatly underestimate overall biodegradation.

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CHAPTER 4

ABIOTIC PROCESSES AFFECTING THE REMEDIATION OF CHLORINATED SOLVENTS

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4.1 INTRODUCTION

Abiotic processes, such as sorption, volatilization and chemical transformation, play an important role in the natural attenuation and treatment of chlorinated solvents. In this chapter, an overview of the principles governing these processes in the context of chlorinated solvent remediation and treatment is presented. This discussion includes a brief introduction to sorption processes and volatilization, with most attention focused on abiotic transformation pathways because of the recent advances in this area and the increasing interest in applying monitored natural attenuation (MNA) to chlorinated solvent plumes. The chapter is not meant to be a comprehensive review of the literature, but rather highlights basic information on key abiotic processes that may impact remedial technology implementability.

4.2 SORPTION PROCESSES

Both the mobility and bioavailability of chlorinated solvents can be significantly influenced by sorption onto aquifer solids. The term sorption does not imply a particular mechanism of removal, but rather broadly describes the partitioning of a chemical from aqueous solution onto or into a solid phase (Stumm, 1992). Sorption of chlorinated solvents can occur onto mineral phases or organic carbon materials present in the aquifer solids (Pankow et al., 1994). The degree of sorption is controlled mostly by properties of the chlorinated solvent (e.g., solubility and polarity) and the aquifer material (e.g., organic carbon and clay-fraction contents), and to a lesser extent by the geochemical conditions of the aquifer (i.e., pH, temperature, ionic strength, and other dissolved chemicals). As a result of sorption processes, chlorinated solvents often move more slowly than groundwater, a process referred to as retardation (Fetter, 1999).

4.2.1 A*b*sorption versus A*d*sorption

For chlorinated solvents (as for most hydrophobic organic compounds) there are thought to be two primary mechanisms of sorption: absorption and adsorption (Stumm, 1992). As discussed in Chapter 2, chlorinated solvents are moderately hydrophobic with $\log K_{ow}$ values ranging from about 1 to 3. The hydrophobic nature (i.e., tendency to not be in water) of most organic contaminants results in a physical partitioning out of water into sediment organic

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matter via absorptive partitioning that is three-dimensional in nature. Sorption onto minerals or other solid materials present in aquifer solids, on the other hand, occurs via an electrostatic or chemical surface adsorption reaction that is considered more of a two-dimensional process (Weber and DiGiano, 1996).

Absorptive partitioning has historically been considered the dominant mechanism for sorption of hydrophobic organic compounds in aquifers containing a significant fraction of organic carbon (fraction of organic carbon, $f_{oc} > 0.001$) (Schwarzenbach and Westall, 1981; Chiou et al., 1983). Surface adsorption to minerals was considered to be significant only in low carbon, high clay aquifers (Karickhoff, 1984). Direct evidence for sorption of organic compounds onto minerals (Perlinger et al., 1993; Mader et al., 1997), however, coupled with studies that were observing more sorption than expected based on absorptive partitioning, led to more recognition of the importance of surface adsorption processes (Mackay et al., 1986a).

In addition to adsorption onto minerals, the role of different types of organic matter has also become more evident. Organic matter in sediments can range from fresh materials containing low carbon and high hydrogen and oxygen contents (i.e., the so-called *soft* carbon, such as peat), or more processed material with high carbon and low hydrogen and oxygen contents (i.e., the so-called *hard* carbon, such as coal and kerogen). Adsorption to the more polymerized soil carbon is now recognized to be a significant sorption mechanism for many organic compounds, including chlorinated solvents (Grathwohl, 1990; Ball and Roberts, 1991; Weber et al., 1992; Jeong and Werth, 2005). The increasing evidence for adsorption to both minerals and polymerized organic carbon has led to a more complete view of sorption including the following mechanisms: (1) absorptive partitioning into *soft* C, (2) adsorption to polymerized *hard* C and (3) adsorption to minerals.

Several research groups have been actively engaged in developing models that incorporate both absorption and adsorption processes to describe chlorinated solvent sorption. For an insightful discussion and synthesis of the literature in this area the reader is referred to a recent review by Allen-King et al. (2002).

4.2.2 Measuring and Estimating Sorption

4.2.2.1 Sorption Isotherms

Sorption of chlorinated solvents is often estimated from batch and column experiments conducted in the laboratory, although a variety of field methods also have been developed (Pankow and Cherry, 1996). In laboratory batch experiments, sorption of trichloroethene (TCE) can be estimated by exposing aquifer solids to dissolved TCE, and measuring the initial and final concentration of TCE in the water after sufficient time for equilibration (C_o and C_W, milligrams per liter [mg/L]). It is important to note that kinetics of sorption can be slow and it can be difficult to conduct the long-term experiments required for equilibration to occur (Pignatello and Xing, 1996; Heyse et al., 2002).

The amount of TCE sorbed is then determined by subtracting the final concentration from the initial concentration based on the mass balance equation for TCE given below. C_S is the amount sorbed, typically in mass of TCE per mass of aquifer solid (milligrams per kilogram [mg/kg]), M is the mass of the solid (kg), and V is the volume of water (L). This assumes that the volume does not change significantly during the sorption experiment. If the final concentration of TCE is measured before reaching equilibrium, the equilibrium partitioning of TCE onto the aquifer material will be underestimated.

$$C_oV = C_WV + C_SM \tag{Eq. 4.1}$$

$$C_S = (C_oV - C_WV)/M \tag{Eq. 4.2}$$

These measurements can be done over a range of dissolved TCE concentrations, and a plot of C_S versus C_W is referred to as a sorption isotherm ("isotherm" indicates that the sorption measurements are collected at a constant temperature).

Figure 4.1 shows two of the more common isotherm models used to describe sorption of chlorinated solvents: linear and Freundlich. Both are equilibrium models, and assume the kinetics of sorption are fast relative to the time scale of the experiment. The linear model is convenient in that a single partition coefficient, K_d (L/kg), derived from the slope of the isotherm, can be used to estimate the amount of sorption. Sorption that is concentration-dependent (i.e., nonlinear sorption), however, has been observed by numerous researcher groups (Allen-King et al., 1996; Xing and Pignatello, 1997; Chiou and Kile, 1998). The nonlinearity is typically described using a Freundlich isotherm with $n < 1$ which captures the decreasing sorption with increasing concentration. At low chlorinated solvent concentrations, however, the Freundlich is approximately linear, and a K_d can be estimated from the linear segment.

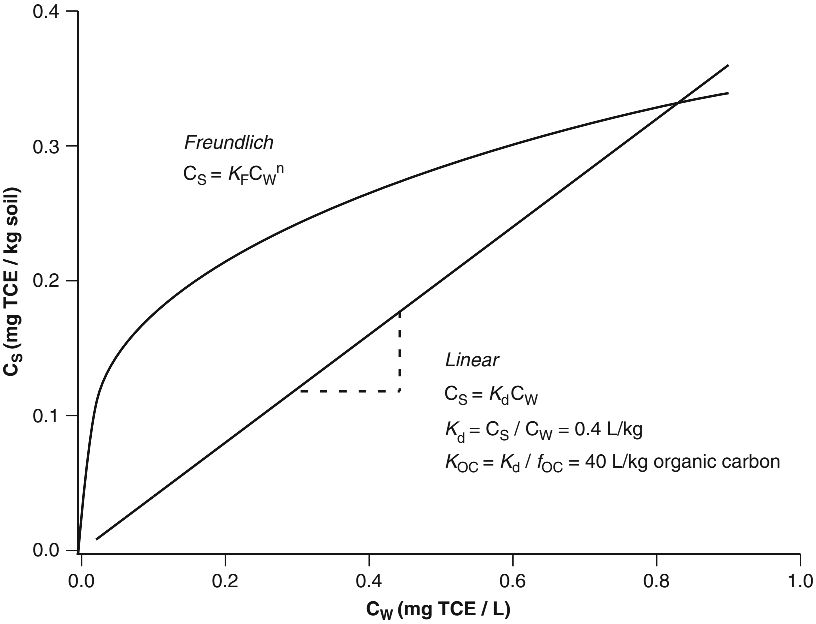


Figure 4.1. Illustration of a linear and nonlinear (Freundlich) sorption isotherm and the corresponding equations. An f_{OC} of 0.01 was used to estimate K_{OC}. The third common isotherm, a Langmuir isotherm, is not shown because a Langmuir pattern with surface site saturation is not typically observed for sorption of chlorinated solvents.

4.2.2.2 K_{ow}-K_{oc}-f_{oc} Paradigm

K_d values measured from a variety of solids and organic compounds have been shown to increase linearly with higher fractions of organic carbon in the solid phase (i.e., $K_d \propto f_{OC}$)

(Schwarzenbach and Westall, 1981; Karickhoff, 1984). These observations have led to the common practice of estimating an organic carbon/water partitioning coefficient K_{OC} (L/kg-carbon) by dividing the K_d by f_{OC}.

$$K_{OC}=K_d/f_{OC} \quad \text{(Eq. 4.3)}$$

Measured K_d values, however, are often not available and methods for estimating K_{OC} values based on properties of the organic compound and aquifer material have been developed. Two properties of the organic compound commonly used to estimate K_{OC} values are K_{OW} and solubility. Solubility (S) tends to be a good predictor of partitioning between organic carbon and water because the less soluble the compound, the more hydrophobic the compound tends to be and the greater its tendency to partition out of water.

The most widely used method for estimating K_{OC} is based on one parameter linear free energy relationships (op-LFERs) developed from correlations between $\log K_{OC}$ and $\log K_{OW}$ that take the form of Equation 4.4 (e.g., Schwarzenbach and Westall, 1981; Karickhoff, 1984):

$$\log K_{OC}=a \log K_{OW}+b \quad \text{(Eq. 4.4)}$$

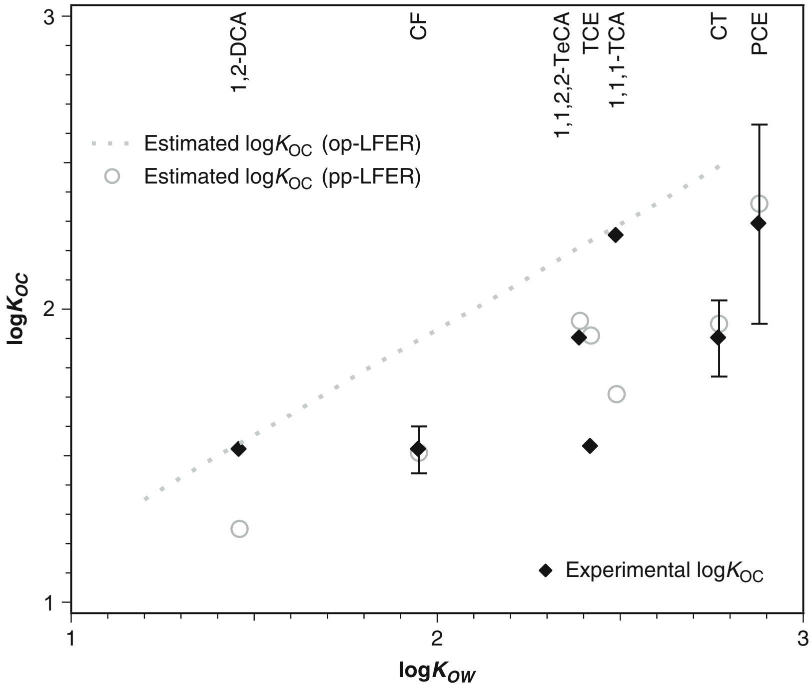


Figure 4.2. Experimental and estimated values of log organic carbon/water partitioning coefficients ($\log K_{OC}$) versus $\log K_{OW}$ values for selected chlorinated solvents. Diamond markers represent experimental values of $\log K_{OC}$ as summarized in Nguyen et al. (2005) plotted versus $\log K_{OW}$ values listed in Table 2.2. Estimated values are based on two example estimation methods reported in the literature. The most common method is a one-parameter LFER based on $\log K_{OW}$ values shown as a dashed line. The widely used one-parameter LFER (op-LFER) developed by Schwarzenbach and Westall in 1981 ($\log K_{OC} = 0.72 \log K_{OW} + 0.49$) is shown as a dashed line (Schwarzenbach and Westall, 1981). A more recent method based on polyparameter LFERs (pp-LFER) is shown in circles (Nguyen et al., 2005).

There are numerous types of these correlations available for many different sets of organic compounds and the reader is again referred to the review by Allen-King et al. for a compilation of correlations and *a* and *b* parameters (Allen-King et al., 2002, Table 3). The practice of predicting sorption behavior based on K_{OW} values and f_{OC} measurement has become so entrenched that it is often referred to as the "K_{OW}–K_{OC}–f_{OC} paradigm". An example calculation to estimate the K_d value for TCE is shown below using the LFER developed by Schwarzenbach and Westall (1981). Predicted K_d values for several other chlorinated solvents are shown as a dashed line in Figure 4.2.

As more studies have been done and more field data have been collected, it has become clear that this approach has some limitations, particularly when applied to compounds that tend to sorb via more adsorptive or site-specific interactions (Karickhoff, 1984; Allen-King et al., 1996; Chiou and Kile, 1998). For example, Figure 4.2 shows marked deviation from linearity for a plot of experimentally determined logK_{OC} values versus logK_{OW} values for nine chlorinated solvents taken from a recent critical review by Nguyen et al. (2005). For more non-polar chemicals, such as many polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), less deviation from linearity was observed in plots of logK_{OC} versus logK_{OW} suggesting that one-parameter LFERs are a reasonable approach for estimating K_{OC} values for these compounds (Nguyen et al., 2005).

Example 1: K_{OW}–K_{OC}–f_{OC} Paradigm
Estimating K_d for TCE

1. Measure or look up logK_{OW} for TCE.

   logK_{ow} = 2.53 (Mackay et al., 1993)

2. Estimate K_{OC} for TCE from a correlation with K_{OW}.

   $\log K_{OC} = a \log K_{OW} + b$

   $a = 0.72 \quad b = 0.49$ (Schwarzenbach and Westall, 1981)

   TCE logK_{OC} = 2.31

3. Measure or estimate organic carbon.

   $f_{OC} = 0.01$ (1% organic carbon (OC) content)

4. Calculate a K_d for TCE from $K_d = K_{OC}\, f_{OC}$

   $K_d = (10^{2.31}$ L/kg OC)(0.01 kg OC/kg solids) = **2.04 L/kg solids**

5. Incorporate K_d into transport equation such as advection dispersion equation (ADE) to predict contaminant retardation. For example, a linear retardation factor, which is the ratio of average linear velocity of the groundwater to that of TCE, can be estimated from:

   $\nu/\nu_{TCE} = R = 1 + \rho_b K_d / \theta_W$ (Pankow and Cherry, 1996)

   ρ_b = soil bulk density and θ_W = water-filled porosity

   R = 1 + (1.81 kg/L)(2.04 L/kg) / 0.33 = **12.1**

This implies that TCE will migrate in such an aquifer about **12** times slower than the groundwater. Note, however, there are some important simplifying assumptions in this estimate: (1) equilibrium, that is, rapid sorption kinetics compared to groundwater flow and reversible sorption; and (2) linear sorption, that is, C_S versus C_W is linear and therefore independent of concentration.

To address some of the limitations of the K_{OW}–K_{OC}–f_{OC} paradigm, polyparameter LFERs (pp-LFERs) have been developed that take into account multiple molecular interactions between organic compounds and water. For comparison, the logK_{OC} values predicted from a pp-LFER are also included in Figure 4.2. The pp-LFER predicts K_{OC} values that are closer to the experimental values for three compounds whose K_{OC} values were determined from multiple experimental measurements—chloroform, carbon tetrachloride and perchloroethene (CF, CT, and PCE, respectively). These results suggest that the pp-LFER may provide a more robust method than the traditional $\log K_{\mathrm{OC}}$–$\log K_{\mathrm{OW}}$ relationships typically used for estimating $\log K_{\mathrm{OC}}$ values for chlorinated solvents (Nguyen et al., 2005).

Another important limitation of the K_{d}–f_{OC} calculations illustrated in Figure 4.1 is that the K_{d} estimates are often much lower than those observed in the field. The greatest deviations appear to be associated with aquifers containing hard carbon materials, such as kerogen or coal, or in aquifers with low concentrations of contamination (Allen-King et al., 2002).

4.2.2.3 Effect of Sorption on Chlorinated Solvent Transport

The influence of sorption on the mobility of chlorinated solvents has been demonstrated numerous times, with perhaps the most famous demonstration being the Stanford-Waterloo experiment (Mackay et al., 1986b). As part of this experiment, PCE, CT and hexachloroethane (HCA) were injected into an unconfined sandy aquifer near the Canadian Forces Base Borden. Chlorinated solvent concentrations were monitored over time and compared to chloride and bromide tracers.

As expected, the PCE and CT plumes were retarded with respect to chloride and bromide. Also, as anticipated, PCE, which is more hydrophobic than CT, moved slower (Roberts et al., 1986). The average retardation factor observed in the Stanford-Waterloo experiment was 4.5 (Roberts et al., 1986), which is relatively low and consistent with the relatively low K_{OW} of these compounds. Retardation factors reported for chlorinated solvents are generally low, often below 10 (Pankow and Cherry, 1996). The measured retardation factors are higher than the values predicted using the K_{OW}–K_{OC}–f_{OC} paradigm outlined above, but are within a factor of two to five.

The plumes also displayed some unexpected behavior, including an increase in retardation factors over time and longer plume lengths than the chloride and bromide plumes (at the same distance). Over the last two decades, an extensive amount of research has focused on understanding and explaining the transport of PCE and CT in this aquifer, and the reader is referred to Allen-King et al. (2006) for recent insights on these plumes.

4.3 VOLATILIZATION PROCESSES

Volatilization is the process by which a chlorinated solvent is transferred into air from either water or a solid phase (Thomas, 1982b). This process influences the fate of chlorinated solvents because solvent vapors can exhibit different reactivities and rates of transport than species dissolved in water or sorbed to aquifer solids. Although chlorinated solvents are generally considered relatively volatile, several variables influence their mass transfer between water and air or solids and air. For example, chemical factors that impact the rate of chlorinated solvent partitioning between water and air include a compound's aqueous solubility (S), its vapor pressure ($p°$), its molecular diffusivities in air (D_{a}) and water (D_{w}), and its equilibrium air-water partitioning coefficient ($K_{\text{air-water}}$) (Thomas, 1982a). Environmental factors such as wind-speed and the degree of mixing in air and water will also contribute.

The following discussion of volatilization begins by examining the simple case of air-water partitioning at equilibrium, where the chlorinated solvent distribution between phases can be predicted using either Raoult's Law or Henry's Law. Next, the role that volatilization plays in subsurface contamination by chlorinated solvents, particularly the transport of chlorinated solvent vapor in the vadose zone, is discussed. Models for estimating the rate of chlorinated solvent volatilization will not be discussed, but the references by Thomas (1982a, 1982b) and

Schwarzenbach et al. (2003) provide detailed presentations of this topic. Treatment strategies (such as air sparging) that take advantage of the high volatility of chlorinated solvents for subsurface remediation are covered elsewhere in this monograph.

4.3.1 Air-Water Partitioning at Equilibrium

As discussed in Chapter 2 (see Figure 2.3), chlorinated solvents will partition between water, air and solids. The focus of this section is their partitioning between water and air in a two-phase system at equilibrium. For air in contact with an aqueous solution of chlorinated solvent, equilibrium is defined as the state in which there is no net rate of solvent transfer between air and water. Of primary interest is the concentration of the chlorinated solvent in air (expressed as a partial pressure with units such as atmospheres [atm]) relative to its concentration in water once equilibrium is established. For this scenario, two possible relationships can be used to describe air-water partitioning. As will be discussed, determining which relationship is most appropriate will depend upon the amount of the chlorinated solvent dissolved in water.

The first approach for describing air-water partitioning is Raoult's Law (Equation 4.5) which states that the equilibrium partial pressure of a chlorinated solvent (p_{RX}) is equal to the product of the mole fraction of the chlorinated solvent in the aqueous mixture (X_{RX}) and the vapor pressure of the chlorinated solvent ($p_{\mathrm{RX}}{}^{\mathrm{o}}$).

$$p_{\mathrm{RX}}=X_{\mathrm{RX}}\cdot p_{\mathrm{RX}}{}^{\mathrm{o}} \tag{Eq. 4.5}$$

In Equation 4.5, X_{RX} represents a measure of the aqueous-phase concentration of a chlorinated solvent. Values of X_{RX} are dimensionless and are defined as the number of moles of dissolved chlorinated solvent divided by the total number of moles present in the aqueous mixture. Values of $p_{\mathrm{RX}}{}^{\mathrm{o}}$, which represent the saturation concentration of a chlorinated solvent in air, are provided in Table 2.2. Thus, for air in contact with an aqueous chlorinated solvent mixture, the equilibrium gas-phase concentration of the solvent is proportional to its concentration in water, and the constant of proportionality for this relationship is the solvent's vapor pressure.

There are limitations to the application of Raoult's Law. Typically, it is only applied when the concentration of the chlorinated solvent in the aqueous mixture is very high (e.g., when X_{RX} approaches 1) or for non-aqueous mixtures in which all chemical components of the mixture possess similar chemical structures (e.g., a mixture of several chlorinated solvents) (Sawyer et al., 1994). When the dissolved chlorinated solvent is present at low concentration Raoult's Law fails, and an alternative approach is required.

In the case of dilute chlorinated solvent solutions, Henry's Law is used to describe equilibrium air-water partitioning. Similar to Raoult's Law, Henry's Law (Equation 4.6) also states that the equilibrium chlorinated solvent partial pressure above an aqueous solvent mixture is proportional to the chlorinated solvent's dissolved concentration.

$$p_{\mathrm{RX}}=K_{\mathrm{H}}{}'\cdot X_{\mathrm{RX}} \tag{Eq. 4.6}$$

Whereas the constant of proportionality in Raoult's Law is the vapor pressure of the chlorinated solvent, Henry's Law uses an alternative proportionality constant, $K_{\mathrm{H}}{}'$, referred to as the Henry's Law constant. The use of $K_{\mathrm{H}}{}'$ rather than $p_{\mathrm{RX}}{}^{\mathrm{o}}$ accounts for unfavorable energetic interactions that occur between the chlorinated solvent and water in relatively dilute solutions.

An important consideration in the application of Henry's Law is the units associated with the chlorinated solvent concentrations in air and water. In Equation 4.6, $K_{\mathrm{H}}{}'$ is expressed in units of pressure, as mole fractions are dimensionless. More commonly, however, Henry's Law constants are reported with the aqueous concentration of the chlorinated solvent ($C_{RX}(H_2O)$) expressed on a molar basis (e.g., moles of RX per L of H_2O), as shown in Equation 4.7.

$$K_H{}' = \frac{p_{RX}}{C_{RX}(H_2O)} \left(\text{units of } \frac{atm \cdot m^3}{mol}\right) \qquad \text{(Eq. 4.7)}$$

Another frequently used alternative is the dimensionless Henry's Law constant ($K_H{}^*$ in Equation 4.8) in which the concentrations of the chlorinated solvent in water and air *both* are expressed on a molar basis (e.g., moles of RX per L of water and moles of RX per L of air, respectively).

$$K_H^* = \frac{C_{RX}(\text{air})}{C_{RX}(H_2O)} \text{ (dimensionless)} \qquad \text{(Eq. 4.8)}$$

The dimensionless Henry's Law constant is important because it can be used to develop expressions for the relative amounts of a chlorinated solvent in a closed air-water system that are entirely dependent upon known system parameters (e.g., the volumes of air and water) and the value of $K_H{}^*$ (see text box for a sample calculation).

For chlorinated solvents, values of the Henry's Law constant can be reasonably approximated from the ratio of the chlorinated solvent vapor pressure ($p_{RX}{}^o$) to the aqueous solubility of the chlorinated solvent (S) (Schwarzenbach et al., 2003). These data are provided for chlorinated solvents in Table 2.2 of Chapter 2. Furthermore, a plot of $p_{RX}{}^o$ as a function of S using these data is shown in Figure 4.3, in which the diagonal dashed lines represent values of the Henry's Law constant. Note that as a result of the units associated with values of $p_{RX}{}^o$ and S in Table 2.2 in Chapter 2, the Henry's Law constants in Figure 4.3 have units of atmosphere·cubic meter per mole (atm·m^3/mol). Figure 4.3 illustrates that while both $p_{RX}{}^o$ and S generally increase

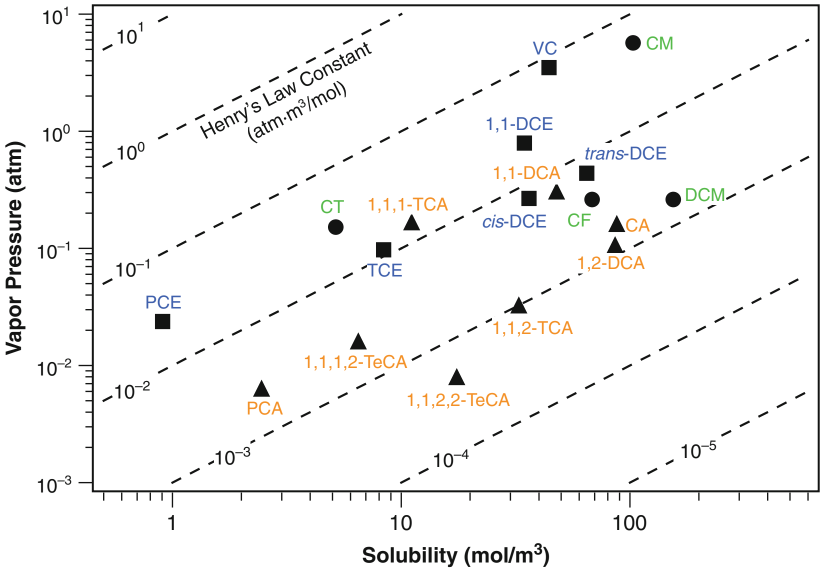


Figure 4.3. Plot of chlorinated solvent vapor pressures as a function of chlorinated solvent solubilities. Values for vapor pressure and solubility are provided in Table 2.2. Dashed lines indicate values of the Henry's Law constant (K_H with units of atm·m^3/mol). Data for chlorinated methanes are shown as circles, chlorinated ethanes as triangles, and chlorinated ethenes as squares. Adapted from Thomas, 1982a.

as the number of chlorine substituents on a solvent decreases, comparable trends in Henry's Law constants are not observed.

Several chemical and environmental variables can influence equilibrium partitioning of a chlorinated solvent in an air-water system. With respect to groundwater contamination, three variables of importance are temperature, the presence of organic co-contaminants and the concentration of dissolved ions (e.g., Na^+, Ca^{2+}, Cl^-, SO_4^{2-} and HCO_3^-). Generally, chlorinated solvent air-water partitioning increases with temperature and ionic strength, whereas the presence of appreciable concentrations of organic co-contaminants (such as other chlorinated solvents) will cause the extent of equilibrium air-water partitioning to decrease (Schwarzenbach et al., 2003).

4.3.2 Vapor Phase Transport of Chlorinated Solvents in the Vadose Zone

While air-water partitioning is likely to be unimportant in saturated groundwater systems, it represents an important process for pollutant source zones present in unsaturated environments such as the vadose zone (Brusseau, 1994). In the unsaturated zone, chlorinated solvent vapors can exist in the air-filled pore space, and the behavior, fate and environmental consequences of such gas phase species must be considered. For example, the downward migration of solvent vapors present in the unsaturated zone can represent an important source of pollution for the underlying groundwater in the saturated zone (Schwille, 1984; Schwille, 1988; Conant et al., 1996).

Unlike dissolved species in aqueous solution, transport of chlorinated solvent vapors is believed to be governed by molecular diffusion (Conant et al., 1996; Jellali et al., 2003), although advection resulting from density gradients may also be important (Mendoza and Frind, 1990a; Mendoza and Frind, 1990b). As molecular diffusivities for chlorinated solvents in air are large relative to water ($D_{air} \sim 10^{-2}$ square centimeters per second (cm^2/s) whereas $D_{water} \sim 10^{-5}$ cm^2/s) (Schwarzenbach et al., 2003), a diffusion dominated transport mechanism allows for the rapid proliferation of a vapor phase contaminant plume, resulting in a much larger area of subsurface contamination than might be anticipated if vapor migration in the vadose zone were ignored (Brusseau, 1994). Aquifer characteristics such as organic matter content (Conant et al., 1996) and water vapor content (e.g., Batterman et al., 1995) will play critical roles in gas phase transport, with partitioning into aqueous phases and organic phases retarding the rate of chlorinated solvent vapor migration.

Example 2: Air-Water-Solid Partitioning
Chlorinated Solvent Mass Balance in a Contaminated Subsurface

Q: Consider a waste site where a total of 150 kg of carbon tetrachloride (CT) has been accidentally discharged into an underground aquifer. The CT plume impacts a total volume in the subsurface of 1×10^6 L, and the impacted aquifer material has an organic carbon content of 1% and a bulk density of 2.0 kg/L. The aquifer solids have a porosity of 0.30 and 50% of the pore space is filled with water, whereas the other 50% is air. From Mackay et al. (1993), CT has a Henry's Law constant of 28.9×10^{-3} atm·m^3/mol at 25 degrees Celsius (°C). From Nguyen et al. (2005), the K_{OC} for chloroform is $10^{1.9}$ L/kg of OC. Assume equilibrium exists everywhere at the site and determine the fraction of CT in the air space, in the water, and sorbed to the aquifer material. How does the partitioning of CT change if the aquifer material has an organic carbon content of 3%? Repeat these calculations for 1,1,2,2-TeCA, which has the same K_{OC} value as CT, but a much smaller Henry's Law constant (0.44×10^{-3} atm·m^3/mol).

A: We start by developing an expression for the total mass of CT in our system, accounting for its presence in water, in air, and sorbed on aquifer solids.

$$Total\ Mass = Mass_{water} + Mass_{air} + Mass_{solid} \tag{i}$$

$$Total\ Mass = C_{water}V_{water} + C_{air}V_{air} + C_{solid}M_{solid} \tag{ii}$$

In (ii) C_{water} has units of mass of CT per L water and C_{air} has units of mass of CT per L air. C_{solid}, on the other hand, uses a different convention with units of mass of CT per kg solid. M_{solid} is the mass of solids present in the aquifer with units of kg.

The fraction of CT in water (f_{water}) is obtained by dividing the mass of CT in water ($C_{water}V_{water}$) by the total CT mass in our system.

$$f_{water} = \frac{C_{water}V_{water}}{C_{water}V_{water} + C_{air}V_{air} + C_{solid}M_{solid}} \tag{iii}$$

At equilibrium, CT air-water partitioning is described by Henry's Law; water-solid partitioning is determined from the K_d value for CT.

$$K_H^* = \frac{C_{air}}{C_{water}} \tag{iv}$$

$$K_d = K_{OC} \times f_{OC} = \frac{C_{solid}}{C_{water}} \tag{v}$$

By incorporating (iv) and (v) into our expression for f_{water} (iii), we obtain:

$$f_{water} = \frac{C_{water}V_{water}}{C_{water}V_{water} + K_H^* C_{water}V_{air} + K_{OC}f_{OC}\, C_{water}\, M_{solid}} \tag{vi}$$

which simplifies to the following expression dependent entirely upon known system parameters.

$$f_{water} = \frac{1}{1 + K_H^* \frac{V_{air}}{V_{water}} + K_{OC}f_{OC}\, \frac{M_{solid}}{V_{water}}} \tag{vii}$$

The fraction of CT in water can now be determined from the known characteristics of the aquifer material.

V_{water} can be calculated from the total site volume (1×10^6 L), the site porosity (0.3) and the percentage of pore space comprised of air (0.5).

$$V_{water} = (1 \times 10^6 \mathrm{L})(0.3)(0.5) = 1.5 \times 10^5 \mathrm{L}$$

V_{air} can be calculated in a similar fashion

$$V_{air} = (1 \times 10^6 \mathrm{L})(0.3)(0.5) = 1.5 \times 10^5 \mathrm{L}$$

The solid to water ratio (M_{solid} / V_{water}) can then be determined from the bulk density of the aquifer material and V_{water}.

$$\frac{M_{solid}}{V_{water}} = \frac{(2.0\ kg/L)(1 \times 10^6 L)}{1.5 \times 10^5 L} = 13.3\ kg/L$$

Before solving for f_{water}, note that our expressions use the dimensionless Henry's Law constant (K_H^*), although we are provided with values of K_H. Conversion between K_H and K_H^* can be accomplished using PV = nRT, where R = 8.205×10^{-5} m^3/mol·K and T is absolute temperature in Kelvin.

$$K_H^*(dimensionless) = \frac{K_H\left(\frac{m^3 \cdot atm}{mol}\right)}{R\ T} = 1.18 \tag{viii}$$

The fraction of CT in water can now be determined from (vii):

$$f_{water} = 0.078$$

and the corresponding mass and concentration of CT in water are calculated as follows:

$$M_{water} = (f_{water})(Total\ Mass) = 11.8\ \text{kg}$$

$$C_{water} = M_{water}/V_{water} = 79\ \text{mg/L} = 79\ \text{ppm}$$

We can now solve for the concentration in air using Henry's Law.

$$C_{air} = (K_H^*)(C_{water}) = 93\ \text{mg/L}$$

This, in turn, allows the total mass of CT in air, and the fraction of CT in air to be calculated.

$$M_{air} = (C_{air})(V_{air}) = 14\ \text{kg}$$

$$f_{air} = M_{air}/(Total\ mass) = 0.093$$

Finally, by mass balance, the results obtained for the amount of CT in air and water can be used to determine the amount of CT sorbed to the aquifer solids.

$$f_{solid} = 1 - f_{water} - f_{air} = 0.83$$

$$M_{solid} = Total\ Mass - M_{air} - M_{water} = 124\ \text{kg}$$

$$C_{solid} = 62\ \text{mg of CT per kg solid}$$

About 83% of the CT is sorbed onto the solids with about 9% in air and 8% in water.

We can now repeat the calculations for f_{OC} = 3% and for 1,1,2,2-TeCA. These results, as well as those derived above, are summarized in the following table.

	CT $f_{OC} = 1\%$	**CT** $f_{OC} = 3\%$	**1,1,2,2-TeCA** $f_{OC} = 1\%$	**1,1,2,2-TeCA** $f_{OC} = 3\%$
f_{solid}	0.83	0.94	0.91	0.97
f_{water}	0.08	0.03	0.09	0.03
f_{air}	0.09	0.03	0.001	0.0006
C_{solid} (mg/kg)	62	70	68	73
C_{water} (mg/L)	79	30	86	31
C_{air} (mg/L)	93	35	2	0.5
M_{solid} (kg)	124	140	137	145
M_{water} (kg)	12	5	13	5
M_{air} (kg)	14	5	0.2	0.08

In all instances, sorption into organic matter in the aquifer material is the dominant partitioning process for both CT and 1,1,2,2–TeCA. As expected, the amount of sorbed chlorinated solvent increases with f_{oc}, whereas the contribution of gas phase partitioning is greatest with increasing Henry's Law constant. Consideration of sorption and gas phase partitioning is important in the context of the abiotic reaction pathways discussed in the subsequent portions of this chapter, as the reactivity of the chlorinated solvent will be influenced by its form in the environment.

4.4 ABIOTIC TRANSFORMATION PROCESSES

This section presents a review of the prominent abiotic transformation pathways for chlorinated solvents. The focus is on natural environments, but where relevant, some engineering technologies will also be discussed. While these transformation pathways may reduce the persistence of chlorinated solvents in subsurface environments, they can also yield product species that exhibit considerably different behavior in groundwater. It is therefore important to understand the factors that influence the distribution of transformation products, as well as the rates of chlorinated solvent transformation.

Abiotic transformation reactions of chlorinated solvents can be divided into two broad categories. The first are those reactions in which the average oxidation state of carbon in the chlorinated solvent does not change as a result of reaction. Common examples of transformation pathways from this class include substitution and non-reductive elimination (or simply, elimination) reactions. The other broad class of reactions is that in which the average carbon oxidation state changes during reaction due to a net transfer of electrons between reactants. Reactions involving electron transfer are known as reduction and oxidation (or redox) reactions. Environmentally relevant examples of reactions from each class are given in Table 4.1 and discussed in more detail below.

Table 4.1. Common Classes of Abiotic Transformation Pathways of Chlorinated Solvents and Environmentally Relevant Examples

Reaction	Relevant Examples
1—No change in average carbon oxidation state	
Nucleophilic Substitution (predominantly S_N2)	
$R\text{-}X + Nuc^- \rightarrow R\text{-}Nuc + X^-$	*Hydrolysis:* $CH_3Cl + H_2O \Rightarrow CH_3\text{-}OH + H^+ + Cl^-$ (chloromethane ⇒ methanol) $CH_2Cl\text{-}CH_3 + OH^- \Rightarrow CH_3\text{-}CH_2OH + Cl^-$ (chloroethane ⇒ ethanol) *Thiol substitution:* $CH_2Br\text{-}CH_2Br + 2HS^- \Rightarrow CH_2SH\text{-}CH_2SH + 2Br^-$ (1,2-dibromoethane ⇒ 1,2-ethanedithiol)
Non-reductive Elimination (predominantly E_2)	
$R_1X\text{-}R_2H + B^- \rightarrow R_1{=}R_2 + BH + X^-$	*Dehydrohalogenation:* $Cl_2HC\text{-}CCl_3 + H_2O \Rightarrow Cl_2C{=}CCl_2 + H_3O^+ + Cl^-$ (PCA ⇒ PCE) $Cl_2HC\text{-}CHCl_2 + OH^- \Rightarrow Cl_2C{=}CHCl + H_2O + Cl^-$ (1,1,2,2-TeCA ⇒ TCE)
2—Change in carbon oxidation state[a]	
Reduction	
Hydrogenolysis $RX + 2e^- + H^+ \rightarrow RH + X^-$	$CHCl_3 + 2e^- + H^+ \Rightarrow CH_2Cl_2 + Cl^-$ (chloroform ⇒ dichloromethane) $CH_3\text{-}CCl_3 + 2e^- + H^+ \Rightarrow CH_3\text{-}CHCl_2 + Cl^-$ (1,1,1-TCA ⇒ 1,1-DCA) $CH_2{=}CCl_2 + 2e^- + H^+ \Rightarrow CH_2{=}CHCl + Cl^-$ (1,1-DCE ⇒ vinyl chloride)
Reductive β-elimination $R_1X\text{-}R_2X + 2e^- \rightarrow R_1{=}R_2 + 2X^-$	$CCl_3\text{-}CCl_3 + 2e^- \Rightarrow CCl_2{=}CCl_2 + 2Cl^-$ (HCA ⇒ PCE) $CHCl{=}CCl_2 + 2e^- \Rightarrow HC{\equiv}CCl + 2Cl^-$ (TCE ⇒ chloroacetylene)
Reductive α-elimination $R_1\text{-}R_2X_2 + 2e^- \rightarrow R1\text{-}\ddot{R}_2 + 2X^-$	$CCl_4 + 2e^- \Rightarrow \ddot{C}Cl_2 + 2Cl^-$ (carbon tetrachloride ⇒ dichlorocarbene) $CH_3\text{-}CHCl_2 + 2e^- \Rightarrow CH_3 - \ddot{C}H + 2Cl^-$ (1,1-DCA ⇒ methyl carbene)

[a] For a discussion of relevant oxidation reactions, please see Chapter 15 in this Volume

4.4.1 Substitution and Elimination Reactions

In the most general terms, substitution and elimination reactions transform chlorinated solvents into new compounds with different chemical structures and less chlorine substituents. Although substitution and elimination reactions are fundamentally different processes, an important shared characteristic is that the average oxidation state of carbon is unchanged by both processes. Thus, although the carbon atoms in chlorinated solvents can exist in many different oxidation states (ranging from –II to +IV), the oxidation state of the chlorinated solvent will always equal that of the reaction product generated via a substitution or elimination transformation pathway.

4.4.1.1 Substitution Reactions

As shown in Table 4.1, substitution reactions involve the addition of a new atom (or group of atoms) to a carbon center of a chlorinated solvent. As a carbon center can be bonded to at most four atoms (called substituents), this addition occurs at the expense of one of the chlorines originally bonded to the reactive carbon. Consequently, the new atom is substituted for chlorine in the reaction product, hence the name "substitution reactions."

For chlorinated solvents, the most environmentally relevant substitution reaction involves the reaction with water. An example is shown in Equation 4.9 for chloromethane (CH_3Cl), which reacts with water to produce methanol.

$$CH_3Cl + H_2O \rightarrow CH_3OH + H^+ + Cl^- \qquad \text{(Eq. 4.9)}$$

This type of reaction, in which a carbon-chlorine bond is broken via reaction with a water molecule (or, as will be discussed later, a hydroxide ion) is commonly referred to as hydrolysis (literally meaning "broken with water"). As in Equation 4.9, the typical products of hydrolysis reactions are alcohols, which can be considered a lesser environmental hazard than chlorinated solvents.

The hydrolysis of chloromethane occurs when the electrons associated with the oxygen in the water molecule are attracted to (or attack) the methyl carbon center, which can be considered slightly electron-deficient because of the electron-withdrawing chlorine substituent. Accordingly, water is called a nucleophile (its electrons make it "nucleus loving"), the carbon center is referred to as an electrophile (its electron deficiency makes it "electron loving"), and the chlorine substituent that is displaced as a result of this reaction is known as the leaving group. As both water and chloromethane are involved in the rate-determining reaction step that simultaneously breaks (e.g., C-Cl) and forms (e.g., C-O) bonds, the overall reaction is bimolecular in nature. Chloromethane hydrolysis is, therefore, classified as an S_N2 reaction, where the abbreviation stands for substitution, nucleophilic, bimolecular.

Although water is not a very reactive nucleophile (Schwarzenbach et al., 2003), it can be considered a key reactant in environmental systems as a result of its high abundance; the concentration of water is ~56 M, whereas the concentration of chlorinated solvents in contaminated groundwater is at most $\sim 10^{-3}$ M under saturated conditions (see Table 2.2). Hydroxide ions (OH^-) represent another environmentally relevant nucleophile. Hydroxide ion is a more reactive nucleophile than water (Vollhardt and Schore, 1994) that also reacts with chlorinated solvents via an S_N2 mechanism. Additional nucleophiles such as NO_3^-, CN^-, HS^- and SO_3^{2-} are also encountered in natural systems, but their reactions with chlorinated solvents are typically not as significant as reactions with water and hydroxide ions because of their relatively low environmental abundance (Schwarzenbach et al., 2003).

An S_N2 hydrolysis pathway (involving either H_2O or OH^-) is only important for a subset of chlorinated solvents. It is only expected to occur at fully saturated carbon centers (i.e., a carbon atom with single bonds to all substituents), such as those present in chlorinated methanes and ethanes. In contrast, S_N2 hydrolysis is not important for chlorinated ethenes such as TCE, PCE or vinyl chloride (VC). Furthermore, this reaction will only exhibit appreciable rates for mono- and dichlorinated species because steric effects generally limit the successful nucleophilic attack at a fully substituted carbon center such as that present in 1,1,1-trichloroethane (TCA, Cl_3CCH_3). Taking these factors into consideration, product distributions and/or reaction kinetics consistent with an S_N2 hydrolysis mechanism have been observed for chloromethane (Heppolette and Robertson, 1959), dichloromethane (Fells and Moelwyn-Hughes, 1958), CF (Fells and Moelwyn-Hughes, 1959), and 1,2-dichloroethane (1,2-DCA) (Jeffers et al., 1989). Note that the identity of the halide leaving group will considerably influence the tendency for a halogenated solvent to undergo an S_N2 reaction, and the following reactivity trend based upon halide leaving group is well-established (Vollhardt and Schore, 1994): R-F << R-Cl < R-Br < R-I. Mono- and dibrominated methanes and ethanes (e.g., 1,2-dibromoethane), therefore, will react via an S_N2 mechanism at a greater rate than their chlorinated analogues (e.g., 1,2-DCA).

4.4.1.2 Non-Reductive Elimination Reactions

Non-reductive elimination reactions always involve the loss of two substituents (e.g., H and Cl) that are located on neighboring carbon atoms of a chlorinated solvent. Unlike substitution reactions, the loss of these substitutents is not accompanied by the addition of a new atom or group of atoms to the parent molecule. Rather, in order to satisfy the bonding requirements of both carbon centers involved in this reaction, elimination pathways result in an increased bond order (e.g., the formation of a double bond from a single bond) between these adjacent carbon atoms.

As an example, pentachloroethane (PCA) readily undergoes non-reductive elimination to yield PCE (Roberts and Gschwend, 1991):

$$Cl_3CCHCl_2+OH^- \rightarrow Cl_2C=CCl_2+H^++Cl^- \qquad \text{(Eq. 4.10)}$$

Equation 4.10 is an example of a bimolecular elimination reaction (abbreviated as E_2), in which a base (OH^-) removes a proton from one carbon center while the C-Cl bond on the neighboring carbon simultaneously dissociates in the rate-determining step. While the electrons from the C-Cl bond remain with the chlorine atom after dissociation to produce a free chloride ion, the electrons associated with the proton remain on the carbon, thereby allowing for the increased bond order that is characteristic of elimination reactions. Accordingly, the characteristic product of chlorinated ethane elimination will be an ethene species possessing one less chlorine substituent. Non-reductive elimination reactions that result in the loss of a proton and a halogen atom from a chlorinated solvent are commonly referred to as dehydrohalogenation. More generally, this type of reaction also can be classified as a non-reductive β-elimination because the proton is removed from the β-carbon of the chlorinated solvent (defined as the carbon atom directly adjacent to the center with the most chlorine substituents). Note that water molecules are also capable of reacting with chlorinated solvents via an analogous bimolecular elimination pathway.

In theory, any chemical with hydrogen and chlorine substituents on adjacent carbon centers can react via a dehydrohalogenation pathway. This reaction is most likely to occur, however, when the majority of electron density associated with the hydrogen atom in question has been removed by neighboring substituents that are electron withdrawing (e.g., additional halogen atoms). Under such circumstances, the hydrogen atom can be considered to behave proton-like, and thereby is prone to removal by either a moderate (e.g., H_2O) or strong (e.g., OH^-) base. This is the case for the hydrogen(s) present on PCA (Roberts and Gschwend, 1991) and 1,1,2,2-TeCA (Jeffers et al., 1989), which represent two chlorinated solvents with relatively high rates of dehydrohalogenation at environmentally relevant pH values. Additional species whose reaction kinetics and/or products are consistent with a bimolecular dehydrohalogenation mechanism include 1,1-DCA, 1,1,2-TCA and 1,1,1,2-TeCA, as well as 1,2-DCA at high pH values (Jeffers et al., 1989).

4.4.2 Reduction and Oxidation Reactions

The second broad class of reactions involves the transfer of electrons between chemical reactants. These reactions are referred to as reduction and oxidation (or redox) reactions. For such reactions, one species serves as the electron donor, also known as the reductant, and another species functions as the electron acceptor or the oxidant. During the reaction, the reductant donates electrons and becomes oxidized, while the oxidant accepts electrons and gets reduced. Whether a chlorinated solvent is acting as an electron donor or acceptor can be determined by monitoring changes in the solvent's average carbon oxidation state, values of which are listed in Table 2.2. Reduction of a chlorinated solvent (to a species such as methane or ethane) decreases the average carbon oxidation state of the compound. In contrast, the average carbon oxidation state of a solvent increases as the result of an oxidation reaction (to a species such as carbon dioxide).

The primary focus of this section is the abiotic reduction of chlorinated solvents. Emphasis will be placed on naturally occurring abiotic reduction reactions, but reductive transformations that have been harnessed in field-scale treatment strategies for groundwater remediation will also be introduced. Abiotic oxidation reactions will not be discussed. These reactions, which tend to be less important in the natural environment but are employed in engineered treatment strategies, are discussed in greater detail in Chapter 15.

4.4.2.1 Reductive Transformation Pathways

Generally, the reduction of a chlorinated solvent results in the replacement of a halogen substituent(s) by a hydrogen atom or the formation of a pi-bond (π-bond) system. Reactions of this kind are often therefore broadly referred to as reductive dehalogenation because the solvent loses halogen substituents during the reduction process. A number of reduction pathways exist, however, and the three most relevant to chlorinated solvents (hydrogenolysis, reductive β-elimination, and reductive α-elimination) are discussed below.

The most straightforward reduction pathway is hydrogenolysis, shown below for the reduction of 1,1,1-TCA to 1,1-DCA (Equation 4.11).

$$Cl_3C-CH_3+2e^-+H^+ \rightarrow Cl_2CH-CH_3+Cl^- \qquad \text{(Eq. 4.11)}$$

As shown in Equation 4.11, hydrogenolysis is a net two-electron transfer that replaces a chlorine substitutent with a hydrogen atom. In theory, all classes of chlorinated solvents (methanes, ethanes and ethenes) can be reduced via a hydrogenolysis pathway. Note that for polyhalogenated species such as 1,1,1-TCA, hydrogenolysis will always yield another chlorinated solvent with a lower degree of chlorination.

Another important pathway is reductive β-elimination, shown in Equation 4.12 for the reduction of 1,1,2,2-TeCA to *cis*- or *trans*-1,2-DCE.

$$Cl_2HC-CHCl_2+2e^- \rightarrow CHCl=CHCl+2Cl^- \qquad \text{(Eq. 4.12)}$$

Reductive β-elimination is also a net two-electron transfer process. Unlike hydrogenolysis, this pathway involves the loss of two halogen substituents from adjacent carbon centers (a process commonly referred to as a dihalo-elimination). A characteristic of reductive β-elimination is that the bond order between the two carbon centers increases (i.e., a single bond is transformed to a double bond, or a double bond becomes a triple bond). This pathway will, therefore, transform a polychlorinated ethane into an ethene with a lower degree of halogenation (e.g., HCA to PCE), whereas polychlorinated ethenes will be reduced to acetylene species (which have a carbon-carbon triple bond). As chlorine substituents on adjacent carbon centers (known as vicinal or neighboring halides) are required for this pathway, reductive β-elimination cannot involve polychlorinated methanes.

The last reductive transformation of note is reductive α-elimination, shown in Equation 4.13 for the reduction of 1,1-DCA.

$$Cl_2HC-CH_3+2e^- \rightarrow \ddot{C}H - CH_3+2Cl^- \qquad \text{(Eq. 4.13)}$$

Reductive α-elimination is another two-electron, dihalo-elimination reaction. Unlike reductive β-elimination, however, the two chlorine substituents are lost from the same carbon center (referred to as the α-carbon). Thus, in order for reductive α-elimination to be a viable reduction pathway for a chlorinated solvent, it must possess multiple halogen atoms on the same carbon center, which are sometimes referred to as geminal (meaning "twin") halides.

A characteristic intermediate in reductive α-elimination is the carbene, which is defined as a neutrally charged carbon center bound to only two substituents and in possession of a lone pair of electrons (Carroll, 1998). Carbenes (such as the methyl carbene in Equation 4.13) are relatively reactive intermediates and consequently will not accumulate in most reductant systems. They participate in a variety of reactions such as coupling and insertion reactions with water molecules (Carroll, 1998) and may therefore allow for reduction products that are quite different from those generated via other reduction pathways.

As a practical consideration, the aforementioned reduction pathways all lead to different product species, and unique pathways may dominate for different combinations of reductants and chlorinated solvents. Moreover, several chlorinated solvents have structural features that may allow them to react by more than one pathway in the presence of a reductant. For instance, *cis*-DCE can react either by hydrogenolysis or reductive β-elimination. Clearly, reductive β-elimination to yield ethene is preferred, as a hydrogenolysis pathway will produce vinyl chloride, which is generally regarded as more toxic.

4.4.2.2 Abiotic Reductants

Abiotic reductants that are commonly found in natural systems include natural organic matter, reduced iron compounds, and reduced sulfur species (Stone et al., 1994). Abiotic reductants capable of reducing chlorinated solvents can be generated via chemical pathways (such as weathering) or microbial pathways (such as microbial respiration) (Rügge et al., 1998, Smolen et al., 2003). Most naturally occurring reductants are thermodynamically capable of reducing the more highly chlorinated solvents, such as PCE, TCE and CT, as shown in the redox ladder presented in Figure 4.4.

The redox ladder is organized by reduction potentials (E_H in volts), which represent a measure of a chemical's redox reactivity. The reduction potentials in Figure 4.4 have been adjusted to pH 7.0 to reflect conditions more relevant to groundwater aquifers. Large, positive E_H values correspond to species whose reduction is thermodynamically favorable ($\Delta G << 0$; as a convention, E_H values are reported for reduction reactions). Species lower on the ladder (at more negative E_H values) can, from a thermodynamic perspective, reduce species higher on the ladder. The redox ladder reveals that several iron and sulfur species are thermodynamically capable of reducing a wide range of chlorinated solvents at pH 7.0. Figure 4.4 also illustrates that a greater number of chlorines on a solvent tends to result in a more positive E_H value. Thus, highly chlorinated solvents (e.g., CT) can usually be considered more easily reduced than species with a lower number of chlorine substituents (e.g., dichloromethane [DCM]), although exceptions to this generalization exist. The focus of the following discussion will be on the most common reductants for chlorinated solvents, specifically reduced iron species (e.g., iron metal and ferrous iron), reduced sulfur species (hydrogen sulfides and polysulfides) and natural organic matter (NOM).

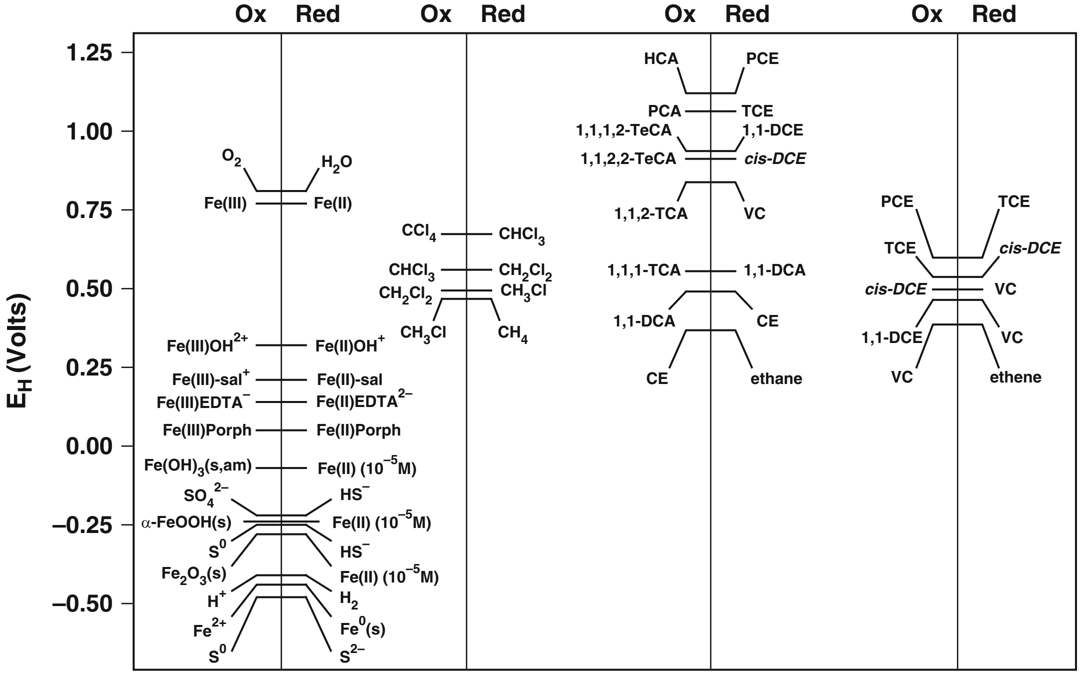


Figure 4.4. Reduction potentials (E_H values) for some environmentally relevant reductants and selected chlorinated solvents. Figure adapted from Schwarzenbach et al., 2003. Unless otherwise noted, E_H values were calculated at pH 7 and a Cl^- concentration of 10^{-3} M. Values of E_H for chlorinated solvents were obtained from Totten and Roberts (2001), while values for reduced iron and sulfur species were taken from Stumm (1992), Haderlein and Pecher (1998) and Bard et al. (1985).

Iron Metal. The majority of work on the abiotic reduction of chlorinated solvents by iron species has focused on zero-valent iron (Fe(0)) because of its use in subsurface permeable reactive barriers (PRBs). A brief introduction to the abiotic reactions involved with iron metal reduction is provided, but the reader is referred to Chapter 16 of this monograph by Gillham et al. for a complete review of the application of Fe(0) to chlorinated solvent remediation.

Iron metal is a strong reductant with a standard reduction potential of -0.44 volts (V). From the redox ladder in Figure 4.4, it is clear that iron metal can thermodynamically reduce most chlorinated solvents. With respect to reduction pathways, it was initially thought that chlorinated solvents were reduced by Fe(0) according to sequential hydrogenolysis pathways (Gillham and O'Hannesin, 1994). For example, the reduction of PCE to ethene via sequential hydrogenolysis is illustrated by the dashed arrows in Figure 4.5.

An obvious disadvantage of dechlorination via sequential hydrogenolysis is the possible formation of vinyl chloride. More recent work, however, has shown that polychlorinated ethenes

(Roberts et al., 1996; Arnold and Roberts, 2000) and ethanes (Arnold et al., 2002; Cwiertny and Roberts, 2005; Song and Carraway, 2005) with vicinal substituents react nearly exclusively via reductive β-elimination. For the chlorinated ethenes included in Figure 4.5, reductive β-elimination (shown using solid arrows) results in the formation of acetylene species that react relatively quickly with Fe(0) to produce fully dechlorinated products such as ethene and ethane.

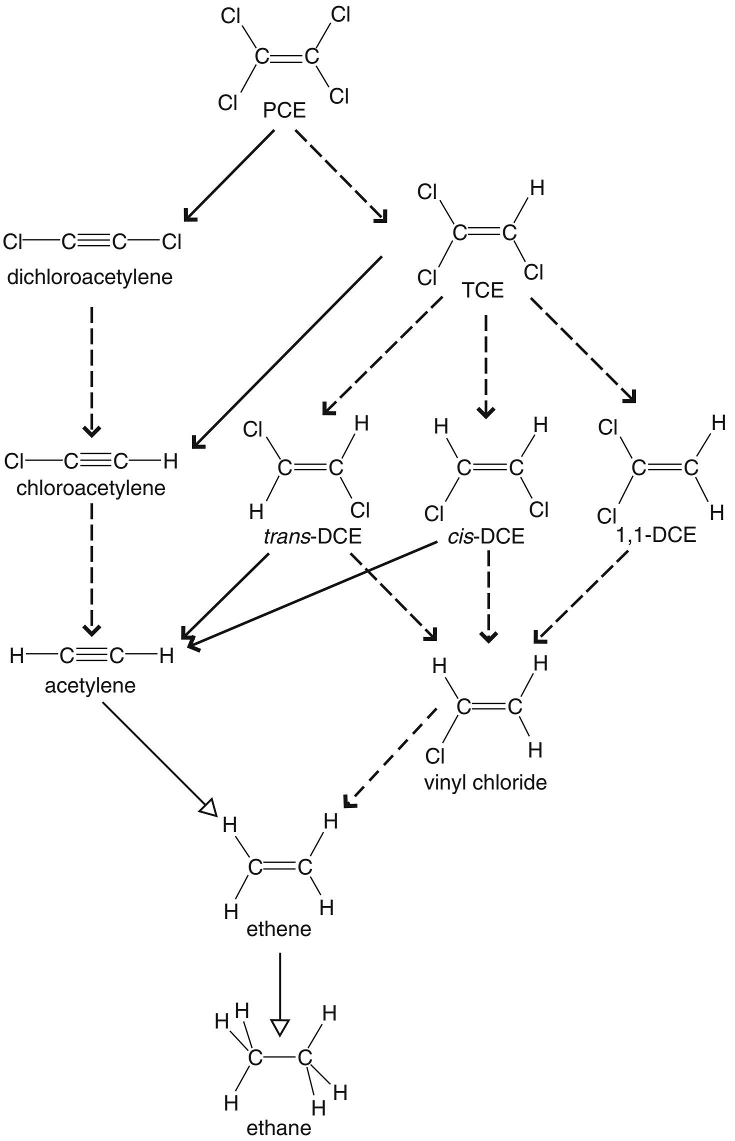


Figure 4.5. Proposed pathways for PCE reduction by Fe(0) (adapted from Arnold and Roberts, 2000). Dashed arrows represent hydrogenolysis pathways, while solid arrows indicate reductive β-elimination reactions, which tend to predominate for most polyhalogenated ethenes in Fe(0) systems. Open arrowheads indicate reductions not involving dehalogenation.

For species with multiple chlorine substituents on only one carbon center (e.g., 1,1,1-TCA), product distributions consistent with α-elimination have been observed. For example the reduction of 1,1-DCE by Fe(0) yielded ethene as the primary reaction product (Roberts et al., 1996; Arnold and Roberts, 2000), and reduction of 1,1,1-TCA yielded products consistent with parallel reductive α-elimination (ethane and ethylene) and hydrogenolysis (1,1-DCA) (Fennelly and Roberts, 1998). Competing α-elimination and hydrogenolysis pathways have also been proposed for CT reduction by Fe(0) (Támara and Butler, 2004).

Despite extensive research focusing on Fe(0) reactivity toward chlorinated solvents, the identity of the relevant reductant remains the topic of some debate. As discussed by Matheson and Tratnyek (1994) and later by Scherer et al. (1998b), numerous electron donors potentially exist in Fe(0) systems. Perhaps the most logical reductant is Fe(0) ($Fe(0) \rightarrow Fe(II) + 2e^-$), which could react with chlorinated solvents either at corrosion pits where it remains exposed to solution (Gaspar et al., 2002), or via the conduction of electrons through the mixed-valent oxide coating that is likely present on the Fe(0) particle surface (Scherer et al., 1998b). Alternatively, products of the corrosion reaction between Fe(0) and water also could be capable of reducing chlorinated solvents. Possible redox active corrosion products include Fe(II), particularly when it is sorbed to the Fe(0) particle surface, and mixed-valent iron oxide phases such as magnetite, green rust and iron carbonate hydroxide, all of which have been observed in column experiments exploring Fe(0) PRB longevity (Kohn et al., 2005). Others have also proposed that reduced forms of atomic hydrogen, which are produced as intermediates during the reduction of water to H_2, represent redox-active agents in Fe(0) systems (Li and Farrell, 2001; Li and Farrell, 2002; Oh et al., 2002).

Ferrous Iron. Several naturally occurring ferrous iron species are thermodynamically capable of reducing many chlorinated solvents. In the subsurface, Fe(II) species may exist as aqueous complexes, sorbed phases, or as part of mineral structures, and all may play a significant role in pollutant reduction (Haderlein and Pecher, 1998; Amonette, 2002). Aqueous Fe(II) at low pH is not a particularly strong reductant with an $E_H^o = 0.77$ V (more than 1,000 millivolts [mV] more positive than Fe(0)). Complexation of Fe(II) with hydroxide ions at higher pH values, however, increases the redox potential, so that aqueous Fe(II)-OH complexes are capable of reducing highly chlorinated solvents. For example, the reduction of HCA and CT by $Fe(II)OH^+$ is thermodynamically favorable at pH 7.0, as illustrated in the redox ladder in Figure 4.4. The few observations of homogeneous reduction of chlorinated solvents by aqueous Fe(II), however, report orders of magnitude slower rates than those observed in the presence of transition metal catalysts or mineral surfaces (e.g., Elsner et al., 2004b; Maithreepala and Doong, 2004).

Numerous laboratory studies have reported heterogeneous reduction of chlorinated solvents by both sorbed Fe(II) phases and structural Fe(II) found in minerals and clays (Haderlein and Pecher, 1998 and references therein). Most of the work conducted with sorbed Fe(II) and structural Fe(II) has been performed in the laboratory with model oxides and clays. Notably, however, several recent studies on the reduction of chlorinated ethenes and methanes by aquifer sediments concluded that Fe(II) species in the form of magnetite (Ferrey et al., 2004) or sorbed (i.e., surface-bound) Fe(II) (Kenneke and Weber, 2003) were the primary reductants.

Fe(II) sorbed on model surfaces, such as Fe oxides and clay minerals, has been shown to reduce chlorinated methanes, such as CT (Amonette et al., 2000; Pecher et al., 2002; Elsner et al., 2004a), and chlorinated ethanes, such as HCA (Elsner et al., 2004b). In an extensive study of a variety of mineral sorbents, Elsner et al. (2004b) found significant differences in rates of HCA reduction by sorbed Fe(II), as shown in Figure 4.6. In general, the fastest surface-area-normalized rates were observed for Fe(II) sorbed on iron sulfides, followed by iron oxides, and then iron carbonate (or siderite, $FeCO_3$) (Elsner et al., 2004b). Interestingly, there are very few reports of chlorinated ethene reduction by sorbed Fe(II). One is the work by Lee and Batchelor (2002a), where quite high concentrations of Fe(II) were used (42.6 millimolar [mM]) and some *cis*-DCE and VC reduction was observed. However, it is likely that the solubility limit for Fe(II) was exceeded in these studies, and redox active Fe(II)-containing solid phases (e.g., green rust, magnetite or ferrous hydroxide) may have formed.

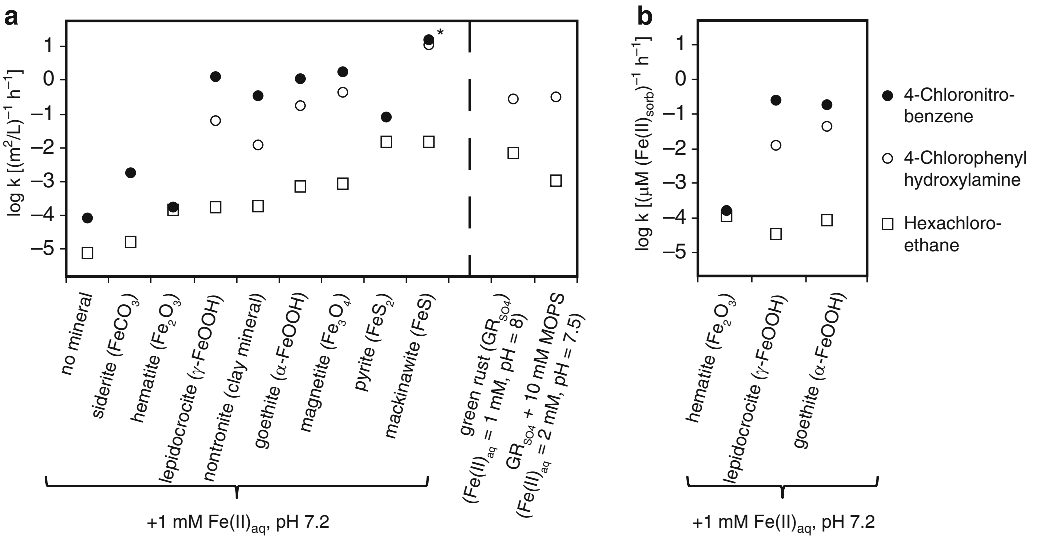


Figure 4.6. Comparison of logarithmic pseudo first-order measured rate coefficients for hexachlorethane reduction by Fe(II) in the presence of a variety of minerals. Open squares are hexachloroethane and reveal a trend of iron sulfides > iron oxides > siderite. Also shown are patterns observed for 4-chloronitrobenzene and 4-chlorophenyl hydroxylamine. Data shown in (a) is surface area-normalized and in (b) is normalized to sorbed Fe(II). The asterisk (*) indicates likely mass transfer limitation. Reproduced from Elsner et al., 2004b (reprinted with permission from the American Chemical Society).

The enhanced reactivity of sorbed Fe(II) is commonly attributed to surface complexation of Fe(II) by hydroxo ligands on the mineral surface, which stabilizes the Fe(III) oxidation state and lowers the Fe(III)-Fe(II) redox potential (Stumm and Morgan, 1996). The sorbed Fe(II) species or phase responsible for contaminant reduction, however, is still unclear. In most cases, the kinetics of contaminant reduction are described as proportional to the concentration of a stable, sorbed Fe(II) species at the mineral surface (determined from the disappearance of Fe(II) from solution). There is growing evidence, however, that both phase transformations and/or electron transfer reactions occur when Fe(II) sorbs on Fe oxides, indicating that the reaction pathways with sorbed Fe(II) are more complex and require additional research (Jeon et al., 2003; Williams and Scherer, 2004; Hansel et al., 2005; Pedersen et al., 2005).

Structural Fe(II) present in Fe(II) or mixed-valent Fe(III)-Fe(II) minerals such as iron sulfides, green rusts and magnetite also have been shown to reduce chlorinated solvents in several laboratory studies. Iron sulfides, such as mackinawite (FeS) and pyrite ($\mathrm{FeS_2}$), have been shown to be very reactive towards most chlorinated solvents (Butler and Hayes, 2002; Hanoch et al., 2006). Both reductive β-elimination and hydrogenolysis have been observed for chlorinated ethene reduction (see Figure 4.5) and there is significant interest in controlling this branching in order to avoid the formation of the toxic VC product (Butler and Hayes, 1999).

Green rusts, which are transient mixed-valent layered double hydroxides composed of $\mathrm{Fe(II)(OH)_2}$ and $\mathrm{Fe(III)(OH)_2^+}$ (Carrado et al., 1988), have been shown to reduce both halogenated ethanes (O'Loughlin and Burris, 2004) and methanes (Erbs et al., 1999; O'Loughlin et al., 2003). Similar to sorbed Fe(II), there are few reports of chlorinated ethene reduction by green rust, with the exception of two studies where partial reduction of chlorinated ethenes was observed with sulfate green rust and in Fe(II) cement slurries where green rust was expected to form (Hwang and Batchelor, 2000; Lee and Batchelor, 2002b).

One of the more commonly occurring mixed-valent iron oxides, magnetite ($\mathrm{Fe_3O_4}$), has often been studied in the presence of aqueous Fe(II), but "control" experiments with magnetite alone typically result in negligible dechlorination (Pecher et al., 2002). Recently, however, there is evidence that CT can be reduced by structural Fe(II) in chemically synthesized magnetite (Danielsen and Hayes, 2004). In this work, as in several studies with Fe(II) reductants, rates increased significantly over a pH range of 6 to 8.

With respect to chlorinated solvent reactivity and reduction pathways, the reduction of CT by either Fe(II) sorbed on Fe(III) (hydr)oxides or Fe(II)-containing mineral phases has been most extensively investigated (Amonette et al., 2000; Pecher et al., 2002; O'Loughlin et al., 2003; Danielsen and Hayes, 2004; Elsner et al., 2004a; McCormick and Adriaens, 2004). CT reduction is believed to initiate via a single electron transfer that cleaves a C-Cl bond and generates a trichloromethyl radical (Figure 4.7), although alternative pathways have also been proposed (Amonette et al., 2000). The fate of this radical intermediate ultimately determines the products of CT reduction. It could either abstract a hydrogen or undergo an additional one electron transfer followed by protonation to yield chloroform (CF), the hydrogenolysis product that is generally more persistent than CT in reduced iron systems. Alternatively, the trichloromethyl radical could undergo an additional reduction step followed by the loss of a chloride ion to yield dichlorocarbene. This reductive α-elimination pathway is more favorable from a treatment perspective, as it can result in the formation of benign, fully dechlorinated end products such as formate and carbon monoxide (as shown in Figure 4.7). Additionally, further reduction of dichlorocarbene may result in the formation of methane (McCormick and Adriaens, 2004). Variations of the reaction pathway in Figure 4.7 also have been suggested for the reduction of CT by Fe(0) (Támara and Butler, 2004; Nurmi et al., 2005), by HS^- in the presence of mineral surfaces (Kriegman-King and Reinhard, 1991), and by iron sulfides (Kriegman-King and Reinhard, 1994).

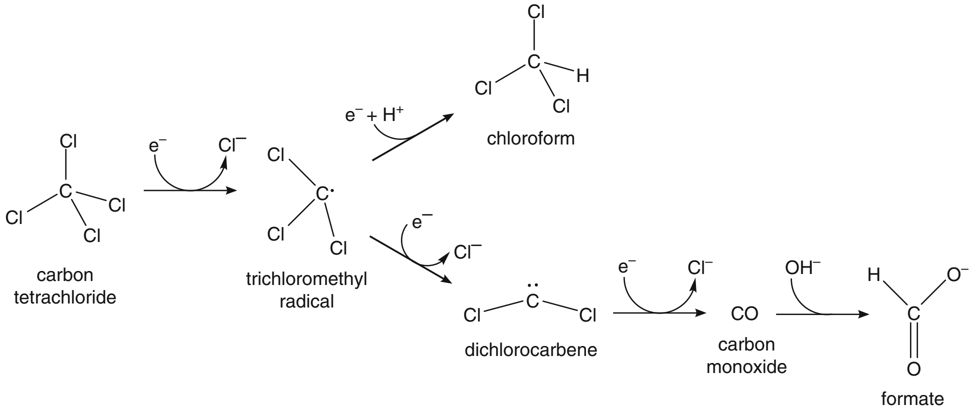


Figure 4.7. Proposed pathways for carbon tetrachloride (CT) reduction by Fe(II) associated with Fe (III) oxide surfaces or Fe(II) containing minerals. Similar reduction pathways also have been proposed for CT reduction in Fe(0) systems (Támara and Butler, 2004), as well as for CT reduction by reduced sulfur species (Kriegman-King and Reinhard, 1992) and vitamin B_{12} (Krone et al., 1991).

Previous investigators have found that several factors can influence the relative rates (or branching ratio) of the hydrogenolysis and reductive α-elimination pathways during CT reduction. For instance Pecher et al. (2002) found that the concentration of CF increased with increasing pH in Fe(II)-containing iron (hydr)oxides systems. The same result was also observed by Danielsen and Hayes (2004) for CT reduction by magnetite. Additional factors that have also been found to influence the relative abundance of CT reduction products include the sorbed concentration of Fe(II) (Pecher et al., 2002), the presence of transition metal additives on the iron mineral surface (O'Loughlin et al., 2003), and the presence of compounds in solution that can provide either hydrogen atoms (Elsner et al., 2004a) or protons (e.g., amine buffers [Danielsen et al., 2005]) that can react with intermediates of CT reduction.

NOM. Natural organic matter, or NOM, can be defined as the structurally diverse mixture of organic macromolecules produced from the decay of terrestrial and aquatic plant matter (Macalady and Ranville, 1998). NOM is traditionally divided into several subclasses based upon its properties. For example, humic substances, which comprise the major organic fraction in soil (Aiken et al., 1985), represent the organic matter that is resistant to further biological decomposition (Macalady and Ranville, 1998). Humic substances are further categorized based upon their aqueous solubilities; humic acid is operationally defined as the fraction that is soluble at high pH values but precipitates at pH 2, whereas fulvic acid is the portion soluble over the entire pH regime (Aiken et al., 1985). As NOM is ubiquitous in both aquatic and terrestrial environments (e.g., the average concentration of dissolved NOM in groundwater is approximately 4 mg carbon/L [Macalady and Ranville, 1998]), its influence on chlorinated solvent fate has been the focus of extensive laboratory investigations.

It is widely accepted that NOM serves as a mediator for the reduction of chlorinated solvents. As shown in Figure 4.8, a mediator facilitates the transfer of electrons between a reductant that is present in excess (referred to as the bulk reductant) and an electron acceptor (in our case, the chlorinated solvent) (Dunnivant et al., 1992). The bulk reductant, typically species such as Fe(II) or HS^-, transfers electrons to the mediator, which in turn serves as the reductant for the chlorinated solvent. The oxidized mediator can then be re-reduced by the bulk reductant, thereby generating a catalytic cycle for chlorinated solvent reduction. Typically, mediators such as NOM are present in relatively low concentrations and do not exhibit considerable reactivity toward chlorinated solvents in the absence of a bulk reductant. Similarly, the bulk reductant also displays only a limited capacity for reducing chlorinated solvents in the absence of a mediator. On the other hand, in systems with both a mediator and a bulk reductant, rates of chlorinated solvent reduction are greater than that anticipated from the summed reactivities of both species.

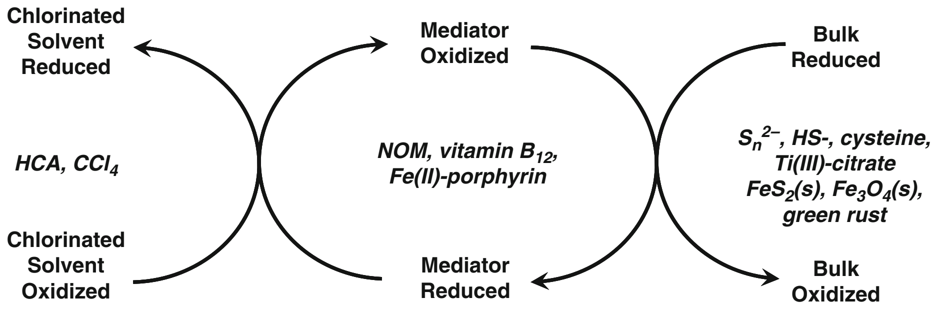


Figure 4.8. Schematic illustrating the catalytic role of mediators for chlorinated solvent reduction, with environmentally relevant examples of each species (adapted from Dunnivant et al., 1992).

The ability of NOM to serve as an electron transfer mediator is often attributed to redox active quinone functional groups (examples of quinone-containing compounds are shown in Figure 4.9) present in its structure (Tratnyek and Macalady, 1989; Schwarzenbach et al., 1990; Dunnivant et al., 1992). For instance, Curtis and Reinhard (1994) examined the reduction of CT and HCA by humic acid in the presence of Fe(II) and HS^-. Consistent with NOM serving as an electron transfer mediator, a 10-fold increase in the rates of CT and HCA reduction was observed in systems containing both a bulk reductant and humic acid. They conducted additional experiments using anthroquinone disulfonic acid (AQDS), which contains a quinone functional group (see Figure 4.9), as a model for structurally complex NOM. Curtis and Reinhard found that the reduced form of AQDS could reduce CT and HCA. Moreover, the pH dependence of the reduction reaction was similar to that observed for the reduction of HCA and CT by humic acid, supporting a role for quinone moieties as the reactive entity in NOM.

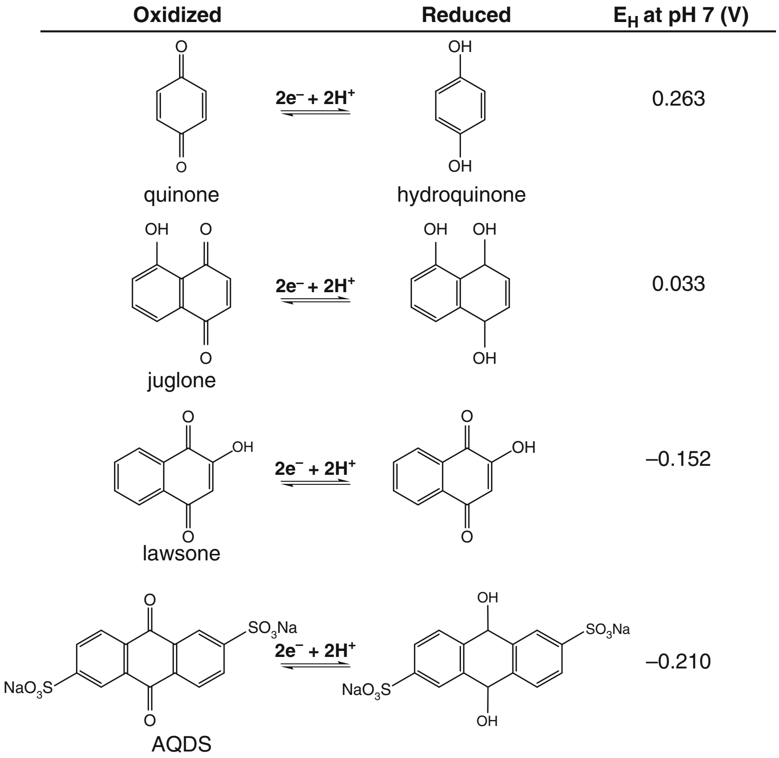


Figure 4.9. Examples of compounds containing a quinone functionality that have been used as models of NOM for mediating chlorinated solvent reduction (adapted from Schwarzenbach et al., 1990). Reduction potentials for each half-reaction are provided, determined at a pH value of 7.

Alternative explanations for the redox activity of NOM have also been proposed. Perlinger et al. (1996) observed that juglone, another model quinone (see Figure 4.9), catalytically reduced HCA in the presence of HS^-, whereas electrochemically reduced juglone was unreactive toward HCA. Based upon these results, the authors proposed that the reactive form of juglone was a product of the addition reaction between juglone and HS^-. A similar hypothesis was suggested in the authors' later works, which examined polychlorinated methane and ethane reduction in juglone/HS^- systems (Perlinger et al., 1998). Subsequent results from additional kinetic and spectroscopic studies (Perlinger et al., 2002) further supported the existence of such a reactive entity in their experimental systems.

It is also possible that complexes between NOM and metal ions play a prominent role in chlorinated solvent reduction. O'Loughlin et al. (1999) examined the reactivity of nine transition metal-humic acid complexes in the presence of the bulk reductant titanium citrate. For Ni complexes, they observed near complete transformation of TCE to ethane and ethene. In fact, later work by this same group (Ma et al., 2001) revealed that Ni complexes with humic acid and NOM were far more efficient as mediators for TCE reduction than quinones, which displayed at best limited reactivity toward TCE.

Although the exact nature of the reactive entities in NOM remains the subject of investigation, NOM must be viewed as a possible reductant for some chlorinated solvents in natural systems. This is particularly true in reducing environments, where reactions with iron and sulfur species, as well microbiological processes (Lovley et al., 1996; Coates et al., 1998), can yield reduced forms of NOM. It also may be necessary to consider the importance of NOM under oxic conditions; recent results of Kappler and Haderlein (2003) indicate that reduced forms of NOM maintain some of their electron donating ability even in the presence of oxygen.

Reduced Sulfur Species. Reduced forms of sulfur represent another possible reductant for chlorinated solvents. These include hydrogen sulfide species (HS^- and H_2S) and polysulfide ions S_n^{2-} (where n refers to the number of sulfur atoms in a polysulfide chain). Each of these species contains sulfur with an oxidation state of −II. For comparison, oxidized forms of sulfur include elemental sulfur (S^0; oxidation state 0), sulfite (SO_3^{2-}; oxidation state of +IV) and sulfate (SO_4^{2-}; oxidation state +VI). Reduced sulfur species are generated from the biologically mediated reduction of sulfate in oxygen-free environments such as those typically encountered in groundwater pollutant plumes.

With respect to their reactivity, reduced sulfur is unique in that it can serve either as a nucleophile in substitution and elimination reactions or as an electron donor for chlorinated solvent reduction. The relative strength of sulfur species as nucleophiles follows the trend $S_n^{2-} > HS^- >> H_2S$ (Barbash and Reinhard, 1989). Based upon the standard reduction potentials in our redox ladder (Figure 4.4), polysulfides are believed to be the strongest reductants. For example, rate constants for the reaction of S^{2-} with HCA, which is proposed to occur predominately via a reductive pathway (Miller et al., 1998), are more than two orders of magnitude greater than rate constants for hydrogen sulfide species (Perlinger et al., 1996). Whether a reduced sulfur species serves as a nucleophile or reductant in reactions with chlorinated solvents will depend upon several factors including the relative abundance of the reduced sulfur species and the chemical identity of the chlorinated solvent.

To date, most investigations have focused on the role of HS^- as a bulk reductant in the catalytically mediated reduction of chlorinated solvents (see Figure 4.8). In experimental systems, natural organic matter (Curtis and Reinhard, 1994), quinone-containing model compounds (Perlinger et al., 1996; Perlinger et al., 1998), and mineral surfaces (Kriegman-King and Reinhard, 1992) serve as catalysts for chlorinated solvent reduction in the presence of HS^-. While reduction of chlorinated solvents by HS^- in the absence of these catalysts has also been observed in these studies, the rates of such reactions are typically much slower. Consequently, it is often assumed that the contribution of direct chlorinated solvent reduction by reduced sulfur species is of relatively little importance in natural systems where redox mediators such as NOM are abundant.

Miller et al. (1998) have suggested, however, that in certain environments the concentrations of reduced sulfur species, particularly polysulfides, can achieve high enough values such that their role as a direct reductant for chlorinated solvents cannot be discounted. They examined the transformation of HCA and PCA in batch systems with water from Mystic Lake, Massachusetts, which contained approximately 7 mM of total hydrogen sulfide species and roughly 80 micromolar (μM) of reactive polysulfide species. Using rate constants for the reaction between reduced sulfur species and HCA calculated by Perlinger et al. (1996) and their own kinetic and product distribution data, they concluded that approximately 20% of HCA disappearance could be attributable to an unmediated reaction between reduced sulfur species and HCA. In particular, polysulfide species were proposed to be the primary reductant. Their results illustrate that in certain environments, microbial sulfate reduction may indeed produce high enough concentrations of reduced sulfur species such that their role as reductants merits consideration.

4.4.3 Reaction Kinetics

The lifetime of chlorinated solvents in subsurface environments will be influenced by the rate at which hydrolysis, dehydrohalogenation, reductive dehalogenation and oxidation reactions occur. If it is assumed that these reactions occur independently of one another and in parallel, a generalized rate expression can be developed. For example, the expression for chloromethane (CM) transformation is as follows:

$$rate\left(\frac{mol}{L\cdot s}\right) = -\frac{d[CM]}{dt}$$
$$= k_{RED}[RED][CM] + k_{OX}[OX][CM] + k_N[CM] + k_B[OH^-][CM] \qquad \text{(Eq. 4.14)}$$

In this expression, [CM], [OX], and [RED] represent the chloromethane, oxidant, and reducant concentrations, respectively. k_{RED} and k_{OX} are second-order rate coefficients with units of $M^{-1}s^{-1}$ for the reduction and oxidation of CM. If more than one reductant or oxidant species is present, additional rate terms would be needed to account for these parallel redox pathways.

The terms k_{N}[CM] and $k_{\mathrm{B}}[OH^-]$[CM] account for the combined rate of CM hydrolysis and dehydrohalogenation at neutral and basic pH values, respectively. Values of k_{N} (which have units of M^{-1}) and k_{B} (which have units of $M^{-1}s^{-1}$) are determined from laboratory experiments that measure the rate of chlorinated solvent transformation resulting from reaction with H_2O and OH^- over a range of pH values. Values of k_{N} and k_{B} are well established for most chlorinated solvents, and these values are summarized in Table 4.2. Note that for many chlorinated solvents, values of k_{B} are several orders of magnitude greater than values of k_{N}. However, the rate of all base-promoted pathways ($=k_{\mathrm{B}}[OH^-][CM]$) also depends upon the concentration of OH^-, which increases with increasing pH. Thus, for most chlorinated solvents, the rate of the neutral hydrolysis and dehydrohalogenation reactions predominates at neutral pH values, whereas the rate of the base-promoted pathway is typically only significant at higher pH values ($pH \geq 10$).

For practical purposes, Equation 4.14 can be simplified by introducing the concept of a pseudo first-order rate constant or k_{obs} value, which represents a measure of the overall reactivity of CM in the system of interest (Equations 4.15 and 4.16)

$$rate\left(\frac{mol}{L\cdot s}\right) = \frac{d[\mathrm{CM}]}{dt} = -k_{obs}[\mathrm{CM}] \qquad \text{(Eq. 4.15)}$$

where

$$k_{obs}\left(s^{-1}\right) = k_N + k_B[OH^-] + k_{RED}[RED] + k_{OX}[OX] \qquad \text{(Eq. 4.16)}$$

The utility of k_{obs} values (which have units of s^{-1}) is that they are composite rate constants that accounts for all CM transformation pathways, and in many instances are easier to determine experimentally than the individual rate constants for parallel reaction pathways. On the other hand, k_{obs} values are limited in that they are usually only applicable to the conditions under which they were measured, making their extrapolation to other conditions, or even field settings, unreliable.

Table 4.2. Experimental Values of k_N and k_B at 25°C Taken from the Literature for Selected Chlorinated Solvents

Species	k_N (s^{-1})	k_B ($M^{-1}s^{-1}$)	Reference
Methanes			
CM	2.30×10^{-8}	6.50×10^{-6}	Heppolette and Robertson, 1959
DCM	3.20×10^{-11}	2.20×10^{-8}	Moelwyn-Hughes, 1949
CF	3.00×10^{-12}	9.00×10^{-5}	Jeffers et al., 1989
CT	5.00×10^{-10}	NO[a]	Jeffers et al., 1996
Ethanes			
Chloroethane	8.50×10^{-9}	6.5×10^{-5}	Jeffers and Wolfe, 1996
1,2-DCA	3.00×10^{-10}	2.00×10^{-6}	Jeffers and Wolfe, 1996
1,1-DCA	3.80×10^{-10}	1.30×10^{-8}	Jeffers et al., 1989
1,1,1-TCA	2.00×10^{-8}	NO	Haag and Mill, 1988
1,1,2-TCA	9.20×10^{-13}	3.70×10^{-3}	Jeffers et al., 1989; Walraevens et al., 1974[b]
1,1,2,2-TeCA	1.60×10^{-10}	1.6	Jeffers et al., 1989; Haag and Mill, 1988
1,1,1,2-TeCA	4.00×10^{-10}	3.50×10^{-4}	Jeffers and Wolfe, 1996
PCA	8.30×10^{-10}	2.70×10^{1}	Jeffers et al., 1989; Roberts and Gschwend, 1991
HCA	NO	1.30×10^{-10}	Jeffers et al., 1989
Ethenes			
1,1-DCE	NO	1.90×10^{-9}	Jeffers et al., 1989
cis-DCE	NO	1.10×10^{-11}	Jeffers et al., 1989
trans-DCE	NO	1.10×10^{-11}	Jeffers et al., 1989
TCE	NO	1.90×10^{-7}	Jeffers et al., 1989
PCE	NO	2.40×10^{-10}	Jeffers et al., 1989

[a] NO = not observed
[b] references for k_N and k_B, respectively

Integration of Equation 4.15 provides a relationship that describes the change in [CM] as a function of time (t) (Equation 4.17) in which $[CM]_0$ is the initial concentration of chloromethane.

$$[CM] = [CM]_0 e^{-k_{obs}t} \qquad \text{(Eq. 4.17)}$$

According to Equation 4.17, the decrease in CM concentration as a function of time follows an exponential decay, such as the concentration profile illustrated in Figure 4.10. Furthermore, by taking the natural log of the integrated rate expression, the following relationship between ln [CM] and t is obtained.

$$\ln[CM] = \ln[CM]_0 - k_{obs}t \qquad \text{(Eq. 4.18)}$$

From Equation 4.18, a plot of the ln[CM] versus t (shown as an inset in Figure 4.10) should yield a line with a slope of $-k_{obs}$ and a y-axis intercept equal to $\ln[CM]_0$.

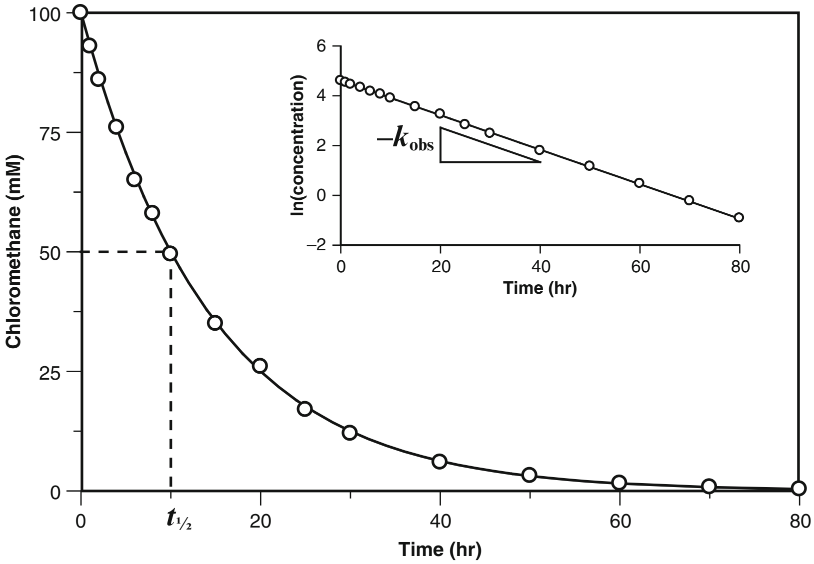


Figure 4.10. Illustration of first-order kinetic behavior for chlorinated solvent degradation in a closed system. The concentration profile follows exponential decay. Dashed lines indicate the half life (or $t_{1/2}$ value) when [CM] = ½[CM]$_0$. Inset shows a first-order plot with the natural logarithm of chlorinated solvent concentration plotted versus time. The slope of such a semi-log plot can be used to determine pseudo first-order rate constants (or k_{obs} values) for chlorinated solvent transformation.

An additional benefit of k_{obs} values is that they can be used to estimate the half life (or $t_{1/2}$ value) of a chlorinated solvent in groundwater. Values of $t_{1/2}$ are defined as the time required for the pollutant concentration in a system to decrease to half of its initial value (the value of $t_{1/2}$ in Figure 4.10 is indicated). Half lives for chlorinated solvents are determined by integrating Equation 4.15 and solving for t when [CM] = ½[CM]$_0$. The result is as follows, where larger k_{obs} values produce shorter half lives.

$$t_{1/2} = \frac{0.693}{k_{obs}} \qquad \text{(Eq. 4.19)}$$

From our expression for k_{obs} (Equation 4.16), it should be clear that values of $t_{1/2}$ for CM (and several other chlorinated solvents) will depend on pH. Specifically, the rate of CM reaction with OH^- will increase with pH, as, by definition, the concentration of OH^- must also be increasing. If oxidation and reduction reactions are neglected, the relationship between chlorinated solvent half life and solution pH can be determined from the published values of k_N and k_B in Table 4.2. The half lives of select chlorinated solvents estimated in this manner over the pH range of 5-10 are shown in Figure 4.11. As Figure 4.11 illustrates, $t_{1/2}$ values for CT and 1,1,1-TCA are independent of pH. This behavior is consistent with the lack of base-promoted reaction pathways for these species. In contrast, values of $t_{1/2}$ estimated for TCE, 1,1,2,2-TeCA, PCA and CF vary considerably over the pH range considered, indicating that these species are able to react with OH^-. A change from pH-independent to pH-dependent $t_{1/2}$ values, such as that observed for CF near pH 6, indicates the approximate pH value at which the contributions from reactions with OH^- become significant.

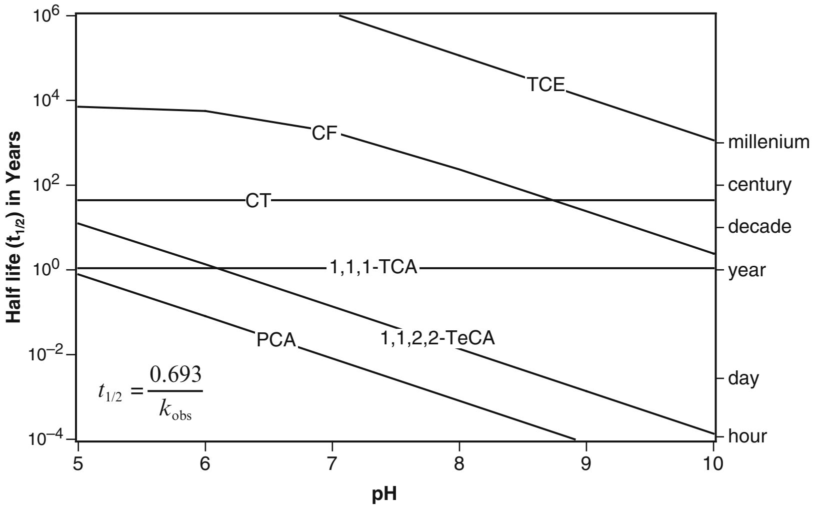


Figure 4.11. Estimated half lives as a function of pH for selected chlorinated solvents undergoing hydrolysis and/or hydrodehalogenation. Half lives were calculated from estimated $k_{obs} = k_N + k_B [OH^-]$ with k_N and k_B values provided in Table 4.2.

The data in Figure 4.11 also suggest that the transformation of chlorinated ethenes by hydrolysis/dehydrohalogenation reactions is relatively unimportant in most environmental systems. The estimated half life for TCE in groundwater at pH 7 is nearly one million years, illustrating why treatment strategies utilizing redox processes (e.g., Fe(0) permeable reactive barriers) are necessary in order to remediate subsurface environments contaminated with chlorinated ethenes. On the other hand, $t_{1/2}$ values for 1,1,2,2-TeCA and PCA are on the order of several days at pH 7. In fact, the dependence of their $t_{1/2}$ values on pH suggests that base-promoted dehydrohalogenation is the predominant reaction pathway over the entire pH range considered, even though the concentration of OH^- is very low for pH values less than 7. The prevalence of the base-promoted dehydrohalogenation of 1,1,2,2-TeCA (to generate TCE) and PCA (to generate PCE) is due primarily to the acidic hydrogen substituents on each compound.

4.4.4 Estimating Rates of Abiotic Transformations

Given the prominent role of chlorinated solvent reductive dehalogenation in both naturally occurring and engineered reductant systems, a method for predicting the reactivity of these contaminants that does not require exhaustive laboratory investigation is desirable. Quantitative structure activity relationships (QSARs), which correlate chlorinated solvent reactivity with molecular properties expected to influence reactivity, are one such predictive tool.

QSARs, also referred to as LFERs, are developed for a class of compounds (e.g., chlorinated methanes, ethanes or ethenes) to explore the influence of structural differences (e.g., the degree of chlorine substitution) on reactivity (Tratnyek et al., 2003). The dependent variable in the relationship, also referred to as the response variable (Tratnyek et al., 2003), is typically a measure of chlorinated solvent reactivity. Common response variables include pseudo first-order rate constants (k_{obs} values with units s^{-1}), surface-area-normalized rate constants (k_{SA} values with units $Lm^{-2}s^{-1}$), or second-order rate constants (k values with units $M^{-1}s^{-1}$). The independent variable, or descriptor variable, is a chemical property of the chlorinated solvent that is expected to influence its reactivity. For example, molecular descriptors commonly used for chlorinated solvent reduction include one- and two-electron reduction potentials (E_1 and E_2, respectively) (Scherer et al., 1998a; Arnold et al., 1999; Lien and Zhang, 2005; Song and Carraway, 2005), the lowest unoccupied molecular orbital energy (E_{LUMO}) (Scherer et al., 1998a; Perlinger et al., 2000; Miehr et al., 2004; Song and Carraway, 2005) and carbon-halogen homolytic bond dissociation energies (D_{RX}) (Liu et al., 2000; Perlinger et al., 2000; Lien and Zhang, 2005).

Table 4.3. Selected QSARs Developed for the Abiotic Reduction of Chlorinated Solvents (adapted from Tratnyek et al., 2003)

Reductant System	Halogenated Solvent Class	QSAR[a]	R^2	Reference
Fe(0)	Methanes, ethanes and ethenes	$\log(k_{SA}) = -1.5(\pm 0.1) \cdot E_{\mathrm{LUMO}} - 5.7(\pm 0.2)$	0.83	Scherer et al., 1998a
Fe(0)	Reductive β–elimination of ethenes	$\log(k_S S_t) = -15(\pm 15) \cdot E_2 + 6(\pm 8)$	0.71[b]	Arnold & Roberts, 2000
Fe(0)	Hydrogenolysis of ethenes	$\log(k_S S_t) = -31(\pm 29) \cdot E_2 + 18(\pm 17)$	0.86[b]	Arnold & Roberts, 2000
Fe(0)	CT, TCE plus other model contaminants	$\log(k_{SA}) = -26(\pm 12^c) \cdot E_{\mathrm{LUMO}} + 4(\pm 1.3^c)$	0.77	Miehr et al., 2004
Iron-reducing sediments	Methanes	$\log(k_{obs}) = -0.081(\pm 0.007\ ^c) \cdot D_{RX} - 0.036(\pm 0.005\ ^c) \cdot \Delta G^{\circ\prime} + 18.51$	0.97	Kenneke & Weber, 2000
Sulfate-reducing sediments	Methanes	$\log(k_{obs}) = -0.089(\pm 0.011\ ^c) \cdot D_{RX} - 0.029(\pm 0.008\ ^c) \cdot \Delta G^{\circ\prime} + 20.64$	0.94	Kenneke & Weber, 2000
Fe(II) on goethite	Methanes	$\log(k_{obs}) = -0.052(\pm 0.013\ ^c) \cdot D_{RX} - 0.028(\pm 0.015\ ^c) \cdot \Delta G^{\circ\prime} + 12.03$	0.78	Kenneke & Weber, 2000
FeS	Methanes	$\log(k_{obs}) = -0.034(\pm 0.016) \cdot D_{RX} - 8.8(\pm 4.9)$	0.82	Butler & Hayes, 2000
Fe(II) porphyin/ cysteine	Methanes and ethanes	$\log(k) = -0.08(\pm 0.01\ ^c) \cdot \Delta G^{\circ\prime} + 2.7(\pm 0.5\ ^c)$	0.96	Perlinger et al., 2000
Juglone/H_2S	Methanes and ethanes	$\log(k) = -0.10(\pm 0.05\ ^c) \cdot \Delta G^{\circ\prime} - 0.2(\pm 1\ ^c)$	0.88	Perlinger et al., 2000

[a] Unless otherwise noted, uncertainties in QSAR coefficients represent one standard deviation.
[b] Represents an R^2 value adjusted for degrees of freedom. [c] Uncertainty represents 95% confidence interval.

Examples of QSARs developed for the reduction of chlorinated solvents in several environmentally relevant systems are shown in Table 4.3. Scherer et al. (1998a) developed linear relationships for the reduction of several chlorinated methanes, ethanes and ethenes using k_{SA} values compiled from previously published investigations (Johnson et al., 1996). Their strongest LFER, included in Table 4.3 and shown in Figure 4.12, was that developed using E_{LUMO} values calculated using computational methods. In a more recent study, QSARs developed by Miehr et al. (2004) included not only the chlorinated solvents CT and TCE, but also several other pollutants including metal cations, metal anions and additional organic compounds. They found that relationships between k_{SA} values and computationally derived E_{LUMO} values reasonably described the reduction of all pollutants by Fe(0) even though a broad range of compounds from different chemical classes was considered. Kenneke and Weber (2000) developed QSARs for the reduction of polyhalogenated methanes in iron-reducing and sulfate-reducing sediments, as well as for their reduction by Fe(II) associated with goethite surfaces. They also presented relationships for polyhalogenated methane reduction by iron sulfides, as did Butler and Hayes (2000) for the reduction of halogenated methanes and ethanes. The practical value of these and other QSARs is that the reactivity of compounds that were not used in the construction of the correlation can be predicted so long as the descriptor variable for that compound is known. It is thought (Tratnyek et al., 2003) that the predictive capabilities afforded by QSARs could be helpful in regulatory decision making processes regarding effective cleanup strategies at hazardous waste sites.

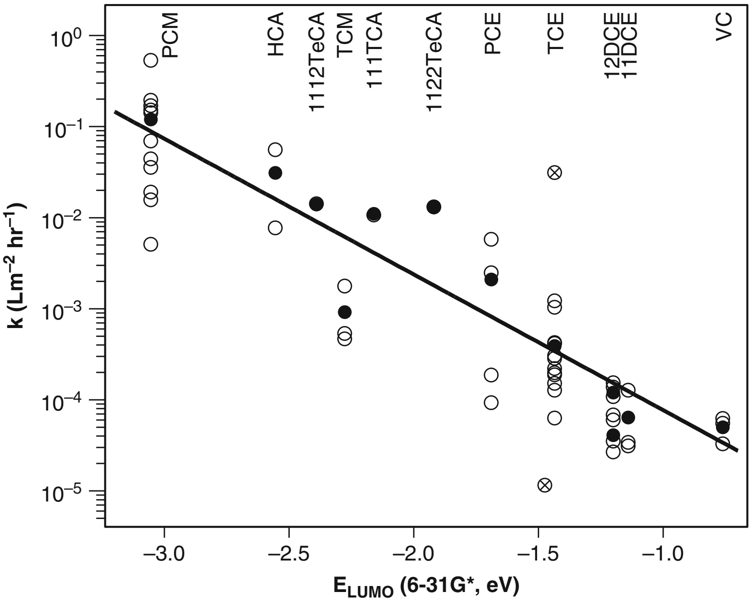


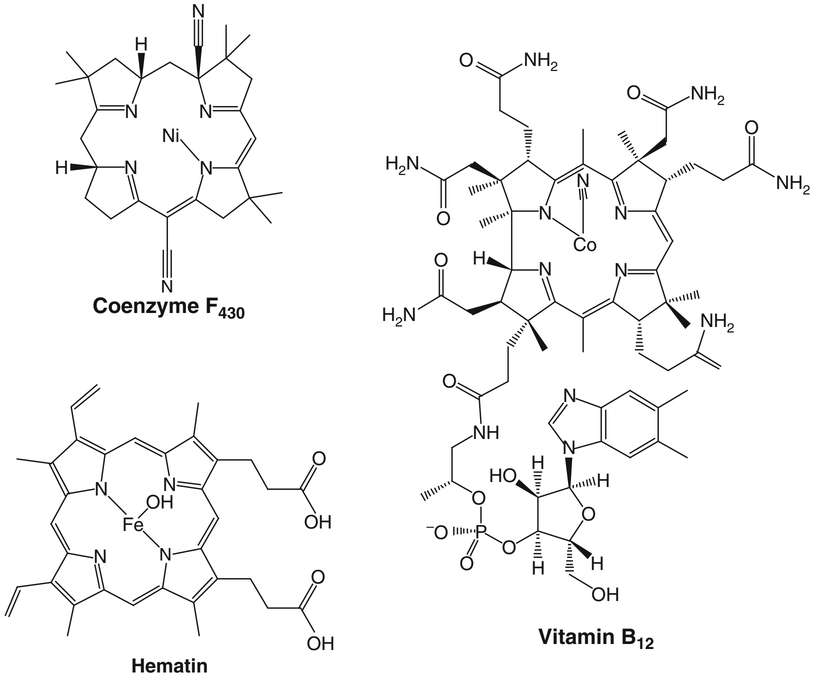
Figure 4.12. Linear free energy relationship for the reduction of chlorinated solvents by Fe(0) constructed by Scherer et al. (1998a). Kinetic data was compiled from rate constants reported in the literature by Johnson et al. (1996), whereas values for the descriptor variable (E_{LUMO}) were determined via computational methods. Reproduced from Scherer et al., 1998a (reprinted with permission from the American Chemical Society).

4.5 COUPLED BIOTIC-ABIOTIC PROCESSES

Although it is appealing to try to separate abiotic and biotic processes, in reality biogeochemical processes are complex and often difficult to decouple. Microbes modify their surrounding chemical environment by respiring to gain energy and assimilating materials to grow. These processes result in modification of both the aqueous and surface chemistry, which can dramatically influence the rate of chlorinated solvent transformation. Here, two examples of coupled biotic-abiotic processes that have been shown to influence chlorinated solvent transformations will be discussed: (1) excretion of reactive extracellular agents and (2) formation of reactive biominerals.

4.5.1 Biocatalysis

In anaerobic environments, bacteria have been shown to degrade chlorinated solvents such as TCE and PCE via a reductive dehalogenation mechanism (see Chapters 3 and 10). In most instances, these biologically-mediated dechlorination reactions appear to be cometabolic processes (Chiu and Reinhard, 1996), meaning that the bacteria do not directly benefit from the reaction. Rather, the chlorinated solvents are reduced by nonselective reagents that are produced by the bacteria for other metabolic functions. It is widely accepted that the reactive agents in these reductive dechlorination reactions are macromolecular metal-organic complexes called metallocoenzymes that are produced by the anaerobic bacteria. Examples of some common metallocoenzymes that react with chlorinated solvents are presented in Figure 4.13 (Gantzer and Wackett, 1991). Each contains a transition metal center that will serve as an electron donor when the metal is present in its reduced form. Thus, the reactive forms of vitamin B_{12} contain a Co(I) or Co(II) center, whereas the fully oxidized Co(III) is unreactive. Similarly, the reactive version of hematin and coenzyme F430 will contain Fe(II) and Ni(I), respectively.


Coenzyme F_{430}

Hematin

Vitamin B_{12}

Figure 4.13. Chemical structures of metallocoenzymes known to function as mediators for chlorinated solvent reduction in the presence of a bulk reductant (after Gantzer and Wackett 1991).

These metallocoenzymes serve as mediators for chlorinated solvent reduction, playing a similar role to other mediators previously described in this chapter (e.g., NOM). Accordingly, metallocoenzymes are typically present in low concentrations in natural environments and require a bulk reductant for the dechlorination reaction to be sustained. The bulk reductant itself is not particularly reactive toward the chlorinated solvent, although it can play an important role in chlorinated solvent reduction. For example, Chui and Reinhard (1995, 1996) found that the identity of the bulk reductant (either titanium[III] citrate or cysteine) influenced the rate and product distribution of CT reduction.

Vitamin B_{12}, which is also referred to as cobalamin, represents perhaps the most commonly studied metalloconenzyme with respect to chlorinated solvent reduction. Cobalamin possesses E_H values of approximately -0.6 and 0.2 V at pH 7 for the reduction of its metal center from Co (II) to Co(I) and Co(III) to Co(II), respectively. In the presence of a bulk reductant, cobalamin can reduce chlorinated methanes (Krone et al., 1989, 1991), ethanes (Schanke and Wackett, 1992) and ethenes (Gantzer and Wackett, 1991; Glod et al., 1997a, 1997b). Generally, its reactivity within a class of chlorinated solvent increases with the number of chlorine substituents (Krone et al., 1989; Gantzer and Wackett, 1991). In fact, interest in the field-scale application of vitamin B_{12} and other metallocoenzymes for the treatment of chlorinated solvents stems primarily from their ability to degrade CT and PCE, which unlike lesser chlorinated compounds are recalcitrant to biodegradation in aerobic environments (Fetzner and Lingens, 1994). With respect to degradation pathways, chlorinated ethenes are proposed to react via parallel hydrogenolysis and reductive β-elimination pathways shown in Figure 4.5 (Burris et al., 1996), whereas CT reduction is analogous to that shown in Figure 4.7 (Krone et al., 1991).

4.5.2 Biominerals

Microbial modification of chemical environments often leads to the formation of inorganic minerals through a process known as biomineralization (Banfield and Nealson, 1997). General trends in both microbial communities and iron mineralogy are illustrated in Figure 4.14 for a sequence of redox zones starting with an oxidizing (aerobic) zone and moving through nitrate-, iron-, sulfate-reducing and methanogenic anaerobic zones. Both Fe(III) and sulfate represent terminal electron acceptors in many aquifers and sediments resulting in formation of reduced iron and sulfur minerals that can reduce chlorinated solvents (Kenneke and Weber, 2003). The change in subsurface iron chemistry is largely a direct result of dissimilatory iron-reducing bacteria (DIRB), that couple the oxidation of organic matter or H_2 to the reduction of Fe(III) to obtain energy for growth (Lovley, 1991; Nealson and Myers, 1992). Biominerals commonly observed include siderite ($FeCO_3$), magnetite (Fe_3O_4), vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$), green rust and maghemite (γ-Fe_2O_3) (Fredrickson et al., 1998; Zachara et al., 2002). In more reducing zones, sulfate-reducing bacteria (SRB) dominate and the production of sulfide from sulfate reduction results in the commonly observed "black" iron sulfides, such as mackinawite (Rickard, 1969).

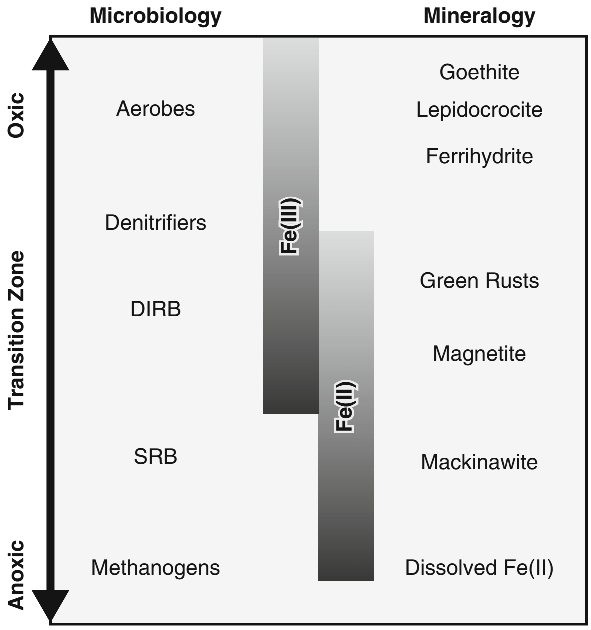


Figure 4.14. Conceptual diagram of dominant microbial-mineral redox zones in the subsurface. Figure originally drawn by Aaron G.B. Williams

The reduction of chlorinated solvents by the chemically synthesized versions of these minerals has been investigated quite extensively (see Section 4.4.2), but fewer studies have measured dechlorination rates in the presence of anaerobes, such as DIRB, SRB and methanogens. Recent work by McCormick et al. (2002, 2004), for example, demonstrated CT reduction by magnetite particles formed from reduction of hydrous ferric oxide by the DIRB species *Geobacter metallireducens*. Interestingly, abiotic rates of reduction by the biomineralized, washed magnetite were found to be significantly faster than the biotic reaction in the presence of cells alone (McCormick et al., 2002; McCormick and Adriaens, 2004).

Gander et al. (2002) have also studied the reduction of 1,1,1-TCA in the presence of FeS and a methanogenic consortium enriched on lactate (Gander et al., 2002). They observed a synergistic effect in the rate of 1,1,1-TCA transformation when FeS and methanogenic consortia were combined that could not be explained by summing the independently measured abiotic and biotic rates. They also found that the supernatant from the cell culture could reduce 1,1,1-TCA, similar to an earlier observation with CT and CF reduction by the supernatant from a pure methanogen culture (Novak et al., 1998). In both cases, soluble, extracellular products appear to react with the chlorinated solvents, but Gander et al. (2002) speculated that the extracellular products may also enhance the reactivity of the FeS by altering the surface redox chemistry. The synergistic interaction observed between FeS and the methanogenic consortium suggests that considering independently determined biotic and abiotic rates may not be sufficient for characterizing rates of chlorinated solvents and that more work is needed to understand coupled abiotic-biotic pathways.

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CHAPTER 5

ENGINEERING AND IMPLEMENTATION CHALLENGES FOR CHLORINATED SOLVENT REMEDIATION

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5.1 INTRODUCTION

This chapter identifies and discusses many of the challenges of evaluating, engineering (designing) and implementing *in situ* remediation technologies for chlorinated solvent plumes in groundwater. Most challenges discussed are not unique to a specific remediation technology, although there are technology-specific challenges. For example, adequate delivery of reagents is the most universal challenge because so many *in situ* remediation technologies rely on injecting treatment reagents into a subsurface that is often highly heterogeneous. The reagents used may be liquids, solids or gases, and the challenges associated with all three of these phases are unique to some extent. While this chapter cannot cover all of the challenges faced during *in situ* remediation, it is hoped that the discussion presented will enable the reader to extrapolate to other challenges not covered.

Remediation practitioners, including coauthors of this book, have generously shared their experience with *in situ* technology implementation.[1] This chapter reflects the discussions the authors had with these experts.

5.2 OVERVIEW

In situ remediation technologies can be thought of as extensions or modifications of technologies used for aboveground treatment of water and wastewater. There are fundamental chemical and biochemical engineering principles that govern the design and performance of these aboveground systems. Project engineers and managers have significant control over the environmental conditions in the reactors used for aboveground treatment. Consequently, these reactors can be designed to have very specific levels of performance that can be predicted with a relatively high degree of certainty (e.g., specific discharge standards typically can be achieved on a routine basis in a wastewater treatment system).

However, *in situ* remediation is more challenging than aboveground treatment for two overarching reasons:

- **It is difficult to "see" below the ground surface**. Practitioners can install a large number of wells and investigation points and still not completely understand the geology and hydrogeology, or the location and distribution of chlorinated solvent contamination.

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[1] Personal communications with Bruce A. Alleman, Brown and Caldwell; Richard A. Brown, ERM; Suthan S. Suthersan, ARCADIS; John T. Wilson, U.S. Environmental Protection Agency (2006).

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- **It is difficult to deliver reagents to the contaminants**. The subsurface is inherently complex and heterogeneous, in contrast to the well-mixed and controlled reactors often used for aboveground water treatment. These complexities make it extremely difficult to achieve complete contact or mixing of treatment chemicals with the contaminants.

These challenges of working in the subsurface were first encountered, and to some extent solved, for the remediation of petroleum hydrocarbons. The experience with fuels thus provided a starting point for treating chlorinated volatile organic compounds (CVOCs) (NRC, 1994). However, *in situ* treatment technologies for CVOCS are typically required to deal with the unique chemical and biochemical challenges inherent to the treatment of CVOCs in general. For example, unlike petroleum hydrocarbons, CVOCs are relatively oxidized and therefore *in situ* reduction is often a more effective approach than oxidation. Furthermore, biological treatment of CVOCs is complex whether it is implemented *in situ* or in an aboveground wastewater treatment system. Finally, the physical properties of CVOCs result in complex distributions in the subsurface, further complicating their remediation.

There are no simple solutions to the challenges of *in situ* treatment, and in some cases, no solutions at all. Rather than "solutions," it may be more appropriate to think of "managing" the challenges, uncertainties and risks at a contaminated site. Managing the challenges of *in situ* treatment of CVOCs can start with the following general approaches:

- **Manage the most significant risks first.** Identify the current and most significant risks to human health and the environment from subsurface contamination, and manage them first and foremost. This approach may include providing vapor intrusion mitigation measures for CVOCs under or near buildings, supplying alternative water supplies or well head treatment when water supplies are impacted, and installing barriers or interceptors to reduce the potential for migration of contaminated groundwater to surface water bodies.
- **Develop realistic expectations.** Appreciation of the general challenges and uncertainties should lead to more realistic performance expectations for *in situ* remediation systems. It can be difficult for some site owners and regulators to accept incomplete and long-term cleanup, as well as the inherent uncertainties in both performance and cost. Still, it is generally more cost effective in the long term to acknowledge the uncertainties and challenges and to communicate them to the affected community.
- **Use treatment trains, and have patience**. It is often prudent to use treatment trains (e.g., applying different remediation technologies in time and/or space). For example, different technologies may be used for locations within a site that have significantly different contaminant concentrations. Natural attenuation is often the most appropriate "polishing" technology in a train of technologies, but it may take many years to achieve the final remedial objectives.
- **Use Triad or observational methods to characterize and remediate sites**. As will be discussed in more detail later in this chapter, these approaches involve thinking through the challenges and uncertainties as part of the design process, developing contingency actions, and using an iterative process of characterization and remediation.

For this discussion, it is assumed that source areas have been addressed in some manner. In practice, it is highly likely that the source area will need to be addressed, that the timing and extent of any source area remedies will be important for plume remediation, and that some source area remedies will have an impact on environmental conditions in the plume in addition to decreasing the maximum flux into the plume. These changes in conditions resulting from source area remediation may be favorable or detrimental to specific plume remedies.

This chapter provides a discussion of challenges to any *in situ* remediation effort at a site with chlorinated solvents in groundwater, and identifies management strategies for each challenge. The specific remedial and characterization technologies are discussed only briefly. More detailed information on specific technologies is available in other chapters of this volume, and general background information on various technologies and engineering approaches is available in other references, including Dupont et al. (1998), USEPA (1999), NRC (1994, 1997, 1999), Siegrist et al. (2001) and Suthersan (1997, 2002).

The challenges identified have been categorized into similar aspects of a remediation project for ease of presentation. The four categories are site characterization challenges, site features challenges, public concern challenges and implementation challenges.

5.3 SITE CHARACTERIZATION CHALLENGES

Site characterizations performed as part of a typical Remedial Investigation are almost always suboptimal for remediation technology selection and especially for system design. Remedial Investigations generally focus on establishing the limits of contamination and assessing the risks first, so remedial designers often encounter large data gaps and significant uncertainties. The specific characterization challenges are grouped into three issues in the following sections: optimizing the level of characterization, insufficient geological and hydrogeological characterization and insufficient contaminant delineation. The site characterization challenges are summarized in Table 5.1.

5.3.1 Optimizing the Level of Characterization

In situ remediation, as stated earlier, has two overarching challenges: one cannot see below the ground surface, and it is difficult to deliver reagents to contaminants in the subsurface. These challenges manifest themselves most notably when deciding on the optimum level of characterization of a site. The degree of characterization of a site can be thought of as a continuum with no data on one end and complete characterization via excavation (if that is physically possible) on the other.

A question that must be asked for every project, is what is the adequate or optimum level of characterization needed to achieve the desired outcome (e.g., cost effective remediation)? Having less than optimum characterization may lead to a number of other challenges. Too much characterization may result in total project costs, characterization plus remediation, being greater than necessary and may also delay remediation. It addition, it should be remembered that additional characterization is likely to be required at various stages in the remediation process (e.g., as part of an interim design for follow-up treatments or technologies), and there may be methods of managing the risks at some sites without the extent of characterization that might be required at other sites. For example, permeable barriers such as permeable reactive barriers (PRBs) have different characterization requirements than remedies employing injection systems (Morgan et al., 2005). The following sections provide additional discussion on the potential impacts of having less than optimum characterization.

5.3.2 Insufficient Geological and Hydrogeological Characterization

If the geology (aquifer matrix and rock types and variations in these types) and the hydrogeology (distribution of groundwater) are not adequately defined, delineation of the plume and the contaminant mass may be incomplete or inaccurate. This may make the selection and design of remedies more challenging. For example, having a less than optimal geologic and hydrogeologic understanding can limit the ability to determine and predict groundwater flow direction and seepage velocity, which will challenge the design of injection well spacing, screen interval and location.

Table 5.1. Site Characterization Challenges

Challenge	Potential Strategies	Notes / Examples
Optimizing the Level of Characterization	Additional Characterization	• Triad approach. • Observational method. • Computer modeling (models and costs should be proportional to potential savings).
	Site-Specific Testing	• Laboratory treatability tests. • Field pilot tests.
	Engineering Solutions	• Contain entire plume (e.g., with PRBs). • Overdesign remedial system.
Insufficient Geologic and Hydrogeologic Characterization	Additional Characterization	• Direct push tools (soil gas probe, cone penetrometer testing [CPT], membrane interface probe [MIP]). • Review area information (regional or nearby site reports). • Field testing (slug test, aquifer pumping, tracers, geophysics).
	Improve Flow Direction Estimates	• Quarterly well-gauging (contours from different seasons). • Examine records for nearby wells that may impact site. • Compare flow direction estimates to contaminant plumes. • Measure vertical gradients (piezometric pressure at different depths). • Evaluate physical site features for impacts on run-off and infiltration.
Insufficient Contaminant Delineation	Improve Vertical Delineation	• Coupled wells with shorter screens. • Diffusion samplers placed at varying depths. • Vertical profiling wells (continuous multi-channel tube [CMT] wells, FLUTe^{TM} samplers, Waterloo profilers, Westbay sampling tools).
	Improve Soil Contamination Estimates	• Detailed soil sampling for volatile organic compound (VOC) distribution. • Larger sample sizes for aquifer solids (consider field preservation methods). • Measure organic matter content in aquifer solids samples (calculate sorbed contaminant mass).

5.3.2.1 Groundwater Flow Direction

It is useful to understand the groundwater flow direction both vertically and horizontally to be able to predict mass transport of the CVOCs (see Chapter 6). Additionally, the flow direction will impact the design of the remedy, such as the method used to distribute reagents, the requirements for groundwater capture or the location of PRBs.

Typically, the horizontal groundwater gradient or piezometric surface is determined by surveying a number of wells and determining the depth to groundwater at these wells.

The gradient is often thought to define the direction of groundwater flow. However, it is not unusual for the groundwater gradient to vary due to seasonal changes in rainfall, use of production wells, and other causes such as changes in the amount of infiltration due to capping or construction. Additionally, the flow of contaminated groundwater may not precisely match the gradient due to the heterogeneity of the aquifer matrix. In these cases, the plume can be diverted and develop at an angle to the groundwater gradient.

The vertical groundwater gradient is also important. For example, if there is a downward gradient that has not been identified, it is possible to conclude that the plume is much shorter than it actually is. A design based on the incorrect information would not treat the farthest downgradient extent of the plume and might therefore not adequately protect downgradient receptors.

5.3.2.2 Seepage Velocity

If the seepage velocity is not known or reasonably approximated, it is difficult to accurately evaluate the transport of contaminants and injected reagents, the amounts of reagents needed, the spacing of injection wells for PRBs or the necessary thickness of a reactive barrier (such as a reactive trench). Seepage velocity can be estimated from a combination of aquifer permeability, aquifer porosity and groundwater gradient. Permeability, the hardest parameter to determine accurately, is often determined from slug tests, which are frequently inaccurate, or by relatively more accurate pump tests (see Chapter 18).

It is important to realize that the estimated seepage velocity generally represents the average seepage velocity, but the transport of contaminants and reagents will likely be more rapid than this average. Because the subsurface often will have one or more layers that are significantly more permeable than the measured average permeability, the contaminant front can spread more quickly than anticipated, and it also can be difficult to predict how fast reagents will be distributed once they are introduced into a formation.

The estimated seepage velocity is particularly useful for designing permeable barriers, especially those that are constructed as back-filled trenches, such as zero-valent iron (ZVI) walls. Although the amount of iron (or other material) placed in these systems, as well as the thickness of the barrier, depends to some extent on the concentration and reactivity of the contaminant within the barrier, these key design parameters are strongly affected by the seepage velocity through the permeable barrier because the velocity controls the effective contact time between the contaminant and treatment reagent.

5.3.3 Insufficient Contaminant Delineation

Obviously it is not possible to remediate CVOCs if their location is not known in three dimensions. Active remediation often involves moving fluids and introducing treatment reagents in sufficient amounts to the locations where contaminants are present or are migrating to in a timeframe that meets project goals. Limitations on delineation efforts due to cost issues or other factors (e.g., access) frequently restrict the extent and the completeness of delineation. The degree of effort, and thus the cost and time required, should be balanced against the savings in remediation time and cost that might result from a better understanding of the mass and distribution of the target compounds and the hydrogeology.

5.3.3.1 Horizontal Delineation

Site investigations frequently focus on the horizontal extent of contamination. In many cases, the full extent of the plume is not determined; more frequently, the horizontal and particularly the vertical distribution of contaminant mass are often incompletely determined. Too frequently, the site geology and hydrogeology are not utilized to assist in the planning of new borings and/or wells. Fate and transport modeling can be used to approximate (by an educated guess) the extent of the plume and possibly the distribution of mass.

In optimizing the characterization for the design of a remediation system, the potential "scale" of the remediation system (e.g., injection well spacing) should be considered. For example, it may be acceptable for regulatory purposes to delineate the extent of a large dilute plume with wells spaced every 150 meters (m) (500 feet [ft]). But if remediation wells need to be spaced every 15 to 30 m (50 to 100 ft), then further characterization may be required in a design investigation. In some cases, refinement of the delineation can be achieved through the observational method discussed in Section 5.3.4.1.

5.3.3.2 Vertical Delineation

The vertical component of flow can be critical to an effective remedial design. Contaminant plumes may have a significant and unrecognized vertical component of flow (Figure 5.1), but it is not unusual for plumes to be delineated using a series of wells screened at the same depth interval. When chasing a plume, it is possible for the far extent of the plume to be "diving" and thus, as shown in the Figure 5.1, the extent of contamination may be underestimated.

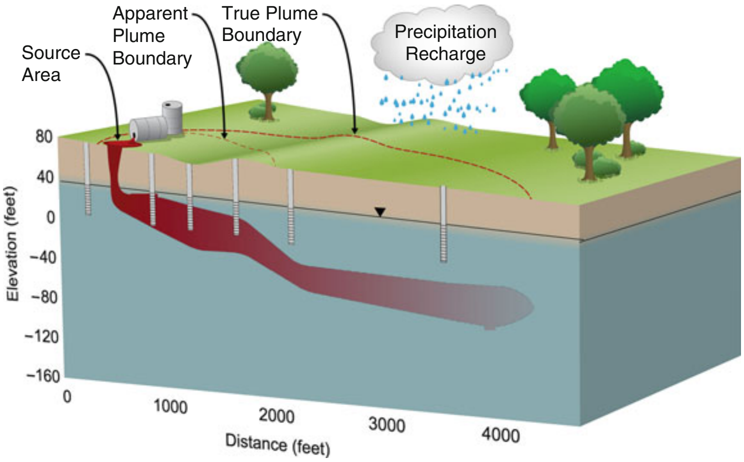

Figure 5.1. Challenges to delineation and design due to vertical flow and improper screen intervals (modified from Wilson, 2003).

5.3.3.3 Vertical Detail

A related and very common issue is the failure to determine a vertical profile of the contaminant concentrations with sufficiently high resolution. Usually, wells are screened over a vertical interval, for example from 1.5 to 5 m (5 to 16 ft). However, the CVOC may well follow preferential flow intervals and thus have higher concentrations in these intervals. As discussed earlier, when wells are screened over a constant depth, the deeper contamination may be missed and the horizontal extent of contamination will not be determined correctly. Wells screened over large intervals will yield data that is an average of concentrations over the entire interval. Sampling techniques and the vertical location of the sampling tool will affect the concentrations in the sample. If the sample represents the higher flow and more heavily impacted interval, then the total contaminant mass in the dissolved phase will be overestimated.

5.3.3.4 Soil and Solids Contamination

At one time, it was common to collect and analyze soil samples in only the unsaturated zone and to use only groundwater data to determine impacts in the saturated zone. This was a more common practice for hydrocarbon sites than for those contaminated with chlorinated solvents. For chlorinated solvents, especially where dense nonaqueous phase liquid (DNAPL) is present in the source area and thus high dissolved phase concentrations are observed in the plume, the vast majority of the contaminant mass may well be associated with the residual and/or sorbed phases. A thorough discussion of DNAPL is presented in Chapter 7 of this volume and by Feenstra and Cherry (1988) and Pankow and Cherry (1996).

When investigations focus on the dissolved phase, they may not adequately account for the residual or sorbed phase, which may represent the majority of the mass. As a result, the total mass is often underestimated and well and/or injection locations may not be optimal. Furthermore, the amount of reagent or operating time will be significantly underestimated. This issue is more important for aquifer matrices with high organic content than for sands and gravels.

In addition to the residual or sorbed phase, a significant amount of contaminant may exist as dissolved contamination in the lower permeability layers. These layers may not be fully represented when collecting groundwater samples from long well screens that collect water mostly from high permeability layers. “Back diffusion” from these lower permeability layers may have a significant impact on the overall performance of a remediation system.

Collection of representative and accurate samples of aquifer solids is very challenging and may be impracticable at some sites. The difficulty in characterizing CVOC sites is a result of the extremely heterogeneous distribution of contaminants at most sites, especially when nonaqueous phase liquids (NAPLs) were present at one time. Contaminant concentrations can vary by orders of magnitude within distances of a few centimeters. Many of the common characterization tools compound this challenge because of the small sample size commonly used. Losses of CVOCs due to volatilization and draining of residual DNAPL are also common challenges to getting accurate samples of aquifer solids. As a consequence, CVOC mass estimates are often very inaccurate and tend to be low.

5.3.4 Site Characterization Strategies

5.3.4.1 Optimizing the Level of Characterization

In general, the strategies for managing the challenges posed by the need to optimize the site characterization activities can be grouped into three general categories: additional characterization, site-specific testing and engineering solutions. These are briefly described below, with examples of technologies or methods that may be useful.

Additional characterization should focus on cost effectively and rapidly obtaining a sufficiently detailed and accurate understanding of the site for remedial design. In general, it is helpful to use the “observational,” or adaptive management method, continuously updating and adjusting the conceptual site model over time (see Section 5.7.1.2). In such cases, less characterization may be adequate. The Triad process is often useful for characterizing a site in a rapid and flexible manner (ITRC, 2007). Computer modeling also may be part of the characterization process, though it is important to ensure the level of modeling (and the costs) is proportional to the potential savings.

Site-specific testing options include laboratory treatability and field pilot testing. This testing can help overcome limitations of the existing site data and can provide focused information needed for design or full-scale treatment.

The engineering solutions that can help include (1) containing the entire plume (e.g., with a PRB) to provide more certain protection despite uncertainty in the conceptual site model (ITRC, 2005), (2) overdesigning the remedial system, again to provide more certain treatment despite the characterization uncertainties and (3) using an observational method to the design and implementation (adapting the design as more is learned during the implementation).

More specific discussions of potential optimization strategies are provided in the following sections. These sections address the two major challenges identified earlier: insufficient geological and hydrogeological characterization of a site and insufficient delineation of the contaminant distribution.

5.3.4.2 Geologic and Hydrogeologic Characterization

The initial step in dealing with an inadequate hydrogeological understanding is to review publications on regional geology or reports from nearby sites to get an initial idea of the site geology and hydrogeology. For field investigations, it is often helpful to use direct push tools (e.g., soil gas sampling, cone penetrometers, membrane interface probes or other direct push tools) often combined with field analytical methods, to obtain more detailed information quickly and at a lower cost. Geophysical tools can be used to provide a broad understanding of the site. Other field-testing techniques that should be considered to better understand the hydrogeology include aquifer pumping, slug tests and tracer studies.

A particular concern is the common difficulty in adequately assessing flow direction, both laterally and vertically. Several techniques can help address this problem:

- Conduct quarterly rounds of well gauging to understand the variations in groundwater flow direction. Develop groundwater contours from data collected during different times of the year.
- Examine records for well usage in the immediate area to understand the impact on groundwater flow direction.
- Compare anticipated groundwater flow direction based on groundwater contours to contaminant distribution.
- Measure vertical gradients by determining the piezometric pressure at various depths in the same well or with wells screened over different intervals.
- Look for changes in physical features of a site, such as new surface contours or construction that could impact run-off and groundwater infiltration.

5.3.4.3 Contaminant Delineation

Four methods can assist in cost effectively improving the understanding of the distribution of contaminants:

- Conduct vertical profile sampling to help understand variations in contaminant concentrations with depth. Use shorter screens with well couples or diffusion samplers placed at multiple depths, especially in wells with long screens.
- Use specially designed wells (e.g., CMT wells, FLUTe^{TM} samplers, Westbay sampling tools and Waterloo profilers) to obtain samples with depth (Parker and Clark, 2002).
- Use more detailed soil sampling for VOC distribution since it is often highly heterogeneous. It also can be helpful to use larger sample sizes than are typically used. When

using larger samples, it can be important to carefully consider field preservation methods as well. Equally or more important is the methodology used to obtain subsamples for analysis.

- Measure the organic matter content (F_{oc}) of the aquifer solids from several samples. This information should be used to estimate the sorbed contaminant mass.

5.4 SITE FEATURES CHALLENGES

Site-specific conditions can pose a wide range of challenges for any *in situ* remediation system. Subsurface features can restrict the types of technologies applicable at a site, and also strongly affect performance, costs and key design parameters. Challenges related to site features are discussed in the following sections and are summarized in Table 5.2.

Table 5.2. Site-Related Challenges

Challenge	Potential Strategies	Notes / Examples
Heterogeneous Subsurface Conditions	Additional Testing and Characterization	• Conduct laboratory and field pilot testing. • Conduct tracer tests or pump tests (to understand the variability in hydrogeology and better target reagent delivery). • Use direct injection techniques to vertically delineate injectivity. • Employ observational method (install some treatment wells, and adjust location of other wells based on performance during initial phases).
	Computer Modeling	• Model several potential designs to identify most efficient distribution strategy. • Model flow paths of injected liquids.
	Engineering Solutions	• Contain entire plume (e.g., with PRBs). • Employ robust treatment technologies (e.g., thermal treatment or subsurface mixing). • Use treatment trains to manage risks from untreated contamination.
	Improved Delivery Techniques	• Use direct push injection (allows injection at closely spaced intervals in low- or high-permeability formations). • Install nested well screens (allows delivery at varying depths). • Use recirculation systems (distribute amendments cross-gradient to groundwater flow and let amendments drift downgradient). • Use pneumatic or hydraulic fracturing to deliver to low-permeability zones (Schnell, 2005). • Drill horizontal wells (particularly for large plumes). • Inject large volumes of low concentrations of electron donor for large plumes. • Inject chase water to increase distribution.
	Modified Reagent Formulations	• Use long-lasting reagents (increase diffusion into lower-permeability areas). • Increase reagent concentrations (increase diffusion, but avoid clogging). • Use thickening additives (e.g., polymers) to improve distribution. • Select technology based on longevity of amendment compared to rate of distribution for specific site conditions.

(*continued*)

Table 5.2. (continued)

Challenge	Potential Strategies	Notes / Examples
Geochemical Constraints	Modify Geochemical Conditions	- Add buffers or pH-adjusting chemicals.
	Selection of Compatible Technologies	- Avoid (or test) biological treatment in high-sulfate aquifers. - Avoid some chemical oxidation technologies in high-carbonate aquifers. - Use oxidation at high-redox sites or reductive technologies in reducing conditions.
Microbiological Constraints	Engineering Solutions	- Add more electron donor and wait to see if *Dehalococcoides* (DHC) populations increase. - Bioaugment after ensuring appropriate geochemical conditions. - Initiate treatment slowly, to avoid build up of toxic levels of byproducts. - Investigate nonbiological attenuation mechanisms (may be sufficient for monitored natural attenuation (MNA) at sites with low contaminant levels).
Ongoing Contaminant Sources	Additional Characterization	- Verify, to the extent possible, that all primary sources (e.g., tanks and pipelines) are removed or sealed.
	Engineering Solutions	- Contain plume at the downgradient edge of the source area (e.g., with PRBs). - Treat the source zone to reduce ongoing flux to the groundwater plume.
Contaminant Mixtures	Technology Selection	- Select a robust technology capable of treating all contaminants (e.g., air sparging for volatile contaminants).
	Engineering Solutions	- Use treatment trains to address all contaminants.

5.4.1 Reagent Delivery in Heterogeneous Subsurface Environments

Another major challenge for *in situ* remediation, in addition to optimizing the level of characterization, is the difficulty in effectively delivering reagents to the heterogeneous subsurface environment. The most common *in situ* remediation technologies for dissolved phase plumes involve delivery of treatment reagents; reagent delivery is the most commonly cited challenge to *in situ* remediation. The following sections discuss some of the most common factors influencing effective contact between remedial agents and contaminants in the subsurface. Because of the widely recognized importance and limitations of technology for delivery and mixing of remedial reagents in the subsurface, an entire volume in this monograph series has been focused on these issues (Kitanidis and McCarty, 2010).

5.4.1.1 Low Permeability

Subsurface solids with low permeability generally impede the migration of contaminants but also limit the distribution of water, treatment reagents and air. Low permeability aquifers may also tend to have high organic matter content, resulting in a high natural demand for chemical oxidants.

The impact of low permeability on delivery of treatment reagents is relatively easy to appreciate by considering Darcy's equation, which governs the transport of fluids in the subsurface. Darcy's equation states that the flow of a liquid is directly proportional to the permeability of the subsurface and the pressure of injection. Since the injection pressure must be kept below the pressure that will cause fracturing of the aquifer matrix or surfacing of treatment chemicals up the bore hole, very little injection flow can be achieved when permeabilities are in the 10^{-4} centimeter per second (cm/sec) range or lower.

Even if injection is possible, it will take a long time for the reagents to reach all of the contaminant mass if the permeability is low (Jackson et al., 2003). For *in situ* chemical oxidation (ISCO) reagents, time is critical. Hydrogen peroxide will decompose and, as with other oxidants, react with the organic matter or reduced metals in the aquifer matrix. If transport is slow, degradation and side reactions will consume the oxidant before it reaches points sufficiently distant from where it was injected. Air sparging also will be difficult since a relatively small radius of influence (ROI) will be achievable.

5.4.1.2 High Permeability

Highly permeable aquifer matrices also can be problematic. Such aquifers are conducive to extensive transport of the contaminants. As a result, very large areas may be impacted (e.g., large plumes). Injected water amended with reagents will not mound, and little lateral migration will occur, resulting in "pin stripe" zones of treatment downgradient of the injection point. As a result, large injection volumes or numerous injection/recovery locations may be required for both recovery and injection. PRBs may have to be robust to accommodate the rates at which VOCs and alternative electron acceptors pass through the barrier. For very permeable aquifers (e.g., coarse gravel), the ROI of air sparging wells may also be small since lateral dispersion will be limited as the air moves upward.

5.4.1.3 Aquifer Heterogeneity

Aquifer heterogeneity is almost a given in subsurface environments, and it should be anticipated at every site. Highly heterogeneous aquifers are highly complex and require special attention.

The heterogeneity typical of the subsurface can severely limit the ability to deliver reagents where needed for several reasons. Preferential migration of CVOCs through more permeable layers can result in plumes that are much larger than predicted from field tests. However, most of the CVOC mass may be located within less permeable zones, over a relatively small lateral area and within limited vertical expanses. In older plumes, especially in heterogeneous formations and in bedrock, CVOCs will have diffused into regions where there is little to no groundwater flow. The mass of contaminants in these locations can range from relatively low to significant portions of the total mass of CVOCs in the formation (Chapman and Parker, 2005). Contaminant mass in low permeability zones is hard to measure since attempts to collect groundwater will likely incorporate water from more permeable zones.

The second critical issue is that injected fluids also will move more readily through the more permeable zones, providing inadequate contact between reagents and contaminants in the low-permeability zones. If the geology is complex, injected fluids are likely to move along the most permeable pathways. Reagents also will distribute more quickly through the more permeable zones and usually to a greater extent than anticipated. Contaminants may have followed the same initial pathways provided they were introduced at the same point. However, contaminants may have diffused into secondary pores and into less permeable aquifer materials. Hence, delivery of reagents into these regions will be difficult and may rely almost entirely on diffusion.

5.4.1.4 Bedrock

Bedrock provides numerous challenges. Groundwater flow through bedrock is controlled by fractures, both vertical and horizontal, that may be hard to locate and that may or may not be interconnected. The effective porosity in bedrock is varied and difficult to determine unless tracer or other tests are performed (Shapiro, 2001). Bedrock porosity, except for karst systems, is much less than that of unconsolidated formations. Thus, due to low porosity, a given volume of bedrock contains a much smaller volume of water than the same volume in an unconsolidated formation. The smaller pore volumes also accommodate a smaller volume of reagent-containing water (Werner and Helmke, 2003). Groundwater velocities can be orders of magnitude larger than for unconsolidated formations. There is some forgiveness to bedrock systems in that the mass of contaminants might be small relative to the impacted volume.

Delineating bedrock systems is often difficult. Depending on the bedrock type, wells located only a few feet from each other may behave in vastly different manners, with achievable groundwater recovery and injectivity rates differing by several orders of magnitude. Wells in bedrock may or may not sample interconnected groundwater; hence, developing meaningful isoconcentration maps can be very difficult. Isoconcentration maps developed for bedrock aquifers are not as useful as those for unconsolidated aquifers. The potential lack of interconnectivity makes it nearly impossible to determine where to install injection wells.

Another concern is the presence of secondary fractures, also thought of as dead-end fractures. Contaminants can diffuse into these fractures over time. For old sites, the mass of remaining VOCs may predominantly reside in the secondary fractures or rock matrix, with relatively little mass residing in the primary fractures (Goldstein et al., 2004). Migration of contaminants into the matrix, where they are largely inaccessible, makes it difficult to remediate the site or to quantify the total mass of contamination present. If the primary fractures are rendered clean, then contaminants will diffuse back out of the matrix and the secondary fractures. However, this diffusion is a very slow process, and contamination may persist over very long periods. Achieving typical cleanup criteria in groundwater within bedrock may require a very long time. However, it may be such that the very slow rate of diffusion out of the secondary fractures and surrounding matrix may be slower than the total effect of the combined natural attenuation mechanisms within the primary fractures.

5.4.1.5 Drilling Conditions

In some formations, the presence of cobbles, depth to water, dense solids, fill or underground utilities, as well as the need to drill within buildings, leads to challenges in locating wells for either investigation or treatment. Installing systems within buildings is frequently difficult or impossible. However, newer drilling methods, such as sonic rigs, are useful in more difficult formations and may permit something close to vertical boring and vertical wells. Some newer wells require less clearance and thus can be used under a greater variety of conditions within buildings.

5.4.1.6 Deep Water Tables and Large Saturated Intervals

For deep aquifers or thick contaminated intervals, such as those found in much of the southwestern United States, drilling and well installation can be very expensive and may eliminate most options for direct injection. For large saturated intervals, the amount of amendments and volume of water required may be cost-prohibitive for technologies that involve delivery of amendments.

5.4.1.7 Strategies to Improve Remediation in Heterogeneous Environments

The strategies for improving delivery of reagents in heterogeneous subsurface environments can be grouped into four general categories: additional characterization and testing, engineering solutions, improved delivery techniques and modified reagent formulations. Many of these strategies are similar to those presented earlier (Section 5.3.4) for managing the challenge of optimizing site characterization.

Additional characterization and testing can include the following:

- Laboratory and field pilot testing, generally done to determine the longevity of reagents in anticipation of long delivery times (this testing may include tests for natural oxidant demand for ISCO technologies [Thomson and Xu, 2005] and estimation of the consumption of electron donors by electron acceptors such as nitrate).
- Tracer tests and/or pump tests to understand the variability in the hydrogeology and better target reagent delivery.
- Direct injections with monitoring to vertically delineate injectivity and better target delivery.
- Use of the observational method (for example, it can be very helpful to install some treatment wells, perform a first phase of treatment, and adjust location of other wells based on performance).
- Computer modeling to improve injection designs in heterogeneous environments (not only can models help predict flow paths for injected liquids, they can also be used to compare different potential design alternatives to identify the most efficient distribution strategy).

Engineering solutions may include using robust technologies (such as thermal treatment or subsurface mixing) and using treatment trains to manage risks from untreated contamination. There are several alternatives for improving delivery:

- Use direct push injection methods to allow injection at closely spaced intervals in low- or high-permeability formations.
- Use nested well screens to control delivery at various vertical intervals.
- Use recirculation systems (injection/recovery) to distribute amendments cross-gradient to groundwater flow and let the gradient distribute the amendments.
- Use pneumatic or hydraulic fracturing to improve the distribution of reagents in low permeability zones (Schnell, 2005).
- Use horizontal directionally drilled wells for large plumes.

Finally, many of the amendments differ in longevity or mobility, and many have been formulated to improve delivery or to meet varying site needs. Some modifications to consider for overcoming heterogeneity are listed below:

- Use long lasting reagents to improve the ability to deliver reagents via diffusion into fractures or lower-permeability layers.
- Use higher concentrations of reagents to foster diffusion, but avoid clogging, in low-permeability or heterogeneous formations.
- Use thickening additives (polymers) in injected solutions to produce thixotrophic fluids that may improve the distribution of chemicals in heterogeneous formations.
- Select technologies based on the expected longevity of the amendment compared to the expected rate of distribution given the specific site conditions.

5.4.2 Geochemical Constraints

The mineralogy and geochemistry of a site are important factors affecting the use of most remediation technologies (Chapelle, 2001). For example, two major considerations in the selection and design of an enhanced reductive dechlorination (ERD) system are the feasibility and the costs required to lower the redox potential to a range where the appropriate microorganisms can function efficiently. Similarly, chemical oxidation and chemical reduction technologies are designed, in part, to manipulate redox potential and in some cases pH. The existing conditions in a given aquifer may not favor a particular technology and may be difficult to manipulate without using large amounts of reagents. For example, it may be impractical in a highly buffered limestone aquifer to achieve the low pH required for some catalyzed hydrogen peroxide (CHP) processes. Other aquifers may have high flow of groundwater that is highly oxygenated and/or has high sulfate content. Thus, the combination of geochemistry and flow rate will consume large amounts of the electron donors needed for reductive dechlorination. The site geochemistry also can strongly affect the performance of ZVI barriers (Wilkin et al., 2003).

Another example of the impact of mineralogy and geochemistry of aquifer solids and groundwater on *in situ* remediation is the wasteful consumption of chemical oxidants due to reactions with non-targeted chemical species. These non-targeted species, such as native organic matter (Thomson and Xu, 2005), compete for chemical oxidants and therefore require addition of greater than stoichiometric amounts. These reactions also make delivery to points distant from the injection location more difficult and increase the time needed to achieve remedial goals. Each of the common ISCO reagents reacts to a different extent with the natural oxidant demand (NOD) resulting from organic matter and reduced inorganic compounds. The efficacy of hydrogen peroxide and persulfate also can be impacted by minerals, especially the amorphous reduced iron and manganese minerals that are typically present in aquifers. Additional information on the impacts of geochemistry on *in situ* chemical oxidation can be found in Chapter 15.

The mineralogy and geochemistry of a site also may be highly heterogeneous, and this heterogeneity can also cause problems for remediation. As with the geology and hydrogeology, the mineralogy of a site can vary widely between different geologic zones and layers that may be spaced as close as centimeters apart. This variable mineralogy may impact the resulting geochemistry and the ability to perform *in situ* remediation. Collecting representative samples of the aquifer matrix to quantify the impacts of the mineralogy on remediation (e.g., through NOD testing) can be challenging, and results obtained may be uncertain.

The combined sources of uncertainty, including uncertainties about reaction rates, the potential for reactions of amendments with native materials, the distribution of amendments within the formation, and the distribution of contaminants within the aquifer, make it very difficult to design efficient remediation systems that deliver sufficient amounts of reagents to degrade all of the contamination without wasteful consumption. In many cases, the potential for excessive reagent consumption is not fully appreciated or understood until remediation has been implemented.

5.4.2.1 Strategies to Manage Geochemical Constraints

Under some conditions, it may be possible to modify the geochemistry through the use of buffers or pH-adjusting chemicals, addition of oxidants or reductants or the addition of amendments such as sulfides to precipitate metals. Otherwise, it will be necessary to select compatible technologies. Considerations for selecting compatible technologies are listed below:

- Select technologies that are compatible with geochemistry. Examples include the use of chemical oxidation if the redox potential is high, or reductive dechlorination or a ZVI wall if the redox potential is low or negative.
- It is generally best to avoid reductive dechlorination if sulfate levels are high (e.g., >500 milligrams per liter) since the electron donor demand may be high.
- Avoid some chemical oxidation processes (e.g., those requiring low pH conditions) if carbonate concentrations are high.
- For aquifers with limited buffering capacity and high pH (>8.0), use lactate or add a buffer with the electron donor when implementing reductive dechlorination.
- Similarly, for aquifers with lower pH values (<5.5) and/or low buffering capacities, inject neutralizing materials such as sodium bicarbonate to prevent the inhibition of dechlorinating bacteria as the pH decreases due to organic acid production.

5.4.3 Microbiological Constraints

As discussed in greater detail in Chapter 3, reductive dechlorination typically depends on both the microbial population and the geochemistry and supply of electron donor. Active bioremediation has become a widely used primary treatment technology, and MNA is also a typical polishing step after active treatment. Hence, it is often important to understand the microbiological potential for biodegradation at a site and to manage problematic biological conditions. Typical microbial challenges include the absence or low numbers of desired microorganisms, and toxic or inhibitory conditions that can limit their desired activities. It is imperative to consider the degradation of intermediate compounds (daughter products), as well as the parent compounds, which may themselves degrade by a number of mechanisms. Stable isotope analysis can help differentiate between dilution/adsorption and the various degradation mechanisms (Slater et al., 2001; Sueker, 2001; Hirschorn et al., 2007).

5.4.3.1 Insufficient Microbial Populations

For biodegradation-based remedies, the microbiology is exceedingly important. If the requisite bacteria are not present, degradation or complete degradation may not occur. The most common example is the absence or low numbers of *cis*-1,2-dichloroethene (*cis*-DCE) degrading bacteria, such as DHC. In the absence of active DHC, complete reduction to harmless products such as ethene will not occur or will occur at too slow a rate to achieve remediation goals in an acceptable timeframe. In some cases, this limitation may be mitigated by other reactions, such as aerobic or anaerobic oxidation or abiotic reactions. In addition, at some sites, native microbial populations will respond to electron donor addition alone while at other sites, bioaugmentation may be necessary. In the last few years, significant advances have been made in identifying and evaluating the microbial populations present in aquifers and groundwater (Koenigsberg et al., 2005; Stroo et al., 2006).

5.4.3.2 Toxicity to Bacteria

Toxicity due to geochemical conditions or due to the presence of toxic chemicals or degradation byproducts may result in a decreased viable microbial population (Talley, 2006). This has not been a widely discussed or studied problem for *in situ* biodegradation compared to the reports for aboveground reactors. *In situ,* the conditions vary widely over even short distances so that micro-conditions may exist where toxic products may accumulate. However, the inhibitory compounds may either be degraded or diluted a short distance away, so there may be no net observable impact. Furthermore, *in situ* biodegradation may involve a lag time followed by a slow growth period during which acclimation to the toxic species may occur.

5.4.3.3 Strategies to Manage Microbiological Constraints

Engineering solutions are available to overcome microbiological challenges in many cases. Some engineering solutions to consider are identified below:

- Add more electron donor (biostimulation) and monitor to determine if complete reductive dechlorination will eventually occur as the numbers of native bacteria increase.
- Bioaugment with DHC-containing cultures after adjusting the redox potential to increase the potential for survival of the added DHC.
- For MNA with low levels of complete reductive dechlorination, investigate whether other attenuation mechanisms (such as cometabolic aerobic biodegradation) are important and sufficient to meet project goals.
- Initiate treatment slowly to avoid accumulation of toxic levels of byproducts.
- Add buffers or select reagents (lactate vs. lactic acid or alcohols) to avoid adverse pH effects.

5.4.4 Ongoing Sources of Contaminants

Cleaning up a chemical spill to groundwater is obviously going to be hampered if fresh contamination continues to enter the treatment zone. The potential for continued releases of CVOCs from the primary source (e.g., tank, pipeline, drums) has been greatly reduced by improvements in product and waste management, as well as the move away from chlorinated hydrocarbons as primary industrial solvents. However, the potential for recontamination does exist at old industrial facilities from unknown waste sources, product tanks and pipelines.

The continued release of contaminants from secondary sources, such as DNAPL source zones, could be a factor that must be considered and dealt with in the remediation of CVOC plumes. Effective containment or source zone treatment should significantly reduce the flux of contaminants into the groundwater plume zone, but there may be some continued mass flux that needs to be considered.

5.4.4.1 Strategies to Manage Ongoing Sources

Ongoing sources of contamination can be managed by additional characterization or through engineering solutions. Additional characterization can be performed to verify, to the extent possible, that all primary sources (e.g., tanks and pipelines) are removed or sealed. However, it is often difficult to exclude ongoing contaminant releases.

The engineering solutions available include addressing the source zone to reduce to a manageable level the ongoing flux to the groundwater plume and implementing PRBs or other forms of containment at the downgradient edge of the source area.

5.4.5 Contaminant Mixtures

While this monograph is focused on dissolved phase chlorinated solvents without the complication of mixtures, it is important to be aware of the impacts of mixtures on remediation technologies since sites with multiple contaminants are common. The challenges posed by mixed plumes result primarily from the failure of some technologies to treat all classes of chemicals present in the aquifer. Even the effectiveness of MNA might be challenged since some classes of compounds degrade poorly under the anaerobic conditions required to degrade most chlorinated compounds. A National Research Council (NRC) report (2005) discusses many of the issues relevant to evaluation and implementation of MNA. There also are differences in reactivity among the various common VOCs. Additionally, mixtures of VOCs can be problematic for chemical oxidation; for example, while chlorinated ethenes react readily with permanganate, chlorinated alkanes are practically inert to permanganate.

Mixtures are not always detrimental. The presence of some hydrocarbons within a plume can create reducing conditions and provide electron donors needed for reductive dechlorination. However, the presence of hydrocarbons, especially when present as mobile or residual light nonaqueous phase liquid (LNAPL), may make finding the bulk of the contamination more difficult, since it may be located at the top of the aquifer (dissolved in residual LNAPL) rather than deeper into the aquifer as would be expected with DNAPLs as sources.

5.4.5.1 Strategies to Manage Contaminant Mixtures

Mixtures require selection of one or more technologies capable of treating all of the contaminants. Key options include (1) selecting a robust technology that can manage mixtures, (2) considering air sparging if all contaminants of concern are volatile or aerobically degradable and (3) using treatment trains to manage mixtures.

5.5 PUBLIC CONCERN CHALLENGES

Remediation is implemented within a regulatory context and may also impact neighboring communities. The concerns of the public, as expressed both in the applicable regulatory requirements and the legitimate concerns of affected individuals, can raise challenges that are not necessarily technical in nature but can still affect *in situ* system designs and operations. Common public concerns are summarized in Table 5.3 and described in the following sections.

Table 5.3. Public Concern Challenges

Challenge	Potential Strategies	Notes/Examples
Regulatory Concerns	Education and Communication	• Inform regulators about technologies, including where technologies may have worked or failed under similar conditions. • Show options with cost estimates and estimated probabilities of success or failure; highlight potential negative impacts if the selected technology were to fail. • Include regulators in the technology selection and conceptual design process. • Conduct pilot tests to demonstrate performance.
	Improve Coordination	• Review regulations and requirements with controlling agency. • Use project staff familiar with the local regulations and regulators. • Determine what has been allowed at similar sites within the same jurisdiction. • Stay current with regulations and anticipate change.
	Use Risk-Based Strategies	• Consult with risk experts to determine if risk based approaches can be used and if such an approach is likely to be beneficial. • Consider MNA, no-further-action (NFA) or technical impracticability (TI) for post active treatment (be prepared to demonstrate, possibly through pilot testing, what reasonably can be expected to be achieved and that the cost effective endpoint has been reached).
	Manage Injection Restrictions	• Contain plume to prevent migration (e.g., with PRBs, impermeable barriers, or hydraulic control system for containment purposes). • Use underground piping between recovery and reinjection points so that groundwater never actually comes above the ground surface (allowed by some agencies). • Demonstrate that reagents will stay near the injection location(s) and that no long term detrimental effects will result from injection of treatment reagents.
Community Concerns	Education and Communication	• Keep the public informed in an honest and easily understood manner. • Provide published descriptions of technologies written in layman's language (e.g., the U.S. Environmental Protection Agency [USEPA] Citizens' Guides, which are available for many technologies; see http://www.epa.gov/tio/pubitech.htm).
Potential Indoor Air Vapor Intrusion	Additional Characterization	• Conduct vadose zone and groundwater sampling (follow approved protocols and consider lithology and depth to water). • Conduct indoor air sampling (consider indoor sources of the compounds of interest and follow approved protocols).
	Engineering Solutions	• Apply an aggressive/fast remedy. • Consider mitigation if risk is uncertain (may include soil vapor extraction or in-building mitigation.

5.5.1 Regulatory Issues

Without regulations, there would be minimal incentive for most remediation projects. Regulations also provide some continuity and guidelines for conducting site investigations and developing approaches to remediation. Regulations provide cleanup goals, both fixed goals such as maximum contaminant levels (MCLs) and alternative cleanup levels (ACLs). Furthermore, from a business point of view, regulations can create a level playing field for business competitors.

5.5.1.1 Unreasonable Expectations

Unreasonable expectations for remediation may be driven by the regulations and the regulators but also by site owners. These unreasonable expectations may include level of effort and time required for remediation, cleanup levels and cost. Unreasonable and unattainable groundwater standards are the most obvious challenge for all *in situ* technologies.

MCLs, and the more stringent limits imposed by some states, are typically difficult or even impossible to obtain site wide in a relatively short period of time with the technologies currently available. TI waivers (USEPA, 1993) were originally designed to be the regulatory solution to this challenge, but TI waivers have turned out to be very difficult to obtain (NAVFAC, 2008).

For some sites, risk-based standards can be used (e.g., Kansas DHE, 2007*)*. Risk-based standards can be established through fairly detailed risk assessment procedures, which can be expensive and run the risk of identifying lower cleanup levels for some sites, or through risk-based corrective action (RBCA) formulas (USEPA, 1995) that have been developed by nearly all states. In most cases, RBCA programs were first developed for petroleum hydrocarbons, but in most states they also apply to chlorinated solvents. While these options are available, it is frequently difficult to get ACLs approved. It may be much easier to obtain a no-further-action (NFA) status for the site or an agreement to proceed to MNA than to obtain an official less stringent cleanup goal.

5.5.1.2 Injection Permits

One potentially significant implementation challenge with technologies involving injection of reagents may be obtaining injection permits or similar permission to inject amendments into groundwater. This requirement can potentially eliminate a specific technology from an entire state. Fortunately, this limitation is becoming less common.

Some agencies preclude or limit the reinjection of untreated, or not completely treated, groundwater. Reinjection under Section 3020b of the Resource Conservation and Recovery Act (RCRA) (ITRC, 2000) requires that hazardous constituents be substantially reduced. However, the USEPA Office of Solid Waste does permit reinjection provided certain conditions are met (Faris et al., 2003). The Safe Drinking Water Act established the Underground Injection Control (UIC) Program (USEPA, 1996), which set these requirements. For sites not covered by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or RCRA, a UIC permit is frequently required.

Additionally, most agencies will want the aquifer to be returned to conditions similar to those observed outside the impacted area after treatment or at least to not exceed applicable standards, including secondary standards. Dissolved metals (such as arsenic for ERD and chromium for ISCO), pH and salinity are common concerns. Frequently, geochemical conditions and metal concentrations will revert over time and distance to pre-contamination conditions (Siegrist et al., 2001).

5.5.1.3 Differing and Evolving Regulatory Requirements

The remediation industry in the United States, and even more so around the world, is challenged by the fact that regulatory requirements differ between states and even within states, as well as between different agencies. This situation is partly due to the differing regulatory programs (e.g., CERCLA vs. RCRA vs. state programs), as well as the differences between regulatory programs and the individual regulators involved. Most of the regulations that guide remediation have sufficient flexibility that their interpretation is critical to the specific requirements for a site. As a consequence, one solution cannot fit all CVOC problems around the country, so the technical solutions that are adopted must be tailored to the particular regulatory climate.

In addition to being variable "spatially," regulations are variable with time—they are continually evolving. For the most part, these changes have been viewed as positive since they are generally more realistic. For example, CERCLA Records of Decision (RODs) are being written to anticipate the use of follow-on technologies that may or may not be specifically designated in the ROD.

5.5.1.4 Strategies to Manage Regulatory Issues

The options available for managing regulatory issues can be grouped into four categories: improved education, improved coordination, use of risk-based strategies and managing restrictions on underground injections.

Alternatives to improve education include the following:

- Inform clients and regulators about technologies, including where technologies may have worked or failed under similar conditions.
- Show options with cost estimates and estimated probabilities of success or failure; include potential negative impacts if the selected technology were to fail.
- Include clients and regulators in the technology selection and conceptual design process.
- Conduct a pilot test(s) to demonstrate performance.

To improve regulatory coordination, practitioners should review regulations and requirements with the controlling agency, utilize project staff familiar with the local regulations and regulators, determine what has been allowed at similar sites within the same jurisdiction(s), stay current with regulations and anticipate change.

Risk-based strategies may be useful, but they often require considerable effort to implement. Strategies to implement include (1) consultation with risk experts to determine if risk based approaches can be used and if such an approach is likely to be beneficial and (2) consideration of MNA, NFA or TI after using active treatment (be prepared to demonstrate what can reasonably be expected to be achieved—this may require a pilot test—and confirm that the cost effective endpoint has been reached).

Managing injection restrictions is not typically difficult, but it can be time-consuming and may require added costs. Some strategies to consider are listed below:

- Use one or more PRBs, an impermeable barrier or a hydraulic control system for containment to prevent releases of injected materials.
- Use underground piping between recovery and reinjection points so that groundwater never actually comes above the ground surface (allowed by some agencies).
- Demonstrate that reagents will stay in close proximity to the injection location(s) and that no long-term detrimental effects will result from injection of treatment reagents.

5.5.2 Community Concerns

Most environmental regulations require that all stakeholders, including those living or operating businesses in proximity to sites, have the opportunity to be informed about site conditions, the potential risks and proposed remedies. Notifications and public meetings are required. Some remedies are less easily accepted by some stakeholders because they have the potential to be disruptive, may be perceived to create additional risks, or appear to be intended to minimize costs without adequately addressing the problem. MNA, for example, often has been seen as a "walk-away" alternative (Norris et al., 2004). Another concern to owners and neighbors is how the remedy might impact the future use of the property (Cook and Friedland, 2005; Greenberg et al., 2005).

In most cases, scrutiny by the regulatory agencies involved is aimed at reducing the probability that risks will not be adequately managed and at concerns regarding the remedy's ability to achieve acceptable goals or the possibility that short-term risks may result from its implementation. As a consequence, community concerns often do not have a significant impact on the implementation of remediation projects since the regulators have addressed them. In some instances, however, this has not been the case and community concerns have either delayed or modified implementation of a project. The disruption that the remediation may cause to a neighborhood is often the most significant community concern in terms of its impact on the selection, design and operation of an *in situ* remedy.

5.5.2.1 Strategies to Manage Community Concerns

Community concerns can be addressed through education and open communication. Practitioners should keep the public informed in an honest and easily understood manner and should provide published descriptions of technologies written in layman's language, such as the USEPA Guides for Citizens, which are available for many technologies.

5.5.3 Potential Indoor Air Vapor Intrusion

The impact of vapor intrusion on indoor air quality has become an increasing concern over the last several years (USEPA, 2002). Vapor intrusion may represent the most immediate and likely exposure pathway to humans for CVOCs in groundwater. Even moderate concentrations of CVOCs in groundwater have the potential to raise concerns about vapor intrusion. As a consequence, vapor intrusion may drive the need to implement groundwater remediation for CVOCs.

The vapor intrusion pathway is challenging because it is difficult to measure conclusively and the true risks are difficult to quantify. For example, it is often difficult to measure the impact of groundwater CVOCs on indoor air since measurements made inside a building can be misleading and, in some cases, a source may be within the structure. There is also significant controversy regarding appropriate modeling to evaluate the risk from vapor intrusion. The Johnson and Ettinger (1991) model is frequently used, although some have suggested it is too conservative while others have claimed it is not conservative enough. Guidance can be found in American Society for Testing and Materials Bulletin E 2600 (ASTM, 2008).

In addition to driving the need for remediation, vapor intrusion considerations may impact the selection and implementation of a remedy. The existence of a potential vapor intrusion problem may preclude use of remedies that take a long time to complete, such as MNA. The use of ERD may result in greater indoor air risks, since vinyl chloride (VC) may be produced and accumulate at some sites. VC is a known carcinogen and is more volatile than its precursors, so indoor air concerns are a common issue at ERD sites. However, VC is readily biodegradable under aerobic conditions, and rapid degradation can occur in the vadose zone (Barbee, 2007). Indoor air risks also can affect the selection or design of air sparging systems because air sparging without adequate soil vapor extraction (SVE) can increase the indoor concentrations of volatiles.

Where vapor intrusion is an existing problem, direct vapor mitigation measures may be incorporated into the remedy. These measures may include SVE systems or sub-slab depressurization systems in buildings (such as systems used for radon control). Typically, these vapor mitigation measures are relatively inexpensive, so it may be prudent to implement them even if there is not conclusive information on a vapor intrusion risk, given the uncertainty regarding the actual risks from vapor mitigation.

5.5.3.1 Strategies to Manage Vapor Intrusion Issues

Vapor intrusion can be addressed through additional characterization and engineering solutions. Considerations for additional characterization include the following:

- Vadose zone and groundwater sampling to determine the extent of the problem; must follow approved protocols and consider lithology and depth to water.
- Indoor air sampling, which can often be costly and inconclusive (any indoor air sampling effort should consider indoor, and possibly outdoor, sources of the compounds of interest and must follow approved protocols).

Engineering solutions include applying an aggressive/fast remedy and considering mitigation if the risk is inconclusive or uncertain. Mitigation may include SVE or in-building mitigation.

5.6 IMPLEMENTATION CHALLENGES

Several of the implementation challenges are related to the ability to implement the selected *in situ* technology. These challenges are discussed in the following sections and summarized in Table 5.4.

5.6.1 Interfering Infrastructure

The location of a plume beneath buildings, streets, and utility lines, including sewers, water lines, gas pipes and communication lines, presents several challenges. In the case of buildings, this may include vapor intrusion issues, as discussed above. The presence of a building may have limited impact if the construction and utilization of the building allow for the installation of monitoring and injection wells or for direct injection techniques. Utility trenches and streets may prevent the construction of PRBs that require trenching. Drilling near utility lines can be done, but it requires identification of the location of the lines and may require hand auguring for five feet before using a drill rig. The consequences of hitting utility lines can be very significant to the contractor, so great care must be taken in working around them.

5.6.1.1 Strategies to Manage Infrastructure Issues

Additional characterization efforts can be helpful at sites with significant infrastructure. Practitioners should carefully review site drawings and have utilities marked by local service. However, one should still use caution as drawings may be in error or outdated.

Table 5.4. Implementation Challenges

Challenge	Potential Strategies	Notes/Examples
Interfering Infrastructure	Additional Characterization	• Review site drawings and have utilities marked by local service (still use caution as drawings may be in error or outdated).
	Engineering Solutions	• Use appropriate drill rigs where overhead space is limited. • Use horizontal or angle drilling. • Install barriers upgradient or downgradient of buildings (use injection technologies for at least a portion of the barrier). • Hand core for 0.6-1.5 m (2-5 ft) below the surface to avoid pipes and other obstacles. • Relocate wells.
Potential for Rebound	Engineering Solutions	• Plan for multiple applications of reagents (especially near sources and low-permeability zones). • Contain treated area (e.g., with PRBs). • Inject more rigorously in low-permeability zones (e.g., closer spacing or use mixing technologies). • Incorporate MNA to manage rebound if it occurs.
	Education and Communication	• Inform interested parties that rebound may occur. • Provide information from similar sites or applications.
Potential Contaminant Mobilization	Engineering Solutions	• Inject at downgradient edge and work towards sources. • Use recirculation systems or injection and recovery/recycle designs. • Install PRBs at the downgradient edge of the treatment zone. • Modify flow by short-term pumping during injection. • Use multiple additions of smaller volumes of amended water.
Well and Formation Fouling	Engineering Solutions	• Inject lower concentrations of reagents (by using larger injection volumes). • Chase with water or dilute acid to push amendments further into the formation. • Surge wells to clear fouling agents. • Pulse additions of amendments (such as electron donors). • Add small amounts of strong oxidizers or acids. • Add biocides, such as chlorine. • Add enzymes. • Add carbon dioxide (CO_2). • Manual scrubbing, including surging of wells.
Difficulty Predicting Performance	Additional Characterization	• Use carefully and appropriately designed laboratory and field pilot tests. • Use carefully and appropriately designed modeling studies. • Review and evaluate case studies from similar sites.

Engineering solutions are also available. Options to consider include (1) use of horizontal or angle drilling to install vapor extraction points, air sparging systems and other subsurface systems to avoid utilities, (2) use of appropriate rigs able to drill where space and overhead clearance is limited, (3) installation of barrier upgradient or downgradient of buildings, (4) use of injection technologies for at least a portion of the barrier, (5) hand coring for 0.6–1.5 m (2–5 ft) below the surface to avoid pipes and other subsurface structures and (6) relocation of wells.

5.6.2 Rebound

At numerous sites, monitoring data taken soon after treatment have shown VOC concentrations reduced to low levels. In many cases, there is an expectation that natural attenuation will address any residual contamination exceeding cleanup standards that have not been met. However, for many sites post-treatment, low levels of VOCs have turned out to be temporary; in some cases, rebounded groundwater concentrations have been higher than the original baseline concentrations.

In general, rebound occurs because fluid-based technologies may easily treat the dissolved phase VOCs in the most readily accessed flow paths but leave residual contaminants behind in less transmissive zones. Once active treatment is complete, additional VOCs enter the monitored groundwater flow path through dissolution and diffusion or as a result of advection from portions of the aquifer that were not monitored and did not receive the amendments used for remediation. McGuire et al. (2006) conducted an extensive review of a large number of DNAPL sites to evaluate rebound. None of the sites achieved MCLs, although typically 70 to 96% reductions in chlorinated solvent concentrations were initially achieved. Sites remediated using ISCO methods had the greatest extent of rebound of any of the technologies examined. ERD-treated sites exhibited relatively little rebound, although the magnitude of any rebound after ERD treatment may be difficult to evaluate because the lingering effects of biological treatment may continue to suppress concentrations for several years after active treatment has stopped.

5.6.2.1 Strategies to Manage Rebound

In addition to educating all interested parties that some rebound may occur, there are some engineering solutions that can be helpful. These include (1) planning for multiple additions of reagents (most likely appropriate near source areas or locations/zones with lower-permeability and/or higher-sorptive capacities), (2) injecting more rigorously (e.g., closer spacing or use matrix mixing) in low-permeability zones, (3) using multiple applications of ERD (Dennis et al., 2005) or ISCO, (4) installing PRBs to contain the contamination and (5) using MNA to manage any rebound that may occur.

5.6.3 Contaminant Mobilization

Expanding a plume by mobilizing contaminants has not been as much of a problem as anticipated in the early days of remediation. For example, at one time, air sparging was thought to have the potential for causing increased migration, but this problem has rarely been observed, especially when intermittent flow (pulsing) designs are implemented. Mobilization can be an issue for some CHP systems and for systems where large volumes of fluids are injected, particularly when high pressures are used. ERD also may result in the net mobilization of CVOCs, in part through the conversion of perchloroethene (PCE; also termed tetrachloroethene) or trichloroethene (TCE) to more soluble byproducts such as dichloroethene (DCE) and VC. This enhanced dissolution may be viewed as a positive if the mobilized products are captured or attenuated downgradient.

5.6.3.1 Strategies to Manage Potential Mobilization

There are several engineering solutions that can be useful to minimize or deal with mobilization of contaminants. These include (1) injecting at the downgradient edge and working towards sources, (2) using recirculation systems or injection and recovery/recycle designs, (3) installing PRBs at the downgradient edge of the treatment zone, (4) modifying flow by short-term pumping during injection and (5) using multiple additions of smaller volumes of amended water.

5.6.4 Fouling of Wells and Formation

The most common problem with operating wells during remediation is fouling, which can be the result of biological growth or activities, mineral precipitation and/or the accumulation of particulate matter. Of these causes, the most frequently discussed challenge is preventing or repairing biofouling—the unwanted growth of microbial populations or biomass that reduce flow through wells or the formation. The most direct cause is the accumulation of polysaccharides, which support the formation of slimy growths. Such growth is most obvious within wells and well bores, but it also can occur in the formation, generally close to the point of injection. Injection of electron donors through wells can lead to biological growth within the well bore and packing or in close proximity to the well. This growth can impede subsequent injection. In some cases, microbial growth away from the well may also reduce permeability, but typically to a lesser extent. This type of permeability loss may alter flow paths in subtle ways and may lead to some redirection of subsequent injections. Several approaches for rectifying biofouling are discussed by Faris et al. (2003), Chopra et al. (2005) and in a recent Department of Defense Environmental Security Technology Certification Program (ESTCP) white paper (ESTCP, 2005).

Implementation of ISCO treatment also can result in permeability losses. For example, the hydrogen peroxide used in CHP applications undergoes decomposition to form oxygen gas, which can then cause gas blockage of pores. This is a temporary problem but can impede subsequent additions, as well as result in temporary and localized modifications to groundwater flow. Reactions of permanganate form insoluble manganese dioxide, which can alter flow patterns. This precipitate accumulation can be especially challenging when permanganate is continuously injected and extracted groundwater is used to make up the permanganate injection solution.

5.6.4.1 Strategies to Manage Fouling

Engineering solutions that can prevent or minimize fouling problems include:

- Injecting lower concentrations of reagents (by using larger injection volumes).
- Chasing with water or dilute acid to push amendments further into the formation.
- Surging wells to clear fouling agents.
- Pulsing additions of amendments (such as electron donors).
- Adding small amounts of strong oxidizers or acids.
- Adding biocides, such as chlorine.
- Adding enzymes.
- Adding CO_2.
- Manual scrubbing, including surging of wells.

5.6.5 Difficulty in Predicting Performance

Many of the challenges discussed above translate into a common challenge of predicting performance of a remedy, especially in the long term. For example, it is difficult to predict how long amendments will last in the aquifer, how long treatment will continue following addition of an amendment, and whether rebound will occur.

Laboratory tests can be useful for evaluating potential interactions with the aquifer matrix. For example, NOD tests for ISCO applications are often used to assess potential oxidant requirements. However, the results from these tests may be challenging to interpret because of the variations in aquifer properties.

Field pilot tests can provide more definitive answers, but they still have significant limitations. Pilot tests can be very useful in helping to understand hydrogeologic conditions if adequate monitoring is conducted during the pilot study. However, given time and budget constraints, pilot tests that are limited to a few months may not provide information on the ultimate performance of a remedy.

Establishing proof that degradation, especially biodegradation, is occurring at a sufficient rate and will continue until site objectives are met is a significant challenge. This is a challenge for most technologies, but it is a particular concern for MNA, ERD and PRBs. The presence of daughter products may be sufficient to support the occurrence of degradation. For TCE and PCE plumes, the presence of products past *cis*-DCE, especially ethene, may be used to indicate biodegradation, but the analysis is not clear-cut. The absence of VC and/or ethene does not necessarily demonstrate that *cis*-DCE is not degrading because alternative pathways (e.g., aerobic biodegradation or abiotic degradation) may occur. These alternative pathways, however, are more difficult to demonstrate. A good discussion on the interpretation of microcosm studies for chlorinated solvents is presented by Wilson et al. (2004). Long and Borden (2006) also discuss the use of column tests for predicting ERD performance.

5.6.5.1 Strategies to Manage Predictive Limitations

Better predictions generally require additional characterization and testing, and using approaches, such as the observational method, that take into account the uncertainty in predicting performance. Measures that may be helpful include using carefully and appropriately designed laboratory and/or field pilot tests, using carefully and appropriately designed modeling studies, and reviewing and evaluating case studies from similar sites.

5.7 ADDITIONAL DISCUSSION OF METHODS TO MANAGE CHALLENGES

Methods for managing remediation challenges were presented in Sections 5.3 through 5.6 with minimal or no discussion. More discussion is included in this section, but it is not intended to be all-inclusive or provide a detailed description of specific management approaches. The reader should consult other sources of information for additional details. Reviews of case histories for similar sites will be especially helpful.

5.7.1 Management Approaches to Optimize the Level of Characterization

There is a continuum in the level of characterization that can be conducted, which impacts the remediation method and extent of the remediation achieved. The following discussion may help optimize the level of characterization.

5.7.1.1 Pre-Design Investigation

One commonly applied approach to managing the level of site characterization is to spend less time and energy on the Remedial Investigation phase and conduct a Pre-Design Investigation. Once the most likely remedies have been identified, the data gaps can be identified more accurately. Important data gaps may include more detail on the localized distribution of VOC mass, as well as improved understanding of site geology, hydrogeology and geochemistry in the areas to be treated. It may be advisable to include analyses of geochemical parameters and microbiological tests. The key is to identify all variables that impact the design, such as information needed to size equipment, to space wells or to estimate reagent requirements.

5.7.1.2 Triad and Observational Method

The Triad approach is a catalyst for more efficient and cost effective evaluation of site conditions, remedy selection and technology implementation (Crumbling et al., 2004). It is intended to guide site investigations from the beginning, but it is also appropriate for addressing delineation efficiencies at any stage of a project. It combines advances in sampling and analytical technologies with a planning approach to ensure data quality, a focus on the information needed for cleanup decisions, and a dynamic work strategy to maximize the benefits of on-site data collection. The Triad approach makes a positive impact by improving site decision making, streamlining site sampling and analysis (which yields program cost savings and shortened timeframes for cleanup), and improving site reuse decisions (see Triad Resource Center at http://www.triadcentral.org/).

The observational method is very similar to the Triad approach in its application of dynamic work planning. It was originally developed for the geotechnical engineering profession to manage uncertainties in the subsurface without excessively large amounts of sample collection (Peck, 1969; Brown et al., 1988; Terzaghi et al., 1996). Key elements of the observational method are (1) remedial design based on the most probable site conditions, (2) identification of reasonable deviations from those conditions, (3) identification of parameters to observe to detect deviations during remediation and (4) preparation of contingency plans for each potential deviation (USDOE, 1997). By using an observational method, less field data are collected initially. Uncertainties and changes in field conditions are managed by developing contingency plans for possible outcomes. These contingency plans may include collecting additional data at designated times or stages of remediation or performing additional remediation.

5.7.1.3 Direct Push Tools

One approach for achieving a more complete vertical profile is the use of direct-push tools that can provide a quick and economical method for identifying the vertical and horizontal extent of impact (Wilson et al., 2005). A wide range of direct push tools is available on the market. Some of these, such as MIPs, can provide real-time readings of relative contaminant concentrations. Adjustments to the sampling program can be made based on these results, and the relatively low costs provide the opportunity to obtain more data when needed.

5.7.2 Delivery Approaches for Difficult Lithologies

Sites where soil conditions make efficient delivery of treatment reagents difficult can be addressed in a number of ways. All of these methods can increase the cost of implementing remediation, although they are likely to reduce overall life cycle costs. The benefits of time should also be considered. Livadas (2003) and Pac et al. (2005) provide discussions of injection/delivery methods.

5.7.2.1 Longer Lasting Reagents

Long-lasting reagents should be selected so that diffusion and desorption have a better opportunity to result in contact between the reagent and the VOCs. For example, potassium permanganate and sodium persulfate typically persist longer than chemically activated hydrogen peroxide or ozone. For reductive dechlorination, emulsified edible oils and Hydrogen Release Compound (HRC®) persist longer than lactic acid (Koenigsberg and Norris, 1999). However, more research is needed to better understand the extent of possible diffusion with these longer-lasting reagents.

5.7.2.2 Monitored Natural Attenuation

MNA requires no active remediation and is thus not affected by delivery issues. However, MNA does require a scientific evaluation and prediction of future conditions and may not necessarily be an acceptable approach for all interested parties, including regulatory agencies or responsible parties.

5.7.2.3 Containment (e.g., Permeable Reactive Barriers)

PRBs and other containment approaches can be advantageous in that reactive reagents and/or adsorbing materials are placed in the path of contaminant migration. Thus, distribution of reagents is not an issue. However, PRBs have a different treatment objective and may not address the overall remedial objective for a specific site.

5.7.2.4 Fracturing Technology

Fracturing technology, either hydraulic or pneumatic, can be used to create fractures that can then be filled with treatment reagents (FRTR, 2002). Hydraulic fracturing creates horizontal fractures that can be relatively thick (a few inches). Reagent solutions can be injected into these fractures. Pneumatic fracturing creates small finger-like fractures that are immediately filled with the treatment reagents. It is still necessary for reagents to move away from either type of fracture to reach the majority of the contaminant mass. This dispersion can be a slow process and is likely to require either a continuous/semi-continuous addition of reagent or a longer-lasting reagent.

5.7.2.5 Recirculation Systems

Recirculation (injection/recovery systems) can be used to accelerate and better control the distribution of reagents. In heterogeneous formations or in deep formations with large plumes, the recovery system will accelerate the delivery of reagents away from the injection point and provide additional control of delivery. These systems are, however, more costly to install and operate than injection-only systems. For deep and large plumes, recirculation may be the only practical method of reagent delivery. For some bedrock sites, injection in one well and pumping water from a cross-gradient well can create the opportunity to access more fractures. The intent of this method is to intercept fractures without having to install a large number of wells. Because bedrock generally has limited porosity, the amount of recovered water requiring treatment will be relatively small.

5.7.3 Managing the Challenges of Performance Uncertainty

There is always significant uncertainty regarding the performance of *in situ* remediation systems. The following subsections discuss potential methods that can help reduce and manage the uncertainty.

5.7.3.1 Groundwater Models

Groundwater models often can be used to help understand and improve appreciation of the uncertainties involved with *in situ* remediation. The history and use of modeling is discussed in detail in Chapter 6. A range of models is available, ranging from simple spreadsheets that require a modest amount of information and can be used by many practitioners to models that require a substantial amount of data and should be used only by highly trained and experienced individuals.

To account for uncertainty in site data and input parameters, statistical tools can be used in conjunction with the models to perform sensitivity analyses. One type of sensitivity analysis is Monte Carlo simulation, which randomly generates values for uncertain variables over and over. These variables are automatically entered into the model and a range of outputs is developed that simulates the range of probable outcomes (see Christians et al. [2006] for application to a PRB design). These methods are useful but should take into account the full range of conditions and data for groundwater chemistry and hydrogeology (Roberts et al., 2002).

5.7.3.2 Laboratory Testing

Laboratory tests (Talley, 2006) can be conducted to determine if the VOCs are degradable by the reagent in question, although this information is for the most part available in the literature. More frequently, laboratory tests can be used to identify problems associated with specific site conditions, whether reactions might go to completion, if reagent consumption might be excessive or whether dissolution of metals may occur (Qui et al., 2004). Laboratory tests also may be used to produce design information for pilot-test and full-scale implementation. However, typical laboratory studies cannot simulate some of the more important factors influencing performance, such as distribution of injected chemicals. Consequently, laboratory tests need to be carefully designed to be able to fill the site-specific data gaps.

5.7.3.3 Pilot Tests

To help resolve uncertainty about reagent consumption and the extent of influence around an injection point, pilot tests may be appropriate. Tests to evaluate the radius of injection and reagent consumption (especially for ISCO) can be relatively short. Pilot tests in plumes will show meaningful changes in VOC concentrations much more rapidly than tests conducted in source areas. Pilot tests should be designed and implemented to obtain answers to specific questions that can be achieved in the allotted time. To determine the ease and extent of reagent delivery, short duration tests with adequate monitoring points are sufficient. To determine if degradation/removal levels can be attained, it is often preferable to conduct tests in low or moderately impacted areas. The same consideration applies when the objective is to reach low contaminant concentrations, such as MCLs. Pilot tests in highly impacted areas are not advisable because the time required to obtain meaningful data may be as long as that required for the entire site to achieve remediation goals. Consequently, pilot tests need to be carefully designed to be able to fill the site-specific data gaps.

5.7.3.4 Phased Implementation of Remedies

Uncertainties in the appropriate design and spacing of wells can be reduced by conducting a pilot test. A more cost effective method than a stand-alone pilot test may be to install a small portion of the remedial system in an initial phase, observe the results, and then incrementally expand the system, modifying the design based on the information gained in earlier phases. This approach is particularly useful for highly heterogeneous sites and sites where the zone of influence of reagent injections is hard to predict. This strategy reduces the potential to overdesign a site. It is also important to avoid spacing wells too far apart because additional wells could be needed at smaller intervals to achieve adequate coverage. In such cases, the total costs may be significantly higher than installing more wells initially because an extra mobilization will be needed.

5.7.4 Treatment Trains to Manage Multiple Challenges

Treatment trains often can provide a solution when a single technology will not address all of the contamination or achieve remediation goals in a cost effective manner. Treatment trains can use one technology to address the most highly impacted area, either through destruction or containment, and a second technology to address the less-impacted portion of the plume or to either polish the source area after aggressive treatment or manage the VOCs that may desorb or enter the groundwater slowly over extended periods. Many sites have included MNA as one component of a remedy (McGuire et al., 2004). The impact of active remedies on future use of MNA should be considered (Norris et al., 2000; Azadpour-Keeley et al., 2004; Sahl, 2005; Sahl et al., 2005). ERD also may be used to initiate the biodegradation component of MNA following implementation of a different technology, such as ISCO. Additionally, it may be desirable to use a follow-on technology to address unintended consequences of a first technology.

Examples of common treatment trains are listed below:

- Air sparging can be used to oxygenate groundwater after ERD. It may be necessary to reestablish aerobic conditions downgradient of the treatment zone, or after treatment is completed, to counteract side effects of anaerobic treatment such as increased solubilization of arsenic or accumulation of VC.
- Adding electron donor to promote reducing conditions might be appropriate where ISCO has resulted in solubilization of hexavalent chromium (which will be reduced to less toxic forms and precipitate under reducing conditions).
- MNA can be implemented for post-treatment once the primary treatment is no longer cost effective.
- MNA can be used in conjunction with another technology to address downgradient and/or lateral areas where VOC concentrations are minimal.
- PRBs frequently are designed to allow VOC concentrations to exit the barrier at concentrations somewhat above MCLs or ACLs.

Design of treatment trains should consider the compatibility of the technologies used. Models are useful tools for determining how MNA can be used and how much it should be depended upon. Mass flux estimates can be used to determine when to stop active treatment and change to MNA.

5.8 SUMMARY

Dealing with the challenges of *in situ* remediation of CVOCs begins with recognizing what challenges may arise. The challenges begin with the inability to see below the ground surface and the inherent variability in the subsurface environment. To fully appreciate these challenges requires some preparation with respect to understanding how contaminants move through formations, the impacts and limitations imposed by lithology and geochemistry, the mechanisms by which various remediation technologies work, and the applicable regulatory requirements. In order to effectively minimize the impacts of a number of the challenges discussed, an optimum level of site characterization information is required. To assist with this optimization, use of the observational method or more formal approaches, such as those incorporated in the Triad Approach, can be used to lead to more cost effective and successful remedies (Simon, 2004; Crumbling et al., 2004; Mack et al., 2004).

The most commonly cited and universal challenge for *in situ* remediation is the delivery of sufficient and appropriate reagent to the exact location of contaminants within an acceptable time. Delivery challenges are especially difficult to meet where site delineation, with respect to both lithology and contaminant mass and distribution, is not optimum. In addition, there are other challenges, including site conditions such as lithology and heterogeneity, that might not be compatible with specific technologies and difficult-to-achieve remediation requirements. Other challenges arise from unintended consequences of the remediation process.

In situ remediation will always present difficult challenges because of the inherent uncertainties associated with the subsurface environment. Practitioners can be more successful in dealing with these challenges by managing the most significant risks first, by developing realistic expectations regarding performance among all interested parties, by using treatment trains or combined remedies to ensure the use of appropriate technologies for different times and locations, and by using adaptive management approaches such as Triad to modify current and subsequent phases based on the results from earlier phases.

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CHAPTER 6

MODELING REMEDIATION OF CHLORINATED SOLVENT PLUMES

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6.1 INTRODUCTION

Analytical and numerical modeling has emerged as a valuable tool for planning and designing groundwater remediation systems. Models have been used in a variety of settings including (1) research into the fundamental processes controlling chlorinated solvent fate and transport, (2) methods for integrating information on site hydrology, geology, contaminant distribution, transport and fate, and (3) applied aspects of plume management and remediation system design. This chapter focuses on currently available models commonly used by practitioners for simulating dissolved chlorinated solvent plumes and includes a brief summary of modeling principles, mathematical expressions useful for representing biodegradation processes, methods for representing dissolved contaminant release from source areas and case studies of models applied to sites. Key challenges that face the groundwater remediation industry from a modeling standpoint include:

- Modeling the complex biological reactions involved in biodegrading chlorinated solvents and being able to simulate the natural attenuation capacity of the groundwater aquifer,
- Understanding the processes controlling remediation of chlorinated solvents and modeling them,
- Predicting remediation impacts using simplified and/or complex models, and
- Evaluating technological efficiencies and performance of technologies used to remediate dissolved chlorinated solvent plumes.

Researchers have been addressing these challenges and developing analytical and numerical models that simulate the fate and transport of chlorinated solvents in the subsurface. Analytical models provide exact solutions to the fate and transport equations whereas numerical models are used to generate estimated solutions that are within an acceptable accuracy relative to the exact solution. This chapter describes these advances in modeling and the resulting models that have been used to simulate chlorinated compounds and their remediation.

6.2 FATE AND TRANSPORT MODELING

Chlorinated solvents released to the subsurface undergo a number of physical, chemical and biological changes as they distribute into the aquifer matrix and groundwater flowing through the matrix. Groundwater flow within the matrix causes the dissolved chlorinated solvents to be transported (or advected) along the flow paths. The heterogeneities and nonuniformity of the aquifer matrix cause microscale spreading, commonly referred to as dispersion. Microbial populations that naturally exist in subsurface media can, given the right

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conditions, metabolize (break down) chlorinated solvents into other organic compounds or effect their complete mineralization. Because of their organic nature, chlorinated solvents can attach (partition or sorb) to the organic fraction of the aquifer matrix, thus slowing their transport in the dissolved phase. In addition, chlorinated solvents can undergo abiotic reactions in the subsurface that affect their fate and transport.

This section will focus on the basics of fate and transport modeling. More detailed and thorough discussions on the physical, chemical, biological and abiotic mechanisms and processes affecting chlorinated solvents can be found in other references including Bedient et al. (1999), Domenico and Schwartz (1998), and Wiedemeier et al. (1999). Information on chlorinated solvents in dense nonaqueous phase liquid (DNAPL) form can be found in Schwille (1988) and Cohen and Mercer (1993). Detailed discussions of modeling principles are available in Zheng and Bennett (1995), Anderson and Woessner (1992) and Bear and Verrujit (1987).

6.2.1 Basic Fate and Transport Equations

In general, the change in dissolved concentrations in an aquifer matrix due to advection and dispersion in mathematical form in one dimension (1-D) is given by:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \qquad \text{(Eq. 6.1)}$$

where C is the contaminant concentration (M/L^3), t is time, D_x is the coefficient of hydrodynamic dispersion (L^2/T), v_x is the average seepage velocity in groundwater (L/T), and x is distance along the flow path. The symbols M, L and T refer to standard units—M is Mass (generally expressed in milligrams [mg] or micrograms [µg]), L is Length (usually expressed in meters [m] or centimeters [cm]), and T is time (generally expressed in days or seconds). Thus, L^2 represents area and L^3 represents volume.

Incorporating sorption into the 1-D advection-dispersion equation is accomplished through the use of a retardation factor (assuming linear reversible sorption):

$$R\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \qquad \text{(Eq. 6.2)}$$

where R is the coefficient of retardation (dimensionless).

In its simplest form, incorporating biodegradation as a first-order reaction into the 1-D advection-dispersion equations results in:

$$R\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \lambda RC \qquad \text{(Eq. 6.3)}$$

where λ is the first-order biodegradation rate coefficient (1/T). The two terms, $\frac{\partial C}{\partial t}$ and λC, do not incorporate a velocity term; thus, they are multiplied by R, the retardation coefficient, to reflect the effects of sorption.

Solving Equations 6.1, 6.2 and 6.3 requires knowledge about the system that is being modeled. This is usually termed *initial* and *boundary* conditions. Initial conditions specify the groundwater contaminant concentrations at the beginning of the simulation (or model run). Boundary conditions, on the other hand, specify the value of the dependent variable (dissolved concentration in this case), or the value of the first derivative of the dependent variable (flux of dissolved concentration), along the boundaries of the system that is being modeled. As an example, if an experiment in a laboratory column is being modeled with a continuous constant source input, initial conditions would include:

$$C(x,0) = 0 \tag{Eq. 6.4}$$

Equation 6.4 means that the initial concentration in the column at any x before the experiment starts (i.e., $t = 0$) is zero. Boundary conditions, on the other hand, define concentrations at either end of the column and would include:

$$C(0,t) = C_o \text{ for } t > 0 \tag{Eq. 6.5}$$

$$C(\infty,t) = 0 \text{ for } t > 0 \tag{Eq. 6.6}$$

Equations 6.5 and 6.6 basically indicate that a concentration of C_0 enters the column on one end and that the concentration beyond the column is zero at all times. Thus, the conditions associated with the particular scenario at hand are defined.

Once the initial and boundary conditions have been specified, mathematical and numerical techniques are used to solve Equations 6.1, 6.2 or 6.3, subject to initial and boundary conditions, such as those given by Equations 6.4 through 6.6.

As an example, the analytical (or exact answer) solution to Equation 6.3 for an instantaneous source (a slug of chlorinated solvent) released into the groundwater is given by:

$$C(x,t) = \frac{M}{(4\pi D_x t)^{1/2}} \exp\left[-\frac{(x - vt)^2}{4D_x t}\right] \tag{Eq. 6.7}$$

where M is the injected mass per unit cross-sectional area. Figure 6.1 shows the results from a scenario analysis using Equation 6.7.

The boundary condition shown in Equation 6.5 designates what is known as a "constant concentration" boundary condition. Other types of boundary conditions used to define sources of chlorinated solvents to groundwater include a "constant flux" boundary condition in which the mass flux (M/V/T) is defined. Constant concentration boundary conditions are typically used to represent dissolution from residual sources, while mass flux boundary conditions are used to represent leakage of chemicals into the groundwater due to the combined effects of infiltration, fluctuations of the groundwater table that cause dissolution from residual sources, and continuous spillage events from tanks, ponds, pits, etc. The difficulty in modeling these processes, as will be discussed in Section 6.4, lies in understanding source behavior over time and estimating the mass flux rate that is "feeding" that groundwater plume.

The advection-dispersion equation also can be written in more than one dimension. In three-dimensional (3-D) terms, the equation is expressed as:

$$R\frac{\partial C}{\partial t} = D_x\frac{\partial^2 C}{\partial x^2} + D_y\frac{\partial^2 C}{\partial y^2} + D_z\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial x} - \lambda RC \tag{Eq. 6.8}$$

where D_y and D_z are the coefficients of hydrodynamic dispersion (L^2/T) in the y and z dimensions.

It should be noted that Equation 6.8 has a 1-D velocity and that is the velocity in the x-direction (or the direction of groundwater flow), and it is only 3-D in the context of dispersion, i.e., dispersion is in the x-, y-, and z-directions. This simplifies the solution greatly and allows Equation 6.8 to be solved analytically once the initial and boundary conditions have been defined. The solution only requires the dispersion coefficients in the transverse (y-direction), and vertical (z-direction) over and beyond the data requirements of the 1-D solution.

M	1000 mg/ft^2
Dx	100 ft^2/s
vx	100 ft/yr

				C(x,t) given by Equation (6.7)		
x (ft)	**t_1** (yrs)	**t_2** (yrs)	**t_3** (yrs)	**C(x,t_1)** (mg/m^3)	**C(x,t_2)** (mg/m^3)	**C(x,t_3)** (mg/m^3)
0	0.1	0.2	0.5	7.322	0.425	0.000
1	0.1	0.2	0.5	11.775	0.692	0.000
2	0.1	0.2	0.5	18.010	1.099	0.000
3	0.1	0.2	0.5	26.205	1.702	0.001
4	0.1	0.2	0.5	36.268	2.571	0.001
5	0.1	0.2	0.5	47.749	3.788	0.002
6	0.1	0.2	0.5	59.797	5.443	0.002
7	0.1	0.2	0.5	71.233	7.628	0.004
8	0.1	0.2	0.5	80.717	10.427	0.006
9	0.1	0.2	0.5	87.004	13.900	0.009
10	0.1	0.2	0.5	89.206	18.072	0.013
12	0.1	0.2	0.5	80.717	28.343	0.029
14	0.1	0.2	0.5	59.797	40.220	0.061
16	0.1	0.2	0.5	36.268	51.644	0.123
18	0.1	0.2	0.5	18.010	60.002	0.238
20	0.1	0.2	0.5	7.322	63.078	0.443
22	0.1	0.2	0.5	2.437	60.002	0.792
24	0.1	0.2	0.5	0.664	51.644	1.358
26	0.1	0.2	0.5	0.148	40.220	2.239
28	0.1	0.2	0.5	0.027	28.343	3.547
30	0.1	0.2	0.5	0.004	18.072	5.399
35	0.1	0.2	0.5	0.000	3.788	12.952
40	0.1	0.2	0.5	0.000	0.425	24.197
45	0.1	0.2	0.5	0.000	0.026	35.206
50	0.1	0.2	0.5	0.000	0.001	39.894
60	0.1	0.2	0.5	0.000	0.000	24.197
70	0.1	0.2	0.5	0.000	0.000	5.399
80	0.1	0.2	0.5	0.000	0.000	0.443
90	0.1	0.2	0.5	0.000	0.000	0.013
100	0.1	0.2	0.5	0.000	0.000	0.000

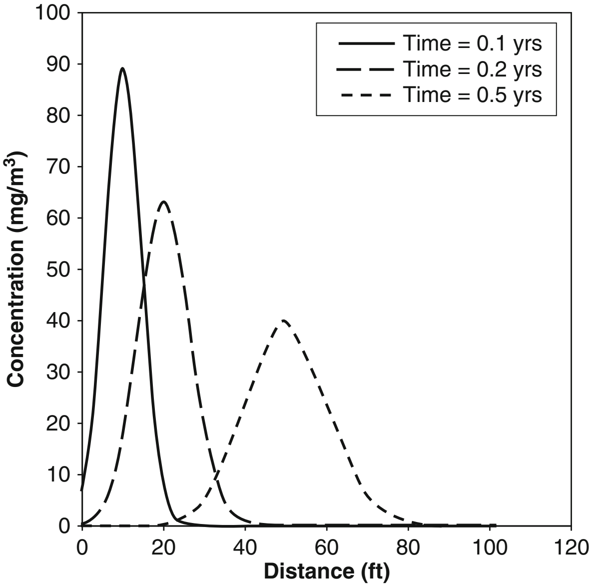


Figure 6.1. Concentrations as a function of time and distance from an instantaneous release in groundwater.

One recent issue has been the accuracy of the Domenico solution (Domenico, 1987), one of the most commonly used solutions for solving the advection-dispersion equation (Equation 6.8) analytically. West et al. (2007) suggested that the Domenico solution not be used because of the error involved in approximation terms employed in the solution. Other researchers (e.g., Falta et al., 2005b; Guyonnet and Neville, 2004; USEPA, 2007) have concluded that the Domenico solution yields reasonably accurate results for most of the cases where it is typically applied.

Unlike Equation 6.8, "fully 2- or 3-D" models require defining velocities in the x, y, and/or z directions along with dispersion in two- or three dimensions. In this instance, the 2-D advection-dispersion equation is given by:

$$R\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D_{xx}\frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial x}\left(D_{xy}\frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial y}\left(D_{yy}\frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial y}\left(D_{yx}\frac{\partial C}{\partial x}\right) - \frac{\partial}{\partial x} \times (v_x C) - \frac{\partial}{\partial y}(v_y C) + \frac{q_s}{\theta}C_s - \lambda RC \qquad \text{(Eq. 6.9)}$$

where q_s is the discharge rate of the source or sink into the aquifer, θ is the effective porosity, and C_s is the concentration associated with the source or sink. As can be seen from Equation 6.9, the input data requirements are much greater in this case and include velocities and dispersion coefficients in two dimensions and source or sink data, as well as reaction and sorption rates. When using a 2-D model, it is assumed that the dissolved chlorinated solvents are completely mixed in the vertical z-dimension or the thickness of the aquifer and that the solvent concentrations measured in monitoring wells are uniform across the aquifer depth. Furthermore, solving Equation 6.9 requires either solving the flow equation in 2-D to obtain velocities or using a groundwater flow model to estimate the velocity field. Solving Equation 6.9 also involves relying on numerical or approximation methods that discretize space and time and have error associated with them (due to their approximating nature). The key advantage of using this modeling approach, however, stems from the ability it provides for simulating the varying conditions across the site, such as subsurface heterogeneities and changes in sources and sinks or reactions over time.

Equations 6.3, 6.8 and 6.9 make use of a simplified biodegradation reaction term, $-\lambda C$. This type of expression is used when biodegradation is assumed to be a first-order process such that the change in concentration over time due to the reaction is a function of the concentration, or:

$$\frac{\partial C}{\partial t} = -\lambda C \qquad \text{(Eq. 6.10)}$$

The resulting concentration from this type of biodegradation kinetic expression is shown in Figure 6.2 for various values of λ. The rate constant, λ, is typically expressed in terms of a reaction half life, the time required for the mass of the biodegrading compound to decrease to half the original mass. The solution to Equation 6.10 is an exponential function of the form:

$$C = C_0 e^{-\lambda t} \qquad \text{(Eq. 6.11)}$$

where C_0 is the starting concentration of the chemical at time = 0. The half life of the chemical is given by:

$$t_{1/2} = \frac{\ln 2}{\lambda} \qquad \text{(Eq. 6.12)}$$

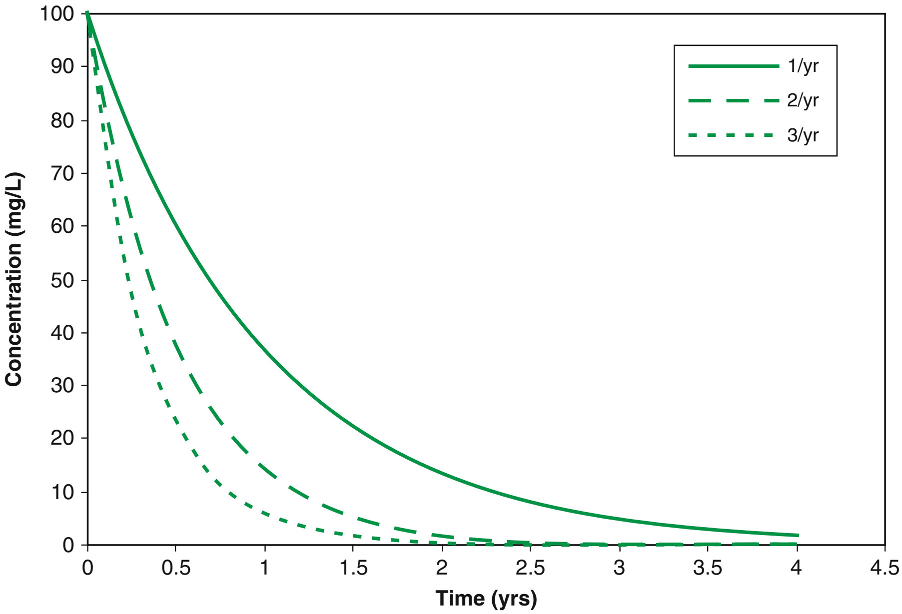


Figure 6.2. Concentration change as a function of time for various values of λ.

The simplified first-order expression given by Equation 6.10 is popular among modelers and practitioners because it requires only one variable to evaluate the effect of biodegradation on a given chlorinated solvent plume, and that is the rate constant, λ. Many acknowledge, however, that estimating this variable from field data is quite complex because field concentrations reflect the combined effect of many processes, such as biodegradation, advection, dispersion and sorption, and it is difficult to separate them out without adequate data gathering and specialized testing. Furthermore, estimating λ from laboratory studies is problematic as well since laboratory experimental conditions are simplified and do not reflect the complexity and the conditions encountered in the subsurface.

A U.S. Environmental Protection Agency (USEPA) Remedial Technology Fact Sheet (Newell et al., 2002) presents methods to estimate biodegradation rates and cautions that different attenuation rates calculated by different methods represent different processes at sites. A concentration vs. time rate represents the attenuation of source materials and is not directly related to a biodegradation rate. Biodegradation rates are lumped together with dispersion in concentration vs. distance rate calculations. Specific methods were identified to calculate biodegradation rates, as discussed below.

Buscheck and Alcantar (1995) derived a relationship that allows calculation of approximate biodegradation rate constants using field data. Their method assumes, however, that a dissolved plume has reached steady-state conditions, an assumption that is not always realized or true for chlorinated solvent plumes. The first-order rate constant is calculated as:

$$\lambda = \frac{v_x}{4\alpha_x}\left[1 + 2\alpha_x\left(\frac{k}{v_x}\right)^2 - 1\right] \qquad \text{(Eq. 6.13)}$$

where α_x is the dispersivity (the dispersivity is related to the dispersion coefficient D_x such that $D_x = \alpha_x v_x$), and $\frac{k}{v_x}$ is the slope of the line formed by making a log-linear plot of contaminant concentration versus distance downgradient along the flow path. Examples of how to apply this method can be found in Buscheck and Alcantar (1995), Wiedemeier et al. (1996) and Chapelle et al. (1996).

In addition to Equation 6.13, Wiedemeier et al. (1999) developed a method that estimates λ by comparing concentrations for the chlorinated compound to those of a tracer that might be present at the site in the subsurface. This tracer could be an inorganic compound (such as chloride), a recalcitrant compound (potentially tri-methyl benzenes) or calibration of groundwater solute transport models to field data. More recently, methods involving carbon and chlorine isotope analysis have been used to quantify biodegradation processes (e.g., Hirschorn et al., 2007; Philp et al., 2007).

Additionally, a number of researchers have catalogued, measured or reported biodegradation first-order rates from the literature for chlorinated compounds. Table 6.1 presents data compiled by Suarez and Rifai (1999) from both laboratory and field studies. Table 6.2 shows decay rates calculated from field sites as determined from calibrations of the BIOCHLOR model (Aziz et al., 2000b).

Another popular biodegradation expression used in modeling because of its simplicity is the zero-order expression. In this expression, the change in concentration as a function of time due to biodegradation is a function of the reaction rate constant:

$$\frac{\partial C}{\partial t} = -\kappa \qquad \text{(Eq. 6.14)}$$

where κ is the zero-order rate constant (1/T). Suarez and Rifai (1999) provided data on zero-order rates for chlorinated solvents from the general literature.

Table 6.1. First-Order Half Lives for Chlorinated Solvents in Years (Laboratory and Field Data) (from Suarez and Rifai, 1999)

	Carbon Tetrachloride	DCA (all isomers)	DCE (all isomers)	PCE	TCA	TCE	Vinyl Chloride
Minimum	0.47	*(no degr.)*	*(no degr.)*	*(no degr.)*	*(no degr.)*	*(no degr.)*	*(no degr.)*
25th Percentile	0.09	*(no degr.)*	0.95	*(no degr.)*	*(no degr.)*	1.87	0.38
Median	0.04	1.87	0.47	0.21	0.19	0.38	0.04
75th Percentile	0.01	0.14	0.04	0.02	0.01	0.08	0.01
Maximum	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Number of Rates	*13*	*25*	*61*	*50*	*47*	*86*	*26*

“no degr.” indicates no degradation (first-order decay rate = 0)

Table 6.2. First-Order Half Lives for Chlorinated Solvents in Years (Model Calibration from Field Data) (from Aziz et al., 2000b)

	PCE	TCE	*cis*-DCE	VC	TCA	DCA
Minimum	0.29	0.22	0.03	0.06	0.22	0.6
Median	0.63	0.58	0.58	0.42	0.29	2.30
Maximum	0.87	2.3	6.9	1.7	0.45	3.9
Number	*3*	*10*	*9*	*7*	*2*	*3*

More sophisticated kinetic approaches for modeling the biodegradation of chlorinated solvents involve the use of Monod kinetics, and incorporate the limitations of multiple substrates, and inhibitory processes. These approaches are discussed in more detail in Section 6.3.

Irrespective of the kinetic expression used to model biodegradation of chlorinated compounds, it is critical to recognize that source behavior over time has a significant influence on the observed concentrations within the plume. A representative site model needs to incorporate adequate expressions to model both processes: biodegradation and source behavior. Typically, residual sources in chlorinated plumes have been described using a starting concentration and a source “decay” rate much like the first-order reaction rate constant discussed earlier and shown in Equation 6.10.

Hausman and Rifai (2005) elucidated the effects of the biodegradation rate constant and the source decay constant on perchloroethene (PCE) concentrations in groundwater, as well as their combined effects. Their analysis considered a relatively short timeframe of 10 years and a longer duration of 100 years. Figure 6.3a illustrates the change in PCE concentrations due to biodegradation, and Figure 6.3b presents the concentration changes due to source decay for the same scenario. Figure 6.4 shows the resulting PCE groundwater concentrations for a biodegrading plume with source decay. It can be seen from Figure 6.3a that biodegradation for both short and long durations has a significant impact on concentrations downgradient from the source area, but has no impact on source concentrations (when assuming a constant non-decaying source). Figure 6.3b, on the other hand, illustrates that source decay affects the concentrations in the source area but has little short-term or long-term impact on downgradient concentrations. The combined effect of these two processes (source decay and biodegradation), however, cause a plume to be shorter and have lower concentrations downgradient from the source. Thus, in modeling chlorinated solvents, it is important to adequately define these processes.

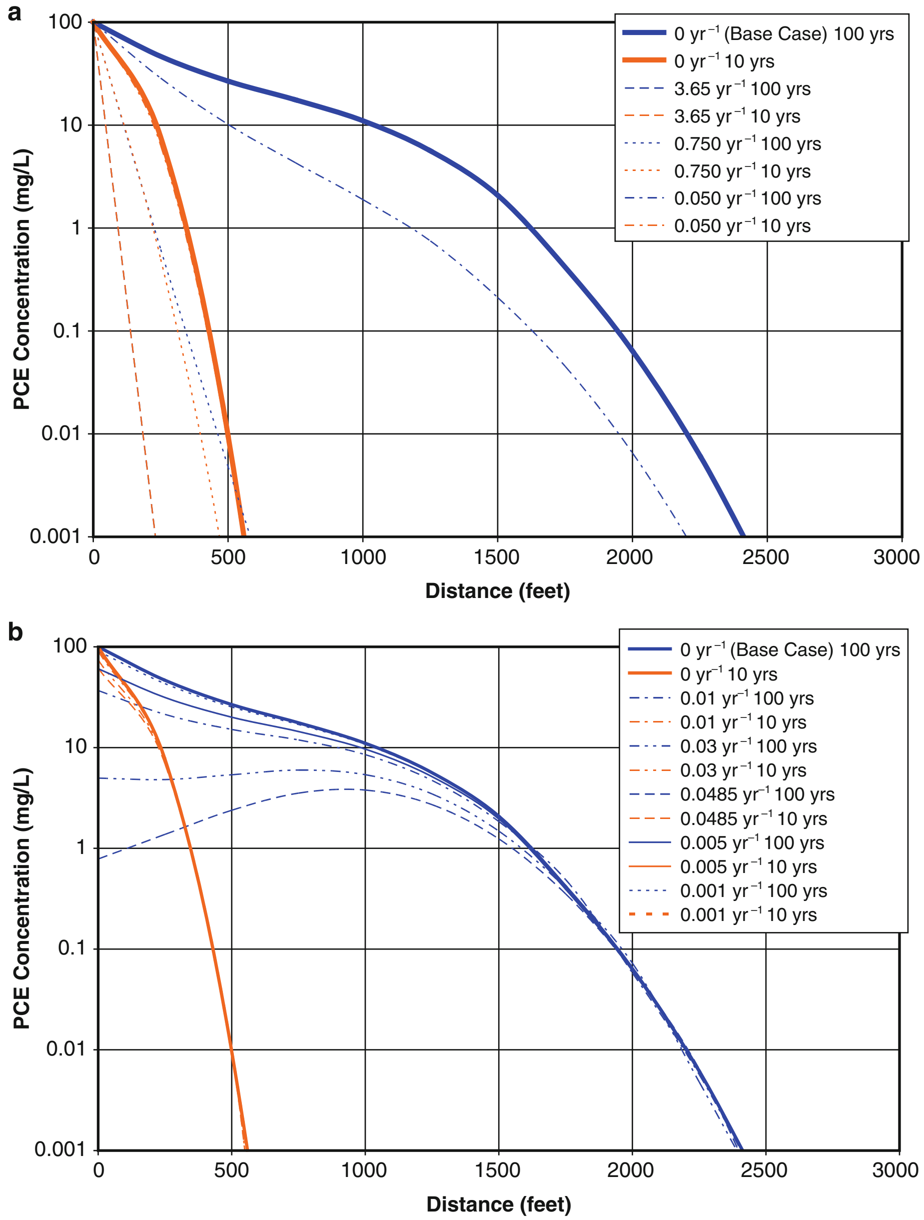


Figure 6.3. Model simulation of PCE downgradient concentrations as a function of (a) biodegradation and (b) source decay (Hausman and Rifai, 2005).

6.2.2 The Modeling Process

Modeling can be a useful analytical tool to better understand contaminant behavior and responses to remediation technologies. However, it is important to recognize that applying a model to a field problem involves uncertainty due to subsurface heterogeneities and the spatial and temporal variations of the physical, chemical and biological processes involved. In addition, mistakes in model applications are common, and models may be misused or applied inappropriately.

However, the benefits of learning and applying models outweigh the drawbacks because models provide:

- An ability to simulate a system or its components,
- An understanding of how a process or mechanism affects contaminant distributions in groundwater,
- A design tool that can be used to evaluate different remediation designs, and
- An "evergreen" process that can be used to continuously update our knowledge about a site.

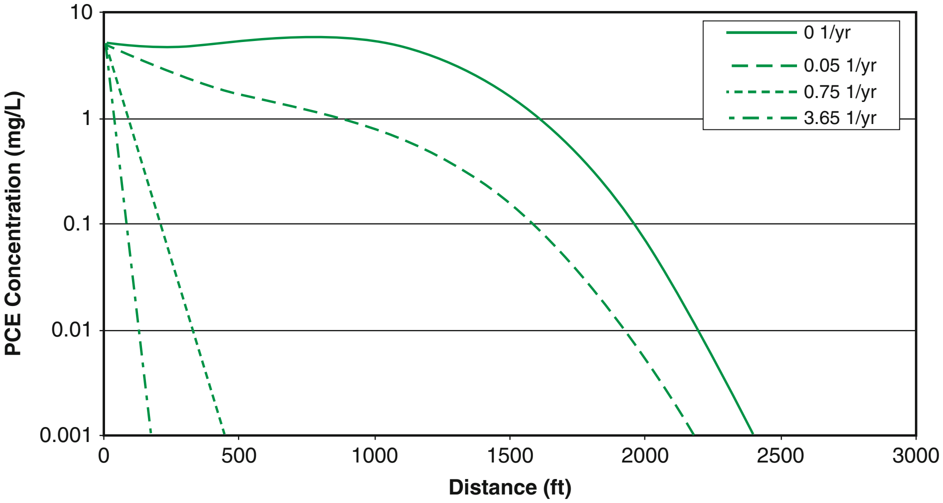


Figure 6.4. Model simulation of PCE downgradient concentrations as a function of biodegradation and a constant source decay value of 0.03 1/yr (Hausman and Rifai, 2005).

The modeling process and models have been described as "garbage in–garbage out." This is because when model set-up, calibration and validation are not rigorously undertaken, model results are suspect and of little value to the stakeholders. Thus, the key controlling factor in undertaking "successful" model development is careful adherence to the modeling process including (1) developing a conceptual model, (2) articulating the modeling objective, (3) analyzing site data to estimate model variables, (4) calibrating and validating the model and, finally, (5) using the model for predictive analysis. The modeling process also involves assessing the uncertainty or confidence in the model results. Uncertainty assessments can be accomplished in a number of ways, as will be seen later, but it is common for modelers to use sensitivity analysis to identify the key model variables that have the most influence on model results. A sensitivity analysis is typically undertaken for the calibrated model as well as the predictive model. The following sections further describe the modeling process.

6.2.2.1 Conceptual Model

The key step to modeling fate and transport at a field site is to gather and analyze all of the relevant information for the site. Then a conceptual model is developed that integrates the collected information and describes many of the variables and processes involved at the site. This process includes the introduction of simplifying assumptions and interpretations of the flow and transport regimes. Preliminary calculations and simple analytical models can be used in this step to help develop a conceptual understanding. For example, Darcy velocities can be estimated and used to develop estimates of plume length if the starting date of contamination is known. The observed plume length then can be compared to these estimates and interpretations regarding chemical and biological processes can be made. If, for example, the observed plume is shorter than expected, it may be due to the combined effects of sorption and biological or abiotic reactions. These processes would then need to be included in the model that is being developed.

Conceptual model development includes defining the hydrogeologic environment (e.g., homogeneous, heterogeneous, layered), the flow regime (confined, unconfined, direction and rate of flow), the source of the contamination (leak or spill start date, what was spilled and how much), and the chemical and biological properties of the chemicals involved (sorption and biodegradation characteristics, for example). Conceptual model development also includes interpreting the groundwater level data, groundwater chemical data and subsurface matrix data and any other types of information gathered at the site. Monitoring well contaminant concentrations and plume maps can be used to develop estimates of plume length over time and attenuation rates within the plume.

The importance of developing an appropriate conceptual model for a site cannot be overstated. The conceptual model is used to guide model selection, model development, parameter estimation, calibration and validation, sensitivity analyses and prediction. Without an appropriate conceptual model, the exercise of modeling is lacking in context and validity. It should be noted that the conceptual model is not static; it is expected to evolve and change as more data are gathered and knowledge of a given site increases. However, Bredehoeft (1994) discusses the "surprise" factor, where many (i.e., perhaps 20–30%) groundwater conceptual models are rendered invalid by new data. Overall, Bredehoeft concludes that developing conceptual models of groundwater systems involves uncertainty ". . . that often is not widely recognized" and that this uncertainty is magnified in long-term predictions using groundwater models. Regardless, modeling without an appropriate conceptual model leads to even greater uncertainty and less confidence in modeling results.

6.2.2.2 Goals of Model Development

The first question that needs to be answered is: What is the purpose of the modeling? It is important to ascertain why the modeling is being done. Typical objectives include (1) understanding a phenomenon or process and how it might affect contaminant fate and transport, (2) establishing likely scenarios that caused the observed contaminant concentrations at a site (source strength, duration of spill, etc.) and (3) predicting future contaminant distributions either under existing conditions or with engineered remediation systems. Defining the objective of the modeling has a strong bearing on model selection, discretization of the modeled domain and the level of effort that must be expended in the modeling study. Additionally, stating the goal for model development defines the expectations and allows model results to be used most appropriately.

6.2.2.3 Data Analysis and Parameter Estimation

The success of model development and application in a given situation relies largely on developing appropriate estimates for the model variables. Information gathered from a site or an experiment should be used to develop these estimates. For example, water level data from monitoring wells or piezometers can be analyzed to estimate the groundwater flow direction and rate. Variables such as hydraulic conductivity, aquifer thickness and flow boundary conditions must then be estimated to calibrate the flow model such that the model-generated flow field matches the observed one.

Once data from a site have been analyzed and integrated into a conceptual model, as discussed earlier, it becomes necessary to begin building the transport model. This requires selecting the dimension of the analysis (1-, 2- or 3-D). It also requires discretizing the spatial and temporal domains. Spatial discretization involves selecting a model grid to represent the site while temporal discretization involves defining what timeframe will be modeled and at what resolution. These are very important considerations that have to be determined on a site-specific basis and depend on which model is being used. Suffice it to say that the spatial domain must be large enough to account for the sources and sinks of water and chemicals in the aquifer that affect the observed plume. The temporal domain depends again on the goal of the modeling and the conceptual model for the site and whether invasive remediation or natural attenuation is to be simulated.

In addition to the spatial and temporal considerations discussed above, initial and boundary conditions must be defined. These conditions also vary from site to site and include considerations such as sources and sinks of water and chemicals into the selected grid, and contaminant conditions within the aquifer prior to the modeled time period. Appropriate selection of initial and boundary conditions eliminates a common problem often encountered in modeling- use of a site model that does not adequately represent the site-specific conditions.

6.2.2.4 Calibration

After the model has been set up and initial estimates of the input parameters have been developed, the model must be calibrated against the site data. In most (if not all) instances, the parameter estimates must be altered until the model's simulated values satisfactorily match their measured counterparts. The calibration process is one of the most critical and valuable steps of modeling. Calibration may be formally accomplished through the use of optimization techniques or less formally by trial and error. Both approaches have advantages and disadvantages, but it is important to understand that the calibration process is not unique. In other words, there are likely many sets of parameter estimates that would produce an acceptable calibration. In one classic study, Freyberg (1988) assigned nine groups of graduate students the same groundwater modeling assignment. Group predictions varied significantly, however, leading Freyberg to conclude that "good calibration did not lead to good prediction." In a more recent study, Saiers et al. (2004) presented a case study where three groundwater models were constructed using different types of groundwater data. The three models gave similar predicted results for groundwater level, but not for flow. Finally, Konikow and Bredehoeft (1992) concluded that "groundwater models cannot be validated, but only tested and invalidated."

The goal in calibration is to select the set of values that most closely represents the likely values of the parameters for the site in question. This, of course, requires identifying the measure of success that will be used to determine if the model is adequately calibrated or not. As an example, in calibrating the model to simulate the observed flow field at a site, a number of goodness-of-fit measures can be used: (1) the modeled flow field can be visually or statistically compared to the contoured flow field from water level data, (2) the modeled water levels at the monitoring wells can be compared to the observed water levels or (3) a combination of the two can be used. When comparing modeled water levels to measured ones or modeled water contours to their observed counterparts, the modeler will need to select a method for estimating the error and an acceptable target for the error (<5% error, etc.). In this way, whether by trial and error or automated calibration, the "best" set of parameter estimates can be selected and the model calibrated.

Recently, there has been a trend to use automatic calibration techniques. Carrera et al. (2005) discussed the overall calibration approach and methods to improve the calibration process. Doherty (2003) proposed a calibration approach for groundwater models using a system of "pilot points" that make nonlinear parameter estimation programs, such as PEST (Doherty, 2005), more flexible and easier to implement. Hunt et al. (2007) compared simple groundwater modeling approaches to more complicated models and concluded that the regularized inversion, which includes many more parameters than conventional approaches, has significant advantages for the modeling process. Kelson et al. (2002) presented the opposite conclusion, where a modest model based on less than 10 parameters yielded similar results to much more complex codes.

6.2.2.5 Validation

The process of validation is just as important as calibration because it allows for greater confidence in model results. Basically, validation involves using a second set of data that is distinct from the data set used for calibration and that was collected at a later point in time than the calibration data set. The calibrated model is then run for the time period between the calibration and validation data sets in order to predict contaminant concentrations for the validation timeframe. Model results are then compared to the validation data and an assessment of closeness of fit is made. If the results are acceptable (i.e., within a predefined margin of error), the validated model can be used for prediction analysis. However, if the validation results are unacceptable, then a recalibration of the model is required using the two datasets (calibration and validation) in order to fine-tune the parameter estimates.

In some instances, validation data sets are not available. In this case, modelers have to rely on a sensitivity analysis to determine which variables have the most impact on the model results and to define and quantify the level of confidence in the model output.

6.2.2.6 Prediction

Once a model has been calibrated and validated, it can be used to predict future contaminant distributions under natural or engineered remediation conditions. Predictions under natural conditions typically involve running the model beyond the present time into the future to determine plume dimensions and concentrations over time. This type of simulation can also include scenarios such as reducing source concentration or mass due to source control technologies. In the same way that a sensitivity analysis is undertaken for the calibrated model, it is necessary to complete a sensitivity analysis for the predictive model to determine the confidence in model results.

Predicting future concentrations using remediation technologies can involve simulating injection and pumping or a change in the flow conditions, as well as possibly a change in source concentrations or flow rates. Caution must be exercised in this instance, because of the uncertainties involved in simulating engineered remediation systems and their performance. For example, if the engineered remediation includes pumping water from the aquifer, then a secondary process of calibration may be required to ascertain that the model adequately represents pumping conditions (e.g., the model can be used to match data from a pumping test in the aquifer). Additionally, it is important to keep in mind that pumping and injection of water into the plume may have an effect on the source definition used in the model, which needs to be recognized. Thus, it is just as important to assess or quantify the confidence in the model results in the predictive mode as it is in the calibration mode.

6.3 MODELING BIODEGRADATION, SORPTION AND ABIOTIC REACTIONS OF CHLORINATED SOLVENTS

Chlorinated solvents can be mineralized and/or partially biodegraded by microorganisms under aerobic and anaerobic conditions, as demonstrated in numerous studies (e.g., Hopkins and McCarty, 1995; Wilson and Wilson, 1985; Fogel et al., 1986; Little et al., 1988; Malachowsky et al., 1994; Wackett et al., 1989; Vanderberg et al., 1995; Nelson et al., 1988; Bouwer and McCarty, 1983; and Folsom et al., 1990). It is generally accepted that enzymes involved in metabolizing a primary substrate such as methane or propane under aerobic conditions or natural organic compounds under anaerobic conditions catalyze the biodegradation of chlorinated solvents (Zhang et al., 1996). However, the biodegradation process may be limited or constrained by a number of factors, including biological limitations and environmental conditions in the subsurface. Microbial considerations include activity loss of critical enzymes, energetic needs for chlorinated biodegradation, metabolic patterns in mixed cultures, and accumulation and disappearance of metabolic intermediates. Subsurface considerations include the carbon content, pH, redox, the dissolved contaminant concentrations, and the presence of several chlorinated solvents with differing biodegradation characteristics, among others.

Key degradation processes for chlorinated solvents include the following (Truex et al., 2006; Wiedemeier et al., 1999):

- Aerobic cometabolism
- Anaerobic cometabolism
- Aerobic direct metabolism
- Anaerobic direct metabolism
- Dehydrochlorination (abiotic)
- Abiotic hydrolysis
- Dichloroelimination (biotic)
- Reductive dechlorination (hydrogenolysis)

Truex et al. (2006) used this list of reactions to show detailed degradation charts for the families of chlorinated ethanes, chlorinated ethenes and chlorinated methanes for aerobic, anoxic and anaerobic geochemical environments.

While mathematical models have been developed to simulate the biodegradation of chlorinated solvents in groundwater, including some of the considerations discussed above, it is important to keep in mind that the models developed to date are far from being able to simulate the complexity of the biodegradation process under field conditions. It is also important to note that appropriately describing the source term for a dissolved chlorinated plume is just as important, if not more important, than fully describing the complexity of the biodegradation process. Additionally, a critical consideration in modeling chlorinated solvents is the need to balance the complexity of the biodegradation model with the available data to support model development and application.

In addition to the first-order model presented in Equation 6.10, Monod kinetics has been a typical starting point for many of the mathematical models developed to date. Monod kinetics relates the transformation rate of the chlorinated solvent to its concentration and the concentration of the microorganisms (whereas the first-order model relates the concentration change to the concentration of the chemical):

$$-\frac{dC}{dt} = kX\frac{C}{K + C} \qquad \text{(Eq. 6.15)}$$

where C is the substrate concentration, t is time, X is the microbial concentration, k is the maximum specific utilization rate of the substrate, and K is the half-saturation constant for the substrate.

Equation 6.15 is based on the assumption that the reaction is limited by the one substrate; however, in practice, there are multiple substrates involved in the biodegradation of chlorinated solvents, necessitating the use of multiple-substrate Monod kinetic expressions:

$$-\frac{dC}{dt} = kX\frac{C}{K_c + C}\cdot\frac{C_e}{K_e + C_e}\cdots \tag{Eq. 6.16}$$

where C_e is the concentration of a limiting electron acceptor or nutrient, and K_e is the half-saturation constant for the electron acceptor or nutrient. Widdowson et al. (1988) and Borden and Bedient (1986) used this approach to develop expressions for aerobic and anaerobic biodegradation of organic compounds.

When competitive inhibition between two substrates is occurring (for example, the chlorinated solvent and a primary substrate), the Monod kinetic expressions are modified to:

$$\frac{dC_1}{dt} = k_1X\frac{C_1}{K_1 + C_1 + \frac{K_1}{K_2}C_2} \tag{Eq. 6.17}$$

$$\frac{dC_2}{dt} = k_2X\frac{C_2}{K_2 + C_2 + \frac{K_2}{K_1}C_1} \tag{Eq. 6.18}$$

where C_1 and C_2 represent the primary substrate and the chlorinated solvent.

The Monod kinetic expression also has been modified to simulate cometabolic degradation of the chlorinated solvents. The reader is referred to Alvarez-Cohen and Speitel (2001), Ely et al. (1997) and Zhang and Bajpai (2000) for detailed discussions on the aerobic and anaerobic kinetic expressions used to simulate cometabolism.

Several issues are noted from Equations 6.16 through 6.18. First, the expression in Equation 6.16 typically replaces the $-\lambda C$ expression in the fate and transport equation for the chlorinated compound (for example, Equation 6.3). This means, however, that one or more fate and transport equations (in addition to that for the chlorinated compound) will need to be solved to determine the concentrations in groundwater of the limiting substrate(s). Second, Equation 6.18 requires defining the microbial concentration, so unless the modeler assumes a constant microbial population concentration, it will be necessary to simulate the growth, death and transport of the microbial population. Thus, it can be seen that using Monod kinetics adds a layer of complexity and increases the data requirements.

A third and equally important consideration is the different time scales between transport and biodegradation. In groundwater, contaminant transport times can range from a few years to several decades. On the other hand, biodegradation half-lives can range from days or weeks to years or even decades. Hence, selection of an appropriate modeling time step is important to increase the probability that modeling results will be accurate. When the reaction half life is much smaller than the transport time, the time step used in modeling should be at the same scale as the reaction half life to yield accurate results. Borden and Bedient (1986) and Rifai et al. (1988) addressed this issue for petroleum hydrocarbons by assuming that the biodegradation reaction is almost instantaneous, thus eliminating the need for very small time steps that increase runtimes. Their method, however, introduces error when used for slow reactions because it assumes that substrates are used in an instantaneous manner, which would not be the case when the reaction is, in fact, slow and occurs at an equivalent time scale as transport.

New models also have been developed to simulate new ideas about sorption and desorption processes. Many numerical models allow the user to select between a linear, Freundlich or Langmuir isotherm (see Chapter 4), while analytical models are often limited to the linear expression. One exception is the RT3D numerical solute transport model, which has the capability to simulate rate-limited sorption processes, where desorption is controlled by a mass-transfer limitation step (Clement, 1997). Similarly, the model developed by Chen et al. (2004) includes a dual-equilibrium desorption approach (Chen et al., 2002) to model the availability effects on desorption processes.

Finally, there has been new research on the potential for abiotically mediated reductive dechlorination of chlorinated solvents by iron in the ferric (Fe(II)) state (Ferrey et al., 2004). This abiotic dechlorination occurs under anoxic conditions when Fe(II)-bearing minerals (magnetite, pyrite, green rust, mackinawite) release electrons for reduction of contaminants via a surface-mediated reaction. Because Fe(II) is relatively soluble under typical groundwater conditions (neutral pH), measurements of total Fe(II) in a soil matrix can include both dissolved and mineral forms. However, oxidation of dissolved Fe(II) is not thought to be capable of reductive dechlorination of contaminants of concern (COCs) in the absence of a solid phase (Lee and Batchelor, 2002a, 2002b), and the reaction appears to be dominated by reactive surface-bound species. Furthermore, dissolved ferrous iron can be scavenged by reduced sulfur species (sulfides) to form insoluble precipitates, such as FeS and FeS_2. These latter species are formed during sulfate-reducing conditions—which can also result in the reduction of Fe(III) to Fe(II)—and are known as acid volatile sulfides (AVS) or chromium extractable sulfide (CES). Certain AVS and CES species are active in promoting reductive dechlorination during anoxic iron oxidation.

Therefore, only a portion of the total Fe(II) present in soil is chemically reactive because of the requirement for surface interactions with the aqueous medium. Measurements of chemically reactive ferric iron must incorporate mineral phase Fe(II) and should be quantified based on the mass of Fe(II) present per mass of soil. Determining the amount of Fe(II) in a soil matrix that can be used for anoxic iron oxidation during abiotic reductive dechlorination follows the AMIBA (Aqueous and Mineralogical Intrinsic Bioremediation Assessment) protocol (Kennedy et al., 2003).

6.4 REPRESENTING SOURCES IN GROUNDWATER MODELING

Groundwater transport models use several different methods to simulate the entry of contaminants into groundwater. For example, some analytical models (described below) require that a vertical plane be used as the source of dissolved concentration to the model. The width and depth of the plane in the saturated zone must be entered into the model, followed by the concentration (in units of mass per volume) leaving the plane. This type of source term assumes that groundwater flows through the vertical plane and picks up dissolved phase contamination that then forms the groundwater plume. Other models require that a dissolved mass vs. time function (in units of mass per time) be entered into source zones. Many numerical models use this type of source term to introduce contaminant mass into a simulated groundwater flow field.

The key point is that most models require that the source term be simplified and entered into the groundwater transport model as a relatively abstract source function. Few commonly used groundwater transport models represent the source term directly as a deterministic function of key source processes, such as DNAPL dissolution, leaching of vadose zone materials or matrix diffusion. Users of these groundwater transport models must simplify and develop a source function outside of the model in order to build a source zone in the model (Figure 6.5). In some cases, a constant source zone (unchanging over time) is used to represent a worst-case scenario of plume growth at a site. In other cases, detailed source functions are developed to represent natural weathering of the source, multiple sourcing events and/or removal actions.

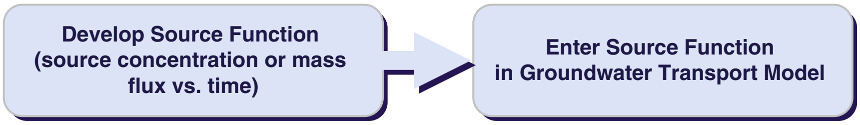


Figure 6.5. Describing the source term in a typical groundwater transport model.

Christ et al. (2006) describe how a number of researchers have developed screening-level models that simulate the change in downgradient groundwater concentrations and source mass over time. It is very difficult with our current state of knowledge to use deterministic models to simulate the changes in source concentrations over time and their associated effects on groundwater concentrations. DNAPL distribution is usually poorly characterized and computational resources are typically constrained (for example, long run-times are undesirable). Thus, having screening models allows an evaluation of source effects without detailed source characterization and with limited computer resources. Christ et al. (2006) evaluated four different screening models—Dekker (1996), Parker and Park (2004), Zhu and Sykes (2004), and Falta et al. (2005a)—all of which employed mass transfer correlations of the following form:

$$K_{eff} = K_o \left(\frac{M(t)}{M_o} \right)^{\beta} \qquad \text{(Eq. 6.19)}$$

where K_{eff} = upscaled mass transfer coefficient, K_o and β are fitting parameters, M(t) = DNAPL mass at time t and M_0 = DNAPL mass at time 0.

The Dekker (1996) model uses a nonsteady, numerically based approach, while the Zhu and Sykes (2004) and the Falta et al. (2005a) models assume simple relationships between mass discharge and mass removal.

The sections below describe some of the key source zone processes and how they can be reduced to source functions for use in groundwater transport models.

6.4.1 DNAPL Sources Zones

The National Research Council (NRC) report (NRC, 2005) on source zone assessment and remediation defines a chlorinated solvent *source zone* as a subsurface reservoir that sustains a plume. The NRC states that the DNAPL-containing region is typically the primary reservoir but also recognizes that DNAPL mass can be transferred to other source *compartments*, such as contaminants sorbed to the aquifer matrix or dissolved into low-permeability zones. These other compartments will then function as source zones to groundwater.

DNAPL source zones can be represented by a continuum of sourcing processes that start with an initial DNAPL release that forms DNAPL pools and fingers in the subsurface. In a few cases, when the mass of DNAPL released is large enough and significant capillary barriers (such as unfractured clay layers) are present, free-phase (continuous) DNAPL can accumulate. Because the saturation (the percent of pore space containing DNAPL) is high, this DNAPL can migrate if pumped or if the underlying capillary barrier is disturbed. Most of the time, however, DNAPL is present in source zones as residual DNAPL or as ganglia of DNAPL in a few pores, instead of one large continuous DNAPL mass.

Shortly after release, the DNAPL present in pools and fingers begins to undergo dissolution and to contribute mass to the groundwater system. DNAPL in unsaturated source zones will be exposed to infiltration of precipitation through the vadose zone, forming a leachate that can then enter the saturated zone. DNAPL that migrates to the saturated zone will begin to dissolve immediately as groundwater moves through the DNAPL source zone.

The source function, also called the *source zone loading rate* or the *mass flux from the source zone*, can be very difficult to predict with typical site characterization data. The site-specific mix of pools, fingers and source loadings from other source zone compartments at a site is called the *source zone architecture*. Because the presence of the DNAPL source materials in these zones can be distributed widely over a very sparse pattern (low average DNAPL saturations) that is controlled by micro-stratigraphic features (very small-scale changes in the texture of the water-bearing unit material), detailed information about the source zone architecture is very difficult to obtain. This complexity is illustrated by the phenomenon that at many DNAPL release sites, actual DNAPL is never encountered during the site characterization process.

The importance of understanding the source zone architecture is linked to its ability to control the source function. For example, the individual source functions of DNAPL pools and DNAPL fingers and other source compartments (such as matrix storage) can be very different. A source zone dominated by DNAPL pools, for instance, may experience only minor changes in concentration and mass flux (also called mass discharge, in units of mass per time), leaving the source zone over time, even if significant mass has been dissolved into the downgradient plume. In contrast, a source zone dominated by DNAPL fingers can show significant changes in mass flux even if relatively little mass has been dissolved from the source zone.

Several researchers have proposed that a power function can be used to relate the change in average source concentration (or mass flux) over time to the change in contaminant mass over time (Rao et al., 2001; Rao and Jawitz, 2003; Parker and Park, 2004; Zhu and Sykes, 2004) (see Figure 6.6). This allows the mass discharge (mass flux) to be related to the source mass mathematically at any time. The power function model is given by:

$$\frac{C(t)}{C_o} = \left[\frac{M(t)}{M_o}\right]^{\Gamma} \qquad \text{(Eq. 6.20)}$$

where C(t) = flux-weighted concentration at time t, C_0 = flux-weighted concentration at time 0, M(t) = source mass at time t, M_0 = source mass at time t_0, and Γ= empirical parameter.

On a very simple basis, sources dominated by DNAPL pools will demonstrate a source function below the 45° line on Figure 6.6, while a source dominated by DNAPL fingers will exhibit a source function above the 45° line. Rao and Jawitz (2003) developed a more detailed description by defining “heterogeneous DNAPL distribution in homogenous media” as causing source functions that fall above the line, while “homogeneous DNAPL distribution in heterogeneous media” will have below-the-line source functions. In practice, source zones at actual sites appear to fall both below and above this line (Stroo et al., 2003; Falta et al., 2005a; McGuire et al., 2006) and a middle-of-the-road approach (the 45° line) is a good starting point for selecting a source function if the source architecture is not known.

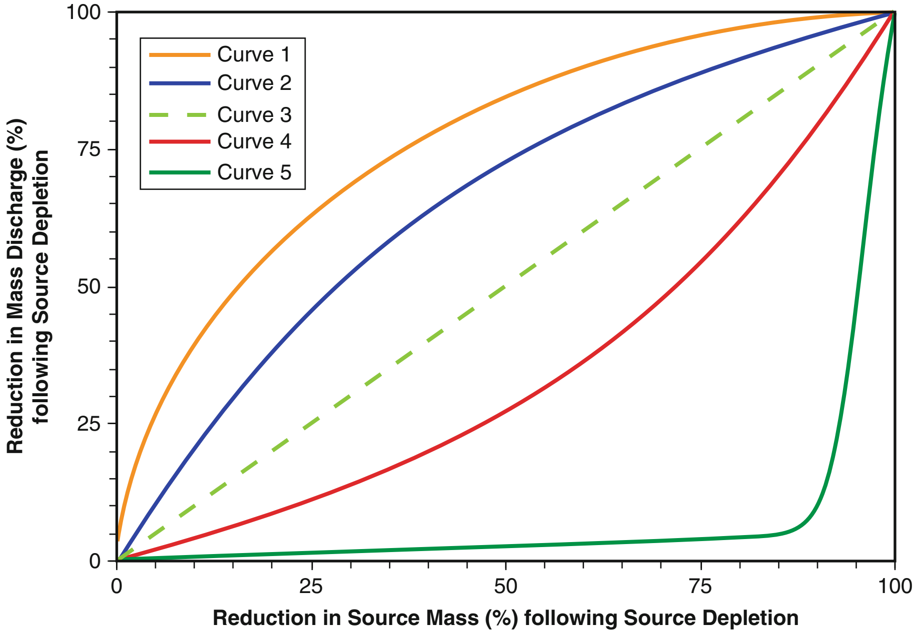


Figure 6.6. Reduction in mass discharge (mass flux) (%) vs. reduction in source mass (%). Adapted from Stroo et al. (2003) where Curve 1 (top curve) is the theoretical relationship from Rao and Jawitz (2003), Curve 2 is the theoretical relationship from Enfield et al. (2002), Curve 3 is from Newell and Adamson (2005), Curve 4 is actual field data from Rao et al. (1997), and Curve 5 is the theoretical relationship from Sale and McWhorter (2001).

Many modeling studies have been performed to evaluate the effects of source remediation on the plume. In theory, the source architecture dominates how the source will respond to partial mass removal in two key metrics: mass flux leaving the source zone, and source longevity. For example, removing half of the mass from the upgradient portion of a DNAPL pool can result in the scenario where the mass flux is not changed by any appreciable amount, but the lifetime of the DNAPL pool (the time it takes for the pool to totally dissolve) will be reduced by half. On the other hand, if a source removal technology evenly removes half of the DNAPL residual ganglia throughout a source zone, the resulting mass flux will drop by half. The overall time until the last ganglia dissolve will not change, however. In practice, source removal technologies do appear to be able to change source zone concentrations significantly. One study of 59 source treatment sites showed an average of over 80% reduction in source zone concentrations due to the effects of source treatment technologies, such as enhanced bioremediation, chemical oxidation and thermal treatments (McGuire et al., 2006).

As indicated above, it is currently difficult to translate site characterization data into useable information about source architecture. One approach to address this issue is to use simple mathematical functions to represent the source function over time. Newell and Adamson (2005) studied four simple potential source functions: step function, linear function, first-order decay and a compound model (a plateau function followed by first-order decay). They concluded that because of the continuing overlay of various source decay processes over time in a source zone, such as DNAPL fingers dissolving first, followed by complete dissolution of any longer-lived DNAPL pools, then long-term depletion of contaminants in storage via matrix diffusion, and then slow release of contaminants via dual-equilibrium-desorption (availability) effects, that source functions at most sites will be dominated by long "tails". Therefore, the use of a first-order decay model, or a companion compound model, was considered to be the most appropriate method to approximate the long-term source function over time (Figure 6.7). Inherent in the use of the planning-level models is that the actual source function will not track the first-order decay model exactly but will exhibit scatter such that different rates of decay over time will be observed. Even so, a first-order or a compound model will capture the essence of a real source function where average concentration and mass flux decline over time with a long-term "tail" over the lifetime of the source.

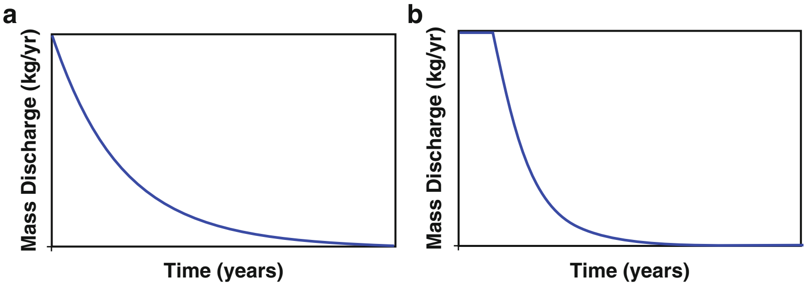


Figure 6.7. Two planning level source functions that simulate the expected "tails" caused by source zone architecture: (a) first-order decay and (b) compound model. The source function tail approximates the effects of various processes such as DNAPL dissolution, matrix diffusion, complex desorption processes, and stagnant zones over time (from Newell and Adamson, 2005; reprinted with permission of John Wiley & Sons, Inc).

There are a number of focused research projects in progress at this time that are attempting to make the development of source functions more deterministic (Table 6.3), where site characterization data can lead to definitive and quantitative descriptions of DNAPL source zone architecture and the resulting source function. If successful, groundwater modelers will be able to use this research to develop more robust and accurate source functions for their models.

6.4.2 Estimating Source Mass

Building source functions often requires some estimate of source mass. Considerable research has been devoted to finding better ways to characterize DNAPL source zones (Table 6.3). Even with advanced source characterization methods, there will be considerable uncertainty in source mass estimation.

One key concept in dealing with source mass estimation is to employ the Observational Approach or some type of adaptive site management (such as the Triad approach). With these approaches, the conceptual site model is continually updated with new information. If a groundwater model is built with a source function that assumes a certain mass and the actual source function begins to stray from the predicted source function, then some type of mid-course correction is needed.

Under the Observational Approach (Terzaghi and Peck, 1948; Peck, 1969; NRC, 2006), the following steps are taken:

- Assess probable conditions and develop contingency plans for adverse outcomes,
- Establish key parameters for observation,
- Measure observational parameters and compare to calculations,
- Compare predicted and measured parameters, and
- Change the design as needed.

This type of adaptive approach is one method to account for uncertainties in estimating source mass.

Tools have been developed to assist in the calculation of source mass. For example, the SourceDK model (Farhat et al., 2004) has source mass calculation tools for estimating source mass based on sampling data.

Table 6.3. Recent Projects Focused on Deterministic Modeling of Source Functions

SERDP/ESTCP Effort	Fact Sheet Location
Decision Support System to Evaluate Effectiveness and Cost of Source Zone Treatment (SERDP No. CU-1292)	http://www.serdp.org/research/CU/CU-1292.pdf
Development of Assessment Tools for Evaluation of the Benefits of DNAPL Source Zone Treatment (SERDP No. ER-1293)	http://www.serdp.org/Research/upload/ER-1293.pdf
Mass Transfer from Entrapped DNAPL Sources Undergoing Remediation: Characterization Methods and Prediction Tools (SERDP No. ER-1294)	http://www.serdp.org/Research/upload/ER-1294-2.pdf
Impacts of DNAPL Source Zone Treatment: Experimental and Modeling Assessment of the Benefits of Partial Source Removal (SERDP No. ER-1295)	http://www.serdp.org/Research/upload/ER_FS_1295.pdf
Diagnostic Tools for Performance Evaluation of Innovative In-Situ Remediation Technologies at Chlorinated Solvent-Contaminated Sites (ESTCP No. ER-0318)	http://www.estcp.org/Technology/ER-0318-FS.cfm
Improved Field Evaluation of NAPL Dissolution and Source Longevity (ESTCP No. ER-0833)	http://www.estcp.org/Technology/ER-0833-FS.cfm
Decision and Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty (ESTCP No. ER-0704)	http://www.estcp.org/Technology/ER-0704-Fact-Sheet.cfm
Integrated Protocol for Assessment of Long-Term Sustainability of Monitored Natural Attenuation of Chlorinated Solvent Plumes (SERDP No. ER-1349)	http://www.serdp.org/Research/upload/ER-1349.pdf
Development of a Protocol and a Screening Tool for Selection of DNAPL Source Area Remediation (ESTCP No. ER-0424)	http://www.estcp.org/Technology/ER-0424-FS.cfm

Note: ESTCP – Environmental Security Technology Certification Program; SERDP – Strategic Environmental Research and Development Program

6.5 DEVELOPED MODELS

Groundwater transport models are typically divided into two groups: analytical models (based on equations) and numerical models (based on discretization of the model domain and numerical solution methods). In general, analytical models are easier to use and apply, while numerical models are more powerful in their ability to represent detailed site features.

6.5.1 Commonly Used Analytical Models

Several commonly used analytical groundwater models that address chlorinated solvent plumes are presented below. It is noted that some of the models discussed are not technically “analytical models” but are modeling tools that rely on analytical solutions in their development.

6.5.1.1 Biochlor

As described by the USEPA, BIOCHLOR is a screening model that simulates remediation by natural attenuation of dissolved solvents at chlorinated solvent release sites (USEPA, 2008; Aziz et al., 2000a). The model can be used to simulate 1-D advection, 3-D dispersion, linear adsorption and biotransformation via reductive dechlorination (the dominant biotransformation process at most chlorinated solvent sites). Reductive dechlorination of dissolved mass is assumed to occur under anaerobic conditions and to follow a sequential first-order decay process. BIOCHLOR includes three different model types:

- Solute transport without decay.
- Solute transport with biotransformation modeled as a sequential first-order decay process.
- Solute transport with biotransformation modeled as a sequential first-order decay process with two different reaction zones (i.e., each zone has a different set of rate coefficient values).

BIOCHLOR includes a decaying source term where the mass flux and the estimated mass were entered into the model (directly for source mass, indirectly via source zone characteristics for mass flux). The model takes the mass flux and divides it by the source mass to get a first-order source zone decay rate. With this option, the source can be simulated as decaying over time in order to demonstrate the impact of the decaying source on the resulting plume.

6.5.1.2 REMChlor

This chlorinated solvent model combines an analytical solution for time-dependent DNAPL source decay and an analytical advection/dispersion model—the Domenico solution—that has been modified to allow for simulation of chlorinated solvent decay chains (Falta et al., 2005a; 2005b). This model can consider independent variations in parent and daughter compound decay rates and yield coefficients in the plume. Multiple reaction zones can be established to simulate the effects of different geochemical environments and remediation schemes. Currently, the authors are enhancing the model with a groundwater-to-indoor air pathway term and a probabilistic engine to incorporate uncertainty analysis. The model has been peer-reviewed by the USEPA and will be distributed via the USEPA’s Center for Subsurface Modeling Support (CSMoS) web page (http://www.epa.gov/ada/csmos/).

6.5.1.3 ART3D

This 3-D analytic reactive transport model simulates homogeneous and constant transport properties (Quezada et al., 2003, 2004). The model includes complex reaction sequences with first-order decay, as well as 3-D dispersion, and can be applied in forward or inverse and stochastic mode. Users can compare model results to data from observation wells at their sites.

6.5.1.4 Natural Attenuation Software (NAS)

This software package includes both analytical and numerical models that can be used to compare the cleanup times associated with monitored natural attenuation (MNA) to active remediation (Chapelle et al., 2003; Widdowson et al., 2004). Natural attenuation processes modeled by NAS include advection, dispersion, sorption, nonaqueous phase liquid (NAPL) dissolution and biodegradation. NAS determines redox zonation and estimates and applies varied biodegradation rates from one redox zone to the next. NAS calculates three key MNA variables:

- *Required Source Reduction:* target source concentration required for a plume extent to contract to regulatory limits (*Distance of Stabilization [DOS]*),
- *Time of Stabilization (TOS):* time required for a plume extent to contract to regulatory limits after source reduction, and
- *Time of Remediation (TOR):* time required for NAPL contaminants in the source area to attenuate to a predetermined target source concentration.

6.5.1.5 MNAtoolbox

This software package can be used to screen sites for the potential implementation of MNA (Brady et al., 2001). *MNAtoolbox* can be used to identify the primary attenuation pathways and to validate the conditions that might prohibit the use of MNA for particular contaminants. Site-specific input parameters are used to gauge the probable effectiveness of attenuation for each contaminant at a given site.

6.5.1.6 BioBalance Toolkit

This software package uses a mass-balance approach to evaluate whether the assimilative capacity of a particular system is sufficient to manage the mass flux of chlorinated solvents emanating from a source zone (Kamath et al., 2006). This modeling platform integrates two planning-level source functions into an analytical model. Users have the option to define the source as either being a vadose zone or submerged source, coupled with the ability to simulate the effects of source management activities by changing the mass flux or the source mass or both. The model includes modules that help estimate the relative abundance of electron donor supply vs. electron donor demand (in units of dissolved hydrogen equivalents), calculate the potential loss of available donor due to the effects of competing electron acceptors, and evaluate plume stability and the relative contribution of various dissolved-phase natural attenuation processes.

6.5.2 Current Numerical Models

A variety of numerical models have been developed to simulate the transport and biotransformation of dissolved chlorinated organic compounds in the subsurface. These include advanced research models capable of simulating multiphase flow, NAPL dissolution and a variety of chemical and biological transformation reactions (Christ et al., 2005). However, the most commonly employed models are based on the groundwater flow model MODFLOW (McDonald and Harbaugh, 1988), and the groundwater solute transport model MT3D (Zheng, 1990). These codes are popular with model developers because of their modular construction, robust numerical methods, good documentation, and continued maintenance and upgrading. These codes are also popular with model users because of the availability of graphical user interfaces (GUIs) including Visual Modflow (http://www.visual-modflow.com), GMS (http://www.ems-i.com), Groundwater Vistas (http://www.groundwater-vistas.com) and Argus ONE (http://www.argusint.com). Contaminant transport and transformation models based on MODFLOW-MT3D include SEAM3D (Waddill and Widdowson, 2000; Widdowson, 2003), BioRedox (Carey et al., 1999; Schreiber et al., 2004), RT3D (Clement, 1997) and PHT3D (Prommer, 2002; Prommer et al., 2003).

6.5.2.1 SEAM3D

SEAM3D is based on the code MT3DMS (Zheng and Wang, 1999) with additional packages for biodegradation via direct oxidation, reductive dechlorination, cometabolism and NAPL dissolution (Waddill and Widdowson, 2000; Widdowson, 2003):

- The biodegradation package simulates the direct oxidation of organic substrates under a range of terminal electron accepting processes (TEAPs). Biodegradation follows Monod kinetics where the degradation rate is controlled by the concentration of electron donor (ED), electron acceptor (EA), a rate inhibition term and the microbial population. The model may be operated under either growth (time-dependent microbial population) or no-growth (steady-state biomass concentration) conditions. The microbial phase is assumed to include as many as nine different bacterial populations that exist as scattered microcolonies attached to the porous medium. Different TEAPs are simulated in a sequential manner where oxygen is consumed first, followed by nitrate, Mn(IV), Fe(III) and sulfate followed by methanogenic fermentation. *cis*-1,2-Dichloroethene (*cis*-DCE) and vinyl chloride (VC) may be degraded via direct oxidation depending on the availability of electron acceptors.
- The reductive dechlorination package simulates biodegradation of PCE, trichloroethene (TCE), *cis*-DCE and VC in the absence of oxygen or nitrate (Widdowson, 2003). Reductive dechlorination is assumed to occur at the maximum rate under methanogenic conditions with somewhat slower rates under Mn(IV)-, Fe(III)- and sulfate-reducing conditions where the current TEAP for each cell is determined by the biodegradation package. Chlorinated ethene degradation rates are assumed to decrease in the order PCE→TCE→*cis*-DCE→VC.
- The cometabolism package is designed to simulate aerobic cometabolism of user-designated compounds (recalcitrants) using methane or petroleum-derived compounds (e.g., toluene) as co-substrates. Recalcitrants may be TCE, *cis*-DCE or VC or any user-defined compound (e.g., methyl tertiary butyl ether [MTBE]).
- The NAPL dissolution package can be used to simulate the dissolution of a multi-component NAPL, where the rate of mass transfer between the NAPL and groundwater is a function of the interfacial mass transfer rate and the difference between the aqueous phase and the equilibrium concentration. For multi-component NAPLs, the equilibrium concentration is calculated using Raoult’s Law.

SEAM3D is a powerful modeling program, allowing simulation of a wide variety of biogeochemical processes. However, this versatility also increases the model complexity and the number of input parameters. For many of the microbial processes, there are no published values of input parameters or methods for independently estimating these parameters. Without accurate estimates of all of the important parameters, it is very difficult to evaluate the accuracy of any model simulation.

6.5.2.2 BioRedox

BioRedox-MT3DMS (BioRedox) is a 3-D, multicomponent solute transport model that was developed to simulate the natural and enhanced bioremediation of chlorinated solvents and petroleum hydrocarbons in groundwater (Carey et al., 1999; Schreiber et al., 2004). BioRedox is based on MT3DMS DoD_3.00.A (Zheng and Wang, 1999) and includes a reaction module and a multicomponent DNAPL dissolution module that are incorporated into the MT3DMS source code.

BioRedox provides the option to simulate conditions that range from a simple scenario with first-order decay for one species to more sophisticated conditions that include the coupled oxidation-reduction of multiple electron donors and electron acceptors. The strength of BioRedox is the flexibility incorporated into the reaction and DNAPL dissolution modules, which allows users to simulate a broad range of site-specific conditions without having to modify the source code.

BioRedox functionality can include simulation of the following processes at a site:

- Biodegradation mechanisms such as oxidation, reductive dechlorination and cometabolism,
- Representation of aqueous and/or mineral species,
- Oxidation of organic compounds (e.g., benzene, toluene, ethylbenzene and/or xylene [BTEX]) coupled to the reduction of inorganic electron acceptors (e.g., oxygen, nitrate, mineral-phase manganese and iron, sulfate and/or carbon dioxide),
- A unique visualization technique that allows users to simultaneously evaluate the effects of simulated redox zones on contaminant distributions that are based on TEAP-specific processes,
- Simulation of halogen accumulation (e.g., chloride production during the reductive transformation of chlorinated solvent species),
- Production of dissolved species such as ferrous iron during the reduction of mineral-phase ferric iron, or the production of methane in the methanogenic zone (BioRedox can assume unlimited carbon dioxide availability so that this species does not have to be represented explicitly in a site model),
- Biodegradation mechanisms, rates and daughter products can vary in each simulated redox zone (e.g., vinyl chloride oxidation in aerobic and iron-reducing zones, and reductive dechlorination in the methanogenic zone),
- Accelerated biodegradation rates that occur during methanotrophic cometabolism (e.g., rapid biodegradation of TCE under aerobic condition when simulated substrates such as methane or toluene exceed a user-defined threshold concentration),
- Reaction rates that are first-order, instantaneous (e.g., BTEX or ferrous iron oxidation under aerobic conditions), or substrate-limited reaction rates,
- Representation of multicomponent inhibition or stimulation by allowing users to specify two biodegradation rates for a given redox zone: one rate that applies when a

co-substrate or an inhibitor is present within a user-defined range of threshold concentrations, and a different rate that applies when the co-substrate or inhibitor is outside the range of threshold concentrations, and

- Multicomponent DNAPL dissolution simulation by calculating the effective solubility for each component and either equilibrium or rate-limited dissolution.

BioRedox is capable of simulating many of the same microbial processes as SEAM3D. However, because BioRedox allows for more simplistic representations of biodegradation processes (including first-order decay and instantaneous reaction kinetics), fewer input parameters may be required, allowing the use of these approaches when calibration data are more limited.

6.5.2.3 RT3D

RT3D (Reactive Transport in 3-Dimensions; Clement, 1997) is also based on the MODFLOW and MT3D codes and is designed to allow users to simulate a variety of processes including oxidative biodegradation, reductive dechlorination and NAPL dissolution. However, RT3D is unique in that it couples the solute transport components of MT3D with an implicit ordinary differential equation solver (Hindmarsh, 1983) allowing the code to be used to simulate a wide variety of chemical reactions. RT3D users can define their own reaction packages in order to adapt the numerical model to a site-specific conceptual model. Consequently, RT3D can be easily adapted as remediation technologies evolve and as the understanding of *in situ* transformation processes improves. This potential is best illustrated by evolution of the RT3D model.

The basic structure of the RT3D model (RT3D v1.0) has remained unchanged since it was first released (Clement, 1997) with seven pre-programmed reaction modules to simulate (1) instantaneous substrate oxidation using oxygen, (2) instantaneous substrate oxidation using multiple electron acceptors, (3) first-order kinetic substrate oxidation using multiple electron acceptors, (4) rate-limited sorption, (5) double Monod kinetics of substrate oxidation using a single electron acceptor, (6) first-order sequential decay of chlorinated ethenes and (7) aerobic/anaerobic biodegradation of chlorinated ethenes. Later, reaction modules were released to simulate NAPL dissolution (Clement et al., 2004) and mixtures of chlorinated ethenes, ethanes, methanes and their daughter products (Johnson and Truex, 2006). Coulibaly et al. (2006) and Jung et al. (2006) recently employed the user-defined module feature in RT3D to simulate emulsified oil transport for chlorinated solvent bioremediation.

The ability to select and/or develop reaction modules to match site-specific conditions is one of the great strengths of RT3D, allowing the model to be used under a variety of conditions including relatively simple sites (e.g., single contaminant and redox condition) with limited input data and highly complex sites (e.g., multiple contaminants degrading under a variety of redox conditions) with much more extensive input data.

6.5.2.4 PHT3D

A variety of coupled transport and geochemical models have been developed to simulate solute transport under conditions where the chemical reactions are fast relative to groundwater flow. In this case, a geochemical equilibrium approach is used to determine the fraction of each species in the mobile, aqueous phase (e.g., Yeh and Tripathi, 1989; Steefel and MacQuarrie, 1996). While this approach may be appropriate for certain reactions (e.g., ion exchange), it is not appropriate for many contaminant biodegradation reactions where reaction kinetics can be much slower than groundwater flow.

PHT3D (Prommer, 2002; Prommer et al., 2003) represents an attempt to merge some of the attractive features of the multi-species biodegradation models (e.g., RT3D) with geochemical models. PHT3D (v1.0) can handle general mixed equilibrium/kinetic geochemical reactions by linking the MODFLOW/BioRedox-MT3DMS flow/transport models with the non-equilibrium geochemical model PHREEQC-2 (Parkhurst and Appelo, 1999). Because the reaction part of the model is based on PHREEQC-2, reaction kinetics easily can be formulated through user-defined rate expressions within the database.

PHT3D will be most useful in situations where complex interactions between organic and inorganic species must be considered. Examples of this type of problem include abiotic degradation of chlorinated solvents in permeable reactive barriers and enhanced anaerobic biodegradation where mobilization of solid-phase species (e.g., Mn, Fe, As) is a concern. PHT3D typically requires a large amount of input data for model calibration. However, much of the geochemical data is already available within the PHREEQC-2 (Parkhurst and Appelo, 1999) and other readily available databases.

6.6 CASE STUDIES

6.6.1 BIOCHLOR Case Study—Cape Canaveral Air Station, Fire Training Area, Florida

Aziz et al. (2000a) applied the BIOCHLOR model to simulate the movement of chlorinated solvents and determine the percent of TCE biotransformation at Cape Canaveral Air Station, Florida. The study focused on a former fire training area on the western edge of the station, about 335 meters (m), or 1,100 feet (ft) east of the Banana River and about 305 m (1,000 ft) northeast of a canal that empties into the river. Fire-training activities at the site from about 1965 to 1985 resulted in contamination of shallow soils and groundwater with a mixture of chlorinated solvents and fuel hydrocarbons. Other constituents of concern at the site are PCE, *cis*-DCE and VC.

The upper aquifer at the site consists of about 3 to 4.5 m (10 to 15 ft) of fine to coarse sand and shell fragments with occasional clay lenses and peat stringers (Wiedemeier et al., 1999). This unit is underlain by the Caloosahatchee Marl, consisting of fine-grained calcareous sand, unconsolidated shells and shell fragments, with some interbedded clay units and peat stringers. About 15 to 18 m (50 to 60 ft) below ground surface (bgs), a clay layer is present within the Marl.

Depth to groundwater at the site ranges from about 0.7 m (2 ft) bgs in wells near surface-water bodies to about 3.4 m (11 ft) bgs in wells northeast of the site (Wiedemeier et al., 1999). The hydraulic gradient is approximately 0.0012 m/m, based on observed static water level measurements, with groundwater discharging to the canal and the Banana River. The hydraulic conductivity for the unconfined aquifer averages about 1.8 centimeters per second (cm/sec) based on slug test results. The effective porosity is assumed to be 0.20.

Prior to determining the amount of TCE biotransformation at the site in 1998, BIOCHLOR was calibrated to match site conditions. For this purpose, the model was used to reproduce the movement of the plume from the best guess for when the release occurred (1965) to 1997 (the data available to Aziz et al. [2000a] for model calibration).

The aquifer was estimated to have a longitudinal dispersivity of 12.2 m (40 ft), based on the intermediate value for a plume length of 243–366 m (800–1,200 ft) (Gelhar et al., 1992). A transverse dispersivity of 1.3 m (4 ft) or 10% of the longitudinal dispersivity, was assumed.

A vertical dispersivity of zero was assumed since the depth of the source was approximately equal to the depth of the aquifer.

6.6.1.1 Contaminant Retardation Factors

Contaminant retardation factors were calculated using:

$$R = 1 + K_{oc}.f_{oc}.\rho_b/n \qquad \text{(Eq. 6.21)}$$

where:

R = coefficient of retardation factor (unitless)
K_{oc} = soil sorption coefficient (liters/kilogram [L/kg])
f_{oc} = fraction organic carbon (kg organic carbon/kg soil)
ρ_b = aquifer bulk density (kg/L)
n = porosity (L/L)

Individual retardation factors of PCE = 7.1, TCE = 2.9, *cis*-DCE = 2.8, VC = 1.4, and ethene = 5.3 were obtained using:

- An estimated aquifer bulk density of 1.6 kg/L,
- f_{oc} of 0.184% based on a laboratory analysis of site aquifer solids,
- K_{oc} values of PCE = 426 L/kg, TCE = 130 L/kg, *cis*-DCE = 125 L/kg, VC = 29.6 L/kg, and ethene = 302 L/kg using literature correlations of solubilities at 20 degrees Celsius (°C), and
- An effective porosity (n) of 0.20.

However, BIOCHLOR uses one retardation factor, not individual retardation factors for each constituent. For this study, the median value of 2.85 was chosen.

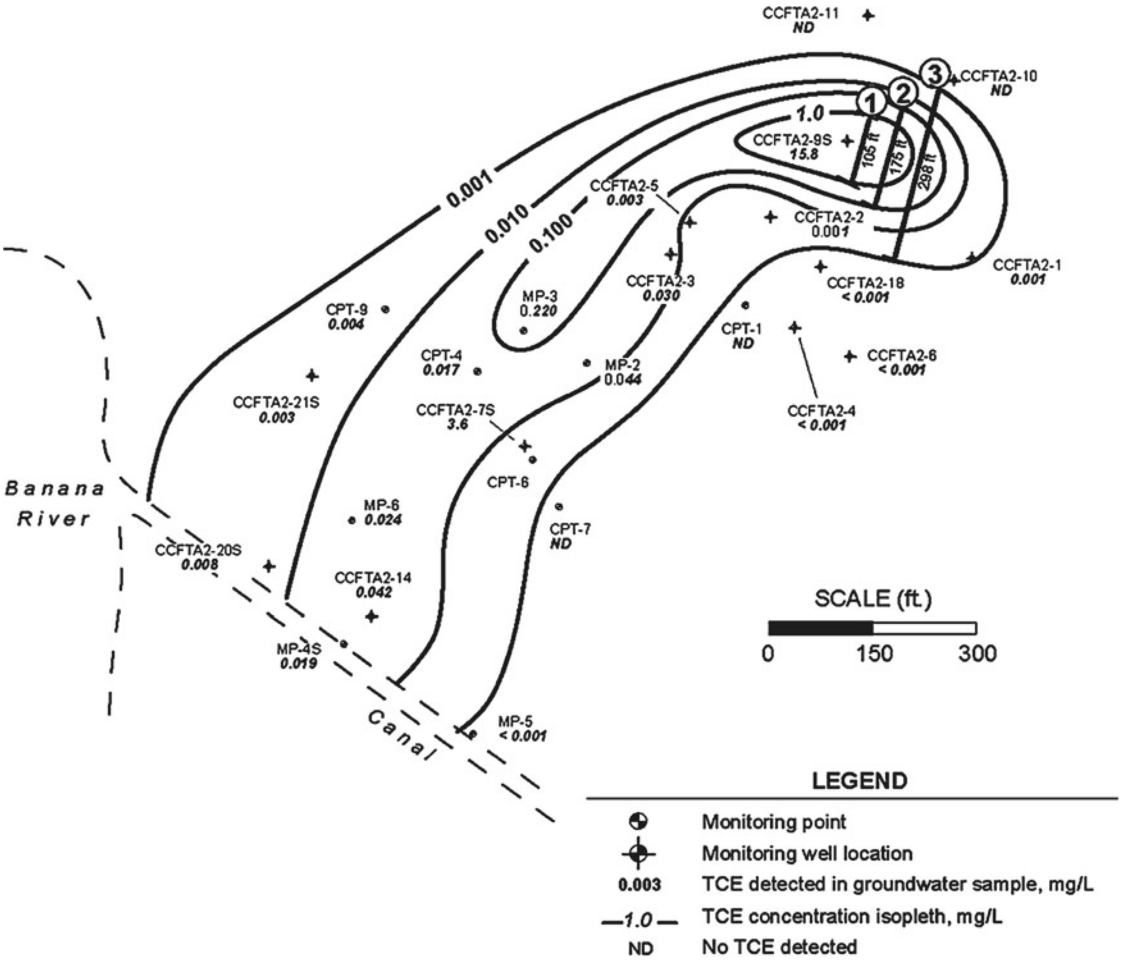
Because the case study focused on the percent of TCE biotransformation, the source area was modeled as a spatially variable source. To obtain the most conservative centerline predictions, the maximum concentrations in the source area were used for the first zone. Concentrations for the other two zones were obtained by taking the geometric means between adjacent isopleths (see Figure 6.8).

A source thickness of 17 m (56 ft) was based on the deepest depth where chlorinated solvents were detected in the aqueous phase. A modeled area length of 330 m (1,085 ft) was calculated as the distance from the source to the receptor (the canal, in this case study). A source width of 213 m (700 ft), significantly larger than the plume width, was used to capture all of the mass discharging into the canal. A simulation time of 33 years was used since the study focused on calculating the percent biotransformation in 1998 and the solvents were released starting in 1965.

Contaminant biotransformation was modeled as a single anaerobic zone based on field dissolved oxygen, oxidation-reduction potential (ORP), and geochemical data that were used to establish anaerobic conditions. Because field-scale rate coefficients and rate data from microcosms were unavailable, literature values were used as the starting rate coefficients. Final rate coefficients were obtained by calibrating the model to field data.

Once the boundary and initial conditions had been defined, the BIOCHLOR model was calibrated by adjusting the biotransformation rate coefficients until the best fit to 1997 field data was obtained as shown in Figures 6.9 to 6.11. Final biotransformation rate coefficients obtained were: PCE→TCE = 2.0 yr^{-1}; TCE→*cis*-DCE = 1.0 yr^{-1}; *cis*-DCE→VC = 0.7 yr^{-1}; and VC→ethene (ETH) = 0.4 yr^{-1}.

Once the model had been calibrated, the percent of TCE biotransformation was calculated as approximately 84% (see Figure 6.12).



BIOCHLOR Source Zone Assumptions

Source Zone	Width (ft)	Actual Source Conc. in 1997 (mg/L)	How Derived
1	105	15.8	Maximum concentration
2	175	0.316	Geometric mean between edge of zone 1 and 2
3	298	0.01	Geometric mean between edge of zone 2 and 3

NOTE: This method of determing widths is different from the method used in BIOSCREEN.

Figure 6.8. TCE site characterization data for Cape Canaveral Air Station, Fire Training Area, Florida for input to BIOCHLOR (from Aziz et al., 2000a).

6.6.2 RT3D Case Study—Simulation of an Emulsified Oil Biobarrier Treating Chlorinated Solvents and Perchlorate

Borden (2007a) applied the numerical model RT3D to simulate the transport and enhanced anaerobic biodegradation of chlorinated solvents and perchlorate in an emulsified oil biobarrier. The biobarrier was installed in a shallow unconfined aquifer impacted by ammonium perchlorate and waste solvent released from a former surface impoundment. The primary COCs at the pilot-test site were perchlorate (ClO_4^-) and 1,1,1-trichloroethane (1,1,1-TCA) with lesser amounts of TCE and related chlorinated volatile organic compounds (CVOCs). The water table aquifer at the site was composed of silty sand and gravel to approximately 5–6 m (16–20 ft) bgs and was underlain by silty clay.

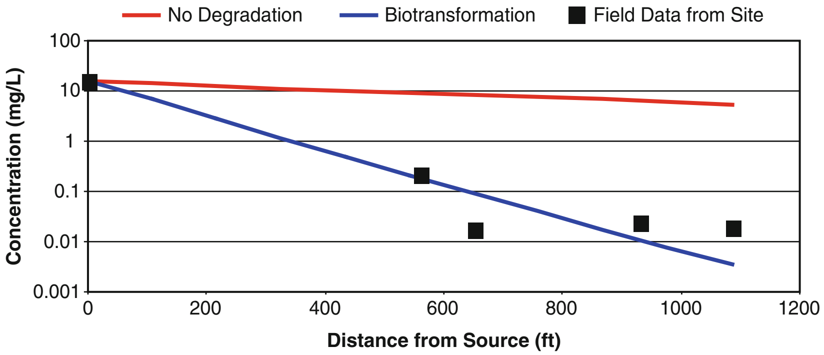


Figure 6.9. TCE centerline concentration output data for Cape Canaveral Air Station, Fire Training Area, Florida (from Aziz et al., 2000a).

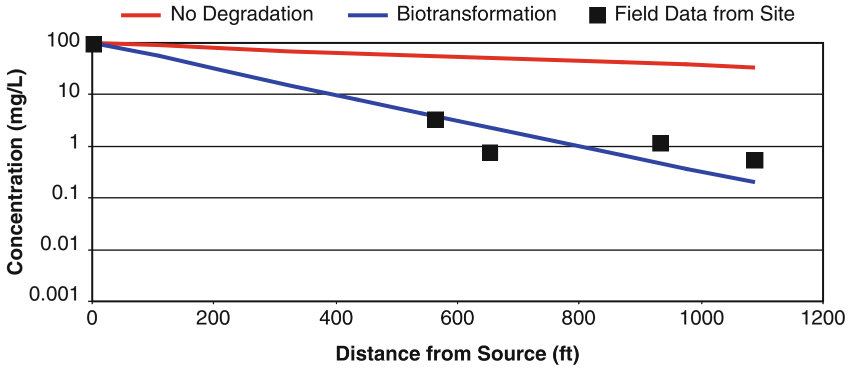


Figure 6.10. *cis*-DCE centerline concentration output data for Cape Canaveral Air Station, Fire Training Area, Florida (from Aziz et al., 2000a).

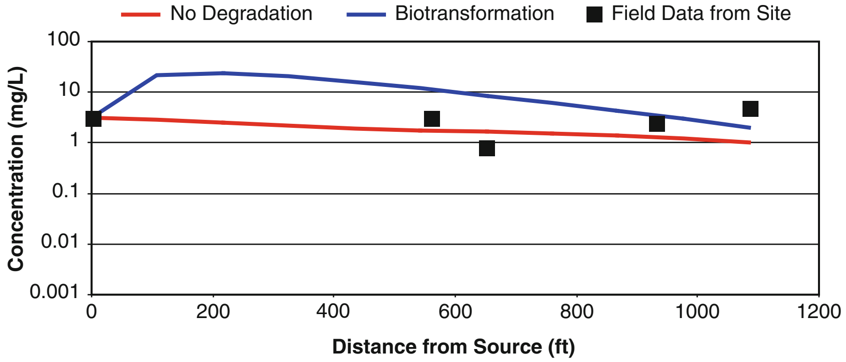
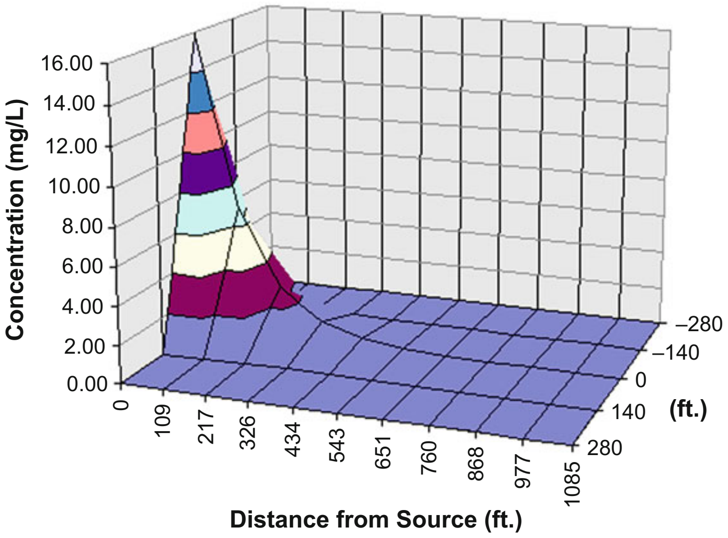
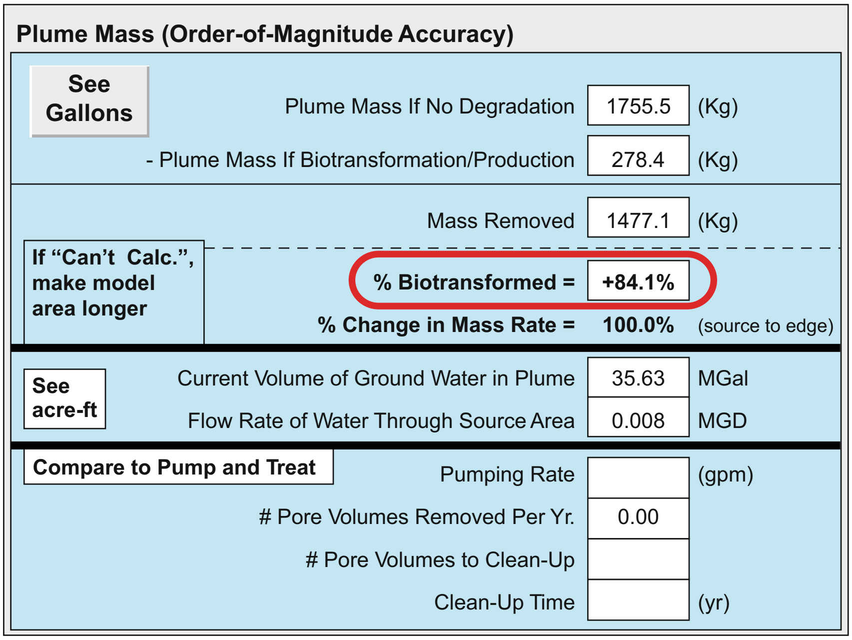


Figure 6.11. VC centerline concentration output data for Cape Canaveral Air Station, Fire Training Area, Florida (from Aziz et al., 2000a).





If "Can't Calc.", make model area longer

Plume Mass If No Degradation: 1755.5 (Kg)

- Plume Mass If Biotransformation/Production: 278.4 (Kg)

Mass Removed: 1477.1 (Kg)

% Biotransformed = +84.1%

% Change in Mass Rate = 100.0% (source to edge)

Current Volume of Ground Water in Plume: 35.63 MGal

Flow Rate of Water Through Source Area: 0.008 MGD

Pumping Rate: (gpm)

Pore Volumes Removed Per Yr.: 0.00

Pore Volumes to Clean-Up:

Clean-Up Time: (yr)

Figure 6.12. Array concentration output data for TCE at Cape Canaveral Air Station, Fire Training Area, Florida (from Aziz et al., 2000a).

The 15.2 m (50 ft) wide biobarrier was installed in a three-step process. First, 10 direct push wells were installed 1.5 m (5 ft) on center, with 3 m (10 ft) of 2.5 cm (1 inch [in]) diameter #20 slotted polyvinyl chloride (PVC) screen. Over a 5-hour period, every other well was simultaneously injected with 42 L (11 gal) of the pre-blended concentrated emulsion (Edible Oil Substrate or EOS) diluted with 166 L (44 gallons [gal]) of water, followed by 625 L (165 gal) of chase water to distribute and immobilize the emulsion. The next day, the remaining wells were treated following the same procedure (Borden, 2007b; Zawtocki, 2005).

Contaminant transport and biodegradation in the emulsified oil barrier and downgradient aquifer were simulated using the sequential decay model (Module #6) within RT3D (Clement, 1997) where:

$$R_A \frac{\partial A}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial A}{\partial x}\right) - \frac{\partial(vA)}{\partial x} + \frac{q_s}{\phi}A_s - k_A S_{oil} A \qquad \text{(Eq. 6.22)}$$

$$R_B \frac{\partial B}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial B}{\partial x}\right) - \frac{\partial(vB)}{\partial x} + \frac{q_s}{\phi}B_s - k_B S_{oil} B + Y_{B/A} k_A S_{oil} A \qquad \text{(Eq. 6.23)}$$

$$R_C \frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) - \frac{\partial(vC)}{\partial x} + \frac{q_s}{\phi}C_s - k_C S_{oil} C + Y_{C/B} k_B S_{oil} B \qquad \text{(Eq. 6.24)}$$

$$R_D \frac{\partial D}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial D}{\partial x}\right) - \frac{\partial(vD)}{\partial x} + \frac{q_s}{\phi}D_s - k_D S_{oil} D + Y_{D/C} k_C S_{oil} C \qquad \text{(Eq. 6.25)}$$

and:

A = aqueous phase concentration (moles/L) for compound A
R_A = retardation factor for compound A
D = dispersion coefficient (m/d^2)
v = velocity (m/d)
ϕ = porosity (dimensionless)
q_s = volumetric water flux per volume of aquifer representing sources and sinks
A_s = source/sink concentration (moles/L) for contaminant A
S_{oil} = sediment oil concentration (g oil/g sediment)
k_A = effective 2nd order decay coefficient (g sediment/g oil - d) for contaminant A
$Y_{B/A}$ = degradation product yield coefficient (moles of B produced per mole of A degraded)

The actual numerical simulations were conducted using GMS 6.0 (Brigham Young University, 2005) to aid in data entry and visualization of model output. Prior to simulating contaminant transport, MODFLOW (McDonald and Harbaugh, 1988) was calibrated to match conditions at the field site. The aquifer was represented as a two-layer system (each layer 1.5 m [4.9 ft] thick) with injection and monitor wells fully penetrating both the shallow and deeper layers. The shallow and deeper layers were estimated to have hydraulic conductivities (K) of 2.1 and 10.7 meters/day (m/d) based on visual observations of soil cores, grain size analyses and slug tests.

Flow and transport parameters were estimated by matching model simulations to results from the non-reactive tracer tests (hydraulic gradient = 0.005, effective porosity = 0.18, longitudinal dispersivity = 0.3 m, horizontal transverse dispersivity = 0.03 m, vertical transverse dispersivity = 0.003 m, bulk density = 1.85 g/cm^3). Following emulsion injection, K was assumed to be reduced by up to 77% due to clogging with accumulated biomass, gas bubbles and/or retained oil (Borden, 2007a). The reduction in K was assumed to be linearly proportional to retained oil concentration where $K_{reduced} = K_{initial} \times (1 - 0.77 \times S_{oil}/\text{Maximum } S_{oil})$. Oil concentration in the sediment (S_{oil}) was determined from numerical simulations of oil droplet transport and retention immediately following emulsion injection and varied from a maximum value of 0.0026 g oil/g sediment adjoining the injection wells to zero in untreated areas (Borden, 2007b).

Contaminant biodegradation was modeled as a second-order process where the contaminant decay rate was assumed to be linearly proportional to both S_{oil} and the contaminant concentration. S_{oil} was determined from prior simulations of oil droplet transport and retention (Borden, 2007b) and assumed constant over the simulation period. The contaminant transport model was first calibrated to match the observed contaminant distribution prior to emulsion injection using specified concentration cells to define the upgradient boundary condition. Contaminant retardation factors were estimated based on published soybean oil-water and octanol-water partition coefficients (Howard, 1990). Long and Borden (2006) found that a linear-equilibrium partitioning approach provided good estimates of the retardation of PCE in abiotic laboratory columns treated with emulsified soybean oil.

Once boundary and initial conditions were defined, the model was calibrated by adjusting the second-order degradation rate (k) for each contaminant until the mean error between observed and simulated steady-state concentrations was less than 0.5% of the average concentration. Estimated second-order degradation rates for each contaminant are shown in Table 6.4. Once calibrated, the model was used to evaluate the effect of alternative barrier designs on chlorinated solvent treatment efficiency.

Table 6.4. RT3D Model Calibration Parameters

	Partition Coefficient (mL/g)	2nd Order Decay Rate (g sediment/g oil–d)	Range of Apparent 1st Order Decay Rate (d^{-1})	Degradation Product	Degradation Product Yield Coefficient (mole/mole)
ClO_4^-	0	310	0 – 0.81	none	NA[a]
TCA	310	132	0 – 0.34	DCA	1
DCA	62	128	0 – 0.33	CA	1
CA	27	42	0 – 0.11	NA	NA

[a] NA – not applicable

6.6.2.1 Full-Scale Barrier Performance

Once calibrated, the model was used to evaluate two different barrier alternatives. For both alternatives, a 10 m (33 ft) wide portion of the barrier was simulated with the model domain extending 15 m (49 ft) upgradient of the barrier and 30 m (98 ft) downgradient. Since only a short section of barrier was simulated, upgradient contaminant concentrations were assumed to be uniform and equal to 9,000 micromolar (μM) ClO_4^-, 57.4 μM TCA, 0.5 μM DCA and 0.08 μM CA.

For Barrier Alternative I, injection wells were spaced 5 m (16 ft) apart, perpendicular to groundwater flow with continuous screens extending through both the shallow and deeper layers. A 20% EOS: 80% water solution was injected in every other well for 0.5 days, followed by chase water for 1.5 days. This procedure was then repeated with the remaining wells. The emulsion and chase-water injection flow rate was 4 m^3/d per well to match the flow rate previously used in the field. The flow rate entering each layer was assumed to be proportional to the layer transmissivity with 16% of the flow entering the shallow, less permeable layer (K = 2.1 m/d) and 84% of the flow entering the deeper, more permeable layer (K = 10.7 m/d).

Figure 6.13 shows the simulated oil distribution in the sediment following injection and the steady-state aqueous contaminant distributions in the shallow, less permeable layer of the aquifer for Barrier Alternative I. In the deeper, more permeable layer, oil was effectively distributed between the injection wells, resulting in a relatively uniform oil-treated zone 13–18 m long along the direction of groundwater flow with a hydraulic retention time (HRT) of 3–4 months (data not shown for the deeper layer). The relatively high residual oil concentrations throughout the deeper layer (0.0037 g/g) combined with the large HRT resulted in very high treatment efficiencies in the deeper layer, with all contaminants reduced below applicable regulatory standards. However, in the shallow layer (shown in Figure 6.13), the oil distribution was much less uniform, varying from 0.0037 g/g near the injection wells to 0.00033 g/g

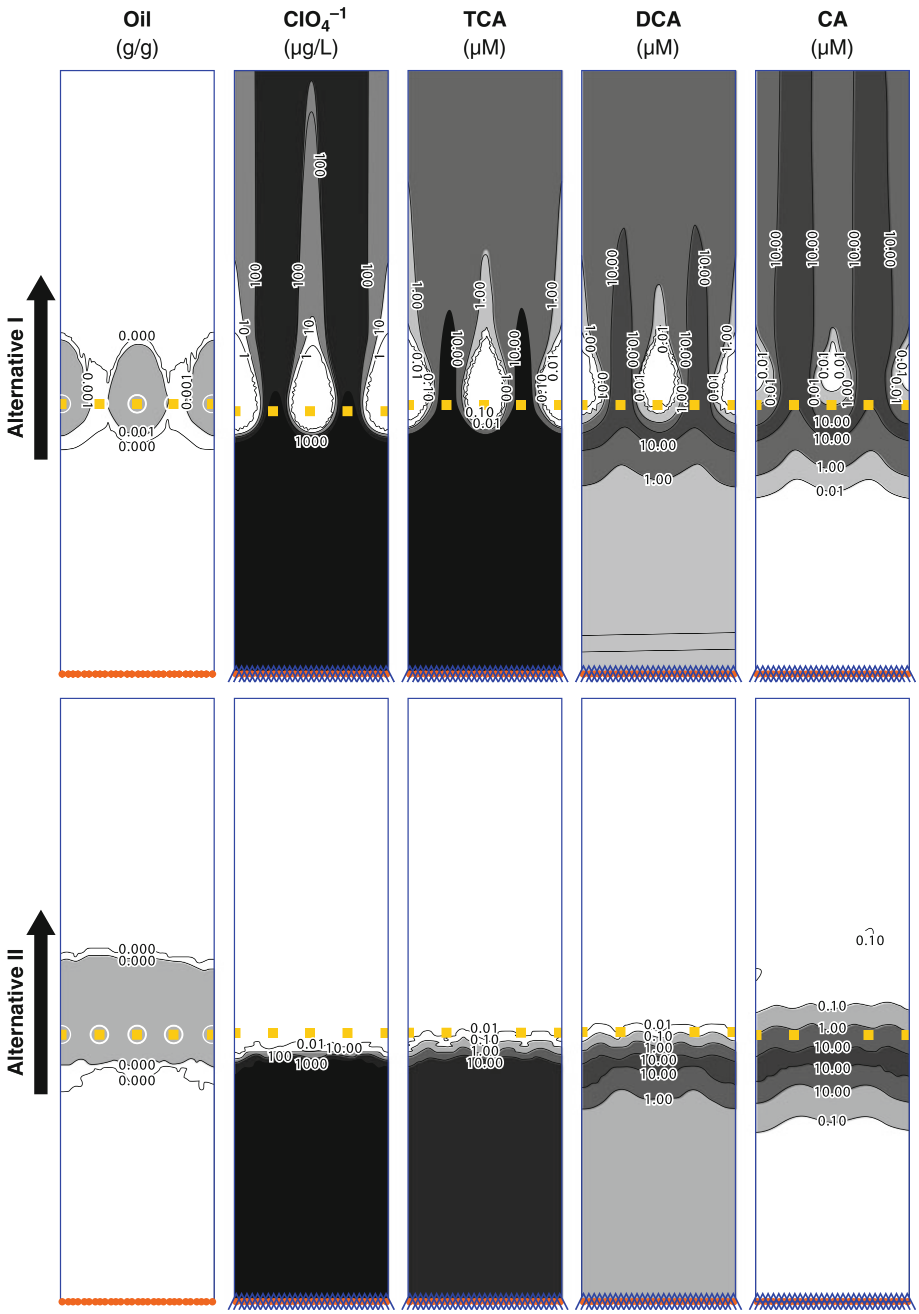


Figure 6.13. Model prediction of oil distribution in sediment following injection and steady-state aqueous contaminant distribution for Barrier Alternatives I and II (from Borden, 2007b).

midway between the injection wells. This nonuniform oil distribution allowed substantial amounts of contaminants to pass untreated through the gaps in the oil-treated zone. Farther downgradient, residual contaminants diffused from the shallow layer into the deeper layer.

Barrier Alternative II used one set of continuously screened injection wells spaced 5 m apart (same as Alternative I) with a second set of injection wells located midway between the first set and screened only in the shallow, less permeable layer. The injection process for the first set of wells was identical to Alternative I. Once the first set of injections was complete, a 20% EOS: 80% water solution was injected into the second set of wells for 0.5 days, followed by chase water for 1.5 days at a flow rate of 0.66 m^3/d per well.

Figure 6.13 shows the simulated oil distribution in the sediment following injection and the steady-state aqueous contaminant distributions in the shallow, less permeable layer for Barrier Alternative II. The modified injection procedure followed in Alternative II resulted in continuous oil-treated zones in both the shallow and deeper layers. The zones of high oil residual saturation ($\sim$ 0.0037 g/g) were 5–6 m long in the shallow layer and 13–17 m long in the deeper layer with HRTs that vary from 4–5 months in the shallow layer to 3–4 months in the deeper layer. The long contact time between the contaminants and oil in both the shallow and deeper layers resulted in very effective treatment, with all contaminants reduced below treatment standards in both the shallow and deeper layers.

6.7 CONCLUSION AND SUMMARY

In summary, and as evidenced by the numerous model development efforts that have been undertaken or are under way for chlorinated solvents, much progress has been made in our ability to articulate and understand the various mechanisms and processes that affect the fate and transport of a chlorinated compound in groundwater. Pilot-scale and large-scale studies at chlorinated solvent sites have greatly assisted the process of model development, application and validation. Additionally, the numerous laboratory- and field-scale biodegradation studies have allowed development of kinetic expressions and biodegradation rate data to support the modeling efforts. Challenges still remain, however, in modeling sources and their behavior over time and in modeling the complexities of the biodegradation process. Research is needed to improve the tools developed to date and their predictive capabilities.

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CHAPTER 7

IMPACTS OF SOURCE MANAGEMENT ON CHLORINATED SOLVENT PLUMES

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7.1 INTRODUCTION

Chlorinated solvent plumes, in aqueous or vapor form, are the products of contaminant source zones. So long as source zones persist, management of plumes will be an ongoing activity. The status of a plume is therefore inextricably linked to its source, and any decision regarding plume management is likely to involve a decision regarding management of the source. As bounding scenarios, sources can decay via naturally occurring processes or they can be actively addressed through engineered measures designed to contain and/or deplete the source. Typically, engineered measures are intended to reduce the magnitude and/or duration of contaminant discharge from a source to an aqueous or vapor phase plume. A typical consequential benefit of source zone treatment is a reduction in the contaminant concentrations downgradient.

This chapter covers the current understanding of the effects of source control on contaminant concentrations in plumes. Two fundamental questions need to be resolved. The first is how source measures reduce downgradient loading to plumes over time ("source function"). The second is how reductions in contaminant loading from the sources translate into downgradient improvements in water quality or soil gas concentrations over time ("plume function").

As a starting point, processes governing the movement and distribution of chlorinated solvents in subsurface environments are described. This background provides an introduction to the mechanisms of contaminant storage, release and transport in source and plumes. Furthermore, it provides an introduction to the 14 compartment model, a graphic tool that is a cornerstone of this chapter.

Next, critical attributes of common geologic settings are identified. Building on the framework described in the National Research Council (NRC) report on source zone assessment and remediation (NRC, 2005), five hydrogeologic type settings are advanced. Each of these type settings has potentially unique mechanisms for storing chlorinated solvents and responses to remedial actions. In this chapter, emphasis is given to the fact that the nature of the problem in each setting evolves with time through early, middle and late stages.

Lastly, the current state of knowledge regarding the effects of source control measures on contaminant concentrations in plumes is reviewed. Given that plumes represent a primary exposure pathway, this issue is critical for determining the need for source control, and the appropriate objectives for source control efforts.

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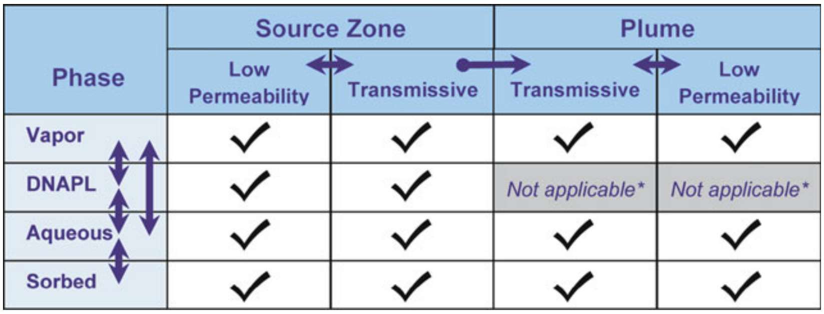
7.2 MOVEMENT AND DISTRIBUTION OF CHLORINATED SOLVENTS IN THE SUBSURFACE

The following presents an overview of processes governing the movement and distribution of chlorinated solvents in source zones and plumes. As a first step, it is critical to recognize that chlorinated solvents in subsurface environments occur in four different phases:

- Dense nonaqueous phase liquids (DNAPL)
- A gas phase in soil vapor
- A dissolved phase in water
- A sorbed phase on aquifer solids

Second, it is essential to recognize that each phase can exist in either transmissive or relatively low permeability geologic media present in source zones or plumes. The differentiation between transmissive zones and low permeability zones is relevant in that water in the more transmissive zones is typically moving much more rapidly than that in the less permeable materials. In most subsurface environments, the water in the lower permeability zones is effectively stagnant. Payne et al. (2008) advances this conceptualization by describing aquifers as bodies containing mobile and immobile pore space. Understanding transfer of chlorinated solvents between transmissive zones (mobile pore space) and low permeability zones (immobile pore space) is essential to understanding remediation of chlorinated solvent releases.

Building on the four phases and transmissive versus low permeability zones, Figure 7.1 identifies 14 compartments in which chlorinated solvents occur in subsurface source zones and plumes. A key attribute of the 14 compartment model is that it provides a holistic view of the problem of chlorinated solvents in subsurface environments.



Phase	Source Zone		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	✓	✓	✓	✓
DNAPL	✓	✓	*Not applicable**	*Not applicable**
Aqueous	✓	✓	✓	✓
Sorbed	✓	✓	✓	✓

Figure 7.1 Subsurface compartments potentially containing chlorinated solvents. Arrows show mass potential transfer links between the 14 compartments. Note: *As per the definition of source zones in NRC (2006), DNAPLs are only present in source zones and consequently are absent in plumes.

As an example, the 14 compartment model can be used to evaluate remediation via groundwater extraction (i.e., pump-and-treat). The primary effect of pump-and-treat is to deplete aqueous phase solvents in transmissive zones. A secondary effect is to enhance the release of solvents stored in other impacted compartments (e.g., DNAPL in transmissive zones and/or dissolved and sorbed chlorinated solvents in low permeability zones). Unfortunately, the release of solvents from these less accessible compartments is relatively slow, even during pump-and-treat, often resulting in a need to continue treatment for decades or even centuries.

The following sections review the key attributes of chlorinated solvent releases through a review of the four phases of concern. It is important to address all four phases in any conceptual model of a chlorinated solvent source. For example, calculating the total mass of solvents in a volume of porous media requires knowing the mass in all four phases (i.e., nonaqueous, aqueous, vapor, and sorbed phases). The total mass therefore is given by Equation 7.1 (from Cohen and Mercer, 1993):

$$\omega_{Total} = \omega_{DNAPL} + \omega_{aqueous} + \omega_{vapor} + \omega_{sorbed} \qquad \text{(Eq. 7.1)}$$

where ω is the contaminant mass per unit mass porous media.

Note that at any point in space, each of the phases is trying to equilibrate with the other phases. Note also that the distribution between the four phases will change over time as the source *weathers*.

7.2.1 DNAPL

Most chlorinated solvents enter the subsurface as separate phase liquids that are denser than water. These liquids are referred to as DNAPL. Less frequently, chlorinated solvents are released as a dissolved phase constituent in water (e.g., solvents in wastewater) and/or as a fractional component in a light nonaqueous phase liquid (LNAPL) such as waste oil. This chapter focuses on DNAPL-related chlorinated solvent releases. Nevertheless, much of the information is also relevant to aqueous- or LNAPL-related releases of chlorinated solvents.

Subsurface environments consist of solids (e.g., soil grains or rock) and void space (soil pores or fracture apertures). The void space contains water above and below the water table. In the unsaturated zone, air coexists with pore water. Compared to air, water is preferentially attracted to solids and forms a continuous "*wetting phase*" that covers the matrix solids and fills the smaller pore spaces. In larger pores, water tends to occupy margins, leaving the remaining central portions filled with air, a "*non-wetting phase.*" Figure 7.2 shows porous media that contain both wetting and non-wetting phases. Recognizing the coexistence of multiple phases (e.g., water, air and DNAPL) closely commingled in tiny pores is a key element of understanding mass transfer between phases.

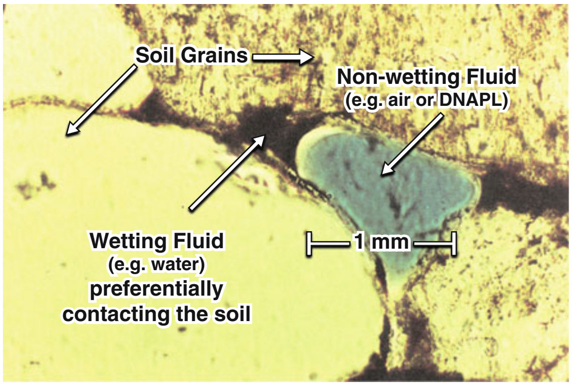


Figure 7.2. Immiscible fluids in the pore space of granular porous media (after Wilson et al., 1990).

Driven by gravity and capillary forces, DNAPL released at the surface migrates downward through the subsurface. Capillary forces reflect the tendency of wetting fluids to be drawn into porous media due to liquid-liquid attraction or liquid-solid attraction (e.g., water being drawn into a dry sponge). Above the capillary fringe, DNAPL displaces air and typically occurs as an intermediate wetting phase between water and air. Over time, volatile DNAPL components partition into soil gas, producing vapor plumes near releases. Given a sufficiently large release, DNAPL will migrate to and below the water table. In the groundwater zone DNAPL displaces water and occurs (typically) as a non-wetting phase. With time, soluble constituents in DNAPL partition into groundwater, forming aqueous plumes in transmissive zones downgradient of the DNAPL zone.

The occurrence of chlorinated solvents as an immiscible non-wetting phase in the saturated zone influences the movement and ultimate distribution of DNAPL. For DNAPL to invade water-saturated media, it must displace the water. This requires that pressure in the DNAPL be greater than the water pressure by an amount known as the *displacement pressure* (Corey, 1994). For a given DNAPL, the displacement pressure is related to the size of the pore. For larger pores the displacement pressure for DNAPL is low, and conversely, for small pores the DNAPL displacement pressure is large.

Given the heterogeneous nature of geologic media and the mechanics of multiphase flow, DNAPL in the saturated zone preferentially invades intervals with the largest pores. Conceptually, this leads to sparse DNAPL bodies described as pools (horizontal subzones) and fingers (interconnecting vertical tubes). This conceptualization is based on field experiments (e.g., Poulson and Kueper, 1992; Kueper et al., 1993) and theoretical developments (e.g., McWhorter and Kueper, 1996).

Initially, the fraction of pore space filled with DNAPL (pore saturation) is large enough that the DNAPL bodies are continuous (i.e., there are interconnected DNAPL-filled pores). With time, the DNAPL is depleted through drainage, dissolution and/or volatilization. These processes reduce DNAPL saturations and transform the continuous DNAPL flow paths into discontinuous ganglia and blobs (Wilson et al., 1990). DNAPL ganglia and blobs are largely immobile as separate phase liquids. Eventually, all of the DNAPL will be transferred to dissolved, vapor and sorbed phases. In all of this it is critical to note that the nature of the problem changes with time.

The architecture of DNAPL pools and fingers within the subsurface is dependent on numerous factors including geology, the rate at which the DNAPL was released, the volume of the release and the age of the release (Feenstra et al., 1996). Figure 7.3 illustrates four conceptual DNAPL architectures in alluvium, containing both granular and fractured media. The presence of a low permeability layer plays a primary role in defining where the pools occur. DNAPL tends to perch above any low permeability capillary barrier. In general, rapid releases are thought to create more horizontal spreading while slower releases create less horizontal spreading (Feenstra et al., 1996). Lastly, DNAPL in fingers is likely to be depleted far more quickly than DNAPL in pools because the geometry and orientation to groundwater flow of DNAPL in fingers creates a relatively large surface area exposed to flushing (Sale and McWhorter, 2001). Therefore, DNAPL in fingers may be present only during the early stages of a release.

Critically absent in Figure 7.3 are representations of vapor plumes, groundwater plumes and solvents sorbed onto aquifer solids. Note that DNAPL is just one of the four phases that can sustain contamination in groundwater and vapor plumes.

7.2.2 Vapor Phase

Vapor phase chlorinated solvents originate from direct volatilization of DNAPL in the unsaturated zone or from evaporation of aqueous phase chlorinated solvent in pore water. Chlorinated solvents are also present as a sorbed phase on solids. Given close commingling of fluids (millimeter or less), chlorinated solvents readily partition between each of the phases.

Under natural conditions the primary transport process for vapor phase chlorinated solvents is gas phase diffusion. This process is dominant because chlorinated solvents are volatile, and because gas phase diffusion coefficients are so much larger than aqueous phase diffusion coefficients (approximately four orders of magnitude greater). At any point in a porous medium, the *effective* diffusion coefficient is strongly dependent on water content. As water content increases, the cross-sectional area available for vapor phase transport decreases and the tortuosity of the flow paths increases. The net result of higher water content is a lower effective diffusion coefficient. Transport of vapor phase chlorinated solvents also occurs via advection of the vapor phase. Advection can be driven by volatilization of DNAPL, changes in atmospheric pressure, density and/or engineered systems (e.g., soil vapor extraction). A comprehensive review of flow of gas in the unsaturated zone due to evaporation of volatile organic compounds is presented in Falta et al. (1989).

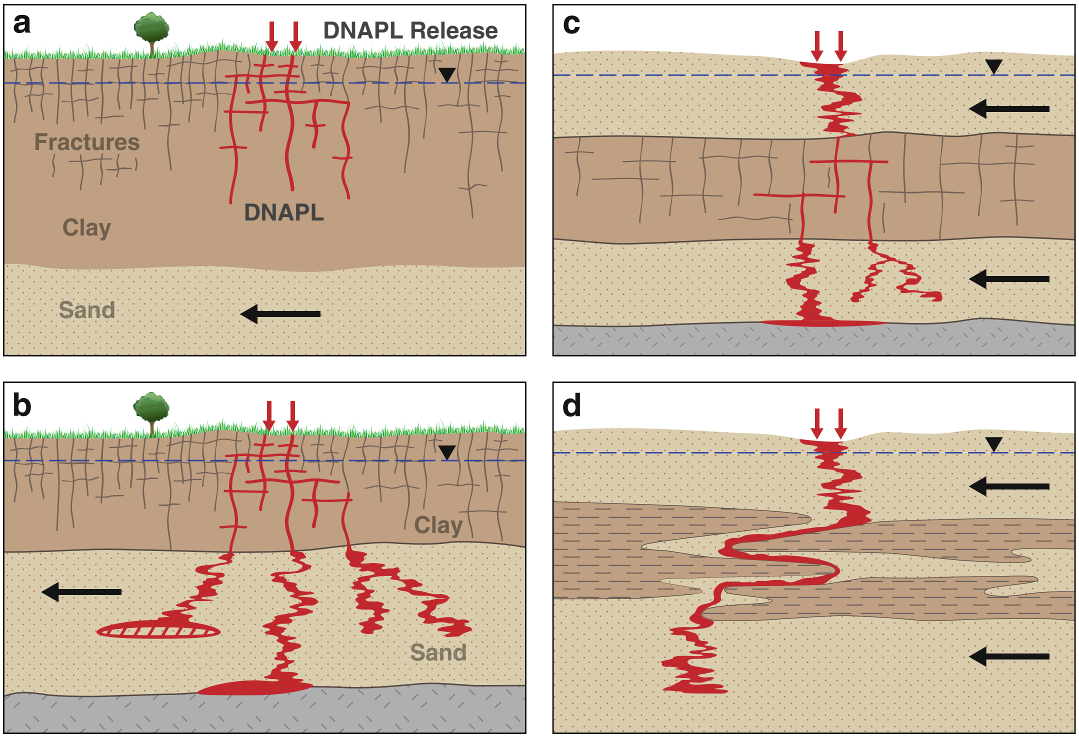


Figure 7.3. DNAPL architecture (after Feenstra et al., 1996).

As vapor plumes advance constituents in the vapor phase partition into pore water and adsorb onto the matrix solids. Initially, this process retards the advancement of vapor plumes. At later times, chlorinated solvents stored in pore water and sorbed to solids can sustain vapor plumes. Degradation of parent chlorinated solvents in unsaturated zones via biologically mediated processes may be uncommon due to presumed aerobic conditions in most unsaturated zones away from source zones. Important exceptions are degradation products such as vinyl chloride (VC), dichloroethene (DCE) and methylene chloride, which readily degrade under aerobic conditions in vapor plumes.

Vapor plumes present two primary challenges. First, they can contaminate underlying groundwater via diffusion and/or by water that percolates through the unsaturated zone. Secondly, vapor plumes can adversely impact indoor air quality. Both of these conditions are common drivers for remedial actions.

7.2.3 Aqueous Phase

As soon as DNAPL encounters water in the subsurface, constituents in the DNAPL begin to partition into water in the pore space. In both saturated and unsaturated zones, mass transfer occurs between phases in small pore spaces where solids, water and DNAPL are closely commingled. Dissolution of DNAPL constituents into water is driven by differences in the constituents' chemical potential in the two phases (Schwarzenbach et al., 1993). Once the chemical potentials in the separate phases equilibrate, the constituents in the aqueous phase reach their effective solubility. The effective solubility of a constituent is a function of the compound's pure phase solubility and its mole fraction in the DNAPL (Feenstra et al., 1996).

Degradation of Chlorinated Solvents

For many years the prevailing opinion was that aqueous phase chlorinated solvents did not degrade under natural conditions in aquifers. However, in the 1980s, researchers (e.g., Vogel and McCarty, 1985; Wilson and Wilson, 1985) demonstrated that biotic processes could degrade chlorinated solvents. This discovery was largely responsible for the acceptance of natural attenuation as a plume management strategy in the late 1990s (Wiedemeier et al., 1998, 1999).

In addition, research conducted in the 1990s indicated that chlorinated solvents can be degraded abiotically via chemical oxidation (Farquar, 1992) and chemical reduction (Gillham and O'Hannesin, 1994). More recently it has been recognized that naturally occurring minerals (e.g., magnetite) can also drive abiotic reduction of chlorinated solvents (Danielsen and Hayes, 2004).

The data below are the average carbon oxidation states of common chlorinated solvents and associated degradation products. In general, chlorinated solvents with higher oxidation states, CT > PCE, CF > TCE, are prone to degradation via reduction. Conversely, chlorinated solvents with lower oxidation states, CM < DCA, VC < DCE, TCA, MC, are prone to degradation via oxidation.

Carbon Oxidation States

↑ Oxidized

	Ethenes	Ethanes	Methanes
4			Carbon Tetrachloride (CT)
3		Pentachloroethane (PCA)	
2	Perchloroethene (PCE)		Chloroform (CF)
1	Trichloroethene (TCE)	Trichloroethane (TCA)	
0	Dichloroethene (DCE)		Methylene Chloride (MC)
-1	Vinyl Chloride (VC)	Dichloroethane (DCA)	
-2	Ethene		Chloromethane (CM)
-3		Ethane	
-4			Methane

Reduced ↓

Over time, aqueous phase advection, dispersion, diffusion and degradation drive dissolved constituents away from DNAPL zones. These processes deplete aqueous phase chlorinated solvents at the water-DNAPL interfaces and allow further dissolution of DNAPL. Ultimately, the rate of DNAPL dissolution is governed either by the rate at which constituents can partition into groundwater (Miller et al., 1990; Powers et al., 1991), or by the rate at which dissolved phase constituents migrate away from the DNAPL (Sale and McWhorter, 2001).

Within transmissive portions of the saturated zone, advective transport produces groundwater plumes that can extend over large distances, as far as miles in some cases. As plumes advance, dissolved phase solvents are lost through sorption, diffusion into low permeability layers, and degradation. At some sites, natural rates of attenuation are rapid enough to create stable or even shrinking plumes (Wiedemeier et al., 1999), and risks to receptors can be addressed through natural processes. Unfortunately, natural attenuation alone is often insufficient to address potential adverse impacts of chlorinated solvent releases.

Dissolved phase constituents also occur in low permeability layers. Note that with the exception of secondary permeability features (fractures, root holes, animal burrows), high displacement pressures typically preclude DNAPL from low permeability layers. Dissolved phase constituents permeate low permeability layers through a combination of diffusion and slow advection. Within low permeability layers, chlorinated solvents are present in both dissolved and sorbed phases. Often, fine-grained low permeability layers have higher sorption capacities due to their greater organic carbon contents and higher surface area per unit volume. Higher organic carbon content increases the contaminant storage capacity of low permeability layers and accelerates the diffusion of chlorinated solvents into the low permeability materials (Freeze and Cherry 1979; Parker et al., 1994; Sale et al., 2008).

As long as the concentration of aqueous phase solvents is greater in the transmissive zones than in the low permeability layer, solvents will be driven into the low permeability layer. This matrix storage can be an important mechanism for attenuation of solvents in plumes. However, once the aqueous concentration of the solvents declines in the transmissive layer(s), solvents will begin diffusing back out of the low permeability layers. This process, back diffusion, can sustain plumes for long periods of time (Liu and Ball, 2002; Chapman and Parker, 2005; AFCEE 2007; Sale et al., 2008). Because back diffusion is far slower than the initial inward diffusion process (Parker et al., 1996), it can sustain plumes for extended periods even after all of the DNAPL is gone (Figure 7.4).

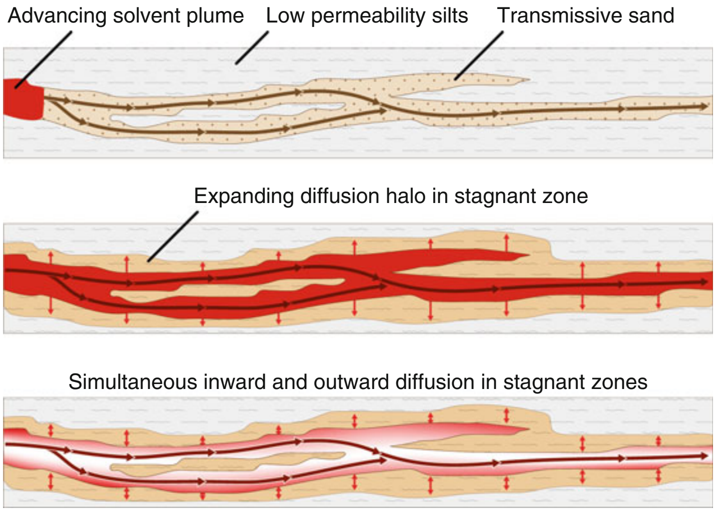
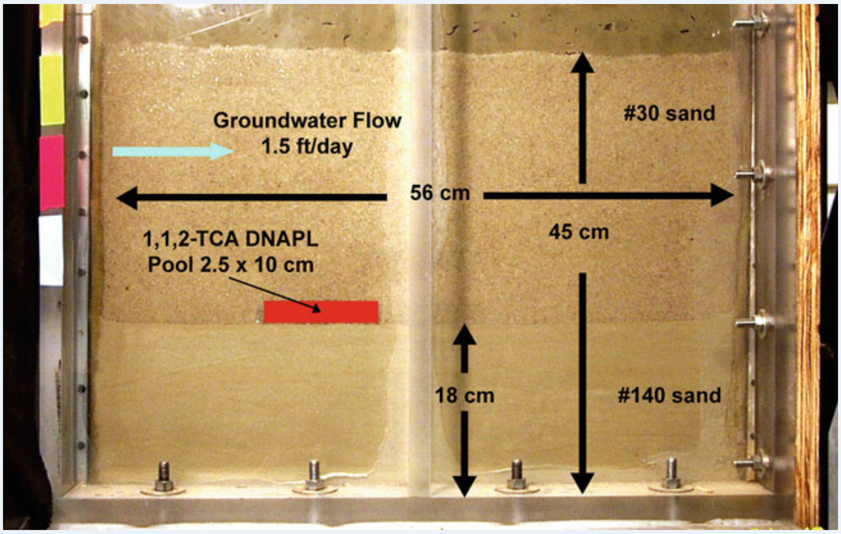


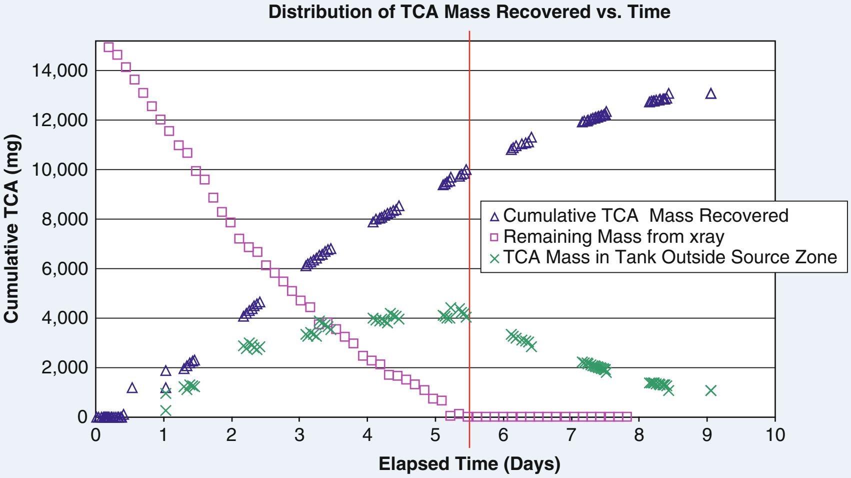
Figure 7.4. Diffusion into and out of low permeability materials, leading to initial plume attenuation and subsequent long-term plume persistence (after AFCEE, 2007).

Source Strength Before and After Complete DNAPL Dissolution

The following experiment illustrates dissolution of DNAPL into aqueous phases in a two layer system (Wilkins, 2005; AFCEE, 2007). Two layers with an approximate two order of magnitude contrast in permeability were present in the sand tank. Water was flushed through the upper transmissive sand layer at a seepage velocity of 1.5 feet per day (ft/day). A 15-gram (g) pool of 1,1,2-TCA was introduced in the transmissive sand immediately above the low permeability layer.



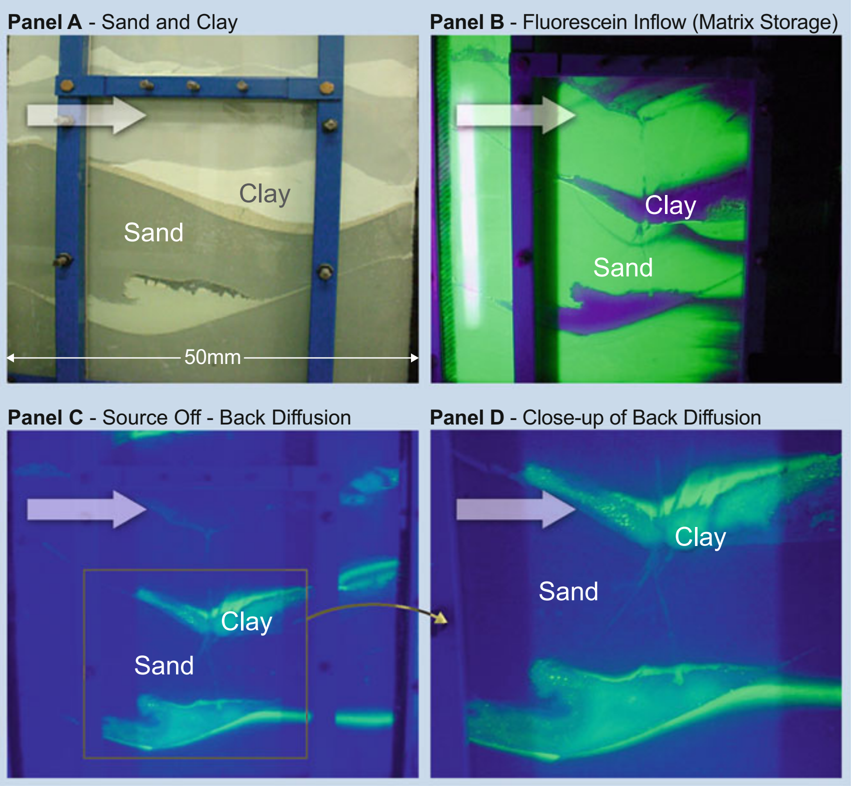
Key results are presented below. The boxes in the graph reflect the amount of DNAPL remaining in the tank as a function of time. This was determined by measuring absorbance with a scanning x-ray source. Results show that the DNAPL completely dissolved in 5.5 days. The triangles depict cumulative aqueous phase discharge of 1,1,2-TCA from the tank. This was based on effluent concentrations and the flow rate through the tank. By the time the DNAPL was fully dissolved, 10 g of TCA had been discharged from the tank via the transmissive layer. The majority of the remaining 5 g had been driven into the low permeability layer via transverse diffusion (data posted as Xs). Sustained discharge of aqueous phase TCA from the tank after DNAPL depletion (triangles) reflected back diffusion of aqueous phase TCA from the low permeability layer. An interesting observation was that the overall rates of contaminant discharge from the tank were similar with and without DNAPL.



Matrix diffusion and back diffusion have received broad attention. Foster (1975), Tang et al. (1981), Sudicky et al. (1993) and Parker et al. (1996) addressed diffusion within granular fractured porous media. Freeze and Cherry (1979), Rao et al. (1980), Sudicky (1983), Sudicky et al. (1985), Goltz and Roberts (1987), Wilson (1997), Liu and Ball (2002), Chapman and Parker (2005), AFCEE (2007) and Sale et al. (2008) addressed diffusion in heterogeneous unfractured granular porous media. The most recent of these publications (Wilson, 1997; Liu and Ball, 2002; Chapman and Parker, 2005; AFCEE, 2007; Sale et al., 2008), specifically recognized that these processes can impact our ability to restore groundwater quality in source zones and in plumes.

Experiment Illustrating Contaminant Storage and Release from Low Permeability Layers

The images below show an experiment in which water containing fluorescein dye was flushed through a tank containing sand and clay layers (Doner, 2007). Initially the fluorescein was attenuated via diffusion into the clay layers (Panel B). Continued flushing without the fluorescein illustrates how back diffusion from the low permeability clay can sustain contaminant levels in a plume occurring in a transmissive zone in the absence of an upgradient source (Panels C and D).



7.2.4 Sorbed Phase

The sorbed phase is the contaminant mass that resides in or on the matrix solids. This fraction of the total mass includes both contaminant adsorption onto solid surfaces and absorption of contaminants into the matrix particles. As the aqueous phase concentrations increase, there is a net flux of contaminants to the sorbed phase. This equilibrium partitioning attenuates the dissolved phase contaminant concentration as the plumes advance. In addition, it creates an *in situ* reservoir of immobile stored contaminants. The initial process of attenuating aqueous phase contamination via sorption is referred to as retardation.

Conversely, as aqueous phase concentrations decrease, contaminants are released from the sorbed phase back into the aqueous phase. This desorption has the net effect of sustaining the aqueous phase concentrations. As a first order approximation, the amount of sorbed contamination is proportional to the fraction of organic carbon (f_{oc}) present in the porous media and the compound's organic carbon partitioning coefficient (K_{oc}), called a linear isotherm. Greater detail is provided in Karickoff et al. (1979) and Schwarzenbach et al. (1993).

To illustrate the relative distribution of the aqueous and sorbed phase contaminant mass, Figure 7.5 plots the contaminant fraction present in the aqueous and sorbed phases given a typical range of f_{oc} values. At relatively high organic carbon content ($f_{oc} = 0.01$), more than 90% of the contaminant mass is present as a sorbed phase. Given high surface areas and deposition in quiescent environments, this is a plausible scenario for silts or clays deposited in an organic rich environment. At the low end of the range of organic carbon content ($f_{oc} = 0.001$), only 10 to 20% of the total contaminant mass may be stored in the sorbed phase.

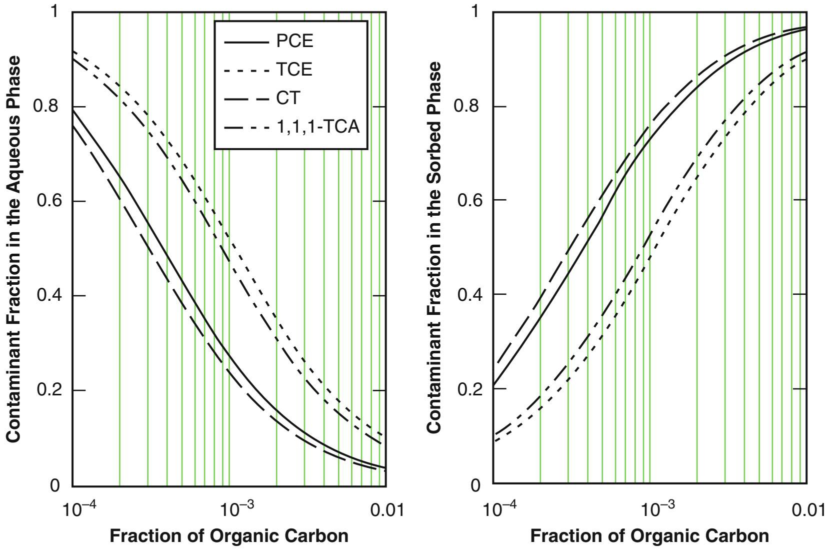


Figure 7.5. Fractions of total contaminant mass in the aqueous and sorbed phases as a function of the fraction of organic carbon (following Schwarzenbach et al., 1993, using parameters for typical saturated soils and K_{oc} values from Allen-King et al., 1996).

More recently, several researchers have determined that sorption and desorption have a linear relationship only at higher concentrations, and at lower concentrations a hysteretic effect is observed due to availability effects (e.g., Pignatello and Xing, 1996). Some researchers call this hysteresis effect *dual-equilbrium desorption* (Chen et al., 2004). Like matrix diffusion, desorption can sustain low-concentration groundwater plumes for long periods of time.

7.3 CRITICAL ATTRIBUTES OF GEOLOGIC SETTING

"Subsurface settings are a product of a set of diverse geologic processes that produce an abundance of variation" (NRC, 2005). These variations play a primary role in controlling the distribution of chlorinated solvents in subsurface environments, understanding how chlorinated solvent releases evolve with time, and resolving the effectiveness of remedial actions. The following sections describe five "type" settings and discuss how solvent releases in each type setting evolve over time.

The NRC describes five general hydrogeologic type settings (Figure 7.6). In the interest of consistency, portions of the following text (in quotation marks) are direct quotes from NRC (2005).

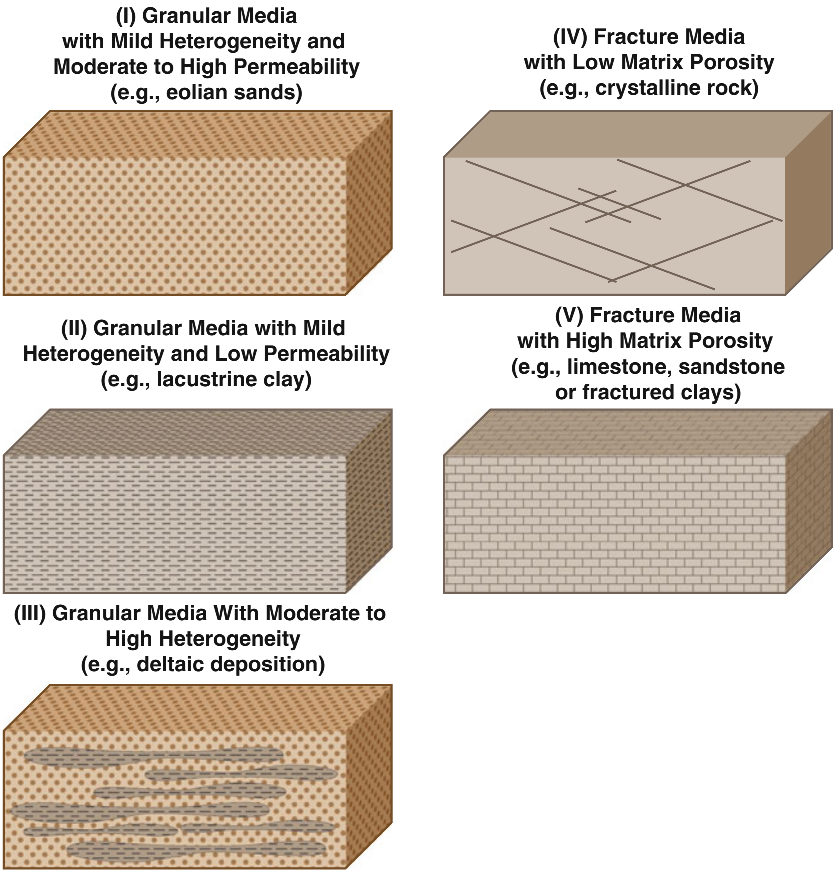


Figure 7.6. Geologic type settings (after NRC, 2005).

7.3.1 Type I—Granular Media with Mild Heterogeneity and Moderate to High Permeability

"Type I media include systems with porosities that are consistent with typical granular media (e.g., 5 to 40%), permeability values that are consistent with sand or gravel deposits ($>10^{-14}$ square meters [m^2] or hydraulic conductivity $>10^{-7}$ meters per second [m/s]), and mild heterogeneity (less than three orders of magnitude). As conceptualized, this material is about as uniform as it can be in nature and thus is relatively uncommon. Deposits of this nature are encountered in association with windblown sands and beach deposits. Examples include beach sands at the Canadian Forces Base Borden, Canada, and dune deposits at Great Sand Dunes National Park, Colorado (Figure 7.7)."

Due to mild heterogeneity and moderate to high permeability, low permeability zones are not dominant in Type I settings. As such, there is little contaminant storage in low permeability layers (sorbed or dissolved). The dominant storage/release mechanism will be associated with DNAPL dissolution and solid-phase sorption.

Figure 7.7. Example of Type I media: Great Sand Dunes National Park (Source: http://www.nps.gov/grsa).

Type I settings are rare. On the other hand, they have been widely used in laboratory tank experiments (e.g., Schwille, 1988). As such, they provide a primary basis for our conceptualization of chlorinated solvents in subsurface environments. A disadvantage of studies conducted in Type I settings is that they provide limited insight into the importance of heterogeneity.

7.3.2 Type II—Granular Media with Low Heterogeneity and Low Permeability

"Type II settings have porosities that are consistent with typical granular media (e.g., 5 to 40%), low spatial variation in permeability (less than three orders of magnitude), low permeability consistent with silt or clay deposits ($k < 10^{-14}$ m^2), and low hydraulic conductivity ($K < 10^{-7}$ m/s). An example is a clay deposit with no significant secondary permeability features (such as fractures, root holes, or animal burrows). These systems are uncommon (especially in the near-surface environment where releases typically occur), although some examples include TCE-contaminated clays at the Department of Energy's Savannah River Site in South Carolina. More typically, low-permeability materials contain significant secondary permeability features and thus fit better into the Type V setting description (see below)."

In Type II settings, the entire zone can be viewed as hydraulically stagnant. The primary contaminant transport process is diffusion. Settings of this nature are difficult to contaminate, and as such, they are not a common concern.

7.3.3 Type III—Granular Media with Moderate to High Heterogeneity

"Type III settings encompass systems with moderate to large variations in permeability (greater than three orders of magnitude) and porosities that are consistent with granular media (e.g., 5 to 40%). Given large spatial variations in permeability (at the scale of centimeters to meters), portions of the zone are comparatively transmissive while others contain mostly stagnant fluids. For the purpose of this analysis, the more transmissive zones in Type III media have permeabilities greater than 10^{-14} m^2 (K > 10^{-7} m/s). Near-surface deposits of this nature are common due to the abundance of alluvium with large spatial variations in permeability and are encountered in either rock or alluvium associated with deltaic, fluvial, alluvial fan, and glacial deposits. Examples include the Garber-Wellington Aquifer in central Oklahoma, the Chicot Aquifer in Texas and Louisiana, and varved sediments near Searchmont, Ontario".

In Type III settings, heterogeneity introduces low permeability zones to the system. These zones initially attenuate DNAPL constituents that partition into groundwater. After the DNAPL is depleted, the low permeability zones sustain groundwater plumes in transmissive zones. The depositional environments that create low permeability zones often favor higher concentrations of organic carbon as well. As a result, low permeability layers may have large sorptive capacities, increasing the potential for diffusion into these materials, and enhancing their ability to sustain dissolved chemical plumes after the original chemical source (DNAPL) has been depleted.

7.3.4 Type IV—Fractured Media with Low Matrix Porosity

"Fractured media with low matrix porosity are common in crystalline rock including granite, gneiss and schist. Examples include bedrock in the Piedmont and Blue Ridge Mountain region of the southeastern United States and plutonic cores of mountain ranges in the western United States (see Figure 7.8 for an example). The primary transmissive feature in Type IV settings is the secondary permeability caused by fractures, because little to no void space exists in the unfractured matrix. The permeability of the unfractured matrix is considered to be less than 10^{-17} m^2 (K < 10^{-10} m/s). However, the bulk permeability of the media is dependent on the frequency, aperture size, and degree of interconnection of the fractures, such that the anticipated range of bulk permeability values is 10^{-15}–10^{-11} m^2 (K = 10^{-8}–10^{-4} m/s). The porosity of both the matrix and the fractures is typically small, less than 1%. However, in regions where crystalline rock has been extensively weathered (e.g., at the top of bedrock), the bulk media can behave more like a porous medium than would be expected from a fractured rock type setting."

In Type IV settings, contaminant transport is primarily limited to fractures and there is little mass storage in low permeability zones due to low matrix porosity. The primary source is likely DNAPL. With time, DNAPL will be depleted from the more transmissive fractures and DNAPL in low flow areas (e.g., dead end fractures) will dominate. Due to the combined effects of low matrix attenuation and low fracture porosity, the contaminant migration velocity at a fractured media site can be very rapid and consequently these sites can have long plumes (Sudicky et al., 1993; Parker et al., 1996).

A primary challenge in this setting is the complexity of the fractures. The fracture frequencies and their capacity to transmit fluid can be highly variable. Furthermore, the degree to which sets of fractures are interconnected also can be highly variable.

7.3.5 Type V—Fractured Media with High Matrix Porosity

"This setting includes systems where fractures (secondary permeability) are the primary transmissive feature and there is large void space in the matrix. The permeability of the unfractured matrix is considered to be less than 10^{-17} m^2 (K < 10^{-10} m/s). The anticipated range of bulk permeability values is 10^{-16}–10^{-13} m^2 (K = 10^{-9}–10^{-6} m/s). The porosity of the fractures relative to the total unit volume is small (<1%). However, unlike Type IV, in Type V hydrogeologic settings, the porosity of the unfractured matrix is anticipated to fall in the range of 1 to 40%. Fractured media with high matrix porosity are commonly encountered in sedimentary rock (e.g., limestone, dolomite, shale and sandstone) and fractured clays. Examples include the Niagara Escarpment in the vicinity of the Great Lakes (see Figure 7.9) and fractured lake-deposited (lacustrine) clays in Sarnia, Ontario, Canada."

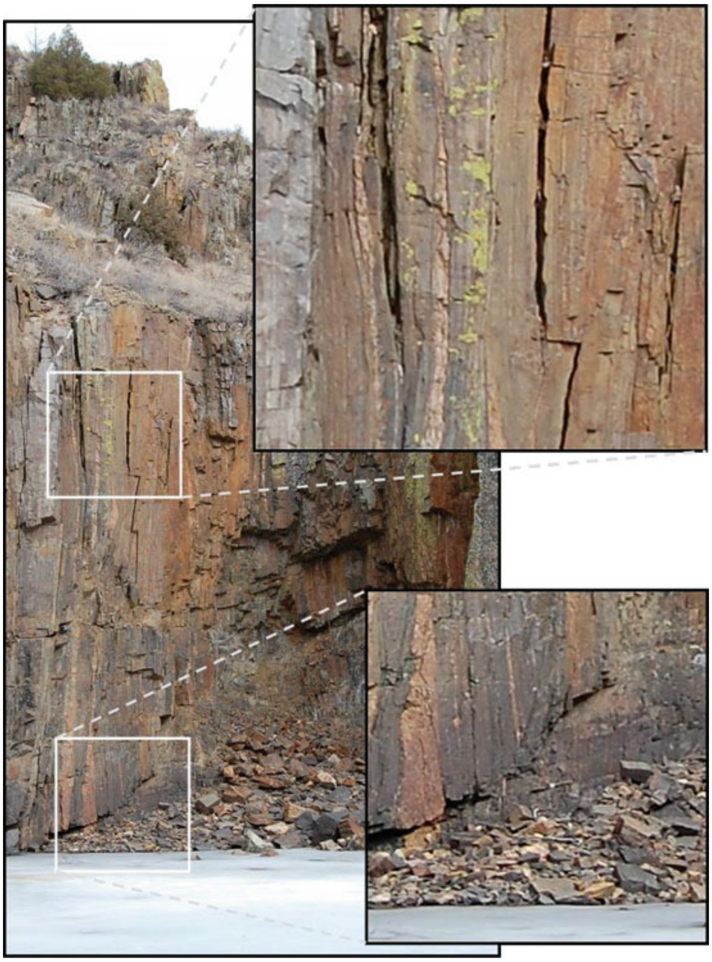


Figure 7.8 Fractured crystalline rock shown as an example of Type IV media (Cache La Poudre River, Colorado).

Type V settings introduce low permeability zones to the system. These zones initially attenuate DNAPL constituents that partition into groundwater by diffusion from the fracture zones into the rock matrix. After the DNAPL is depleted, back diffusion can sustain dissolved phase concentrations in groundwater flowing in the fractures. For systems where the matrix material has large sorptive capacities, the stagnant zones will act as a contaminant sink and accelerate the rates of natural DNAPL depletion. Due to limited mass storage in fractures, rapid depletion of DNAPL may occur via natural processes (e.g., Parker et al., 1994).

"An important variant of the Type V setting is karst, which is common in carbonates (e.g., limestone or dolomite). In this scenario, transmissive zones include sinkholes, caves and other solution openings that vary widely in aperture and have the potential to store and transport significant contaminant mass (see Figure 7.9). Permeability in karst terrains varies over tens of orders of magnitude from low permeabilities between fractures to open channel flow in channels and caves (Teutsch and Sauter, 1991; White, 1998; White, 2002). Karst is characterized by both rapid transport along sparse dissolution features and a high ratio of stagnant to transmissive zones. As such, it is one of the most challenging hydrogeologic settings to characterize and manage."

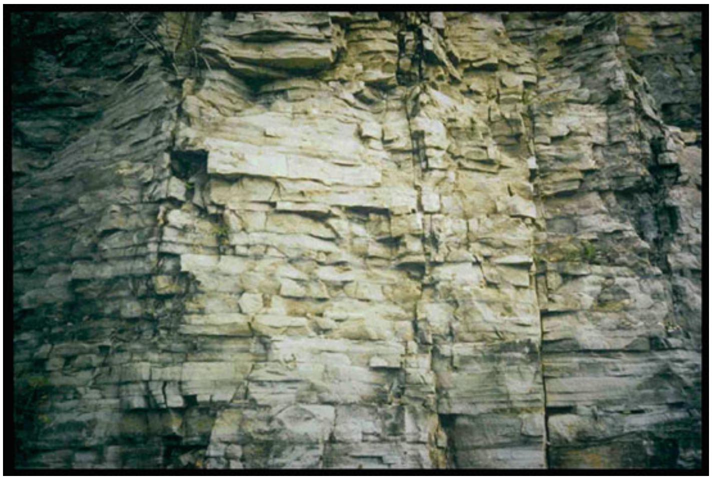


Figure 7.9. Bedding planes, joints, and vertical fractures in carbonate rock, Southern Ontario, Canada (courtesy of Dr. Beth Parker).

7.3.6 Source Zones Containing Multiple Type Settings

Source zones, especially those above a certain size, may encompass more than one hydrogeologic setting. This commonly occurs in the case of shallow alluvium over bedrock. For example, in the Piedmont region of the southeastern United States one can find fluvial deposits (Type III) and saprolite (Type V) overlying fractured crystalline rock (Type IV) (Figure 7.10). Selecting characterization tools and source management technologies is challenging under these conditions, because although contamination may exist throughout, the appropriate tools for one hydrogeologic setting may not work in the adjacent hydrogeologic setting.

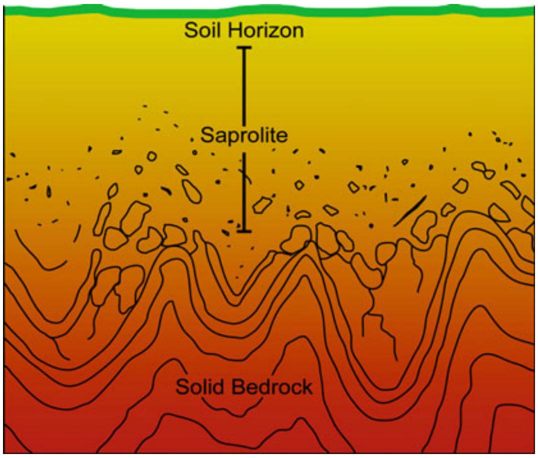
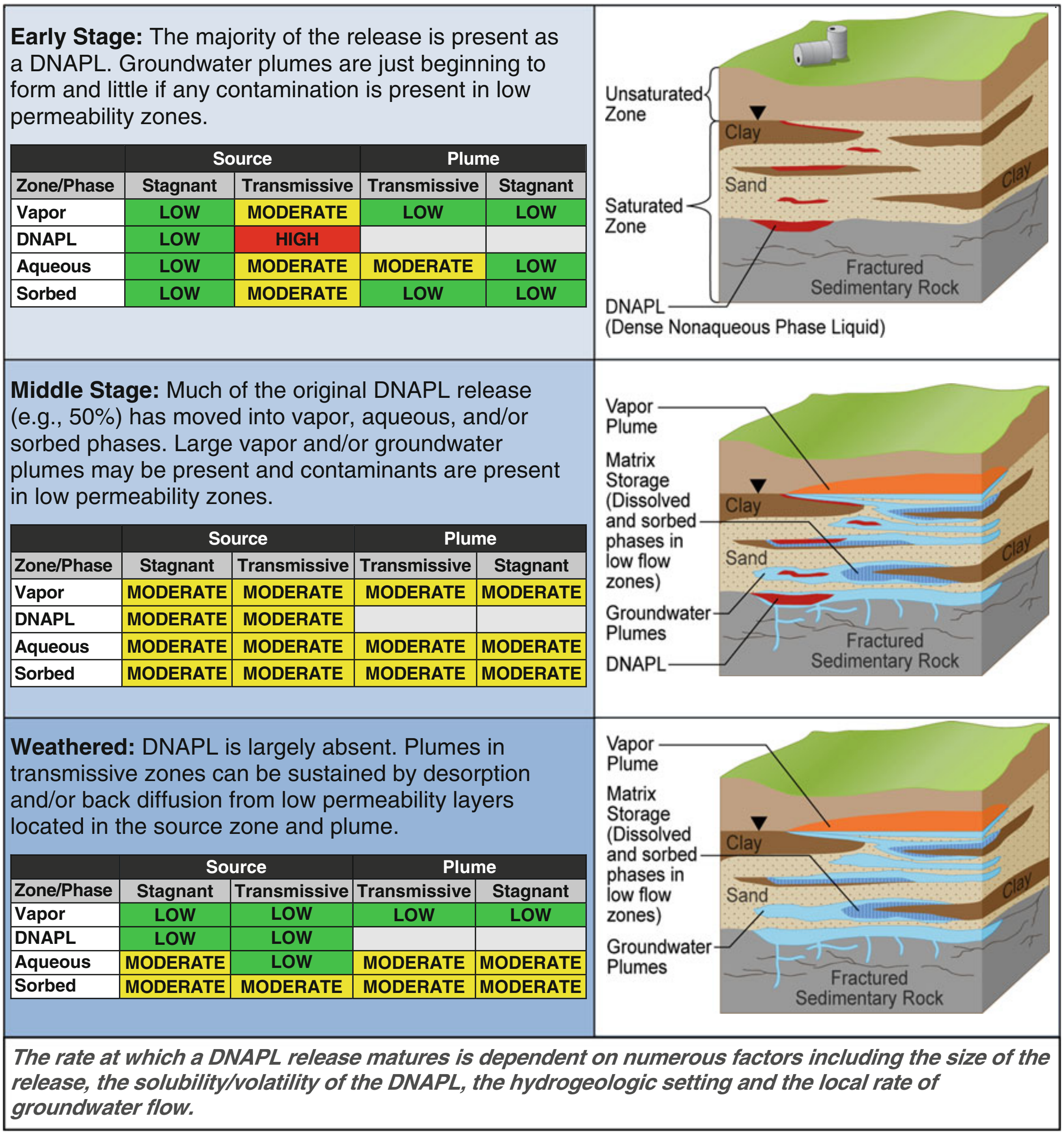


Figure 7.10. Mixed hydrologic settings of highly weathered saprolite overlying crystalline bedrock.

7.4 EVOLUTION OF CHLORINATED SOLVENT SITES

It is critical to recognize that chlorinated solvent releases evolve with time. This process is conceptualized in Figure 7.11 for a Type III setting (Granular Media with Moderate to High Heterogeneity) underlain by a Type V setting (Fractured Media with High Matrix Porosity). In the early stage the problem is about DNAPL. During the middle stage, the problem concerns all phases in transmissive and low permeability zones in the source and the plume. At the late or weathered stage, DNAPL is fully depleted and the problem is dominated by solvents stored in low permeability zones.



Early Stage: The majority of the release is present as a DNAPL. Groundwater plumes are just beginning to form and little if any contamination is present in low permeability zones.

	Source		Plume	
Zone/Phase	Stagnant	Transmissive	Transmissive	Stagnant
Vapor	LOW	MODERATE	LOW	LOW
DNAPL	LOW	HIGH		
Aqueous	LOW	MODERATE	MODERATE	LOW
Sorbed	LOW	MODERATE	LOW	LOW

Middle Stage: Much of the original DNAPL release (e.g., 50%) has moved into vapor, aqueous, and/or sorbed phases. Large vapor and/or groundwater plumes may be present and contaminants are present in low permeability zones.

	Source		Plume	
Zone/Phase	Stagnant	Transmissive	Transmissive	Stagnant
Vapor	MODERATE	MODERATE	MODERATE	MODERATE
DNAPL	MODERATE	MODERATE		
Aqueous	MODERATE	MODERATE	MODERATE	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE

Weathered: DNAPL is largely absent. Plumes in transmissive zones can be sustained by desorption and/or back diffusion from low permeability layers located in the source zone and plume.

	Source		Plume	
Zone/Phase	Stagnant	Transmissive	Transmissive	Stagnant
Vapor	LOW	LOW	LOW	LOW
DNAPL	LOW	LOW		
Aqueous	MODERATE	LOW	MODERATE	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE

The rate at which a DNAPL release matures is dependent on numerous factors including the size of the release, the solubility/volatility of the DNAPL, the hydrogeologic setting and the local rate of groundwater flow.

Figure 7.11. Evolution of a chlorinated solvent release in a Type III setting as a function of time. Red, yellow and green compartments indicate high, moderate and low importance of the compartments, respectively. Noted conditions are plausible but not necessarily the only possibility.

Building on the themes in Figure 7.11, Figure 7.12 illustrates the evolution of chlorinated solvent contamination in all five type settings. It is important to note that the described distributions are plausible for each type setting but are not necessarily the only possibilities. Other distributions in the noted setting at the described stages are possible. For example, vapor plumes may or may not be present depending on the release mechanism and/or the depth to groundwater. Figure 7.12 can be simplified from 15 to 6 scenarios by recognizing that:

- Type Settings I and II rarely exist in natural settings. Even the well-studied Canadian Forces Base Borden site, which is widely viewed as uniform sand, has three orders of magnitude spatial variation in hydraulic conductivity (Sudicky, 1986) and is underlain by lacustrine clay. Contaminated Type II sites are even less common, and where they do exist, they are very difficult to contaminate.
- Most of the sites we currently deal with are at least 20 years old, and often much older. As such, early stage sites are rare.

Given the limited frequency of Type I settings, Type II settings and early stage conditions, Figure 7.13 illustrates the 6 primary scenarios of concern for chlorinated solvent releases. At complex sites it may be difficult to develop a single 14 compartment model that describes conditions throughout an entire release. In these cases it may be useful to divide a release into separate blocks, as shown in Figure 7.14.

The 14 compartment model provides a holistic view of chlorinated solvents sites, which is essential in making informed decisions. Dealing with all of the compartments could be problematic, but it is better to be forewarned than surprised, which occurs frequently at chlorinated solvent sites. In the past, DNAPL sites have been characterized all too often using only water quality data from wells. Groundwater data is essential in resolving potential groundwater exposure pathways, but it typically provides little if any information about vapor, DNAPL or sorbed phases in transmissive zones and no information regarding contaminants in low permeability zones. When using the 14 compartment model as the primary site characterization tool, water quality data from wells may provide insight into only two of the 14 compartments, which may miss the majority of the problem.

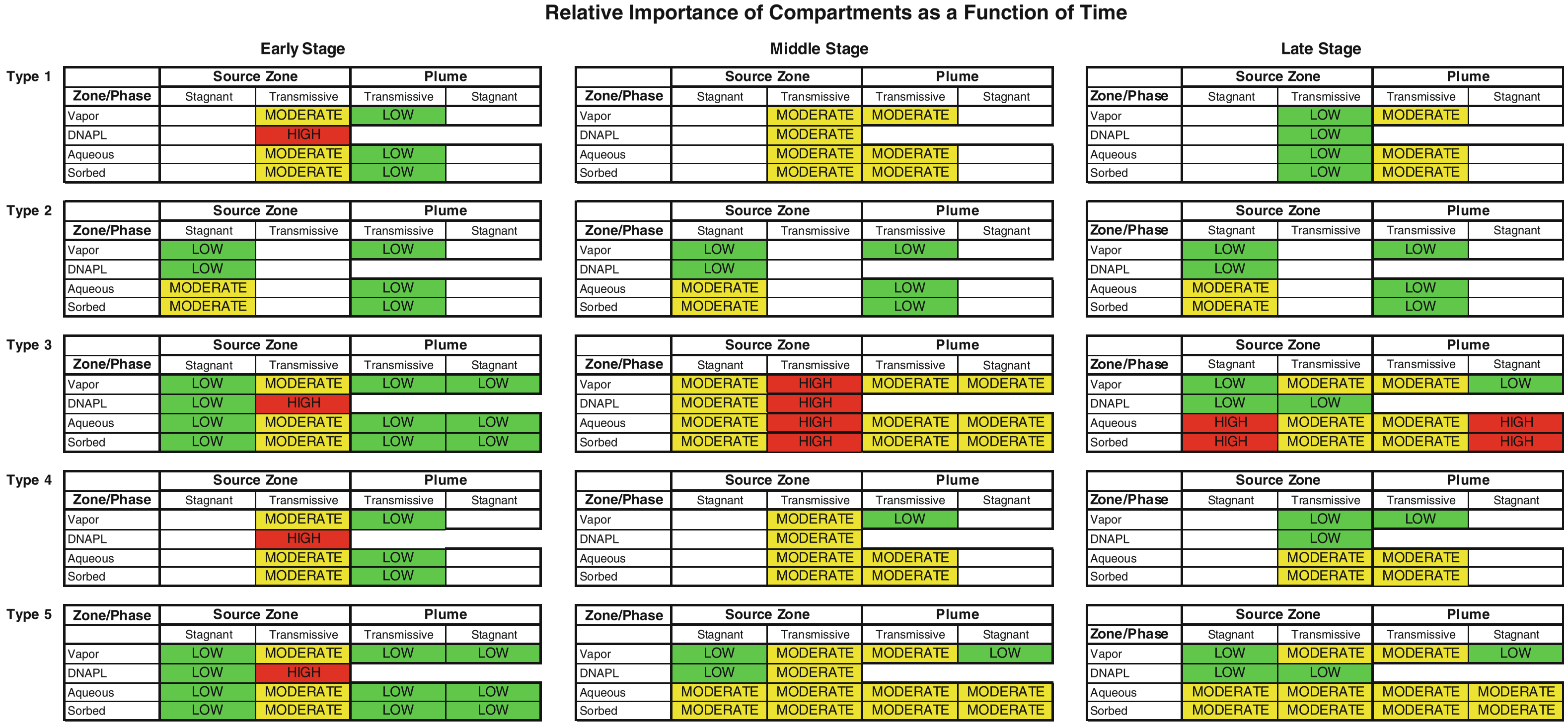
7.5 EFFECTS OF SOURCE DEPLETION OR CONTAINMENT ON PLUMES

It is fundamental to the process of making decisions regarding source zones to resolve (in advance) how the remedial actions will affect key metrics including (1) contaminant discharge from source zones and (2) contaminant concentrations in plumes.

For sources, the critical issue is often the magnitude and/or duration of contaminant discharge in units of mass per time (also called contaminant mass flux). For plumes, the critical issue often is the aqueous concentrations.

The contaminant discharge from sources can be reduced via containment and/or depletion. Common containment measures include physical barriers, hydraulic capture and/or permeable reactive barriers. Ideal containment measures provide an instantaneous and permanent boundary downgradient of the source, with zero or near zero contaminant flux crossing the boundary. Functionally, containment provides a step function change in contaminant loading to a downgradient plume.

Common source depletion approaches include excavation, soil vapor extraction, *in situ* chemical oxidation, *in situ* chemical reduction (biotic or abiotic) and conductive heating. These measures are likely to provide fractional depletion of the contaminant mass in the source zone and a corresponding factional reduction in the magnitude and/or duration of the contaminant loading to the plume. What remains in the source after depletion is likely to feed contaminants to the downgradient plume at a rate that decays with time (e.g., Newell and Adamson, 2005; Falta, 2008).



Relative Importance of Compartments as a Function of Time

Type 1

	Early Stage				Middle Stage				Late Stage			
	Source Zone		Plume		Source Zone		Plume		Source Zone		Plume	
Zone/Phase	Stagnant	Transmissive	Transmissive	Stagnant	Stagnant	Transmissive	Transmissive	Stagnant	Stagnant	Transmissive	Transmissive	Stagnant
Vapor		MODERATE	LOW			MODERATE	MODERATE			LOW	MODERATE	
DNAPL		HIGH				MODERATE				LOW		
Aqueous		MODERATE	LOW			MODERATE	MODERATE			LOW	MODERATE	
Sorbed		MODERATE	LOW			MODERATE	MODERATE			LOW	MODERATE	

Type 2

	Early Stage				Middle Stage				Late Stage			
	Source Zone		Plume		Source Zone		Plume		Source Zone		Plume	
Zone/Phase	Stagnant	Transmissive	Transmissive	Stagnant	Stagnant	Transmissive	Transmissive	Stagnant	Stagnant	Transmissive	Transmissive	Stagnant
Vapor	LOW		LOW		LOW		LOW		LOW		LOW	
DNAPL	LOW				LOW				LOW			
Aqueous	MODERATE		LOW		MODERATE		LOW		MODERATE		LOW	
Sorbed	MODERATE		LOW		MODERATE		LOW		MODERATE		LOW	

Type 3

	Early Stage				Middle Stage				Late Stage			
	Source Zone		Plume		Source Zone		Plume		Source Zone		Plume	
Zone/Phase	Stagnant	Transmissive	Transmissive	Stagnant	Stagnant	Transmissive	Transmissive	Stagnant	Stagnant	Transmissive	Transmissive	Stagnant
Vapor	LOW	MODERATE	LOW	LOW	MODERATE	HIGH	MODERATE	MODERATE	LOW	MODERATE	MODERATE	LOW
DNAPL	LOW	HIGH			MODERATE	HIGH			LOW	LOW		
Aqueous	LOW	MODERATE	LOW	LOW	MODERATE	HIGH	MODERATE	MODERATE	HIGH	MODERATE	MODERATE	HIGH
Sorbed	LOW	MODERATE	LOW	LOW	MODERATE	HIGH	MODERATE	MODERATE	HIGH	MODERATE	MODERATE	HIGH

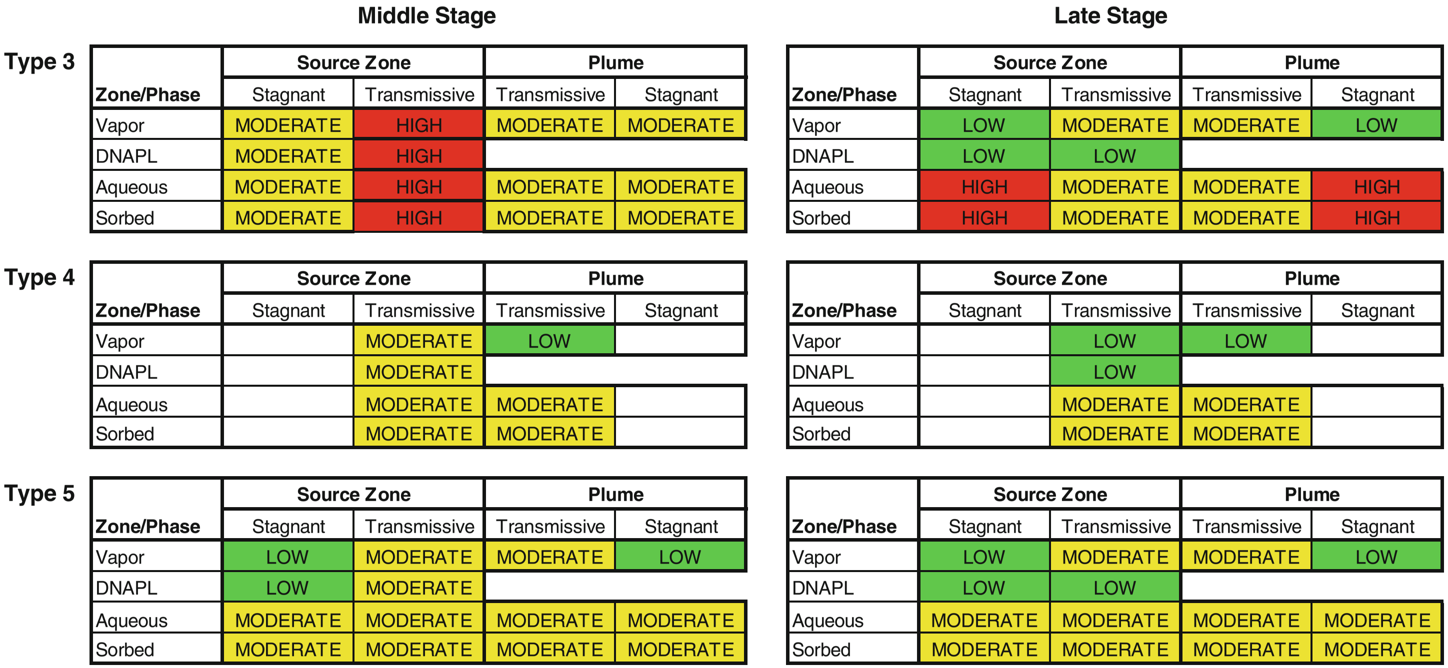
Type 4

	Early Stage				Middle Stage				Late Stage			
	Source Zone		Plume		Source Zone		Plume		Source Zone		Plume	
Zone/Phase	Stagnant	Transmissive	Transmissive	Stagnant	Stagnant	Transmissive	Transmissive	Stagnant	Stagnant	Transmissive	Transmissive	Stagnant
Vapor		MODERATE	LOW			MODERATE	LOW			LOW	LOW	
DNAPL		HIGH				MODERATE				LOW		
Aqueous		MODERATE	LOW			MODERATE	MODERATE			MODERATE	MODERATE	
Sorbed		MODERATE	LOW			MODERATE	MODERATE			MODERATE	MODERATE	

Type 5

	Early Stage				Middle Stage				Late Stage			
	Source Zone		Plume		Source Zone		Plume		Source Zone		Plume	
Zone/Phase	Stagnant	Transmissive	Transmissive	Stagnant	Stagnant	Transmissive	Transmissive	Stagnant	Stagnant	Transmissive	Transmissive	Stagnant
Vapor	LOW	MODERATE	LOW	LOW	LOW	MODERATE	MODERATE	LOW	LOW	MODERATE	MODERATE	LOW
DNAPL	LOW	HIGH			LOW	MODERATE			LOW	LOW		
Aqueous	LOW	MODERATE	LOW	LOW	MODERATE	MODERATE	MODERATE	MODERATE	MODERATE	MODERATE	MODERATE	MODERATE
Sorbed	LOW	MODERATE	LOW	LOW	MODERATE	MODERATE	MODERATE	MODERATE	MODERATE	MODERATE	MODERATE	MODERATE

Figure 7.12. Illustration of plausible distributions of chlorinated solvent as a function of type setting and the stage of release. White boxes are considered to be absent in the type setting. Red, yellow and green compartments indicate high, moderate, and low importance of the compartments, respectively. Note conditions presented are plausible in the noted situations but not necessarily the only plausible scenario.



Middle Stage

Type 3

Zone/Phase	Source Zone Stagnant	Source Zone Transmissive	Plume Transmissive	Plume Stagnant
Vapor	MODERATE	HIGH	MODERATE	MODERATE
DNAPL	MODERATE	HIGH		
Aqueous	MODERATE	HIGH	MODERATE	MODERATE
Sorbed	MODERATE	HIGH	MODERATE	MODERATE

Type 4

Zone/Phase	Source Zone Stagnant	Source Zone Transmissive	Plume Transmissive	Plume Stagnant
Vapor		MODERATE	LOW	
DNAPL		MODERATE		
Aqueous		MODERATE	MODERATE	
Sorbed		MODERATE	MODERATE	

Type 5

Zone/Phase	Source Zone Stagnant	Source Zone Transmissive	Plume Transmissive	Plume Stagnant
Vapor	LOW	MODERATE	MODERATE	LOW
DNAPL	LOW	MODERATE		
Aqueous	MODERATE	MODERATE	MODERATE	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE

Late Stage

Type 3

Zone/Phase	Source Zone Stagnant	Source Zone Transmissive	Plume Transmissive	Plume Stagnant
Vapor	LOW	MODERATE	MODERATE	LOW
DNAPL	LOW	LOW		
Aqueous	HIGH	MODERATE	MODERATE	HIGH
Sorbed	HIGH	MODERATE	MODERATE	HIGH

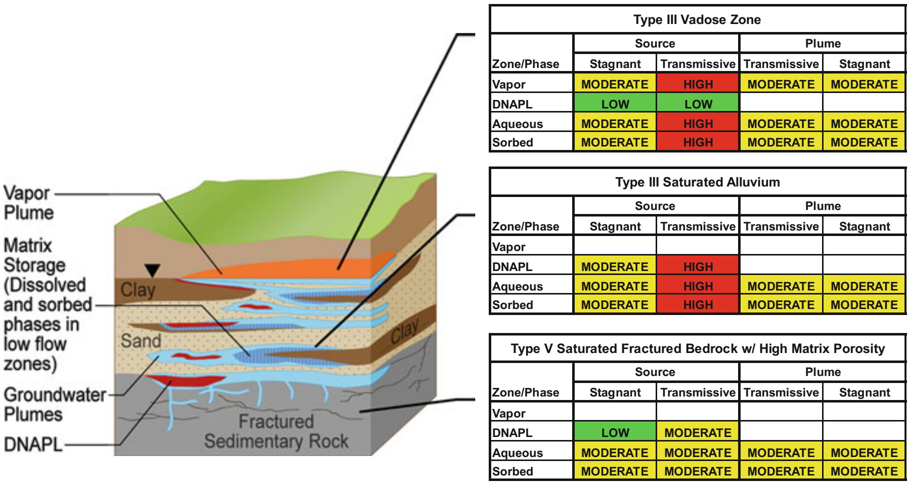
Type 4

Zone/Phase	Source Zone Stagnant	Source Zone Transmissive	Plume Transmissive	Plume Stagnant
Vapor		LOW	LOW	
DNAPL		LOW		
Aqueous		MODERATE	MODERATE	
Sorbed		MODERATE	MODERATE	

Type 5

Zone/Phase	Source Zone Stagnant	Source Zone Transmissive	Plume Transmissive	Plume Stagnant
Vapor	LOW	MODERATE	MODERATE	LOW
DNAPL	LOW	LOW		
Aqueous	MODERATE	MODERATE	MODERATE	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE

Figure 7.13. Six primary scenarios of concern for chlorinated solvent releases.



Type III Vadose Zone

	Source		Plume	
Zone/Phase	Stagnant	Transmissive	Transmissive	Stagnant
Vapor	MODERATE	HIGH	MODERATE	MODERATE
DNAPL	LOW	LOW		
Aqueous	MODERATE	HIGH	MODERATE	MODERATE
Sorbed	MODERATE	HIGH	MODERATE	MODERATE

Type III Saturated Alluvium

	Source		Plume	
Zone/Phase	Stagnant	Transmissive	Transmissive	Stagnant
Vapor				
DNAPL	MODERATE	HIGH		
Aqueous	MODERATE	HIGH	MODERATE	MODERATE
Sorbed	MODERATE	HIGH	MODERATE	MODERATE

Type V Saturated Fractured Bedrock w/ High Matrix Porosity

	Source		Plume	
Zone/Phase	Stagnant	Transmissive	Transmissive	Stagnant
Vapor				
DNAPL	LOW	MODERATE		
Aqueous	MODERATE	MODERATE	MODERATE	MODERATE
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE

Figure 7.14. Use of multiple 14 compartment scenarios to describe a complex site.

Note that the ability to make *a priori* predictions of how source depletion affects contaminant discharge at a field scale is limited. Challenges include the complexity of field scale sources, the rigor with which subsurface conditions can be resolved (before and after treatment), and the long time periods that are typically required to resolve field-scale responses to source depletion measures.

The second issue, how the contaminant concentrations in the dissolved plumes will respond to upgradient reductions in contaminant loading, can be equally challenging. Reduced loading to plumes can promote desorption of contaminants stored in transmissive zones and/or the back diffusion of contaminants stored in low permeability zones within the plumes. Both processes can sustain plumes for extended periods (Chapman and Parker, 2005; AFCEE, 2007; Sale et al., 2008).

Given uncertainties in our current knowledge of both sources and plume function, opinions about how groundwater plumes respond to interception and/or source depletion are diverse. Nevertheless, sound decisions for chlorinated solvent sites hinge on understanding how source control measures will affect plumes. With this in mind, the following sections review the more prominent perspectives regarding the effect of source control measures on the contaminant concentrations in plumes.

7.5.1 The Big Picture

Expert panel reports by the U.S. Environmental Protection Agency (USEPA, 2003) and the National Research Council (NRC, 2005) have captured the current consensus on two key issues. First, given effective execution, current source technologies are capable of depleting a large portion of the chlorinated solvents present in the subsurface, significantly reducing the total loading of chlorinated solvents to plumes. Second, in most instances, sufficient amounts of chlorinated solvents will remain after treatment (in source zones and/or plumes) to exceed typical regulatory criteria (maximum contaminant levels [MCLs]) in groundwater for extended periods.

Managers who must make decisions regarding source treatment are therefore confronted with the following:

- On the one hand, source treatment will reduce the ultimate total mass of contaminants in downgradient plumes, and will likely result in reduced plume extent and/or longevity. Although there probably still will be contaminants remaining in the source and plume even after source treatment, the benefits may be significant from an economic or regulatory point of view.

- On the other hand, no matter what type of treatment is done, there may be an ongoing expectation to address what remains through further investments in source depletion and/or plume management. These ongoing site care requirements can lead to questions about the value of any source treatment, especially since the cost of source treatment can be substantial.

Reconciling these perspectives is critical to moving forward. Pragmatically, this requires striking a balance between what can be done and living with the inevitable imperfections of what will remain. The significant uncertainties regarding the impacts of source management remain, and complicate the efforts to strike the right balance. However, research continues to address these uncertainties. The following section provides a summary of recent research on the effects of source management on the source function, and on the plume response to source treatment.

7.5.2 Source Function

Sale and McWhorter (2001) evaluated how DNAPL depletion governs downgradient water quality by modeling heterogeneous distribution of DNAPL bodies in uniform porous media. A technique involving superposition of multiple analytical source terms allowed for analysis of DNAPL dissolution rates throughout complex sets of sparse DNAPL bodies in a uniform porous medium (Type I Setting). A primary observation from this modeling effort was that most contaminant loading to groundwater plumes occurs at the upgradient edges of the DNAPL bodies. As long as the upgradient edges of DNAPL bodies remain, significant loading to downgradient plumes will continue.

From this observation, Sale and McWhorter (2001) concluded that “removal of the vast majority of DNAPL will likely be necessary to achieve “significant near-term improvements in groundwater quality.” According to McWhorter and Sale (2003), the meaning of “significant near-term improvements in water quality” was achievement of the multiple order-of-magnitude reductions in aqueous concentrations that are typically required to attain risk-based MCLs. Similar limited reductions in contaminant loading with DNAPL depletion have been reported by Suchomel et al. (2007). Sale and McWhorter (2001) also recognized other potential benefits of partial depletion of DNAPL, including reduced source longevity, reduced site care requirements and enhanced effectiveness of natural attenuation processes.

However, Rao and Jawitz (2003) contend that “in heterogeneous formations, significant contaminant flux reductions can be realized.” In support of this position, they presented a one-dimensional analytical solution that addressed a system with uniform DNAPL in a nonuniform flow field (Type III setting). The modeling results indicated that DNAPL depletion on the order of 70 to 90% could yield reductions in loading to downgradient plumes by 70 to 98%.

McWhorter and Sale (2003) believe there is little difference between the conclusions of the two papers, if the goal is to attain MCLs throughout the source zone. In their analysis, Rao and Jawitz (2003) shifted the location of the envisioned water quality benefits from the source zone to the downgradient plumes. Specifically, they envision that upgradient reductions in contaminant loading will produce downgradient water quality improvements that result in stable or shrinking plumes. In practical terms, source treatment may be beneficial if it removes enough source material to allow a natural attenuation remedy to be protective, and/or attainment of MCLs within a reasonable time frame. That decision will largely be based on an estimate of the source strength after treatment, combined with estimates of the natural attenuation capacity of the downgradient aquifer.

Estimates of the achievable reductions in source strength are available from the laboratory studies of Suchomel et al. (2007). These researchers created sparse DNAPL zones in tanks filled with uniform sand (Type I Setting) and compared the effects of partial removal of the DNAPL in systems either dominated by DNAPL as a continuous phase in pools, or with DNAPL occurring primarily as isolated ganglia. They concluded that “in the ganglia dominated system greater than 70% mass (DNAPL) removal was required before measurable reductions in plume concentration and mass discharge were observed.” Furthermore, they observed that “for pool dominated source zones substantial reductions (>50%) in mass discharge were realized after only 50% mass removal.” Hence, it appears reasonable to conclude that fractional depletion of DNAPL will fall well short of attaining MCLs, but will yield reductions in downgradient loading to plumes.

Field measurements of the impacts of source treatment are also available (McGuire et al., 2006). Researchers evaluated water quality data from 59 chlorinated solvent sites before and after source depletion. Four source treatment technologies were included in the survey: chemical oxidation, enhanced bioremediation, thermal treatment, and surfactant/cosolvent flushing. Performance was evaluated by examining temporal groundwater concentration data before and after source remediation was performed. The results (Figure 7.15) indicated that “all four technologies have median concentration reductions of 88% or greater for the parent chlorinated volatile organic compound (CVOC). Approximately 75% of the source depletion projects were able to achieve a 70% reduction in parent compound concentrations. Based on current data, none of the 59 source depletion projects was able to meet maximum contaminant levels throughout the treatment zone for all CVOCs.” Of course, these results are dominated by the impact on only one of the 14 compartments (the aqueous phase within the transmissive fraction of the source zone), because these are by far the most common measurements available. The masses remaining in other compartments may differ markedly between treatment approaches, but the failure to meet MCLs in source zone groundwater implies a continued need to manage the source, and continued releases of contaminants to the plume.

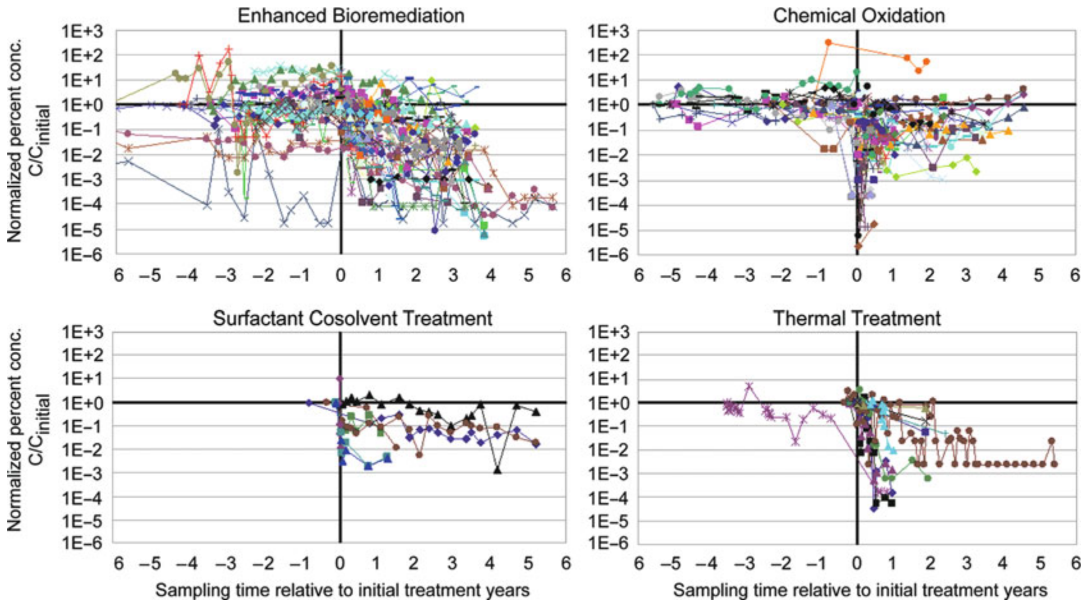


Figure 7.15. Temporal concentration records for wells at source depletion sites (from McGuire et al., 2006).

7.5.3 Plume Responses

Research has consistently shown that partial source DNAPL removal is unlikely to achieve MCLs (in the near term) throughout source zones (Sale and McWhorter, 2001; Rao and Jawitz, 2003; USEPA, 2003; NRC, 2005; McGuire et al., 2006; Suchomel et al., 2007). On the other hand, the research does suggest that attainable reductions in downgradient loading may yield beneficial improvements in downgradient water quality. The following explores the current state of knowledge regarding plume responses (plume function) to upgradient reductions in contaminant loading.

Wiedemeier et al. (1998) pointed out that select chlorinated solvents are attenuated via biotic processes. Typically this occurs at sites where reducing conditions exist in plumes due to the co-release of a fuel hydrocarbon. More recently it has been demonstrated that naturally occurring minerals can drive abiotic degradation of chlorinated solvents in plumes (Danielsen and Hayes, 2004). Active attenuation of dissolved phase chlorinated solvents, even at slow rates, can result in plumes that are naturally either stable or shrinking. Further, it can provide effective control of any residual contaminants stored in lower-permeability materials within the plume.

Given stable or shrinking plumes, two perspectives arise. First, in the absence of an expanding plume and with no current exposures, actual risks may be negligible and there may be no need for further action. Secondly, the rate at which a plume is shrinking can be enhanced and/or its overall longevity can be reduced through reduction of the upgradient source. Chapelle et al. (2004) supported the latter point through review of data from a site in Kings Bay, Georgia. Results indicated that "source-area removal actions, particularly when applied to groundwater systems with a significant natural attenuation capacity, can be effective in decreasing the areal extent and contaminant concentrations of chlorinated ethene plumes."

However, some chlorinated solvents plumes show little if any biotic attenuation, and therefore may be unacceptably large or still expanding. Large and expanding plumes are often problematic due to ongoing resource degradation and the potential for future impacts to receptors. Another potential problem in plumes with low degradation rates is that dissolved phase contaminants can accumulate in low permeability zones via diffusion. As discussed earlier, upgradient reductions in contaminant loading that reduce the dissolved phase concentrations in transmissive zones can also drive release of contaminants stored in plumes via desorption and/or back diffusion out of low permeability layers (Chapman and Parker, 2005).

Back diffusion from low permeability layers in granular porous media can sustain plumes for decades after complete removal of sources (Sale et al., 2008). Field data from F.E. Warren Air Force Base (AFB), Wyoming (Figure 7.16) demonstrate the potential for sustaining plumes through back diffusion. An iron permeable reactive barrier was installed in 2000, decreasing the TCE concentrations at the barrier by multiple orders of magnitude, to values of less than 5 micrograms per liter (μg/L). After five years, TCE concentrations 40 and 60 feet (12 and 18 m) downgradient of the barrier dropped by only one order of magnitude. The sustained concentrations of TCE downgradient of the barrier are attributed to desorption and back diffusion from low flow zones.

The prior discussion demonstrates the importance of considering both the plume and source characteristics when deciding how to manage sources. The mass stored in the plume and the rate of attenuation of that mass can largely determine the plume response to source depletion. If a relatively large fraction of the mass is in the plume, and if its attenuation is slow, even complete source removal may have relatively little effect on restoration time frames. On the other hand, if the attenuation rate is sufficient to handle any residual mass remaining in the source and plume after treatment, source depletion can greatly reduce the plume longevity and the costs for continued site management after active remediation. Thus, adequate characterization of the source, and the plume, is needed to predict the response of a given plume to a given level of source reduction.

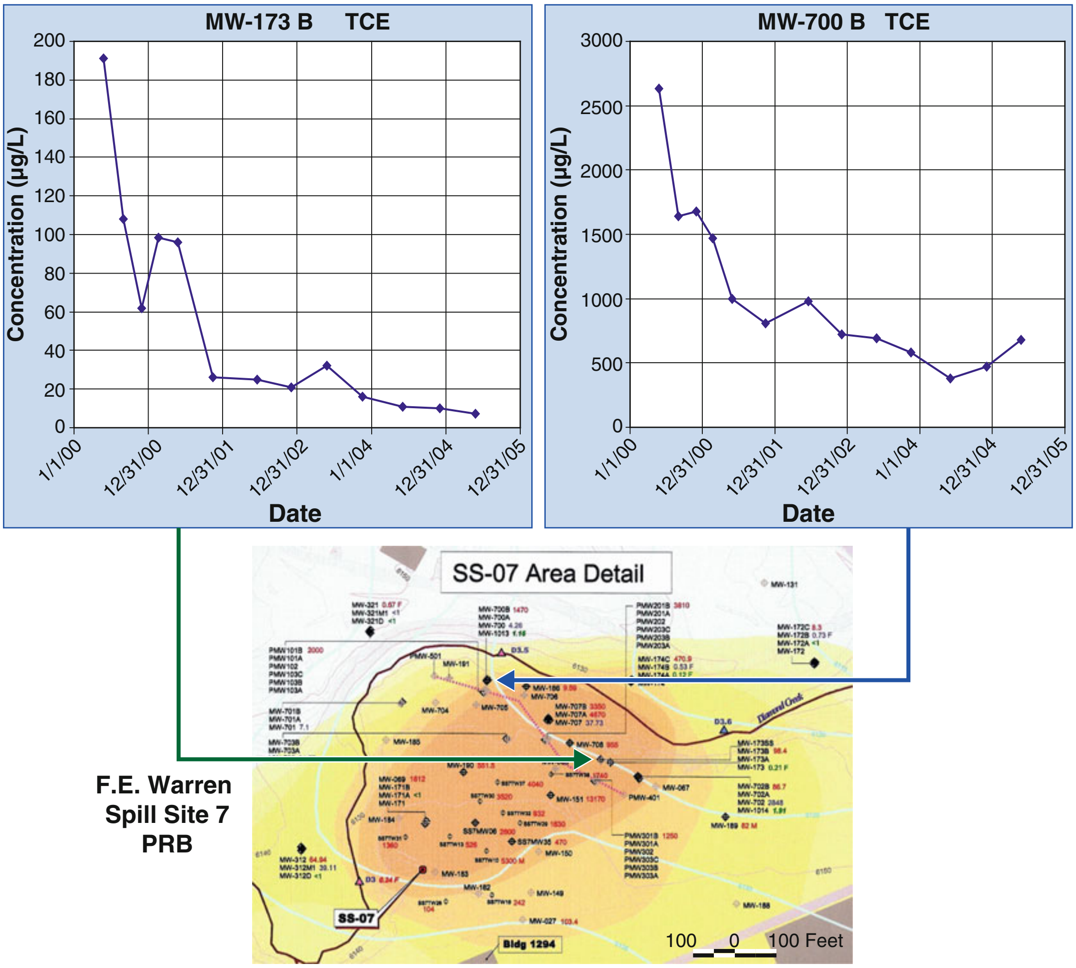


Figure 7.16. Field data from F.E. Warren AFB (courtesy of F.E. Warren AFB and AFCEE).

Currently, a number of researchers are developing models that simultaneously address source strength and plume response as a function of time (e.g., Newell and Adamson, 2005; Chapman and Parker, 2005; Falta, 2008; Sale et al., 2008). Each of these efforts has its merits and limitations. In all cases, the primary challenges include capturing the physics of the problem and acquiring the necessary inputs to run the models. The remainder of this section summarizes these different model development efforts.

Falta (2008) presents an analytical solute transport model called REMChlor that includes the effects of both source and plume remediation. A limitation of the model is that it does not address contaminants stored in low permeability zones in the plume (Falta, 2005). A REMChlor simulation result is shown in Figure 7.17 for a hypothetical PCE release that occurred in 1975. By 2005 a large plume of PCE and its daughter products (TCE, DCE and VC) existed down-gradient of the source. Only the TCE component is shown in Figure 7.17. This model scenario assumes that 90% of the DNAPL source mass was removed in 2005, leading to a 90% reduction in the PCE mass discharge to the plume. Plume remediation was assumed to start in 2005, and extend for 20 years. The plume remediation assumes that the PCE and TCE decay rates can be enhanced over the first 400 m of the plume by the addition of an electron donor. An aerobic treatment zone is assumed to extend from 400 m to 700 m, but the PCE and TCE are assumed to not degrade in this environment (where the DCE and VC are rapidly degrading).

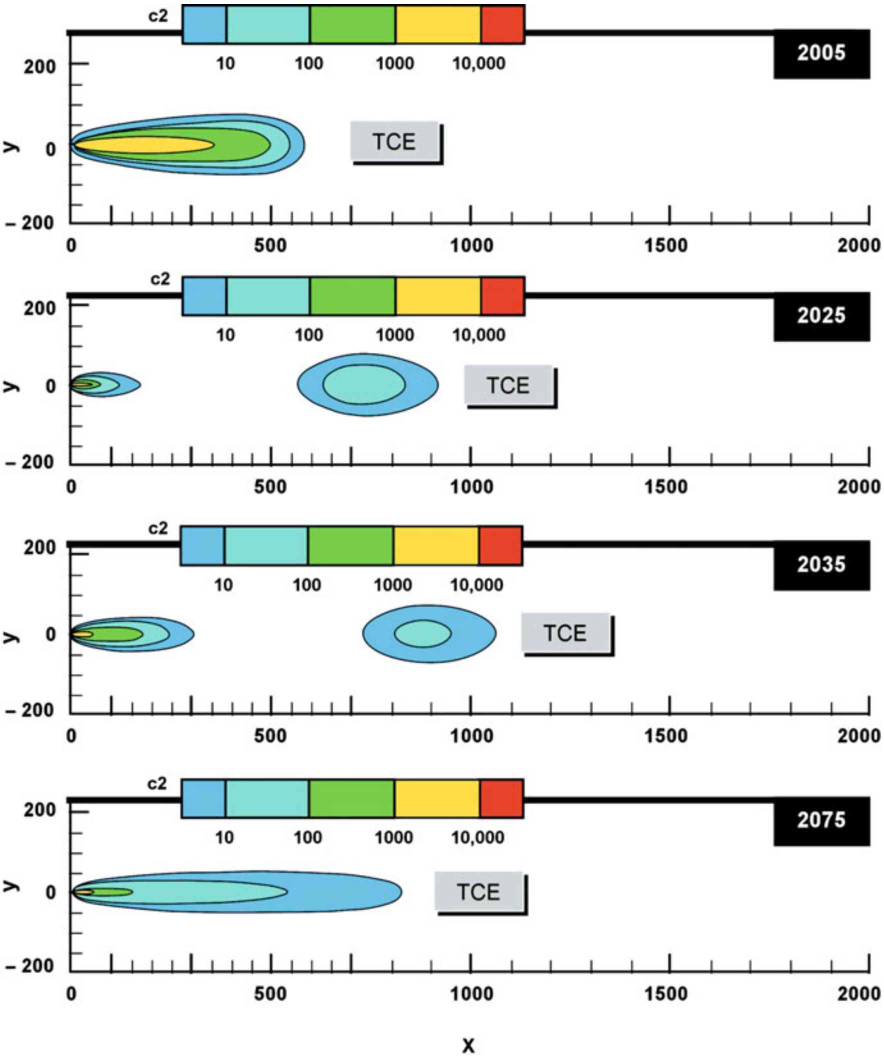


Figure 7.17. Simulated plume concentration (μg/L) after 90% reduction in source mass + remediation of first 400 meters of plume, both occurring in 2005 (Falta, 2008). x and y in meters.

As shown in Figure 7.17, the leading edge of the TCE plume continues to advance for some time, despite the source and plume treatments. This continued expansion occurs because this contaminant mass is beyond the treatment zones at the start of remediation (referred to as "the horse has already left the barn" scenario by some). Note also that a small plume regenerates from the remaining source material once the plume treatment is stopped. Although it is weaker than the original plume, in 70 years, the regenerated plume is almost the same length as the original 2005 plume.

Newell and Adamson (2005) developed mass balance-based, planning level models to provide estimates of the reduction in remediation timeframe (RTF) for a given amount of source depletion (source mass or flux reduction following intensive treatment). As a shared framework for assessment, the models use the time required to reduce the contaminant discharge from the source zone to below a mass flux goal as a metric. Impacts of source treatment on the RTF are assessed using a number of different types of source zone decay patterns, such as a *First-order Decay* model to represent a middle-of-the-road approach with a linear relationship between mass remaining and flux, or a *Compound* model to address situations where limited changes in the mass flux are achieved until a large percentage of the mass has been removed. These models are of interest in terms of providing:

- Absolute RTF estimates in years as a function of current mass discharge rate, current source mass, the remediation goal and the reduction in discharge rate and source mass immediately after treatment, and
- Relative RTF estimates as a fraction of the remediation timeframe for monitored natural attenuation (MNA) in the decision to proceed with source depletion or to use a long-term containment or MNA approach.

As an example of the first-order source decay scenario, a chlorinated solvent source in a homogenous aquifer (Type I) might require a remediation timeframe of 184 years of mass discharge before concentration goals are achieved, due to slow source decay and the resulting decrease in flux as the source ages. If an initial source treatment (e.g., *in situ* chemical oxidation or enhanced bioremediation) successfully removed 70% of the source mass and reduced the mass flux by 70%, then the remediation timeframe would decrease to 136 years (a decrease of 26%). This simple method demonstrates that while source treatment can reduce the time to cleanup, the removal of significant amounts of source mass does not necessarily result in an equivalent reduction in the remediation timeframe.

Note that this approach is focused on the source function and not the plume function, such that concentration goals must be attained at the downgradient edge of the source zone. However, the inclusion of a source decay term in effect incorporates the concept of storage and release of mass in low permeability layers within the source zone.

Chapman and Parker (2005) studied an industrial site where a TCE source was isolated from the adjacent alluvial aquifer for 42 years after the release by a sheet wall enclosure. Field data and modeling indicate that back diffusion out of an underlying aquitard and desorption were sustaining the aqueous concentrations of TCE in the transmissive alluvium. Specifically, monitoring results from two wells located 330 m downgradient of the source in transmissive alluvium indicated slightly more than one order of magnitude improvements in downgradient water quality eight years after source containment. Field data demonstrated that back diffusion was sustaining contaminant concentrations in the transmissive portion of the plume.

Extrapolation of the observed water quality data suggests that the current levels of TCE in the plume downgradient of the source enclosure will persist at levels an order of magnitude above the MCL for more than a century. Detailed mass estimates indicated that approximately 3,000 kg of TCE was dissolved in the underlying aquitard in the first 280 m downgradient of the sheetpile enclosure, compared to between 5,000 and 20,000 kg of DNAPL trapped within the enclosure. In other words, a new "source zone" containing no DNAPL was created by matrix diffusion downgradient of the DNAPL source. This new source zone represented between 15 and 60% of the remaining DNAPL mass at the site.

Complementary modeling was performed using a numerical model developed by Therrin and Sudicky (1996), which is now referred to as HydroGeoSphere. Finite element numerical methods were employed to model a two-dimensional cross-section with a domain of 300 m long and 15 m high. The domain was discretized using a total of 120,000 finite element hexahedral blocks and 241,602 nodes. Tighter vertical node spacing was used near the contact between the transmissive alluvium and underlying aquitard. Predicted water quality trends were similar to those observed in the field data. Extrapolation of results out to 100 years after containment indicated an approximate two order of magnitude improvement in downgradient water quality. A promising attribute of the modeling is that it suggests that (given sufficient domain discretization and model inputs) numerical models can be used to simulate contaminant storage and release processes in plumes.

More recently, Sale et al. (2008) presented an exact two-dimensional analytical solution for the scenario of a transmissive layer overlying a stagnant no-flow layer. A DNAPL-like source located at the contact between the upper transmissive and lower stagnant layer was considered. The source discharged contaminant at a constant rate for five years. Downgradient water quality in analog wells was considered in wells located 1, 10, and 100 m downgradient of the source while the source was active and for an additional 15 years afterward. Typical flow conditions were considered and sensitivity to retardation factors and rates of contaminant degradation were evaluated.

Results are presented in Figure 7.18. In general, rates of cleanup of downgradient water quality improved after source removal, showing shorter half lives and lower retardation. In the best case (lower left-hand corner) downgradient water quality was below clean up levels in the time it takes the water to travel from the source to the wells. This outcome reflects limited accumulation of contaminants in the plume due to active contaminant attenuation via degradation. For the remaining scenarios, the greatest improvements in downgradient water quality occurred close to the source, with diminishing improvements as one progresses downgradient. These outcomes reflect the accumulating effect of back diffusion and desorption at larger downgradient distances. Furthermore, for the remaining scenarios the anticipated downgradient improvements in water quality, at 100 m given complete source removal, was in the range of one to two orders of magnitude 15 years after removing the source.

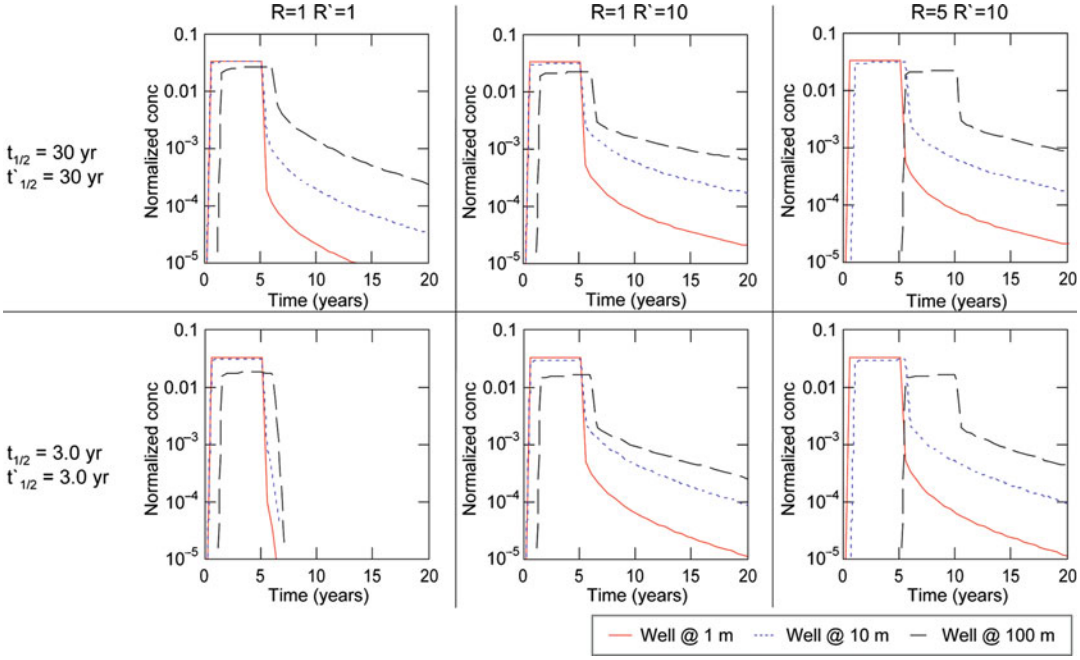


Figure 7.18. Sensitivity concentrations in wells to contaminant half life, retardation coefficient, and downgradient distance from the source. Seepage rate is 0.3 m/day, from the source is on from 0 to 5 years, and the wells have 3-m screens that are completed immediately above the sand-silt contact. R and R′ are the retardation coefficients and k and k′ are the half lives for the transmissive and stagnant layers, respectively. From Sale et al., 2008.

It should be noted that previous compilations of concentration and plume length data for petroleum hydrocarbon releases have demonstrated a similar long-term persistence of plumes due to factors such as slow back diffusion and desorption (Newell and Connor, 1999). This behavior occurs as plumes age and some transition into an "exhausted" state, such that the rate of change in concentration and plume size slows significantly even after depletion of NAPL. These studies provide clear evidence that this type of plume response is likely a widespread occurrence not restricted to chlorinated solvents.

7.6 SUMMARY

Plumes are inextricably linked to their sources. Given this linkage it follows that decisions regarding management of plumes are likely to involve decisions regarding management of sources. A common perception has been that removing the source will result in removing the plume (after several years of flushing). Unfortunately experience has made clear that the relationship between sources and plumes is complicated and that plumes can persist long after their sources are depleted. The degree to which plumes can persist is governed by site specific attributes (e.g., geology, hydrology, contaminants properties, bio-geochemistry, release volume. . .) and the fact that fundamental aspects of releases evolve with time.

As a starting point, this chapter advanced the concept that there are 14 compartments (8 in source zones and 6 in plumes) that can store and release contaminants. This concept builds on recognition that there are four phases of concern (vapor, DNAPL, aqueous and sorbed) that can occur in transmissive zones with active groundwater flow and low permeability zones where diffusion is a primary transport process. A key value of the 14 compartment model is that it advances a holistic view of the problem of chlorinated solvent releases. Historically, success with managing plumes (and source zones) often has been constrained by failing to take into account all of the consequential compartments.

Clearly, chlorinated solvent releases evolve with time. At the early state, the primary issue is presence of DNAPL in source zones. With time, DNAPL is depleted through dissolution and/or volatilization. However, plumes form and contaminants may be slowly driven into low permeability zones via diffusion and slow advection. At a middle stage, most if not all of the compartments are impacted. Finally, at this stage, little if any DNAPL remains and the critical compartments are aqueous-sorbed phases in low permeability zones. A common feature at late stage sites is a large dilute groundwater plume with chlorinated solvents concentrations in the range of 10s to 100s of µg/L. Furthermore, at late stage, sites little remains to differentiate source zones and plumes.

Given that most releases are 10, 20, 30 or even 50 years old, many sites have progressed to middle or late stages where contaminants are present in low permeability zones, both in the source and in the plume. The key concerns with contaminants in low permeability zones are their potential to sustain plumes for extended periods of time and their constrained effects on the benefits of technologies that solely address contaminants in transmissive zones. Flushing out the plume (i.e., pump-and-treat) is a slow, inefficient process when there are contaminants in the low-permeability compartment.

Over the past decade, the effects of source control measures (depletion or containment) on plumes has been the focus of rigorous debate and research. It is now clear that source treatment will reduce the ultimate total mass in downgradient plumes, and will likely result in reduced plume extent and/or longevity. However, in most instances it is likely that contaminants will remain and persist for extended periods, leading to a sense that no action will get a site to closure. Reconciling these perspectives is critical to moving forward in risk management and site remediation. A pragmatic approach would be to strike a balance between what can be done and living with the inevitable imperfections that remain.

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CHAPTER 8

DNAPL SITE CHARACTERIZATION ISSUES AT CHLORINATED SOLVENT SITES

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8.1 INTRODUCTION

Past releases of chlorinated solvents generally occurred as dense nonaqueous phase liquids (DNAPLs). Because DNAPLs are heavier than water and are sparingly soluble, they pose difficult characterization, remediation and long-term management challenges. At such sites, a distinction is made between the source zone, which includes portions of the subsurface where DNAPL is or was present as a separate phase, and the downgradient plume of dissolved contamination resulting from groundwater flow through the source zone. Site management frequently involves attempting to contain or deplete contamination in both of these areas. During the past two decades, several promising *in situ* technologies (e.g., chemical oxidation, thermal extraction and cosolvent/surfactant flushing) have been applied at many sites to remove or destroy contaminants in DNAPL source zones. Yet the U.S. Environmental Protection Agency (USEPA) Expert Panel on DNAPL Remediation (USEPA, 2003) concluded that:

"As far as the Panel is aware, there is no documented peer-reviewed case study of DNAPL source zone depletion beneath the water table where U.S. drinking water standards, or MCLs [maximum contaminant levels], have been achieved and sustained throughout the affected subsurface volume, regardless of the in-situ technology applied."

A key factor limiting remediation success is the difficulty of adequately delineating and characterizing the DNAPL source zone. As an introduction to this chapter, a number of related DNAPL characterization issues/observations are listed. These are discussed throughout this chapter and include:

- In most cases, DNAPL source zone(s) and architecture must be delineated (and distinguished from downgradient dissolved plumes) in order to effectively manage site contamination.
- Characterization efforts need to focus on traditional goals (such as defining the nature and extent of contamination) and on acquiring data to evaluate remediation options.
- Remediation goals and strategy should be formulated based on the conceptual site model (CSM) early in the characterization process to ensure collection of appropriate remediation data. The CSM encompasses the site stratigraphy (layering), DNAPL release areas, depth to groundwater, groundwater flow directions and rates, approximate location of DNAPL, DNAPL architecture (i.e., pooled where free-phase DNAPL occupies most, but not all, of void spaces in more-permeable zones, or at residual saturation where disconnected globules are trapped by capillary forces) and other important site features.
- An outside-in characterization approach guided by the CSM should be used to minimize undesirable spreading of DNAPL.

H.F. Stroo and C.H. Ward (eds.), *In Situ Remediation of Chlorinated Solvent Plumes*,
doi: 10.1007/978-1-4419-1401-9_8,

- Characterization tools (e.g., direct-push technology) have advanced, but many challenges remain, especially for fractured rock and deep DNAPL source zones.
- Characterization uncertainties and requirements increase with age of release, subsurface complexity, and at sites with large and multiple DNAPL source zones.
- For large DNAPL source zones, it only may be possible to define them generally.
- Direct observation of DNAPL is often difficult (e.g., DNAPL at residual saturation will not flow into a well) and indirect methods are used to infer DNAPL presence based on elevated contaminant concentrations in groundwater, soil gas and soil.
- There is a recent focus on characterizing the downgradient mass flux coming from the DNAPL source; however, tools to characterize flux are limited and not well tested.
- DNAPL left in the subsurface after remediation is due to both incomplete characterization and remediation.

Given the complexity of DNAPL site characterization, it is advantageous to use a dynamic and flexible investigation workplan based on a CSM that is refined iteratively as new data become available. This is illustrated in Figure 8.1, which shows that characterization continues into remediation. An overarching goal of data collection is to sufficiently understand site stratigraphy, groundwater flow conditions, contaminant distribution and contaminant behavior in order to guide site management decisions. At the outset, DNAPL site investigation depends on the purposes of the characterization effort.

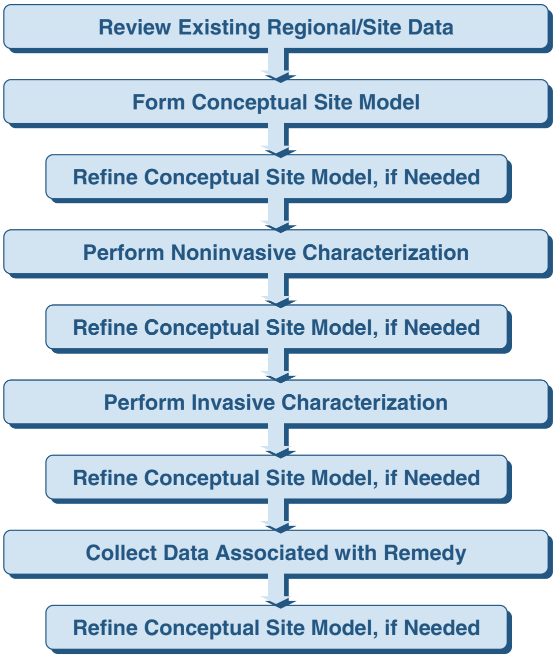

Figure 8.1. Data collection followed by hypothesis testing leads to continued refinement of the CSM.

8.2 PURPOSES OF SITE CHARACTERIZATION

Data collection at a contamination site can serve several functions. Prior to designing a data collection program, the use and value of the data needs to be understood to promote the acquisition of sufficient and appropriate information. Environmental data may be collected to (1) estimate the nature and extent of contamination, (2) determine present and future risk and (3) make and monitor remedial decisions. Each of these purposes is discussed briefly below.

8.2.1 Estimate Nature and Extent of Contamination

Historically, the focus on the nature and extent of contamination was regulatory-driven and centered on the groundwater contaminant plume. For suspected DNAPL sites, in addition to characterizing the aqueous plume, determining nature and extent includes estimating whether or not DNAPL is present, and if so, attempting to delineate its spatial distribution and saturation characteristics (collectively referred to as its architecture) that have resulted from percolation, entrapment and phase-partitioning. The source zone can include (1) immobile DNAPL trapped at residual saturation in pore spaces by capillary pressure or at higher saturation pooled in geologic traps, (2) mobile DNAPL, (3) sorbed contaminants, (4) dissolved and volatilized contaminants in water and gas, respectively, and (5) diffused contaminants in fine-grained media (also known as matrix diffusion). All of these components can serve as long-term sources of dissolved groundwater contamination. The downgradient plume of dissolved contamination created by groundwater flow through the DNAPL zone typically occupies a much greater area than the source zone and can substantially increase risks to receptors and the environment. Nature and extent information is required to manage both the dissolved plume and the DNAPL zone. The level of detail required for characterization depends on the specific questions and/or goals considered for the site and the complexity of site conditions (SERDP, 2006). In the discussion below, the following aspects of the nature and extent of contamination are discussed: (1) aqueous plume characteristics and behavior, (2) DNAPL architecture and (3) DNAPL characteristics, mobility and age.

8.2.1.1 Aqueous Plume Characteristics and Behavior

Information on the aqueous plume includes (1) where it starts relative to the DNAPL source area, (2) where it ends (both vertically and horizontally), (3) its composition, (4) the subsurface assimilative capacity (e.g., biodegradation rates and degradation products, if any), (5) its behavior (stable, shrinking or expanding) and (6) the amount of mass sorbed and/or diffused into fine-grained material, as well as the mass dissolved in the plume.

The extent of the aqueous plume is determined by groundwater sampling using wells and/or direct-push methods. Distinguishing where the DNAPL source zone ends and the aqueous plume begins may be difficult because elevated concentrations persist some distance downgradient of the source zone. Insight into DNAPL composition can be gained from analysis of downgradient water quality data. One complication is that some biodegradation products may occur as impurities in the DNAPL source. An examination of spatial and temporal concentration trends may help sort out chemicals that are in the DNAPL versus those that are degradation products.

The volume of the aquifer impacted by aqueous plume contaminants is a function of the DNAPL source zone size, the DNAPL dissolution rate and the assimilative capacity of the aquifer. Assimilative capacity can be estimated by (1) comparing measurements of contaminant mass discharge from the source zone (mass per time [M/T]) and the contributing area perpendicular to flow at two or more distances along the plume flowpath, or (2) examining contaminant concentration data at individual wells within the plume. By fitting the data to an equation that describes contaminant transport and degradation, the assimilative capacity can then be characterized using a lumped mass loss term such as a first-order decay parameter (though more advanced approaches may be needed). If the assimilative capacity is sufficient, the aqueous plume will be stable or shrink in size over time. Evaluation of plume and chemical-versus-time trends at individual wells typically requires multiple sampling events over at least a few years.

Estimates of the contaminant mass distributed between water (dissolved), solids (sorbed), air (volatilized in the vadose zone) and nonaqueous phase liquid (NAPL), if present, can be made by analysis of soil (or rock) samples and use of equilibrium partitioning equations (Mariner et al., 1997). Chemical specific sorption coefficients (K_d values, also known as the soil/water distribution coefficient), can be calculated as $K_d = K_{oc} \times f_{oc}$ by analyzing soil samples for their fraction of total organic carbon content (f_{oc}) and using the chemical's organic carbon partition coefficient (K_{oc}), which is typically obtained from published values (e.g., Howard and Meylan, 1997). Contaminant mass diffused into fine-grained unconsolidated media and rock (and diffusive flux) also can be estimated based on analyses of soil and crushed-rock core samples, and estimates of matrix porosity and diffusion coefficient data. The amount and distribution of sorbed and diffused mass will have uncertainties and will act as a continuing source, even downgradient of the DNAPL source area (e.g., Wilson, 1997). This is discussed further below for the DNAPL source zone.

8.2.1.2 DNAPL Architecture

In permeable zones within unconsolidated media, relatively rapid groundwater flow may have dissolved much or nearly all of the DNAPL that was retained at residual saturation in fingers during its downward penetration (Anderson et al., 1992; Sale and McWhorter, 2001; Parker et al., 2003). Non-wetting DNAPL that pooled, spread and attained higher saturation in permeable lenses over finer-grained layers tends to dissolve at a slower rate due to reduced contact area with flowing groundwater (Johnson and Pankow, 1992), but over decades, dissolution may have removed or greatly diminished the volume of DNAPL in such zones (Parker et al., 2003). The remaining DNAPL typically persists in the less-flushed, finer-grained, lower-permeability layers where substantial contaminant mass likely migrated by advection (e.g., through fractures) and diffusion (SERDP, 2006). For example, in sand and gravel aquifers, field investigations at older sites show that a large fraction of the total contaminant mass is found in confining layers above or below aquifers or in low-permeability beds within an aquifer (Chapman and Parker, 2005; Parker et al., 2003; Parker et al., 2004). A conceptual model of DNAPL release, penetration, redistribution, and evolution in sandy aquifers presented by Parker et al. (2003) is illustrated in Figures 8.2 and 8.3.

In fractured aquitards (i.e., silts/clays and shales/mudstones) where the bulk hydraulic conductivity is low, DNAPL penetration can occur via fractures and, after a few years to decades, nearly all the contaminant mass may reside in the low-permeability matrix blocks (i.e., non-fractured, porous zones between the fractures) due to dissolution and diffusion (SERDP, 2006; Goldstein et al., 2004; O'Hara et al., 2000). Similarly, in fractured sedimentary rock (e.g., sandstone and limestone), substantial contaminant mass typically exists in the porous, low-permeability matrix blocks between the fractures that once contained DNAPL (Parker et al., 1994; Sterling et al., 2005). However, in crystalline rock (e.g., granite, gneiss and basalt), most of the contaminant mass likely resides as DNAPL in dead-end fractures or smaller aperture fractures with less mass in the very low-porosity blocks between fractures. The complex distribution of contaminant mass and the importance of diffusion in fractured media, which is illustrated conceptually in Figure 8.4, increases the difficulty of DNAPL zone characterization.

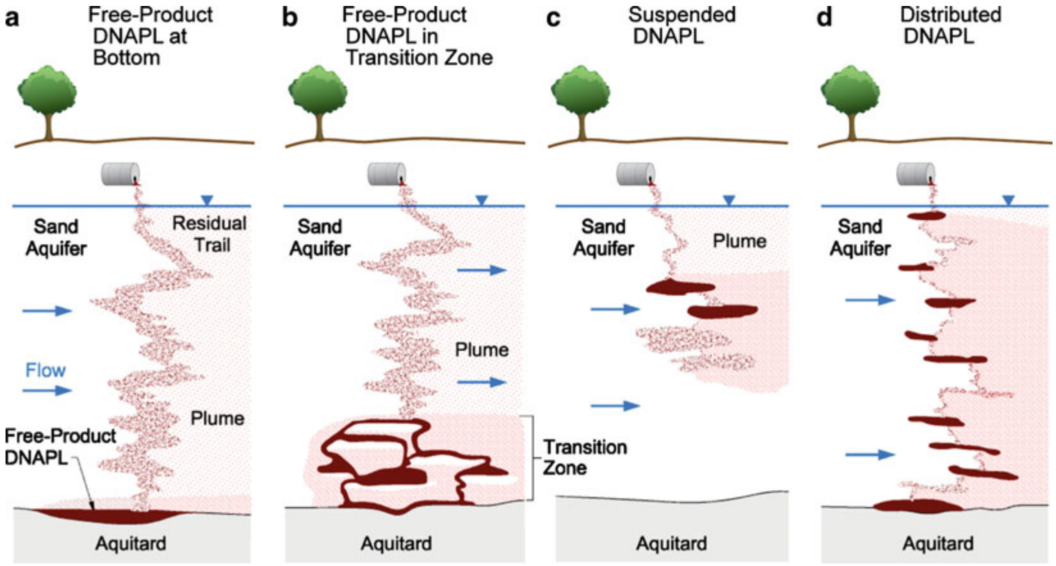

Figure 8.2. Schematic representations of four scenarios for DNAPL source zones in sandy aquifers: (a) DNAPL leaves a trail of residual DNAPL as it penetrates to the base of a uniform sand aquifer where it pools above an aquitard; (b) DNAPL penetrates through homogenous sand and accumulates in a layered transition zone; (c) layers of residual and pooled DNAPL are suspended in a sand aquifer; and (d) DNAPL forms multiple layers distributed throughout the aquifer thickness (modified from Parker et al., 2003).

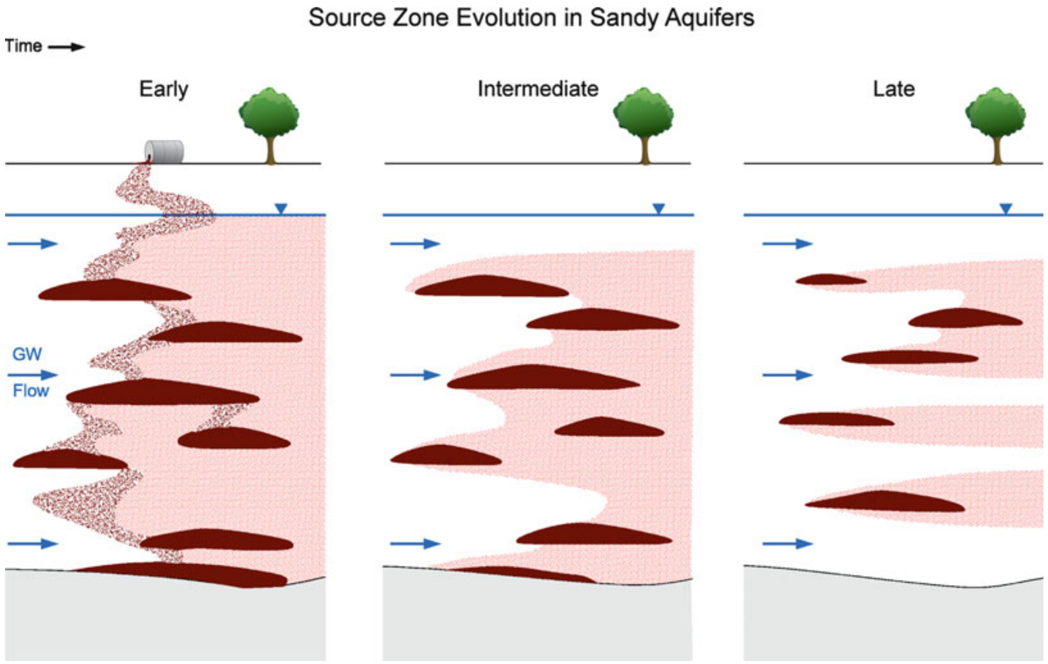

Figure 8.3. Conceptual illustration of the evolution of a layered DNAPL source zone showing complete dissolution of residual trails, shrinkage of some DNAPL layers, and complete removal of others due to decades of groundwater flushing (modified from Parker et al., 2003).

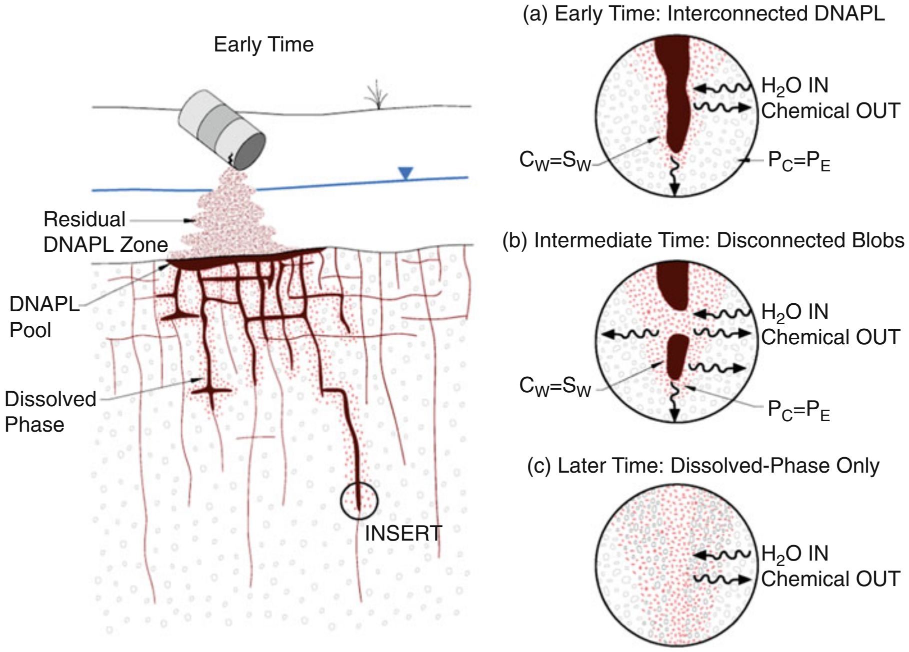

Figure 8.4. Conceptual model of DNAPL in individual fractures: (a) early time invasion of non-wetting DNAPL, dissolution, and diffusion into adjacent porous media; (b) intermediate time showing disconnected NAPL blobs resulting from mass loss by diffusion; (c) later time after diffusion into the matrix has caused the DNAPL to disappear. Back-diffusion provides a long-term source of dissolved contamination to the fracture system after the chemical gradient has been reversed by natural or engineered flushing (modified from Parker et al., 1994).

Delineating the architecture of subsurface DNAPL can be critical to site characterization and remediation. Typically, residual DNAPL is easier to remove and contributes more mass to downgradient dissolved plumes than pooled DNAPL. DNAPL present in granular and fractured media tends to reside in thin layers and fracture zones, respectively. Because the mass distribution is typically controlled by small-scale features, high resolution sampling of cores may be required to determine DNAPL architecture in most sources zones. The sampling scale needed to delineate DNAPL architecture will vary as a function of site stratigraphy, contaminant age (length of time in the subsurface) and type (physical properties), and remediation objectives.

At many sites, estimation of the total contaminant mass in the source zone may remain uncertain by a factor of 10 or more due to the complex contaminant distribution in the subsurface (SERDP, 2006). If DNAPL is mobile and flows into a well, its presence (but perhaps not its source elevation) can be identified using discrete-interval sampling devices and/or oil-water interface probes. Attempts to characterize the architecture of DNAPL at and above residual saturation, however, generally rely on detailed examination of core samples, use of specialized probes, and inferences derived from vertical profiling of groundwater quality.

An essential aspect of source zone characterization involves inspecting low-permeability strata that can entrap, store and eventually release (by back-diffusion) substantial contaminant mass. This generally cannot be accomplished by sampling groundwater from wells or with other monitoring systems that preferentially interrogate higher-permeability layers. Rather, there must be an emphasis on the use of cores to yield insight into (1) small-scale geologic features that provided preferential pathways for DNAPL migration during source zone formation, and (2) the distribution of low-permeability zones that serve as reservoirs for contaminant mass storage (derived from mass transfer processes and/or residual DNAPL entrapment) and are not readily flushed by groundwater flow (SERDP, 2006). For large DNAPL source zones, application of extensive detailed coring will likely be limited by cost and it may only be practicable to determine generally where the DNAPL source zone is located (i.e., by drawing its estimated outline on a map).

8.2.1.3 DNAPL Characteristics, Mobility and Age

DNAPL in the subsurface is acted on by three forces: (1) gravitational (pressure due to gravity), (2) capillary (capillary pressure) and (3) hydraulic (also known as viscous force or hydrodynamic pressure). DNAPL movement and retention in the subsurface are influenced significantly by DNAPL properties, such as density and viscosity, and capillary forces. In general, capillary forces tend to trap DNAPL while gravitational and hydraulic forces tend to mobilize DNAPL. DNAPL flow occurs when the vector sum of the gravitational and hydraulic forces exceed the capillary force. It is important to determine whether DNAPL is continuing to move, is trapped at residual saturation, and/or is pooled and potentially mobile (e.g., drilling through it and the underlying capillary barrier could mobilize DNAPL deeper).

Properties that control capillary force, and thereby influence DNAPL mobility, include interfacial tension, pore size and wettability. Wettability refers to the tendency of one fluid to spread over and adhesively coat a solid surface in the presence of another fluid; it depends on interfacial tension and is a major determinant of flow, entrapment, distribution and recoverability of DNAPL in the subsurface. The fluid that preferentially spreads over solid surfaces is known as the wetting fluid, and the fluid repelled by capillary forces is the non-wetting fluid. Most natural porous media that have not been invaded by DNAPL, are generally strongly water-wet. Non-wetting DNAPLs tend to have lower residual saturations (by a few percent) than wetting DNAPLs.

Phase partitioning and redistribution of contaminant mass that occurs over time in porous and fractured media must be considered in designing a data collection program. Partitioning causes multi-component DNAPL to selectively lose its more volatile and soluble components with time. Such weathering typically results in changes in viscosity, density and wettability. Due in part to the effects of weathering, DNAPL properties (such as density, viscosity, interfacial tension and wettability) and composition are best determined by analysis of representative DNAPL samples (if obtainable). Properties of subsurface NAPL may also differ from pure products (and textbook values) due to release (spill/discharge to the environment) of off-specification material and mixtures.

An important aspect of contaminant nature and extent is the age of the source zone due to its influence on migration history, contaminant partitioning and existing DNAPL architecture. At many DNAPL contamination sites, chlorinated solvents were released to the subsurface more than 20 years ago (between 1950 and 1985) and have migrated via heterogeneous pathways that are characterized by vertical fingers ending in lenses where lateral spreading occurred due to subtle changes in media capillary properties. Coal tar and creosote DNAPLs derived from manufactured gas plant and wood-treating operations were released initially at some sites more than 100 years ago.

8.2.2 Determine Risk

Risks associated with DNAPL include the threat of uncontrolled mobilization resulting from characterization and remediation activities (e.g., cross-contamination) and more traditional risks related to chemical exposure. Careful delineation of DNAPL architecture helps reduce the potential for inducing unwanted DNAPL migration into previously uncontaminated aquifers, and can help determine if investigation or remediation work caused such DNAPL movement (i.e., based on comparison of data collected before and after fieldwork).

Sufficient data need to be collected to determine the exposure pathways and associated risks posed by a contamination site. Exposure pathways commonly of concern at DNAPL sites include impacts to (1) drinking water wells, (2) discharge to surface water bodies and (3) vapor transport to buildings. Potential impacts to surface water may require examination of the attenuation processes within the transition zone between surface water and groundwater. There are several well-publicized sites where the indoor-air pathway has been shown to cause elevated human health risk due to migration of chlorinated solvent vapors through the vadose zone (SERDP, 2006). In November 2002, the USEPA issued the Vapor Intrusion Guide, which provides conservative groundwater concentration screening limits for the groundwater-to-indoor-air exposure pathway and recommends application of site-specific vapor sampling and/or modeling analyses if screening limits are exceeded (USEPA, 2002). These conservative screening limits suggest that the presence of low part per billion (ppb) levels of chlorinated solvents in groundwater could pose an unsafe indoor air exposure, triggering the need for a site-specific evaluation wherever buildings overlie solvent plumes. Consequently, in addition to groundwater data, vapor data may need to be collected and could be a driver for remedial action if vapor transport to a building is suspected.

8.2.3 Make and Monitor Remedial Decisions

Enough work has been performed at DNAPL sites to identify potentially applicable remedial options at the beginning of a characterization effort. The investigator should be familiar with potential remedial options and associated data requirements to ensure that data needed to make remedial decisions are collected during site characterization. Examples of these types of data include monitored natural attenuation (MNA) parameters (e.g., dissolved oxygen, electron acceptors and degradation products) and DNAPL properties, such as composition, density, viscosity and interfacial tension.

In addition, remediation provides an opportunity to obtain additional data that may be used to update the CSM (Figure 8.1). Remedial activities, such as installation of wells, produce subsurface samples that can be used for contaminant and lithological delineation. Monitoring responses (pressure changes, flow rates, chemical concentrations) to injection of treatment agents or extraction of fluids can provide valuable information regarding media properties as well as contaminant conditions and behavior. To develop characterization data from remedial actions requires integration of investigation and remediation efforts that are often seen as sequential activities. Adaptation of the Triad approach (Crumbling, 2001; Crumbling et al., 2001) to remedial activities is a means of more fully integrating site characterization and remediation. The Triad approach is an attempt to rely on past general experience along with site-specific, flexible planning that allows decisions to be made in the field using real-time data, where the goal is to optimize characterization and remediation decisions.

Implementing DNAPL source zone depletion technologies can lead to changes in subsurface properties that need to be monitored both in the source zone targeted for treatment and downgradient as groundwater and vapors migrate from the source zone during and after treatment. For example, changes in subsurface properties caused by remediation can occur in (1) water chemistry (e.g., depressed pH, increased ionic strength), (2) microbial populations (e.g., reduced biomass, increased activity and changed community structure), (3) porous media properties (e.g., reduced permeability, altered surface chemistry), and (4) subsurface temperatures (e.g., elevated temperatures) (Crimi and Siegrist, 2003; Kavanaugh et al., 2003; Siegrist et al., 2001).

In addition, there is increased interest in developing monitoring approaches to allow reliable estimation of the contaminant mass discharge before, during and after remediation of source zones. This interest has developed, in part, because total mass removal is rarely, if ever, achieved, and there is a desire to assess the positive impact of partial mass removal (i.e., a reduction in mass flux—contaminant mass per unit area per unit time). However, estimates of contaminant mass flux are frequently subject to considerable uncertainty because the contaminants often emanate from sources in complex distributions and settings that cannot be easily defined. The mass flux can be even more difficult to estimate reliably during and after remediation if its distribution becomes more sparse and difficult to detect.

Finally, another aspect of post-remedy site characterization is long-term monitoring (LTM). LTM is defined as monitoring conducted after a remedy has been selected and implemented, and is used to evaluate the degree to which the remedial measure achieves its objectives (USEPA, 2005b). It provides another opportunity to obtain data and update the CSM. An important aspect of LTM is that it represents a significant, persistent, and growing cost for entities involved in remediation. Consequently, efforts are being made to optimize LTM and reduce long-term costs. This optimization may take the form of reduced samples in time and space and/or more efficient sampling (e.g., sensor systems or diffusion samplers).

8.3 CHARACTERIZATION APPROACH AND METHODS

As noted above, given the inherent complexity and cost of DNAPL site characterization, it is advantageous to use a dynamic and flexible workplan based on a CSM that is refined iteratively as new data becomes available (Figure 8.1). This observational approach (Terzaghi and Peck, 1948) tends to optimize use of resources and reduce characterization inadequacies.

The first step (Table 8.1 and Appendix 8.A) in developing a CSM and locating DNAPL sources is to review available information regarding (1) site history (chemical use, storage, release, and disposal records, historic aerial photographs, employee/witness interviews) and (2) environmental conditions (geologic, hydrogeologic, and site-specific investigation reports). Using this information, a CSM (or a set of alternative models) is formulated based on limited understanding of stratigraphy, groundwater flow, DNAPL release areas and distribution, and contaminant partitioning and transport.

The CSM forms the basis for designing a data collection program, which is phased and may initially rely on noninvasive and minimally-invasive methods (e.g., soil gas and surface geophysical surveys) prior to drilling/probing. A common strategy used at chlorinated solvent sites to reduce the risk of inducing unwanted DNAPL movement due to invasive investigation is to employ an outside-in approach whereby invasive characterization work is initiated outside of suspected DNAPL areas prior to drilling/probing in the source zone. Such an approach improves understanding of stratigraphy, groundwater flow and contaminant distribution while minimizing the risk of cross-contamination by drilling through a DNAPL zone. Stratigraphic information can help identify preferential pathways and traps for DNAPL. Dissolved concentrations in groundwater, which is an integrator of contamination, can be used along with site history information to backtrack to DNAPL source zones. Source investigation methods are then selected that provide desired characterization and remediation data and minimize the risk of DNAPL mobilization.

Table 8.1. Applicability of Methods for Characterizing DNAPL Source Zones and Downgradient Aqueous Plumes

Characterization Method	DNAPL Source Zone	Down-gradient Aqueous Plume	Comment (primarily used to characterize: S=Stratigraphy, H=Hydraulics/ Hydrogeology, N=NAPL, C=Contamination, O=in Unconsolidated Media, R=in Rock)
Desktop review of existing information	Yes	Yes	Initial step in development of a CSM; used to guide subsequent investigation
Soil gas survey	Maybe*	Rarely	Minimally invasive screening tool to help delineate volatile organic compounds (VOCs) in vadose zone; [N,C,O]
Surface geophysical methods	Yes	Yes	Noninvasive surveys to help delineate stratigraphy, buried waste, fracture zones, and conductive plumes; DNAPL is a poor geophysical target; interpretation is somewhat ambiguous; [S,H,C,O,R]
Soil/rock core sample examination	Yes	Yes	[S,H,N,C,O,R]
Organic vapor analysis	Yes	Yes	Screening tool for VOCs and NAPL
Ultraviolet (UV) fluorescence inspection	Maybe*	No	Can illuminate fluorescent NAPLs (e.g., those containing polycyclic aromatic hydrocarbons [PAHs]); subject to interference
Hydrophobic dye shake test	Yes	No	Used to reveal NAPL presence
NAPL FLUTe^{TM} liners	Yes	No	Used to reveal NAPL presence in retrieved core
Chemical analysis of soil and rock	Yes	Yes	Used to delineate contaminant distribution and infer NAPL presence/absence
Direct-push methods			Limited by penetration resistance; [S,H,N,C,O]
Geoprobe®	Yes	Yes	Well-developed suite of characterization tools
Cone penetrometer testing (CPT)	Yes	Yes	Well-developed suite of characterization tools
Membrane interface probe (MIP)	Yes	Yes	High-resolution screening tool used to help delineate immiscible phase and dissolved VOCs
Laser-induced fluorescence (LIF)	Maybe*	No	Used to delineate fluorescent NAPLs (e.g., containing PAHs); subject to interference
Hydraulic conductivity testing	Yes	Yes	Cross-contamination risk; [H,O,R]
Examining drill core/cutting samples	Yes	Yes	Cross-contamination risk; [S,H,N,C,O,R]
Hydraulic head surveys	Yes	Yes	Defining the groundwater flow field; [H,O,R]
Groundwater quality profiling (vertical)	Yes	Yes	Can provide detailed 3-dimensional (3-D) groundwater chemistry data; used to help delineate DNAPL zone by back-tracking; [H,N,C,O,R]

(*continued*)

Table 8.1. (continued)

Characterization Method	DNAPL Source Zone	Down-gradient Aqueous Plume	Comment (primarily used to characterize: S=Stratigraphy, H=Hydraulics/ Hydrogeology, N=NAPL, C=Contamination, O=in Unconsolidated Media, R=in Rock)
Waterloo Profiler® and similar other direct-push tools	Yes	Yes	Can provide detailed vertical (and 3-D) snap-shot characterization of groundwater chemistry
Multi-level monitoring systems	Yes	Yes	Used to measure dissolved chemistry and hydraulic heads in multiple discrete intervals in a single well
DNAPL profiling	Yes	No	[N,C,O,R]
NAPL in well surveys	Yes	No	Reveals NAPL presence; cross-contamination risk
Downhole NAPL FLUTe™	Yes	No	Provides log of NAPL distribution with depth at borehole location; cross-contamination risk
Partitioning interwell tracer test (PITT)	Yes	No	Provides estimates of DNAPL saturation and volume; subject to error; very expensive; [H,N,O,R]
Mass flux calculation methods	No	Yes	Used to estimate contaminant mass flux to groundwater downgradient from a source zone; provides a measure of remediation benefit; [H,C,O,R]
Borehole geophysical methods	Maybe	Maybe	Particularly useful for delineating stratigraphy, bedrock fractures, and vertical flow in wells; cross-contamination risk; [S,H,NC,O,R]
NAPL property measurement	Yes	No	For characterizing NAPL properties that affect mobility and remediation

*Note: Soil gas surveying is applicable to volatile chemicals; fluorescent methods are applicable to fluorescent NAPL; this table is general in nature, see Appendix 8.A for details.

An extensive compilation of DNAPL site characterization tools and methods (including detailed information describing method process, use, limitations and reference citations) is provided in Appendix 8.A. The applicability of many of these methods to characterize DNAPL source zones and downgradient aqueous plumes is summarized in Table 8.1. Kram et al. (2002) compared implementation costs for many of the DNAPL characterization methods presented in Appendix 8.A, and concluded that direct-push sensors (cone penetrometer testing [CPT], laser-induced fluorescence [LIF] and membrane interface probe [MIP]) and the downhole NAPL FLUTe™ liner methods are particularly cost-effective components of integrated DNAPL site characterization.

Due to variation in site conditions, objectives and constraints, there is no standard strategy or assemblage of methods and tools that can be prescribed for source zone characterization. DNAPL source zone characterization in unconsolidated and fractured rock media is discussed below.

8.3.1 Source Characterization in Unconsolidated Media

Two exemplary studies that evaluated the efficacy of multiple characterization methods to delineate DNAPL source zones in sandy aquifers were presented by Parker et al. (2003) and Griffin and Watson (2002a; 2002b). The results of a third study (Einarson et al., 2000), which applied eight innovative characterization tools to investigate a dissolved methyl tertiary butyl ether (MTBE) plume in heterogeneous alluvium, are highlighted in Box 8.1.

Box 8.1. Comparison of Eight Innovative Site Characterization Tools

Einarson et al. (2000) applied eight characterization tools to investigate a MTBE plume at Site 69, Vandenberg Air Force Base, California. The tools were applied in a shallow heterogeneous mixture of sand, silt and clay alluvium. The first group of tools focused on determination of stratigraphy. The first tool applied was *dipole-dipole surface resistivity*, which allows rapid noninvasive screening. The tool was able to distinguish sandy layers (high resistivity) versus a clay layer (low resistivity). Next, continuous soil cores were obtained using the *Enviro-Core® system*. Core recovery with the small-diameter system (2.25 inch outer diameter (OD)) was 60% and with the larger-diameter system (3.5 inch OD) was 80%. This caused important stratigraphic features to be missed. Soil cores collected with the *Waterloo Piston Sampler™* demonstrated the best recovery (>90%) and were used for lithologic logging and geotechnical and chemical testing. Stratigraphy also was determined using continuous electrical conductivity measurements made using the *GeoProbe® electrical conductivity (EC) probe* and using the *CPT-resistivity probe*. The EC probe showed good correlation with the core log and the CPT tool for coarse-grained deposits; a fine-grained confining unit (identified by CPT probes and soil coring) was not identified by the EC probe. The remaining tools were used to define groundwater conditions and the contaminant distribution. Depth-discrete, one-time groundwater samples were collected using the *Waterloo Groundwater Profiler™*, a direct-push tool. The Profiler was found to be of limited use due to the presence of interstitial fines that frequently plugged the external ports on the sampling tool. Sampling flow rates were low and the tool often needed to be removed, cleaned, and reinserted. Traditional bundle piezometers could not be utilized due to the presence of cohesive, fine-grained sediments. Instead, six permanent multilevel monitoring systems were installed using the continuous, multi-channel tube (*CMT) multilevel monitoring system* from Solinst. This was used to collect water-level and water quality data. Finally, the *GeoProbe® MIP* was used to semi-quantitatively identify contaminated zones without collecting a soil or groundwater sample. The MIP proved to be a useful tool to quickly delineate contaminated zones.

Several techniques were used by Parker et al. (2003) between 1996 and 2000 to delineate chlorinated solvent (trichloroethene [TCE] or perchloroethene [PCE]) source zones at five industrial sites where DNAPL had been released into sandy aquifers between 1950 and 1980. At each site, the DNAPL source zone had weathered due to contaminant dissolution in groundwater, and the source was present in a glaciofluvial or beach sand aquifer, with a varying degree of layering and textural heterogeneity, which is underlain by a finer-grained aquitard (typically clayey silt). Source zone characterization was achieved by testing soil and groundwater samples obtained at very close vertical spacing using direct-push methods for NAPL and contaminant concentrations. Where present, as illustrated conceptually in Figures 8.2 and 8.3, DNAPL was found to occur in one or a few thin layers (1 to 30 centimeters [cm] thick) that were positioned within distinct grain-size zones (e.g., finer-grained sandy sediments within a coarser sand unit), or at contacts between sedimentary layers, or without any apparent textural relationship. Parker et al. (2003) concluded that collection of continuous cores with subsampling at very close vertical spacing (5 cm or less) was essential for delineating DNAPL presence. Methods used to characterize DNAPL source zones at these sites are described, and findings regarding their application are presented in Table 8.2. An example of core subsampling results is provided in Figure 8.5.

Table 8.2. Review of DNAPL Source Zone Investigation Techniques by Parker et al. (2003) (reprinted from Vadose Zone Journal courtesy of Soil Science Society of America).

Method	Study Findings
Sample Collection Method	
Waterloo Groundwater Profiler® A direct-push device for collecting depth-discrete groundwater samples in unconsolidated granular deposits (Pitkin et al., 1999). Under favorable conditions, it allows rapid groundwater sampling at multiple depths in the same hole without retrieving, decontaminating and re-driving the tool between samples, with no drill cuttings and little generation of purge water.	"The depth-discrete groundwater sampling done using the Waterloo Profiler served, for screening purposes, to identify high-concentration zones where DNAPL occurrence was most-probable. This sampling only rarely identified actual DNAPL layers, because the sample spacing was too large, and because of dilution caused by the depth integration of each sample, given the thinness of the DNAPL layers typical of these source zones." [p. 133] "Samples can be collected at vertical spacings as close as 15 cm without causing overlap of sample zones in the aquifer. In finer-grained silty of clayey zones, the time required to obtain sufficient sample volume may be large, so that sampling in such zones is not practical." [pp. 119–120]
Direct-Push Piston Sampler Cores were collected using a piston core barrel described by Zapico et al. (1987) that was driven using the air-hammer and scaffolding method of Starr and Ingleton (1992) or a direct-push rig (Einarson, 1995).	"The ability to collect relatively undisturbed cores using the piston corer, which provided excellent recovery (typically >95%) [and retains pore fluids], was essential for subsequent core examination and subsampling procedures." [p. 120]
NAPL Identification Methods	
Drainable Core Technique (DCT) At two sites, cores were subjected to a draining procedure in an attempt to distinguish between free product and residual DNAPL. The DCT was performed on cores contained in aluminum samples tubes (and maintained in a vertical position) that were collected using the piston core barrel. The core was then drained sequentially from top to bottom at closely spaced intervals (typically 2.5 to 5.0 cm) by drilling holes (3 millimeters [mm]) into the core tube, and collecting fluids that drain from each depth into a glass vial.	"Where DNAPL flowed from an interval, it typically flowed first followed by water. After fluid drainage ceased from an interval, usually after about 10 minutes, the volumes of fluid (water/DNAPL) that drained from the interval were recorded and draining of the next interval was started. . .Application of the DCT typically requires several hours for each core, although several cores can be drained concurrently to increase efficiency." [p. 120] "The drainable core technique is the most time-consuming of the field methods, and it was particularly useful at only one of the five sites. This technique did not always yield DNAPL from finer sand layers, even when we were certain that free product existed in these layers. Even when cores do produce DNAPL, the conditions within the core allowing DNAPL drainage are not controlled or monitored. Therefore, this method is not widely applicable." [p. 133]
Sudan IV Hydrophobic Dye Shake Test on Core Samples Core subsamples were taken using stainless steel sampler and plunger devices at close vertical spacings (typically 2.5 to 10 cm) to detect NAPL using the Sudan IV hydrophobic dye test (Cohen et al., 1992) and for laboratory analysis of VOCs.	"Continuous cores subjected to Sudan IV sampling at extremely close spacing, 5 cm and sometimes closer, were required to find DNAPL and define layer thicknesses at each of the five sites. The DNAPL was not visible in the cores without using the Sudan IV dye test. The core samples analyzed for VOCs, which were generally taken at the same

(*continued*)

Table 8.2. (continued)

Method	Study Findings
Each dye test sample was extruded into a 25-milliliter (mL) glass vial containing a small amount of Sudan IV powder and a few milliliters of deionized water. The dye dissolves in organic NAPL that it contacts, causing it to turn red, if present.	vertical spacing as the Sudan IV samples, corroborated the Sudan IV results. However, if the VOC results had been used alone, the DNAPL identifications would have been uncertain because the calculation procedure used for DNAPL identification depends on estimates of porosity and sorption." [p. 133] "Estimates of DNAPL saturation [based on chemical analyses at the Ontario site] for all samples identified containing DNAPL by the Sudan IV screening test. . .indicated a range from $<$1 to 35%, with a mean of 7%. Therefore, the Sudan IV method indicated good sensitivity for DNAPL detection, even for sample depths where the DNAPL saturation was very low." [p. 129] "Of the three methods for finding DNAPL (DCT, soil VOC analyses and chemical partitioning calculations, and the Sudan IV hydrophobic dye method), the Sudan IV method is the most direct and provides results rapidly in the field as sampling proceeds." [pp. 133–134]
Chemical Partitioning Calculation Procedure Applied to VOC Analyses The total concentration of TCE or PCE detected in a core subsample was compared to the minimum concentration that would be expected in a sample containing DNAPL TCE or PCE based on the method described by Feenstra et al. (1991).	"The core samples analyzed for VOCs, which were generally taken at the same vertical spacing as the Sudan IV samples, corroborated the Sudan IV results. However, if the VOC results had been used alone, the DNAPL identifications would have been uncertain because the calculation procedure used for DNAPL identification depends on estimates of porosity and sorption." [p. 133]
Measuring DNAPL Thickness in Monitoring Wells Using an interface probe or other device.	"Free product thicknesses measured in conventional monitoring wells at three of the sites indicated major DNAPL pools, but these measurements do not represent what is actually in the ground, because the wells do not indicate the layered (vertically discontinuous) nature or position of the DNAPL distribution. Therefore, estimates of the DNAPL volume in these source zones based on product thickness in conventional wells were grossly exaggerated relative to estimates based on the measured thicknesses of the individual layers. Another implication of the finding that the DNAPL zones consist of thin layers rather than thick pools is that the DNAPL has much less potential for downward remobilization, except in situations where wells cause short-circuiting of free-product layers." [p. 134]
Not Used	
Partitioning Interwell Tracer Test (PITT) Jin et al. (1995)	"The occurrence of DNAPL layers in less permeable zones, or in geologically layered transition zones, is disadvantageous for PITT because of the propensity for the tracer to bypass such zones." [p. 134]

(*continued*)

Table 8.2. (continued)

Method	Study Findings
Membrane Interface Probe (MIP) Christy (1996)	"Probes such as MIP offer potential to locate high-concentration zones of chlorinated solvent contamination, but quantification to the degree necessary to differentiate highly sorptive zones from DNAPL, residual from free-product DNAPL, or the vertical separation of thin layers of DNAPL is unlikely." [p. 134]

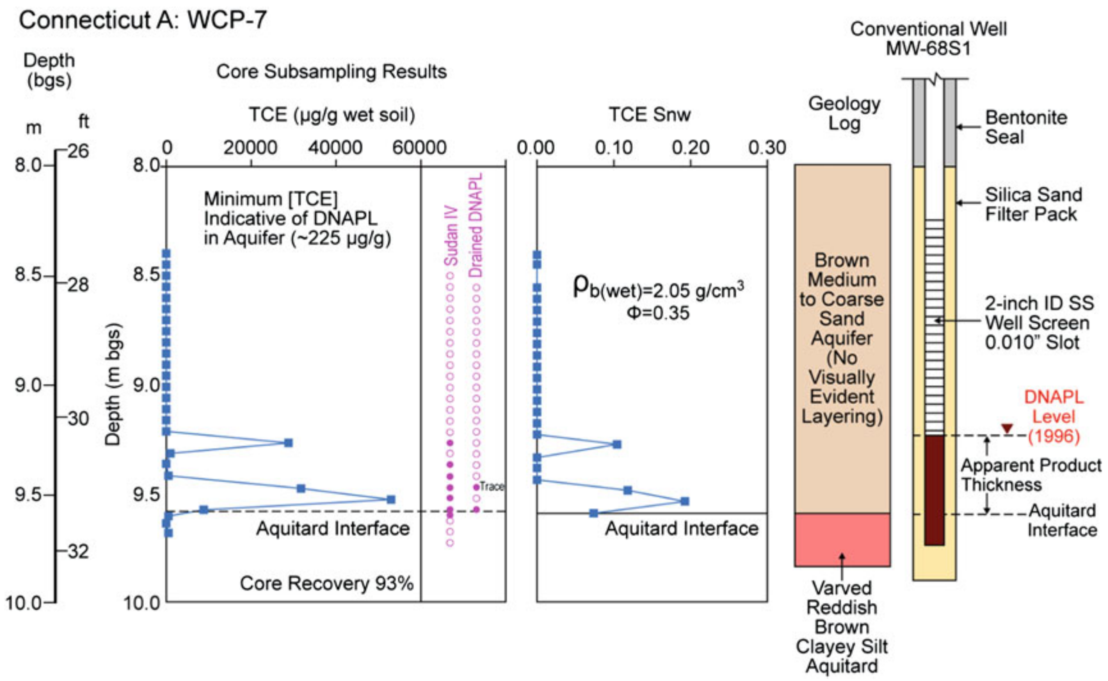

Figure 8.5. Example profile of DNAPL source zone characterization method results next to a conventional monitoring well showing DNAPL accumulation at a site in Connecticut. TCE DNAPL saturations were estimated using soil analytical data (modified from Parker et al., 2003).

A separate investigation was performed by Griffin and Watson (2002a; 2002b) to evaluate DNAPL characterization methods at a site in Florida where Freon 113 and TCE had been released in a sandy aquifer as early as the mid-1960s. Study methods included a high-resolution seismic geophysical survey, field screening of soil cores with a flame ionization detector (FID)/organic vapor analyzer (OVA), reaction with Sudan IV hydrophobic dye, ultraviolet light fluorescence, Geoprobe MIP logging and phase equilibrium partitioning calculations based on laboratory analysis of soil samples. The researchers concluded that:

> "… [I]t appears that an effective strategy for identifying and delineating DNAPL at a similar site would be to initially evaluate existing groundwater quality data to estimate the 1% solubility isopleth boundary for the contaminant(s) in question (an outer boundary supported by the results of this study). The likely DNAPL intervals can then be delineated using the MIP system and confirmed by laboratory analysis of subsequent soil samples."

Example results of DNAPL field tests and findings specific to each characterization method are presented in Tables 8.3 and 8.4.

Comparing the findings of these two studies reveals some differences that may reflect site characteristics, method implementation and/or study focus. For example, the hydrophobic dye shake test worked well for Parker et al. (2003), but was not effective for Griffin and Watson (2002a; 2002b). This difference illustrates some of the difficulties in characterizing DNAPL sites and the possible need to use multiple DNAPL detection methods.

Table 8.3. Comparison of Representative DNAPL Field Test Results (Griffin and Watson, 2002b)

Boring ID and Depth (ft bgs)	Visual Observation	UV Lamp	Sudan IV Shake Tests	FID/OVA Screening (ppm)	Flute Liner Indication	Soil Analytical Result (mg/kg)
SB-5 @ 38’	ND	ND	ND	3,800	None	**Freon – 304**
SB-6 @ 23’	ND	ND	ND	1,700	None	Freon – 8.14 TCE – 0.047 *cis*-DCE – 0.007
SB-6 @ 30’	ND	ND	ND	1,700	None	Freon – 3.54 TCE – 0.063 *cis*-DCE – 0.008
SB-6 @ 39’	ND	ND	ND	1,900	None	Freon – 0.060
SB-6 @ 45’	ND	ND	ND	3,000	Trace - ???	Freon – 0.065
SB-12 @ 41’	ND	ND	ND	NM	Trace - ???	ND
SB-12 @ 57’	ND	ND	ND	NM	None	Freon – 0.143
SB-12 @ 69’	ND	ND	ND	3,000	Dark Stain	Freon – 0.007
SB-14 @ 46’	ND	ND	ND	5,000+	None	**Freon – 897**
SB-14 @ 50’	ND	ND	ND	3,700+	Dark Stain	**Freon – 614**
SB-14 @ 52’	ND	ND	ND	3,300+	Dark Stain	**Freon – 3340**
SB-14 @ 53’	ND	ND	ND	NM	Dark Stain	**Freon – 857**
SB-14 @ 54’	ND	ND	ND	IND	Dark Stain	**Freon – 680**

Notes: bgs = below ground surface; ID = inner diameter; IND = indeterminate; mg/kg = milligrams per kilogram; NM = not measured, ND = not detected; ppm = parts per million. Analyte in bold is considered indicative of NAPL (Freon > 84 mg/kg and TCE > 364 mg/kg based on method described by Feenstra et al.,1991).

8.3.2 Source Characterization in Fractured Media

In recent years, there has been an increased focus on characterizing contamination in fractured media. A 1998 workshop and a 2001 international conference on fractured media were sponsored by the USEPA, the Ontario Ministry of Environment, and others (Steimle, 2002; USEPA, 2001). In 2004, the USEPA and the National Ground Water Association convened another fractured rock conference (Kinner et al., 2005). In addition to these efforts, the American Society for Testing and Materials published a standard guide for monitoring karst and fractured rock (ASTM, 1995) and some states (e.g., Minnesota) published guidance on investigations in karst areas (MPCA, 2005). Even with this recent attention, characterization of fractured media is still a challenge and there is no one strategy that fits all situations. Instead, the practitioner must select methods and tools that best match data needs and site conditions and reduce cross-contamination risks. Thus, an outside-in approach is recommended where fractured media beyond the source zone are characterized before performing invasive work in the source zone.

Table 8.4. Evaluation of DNAPL Source Zone Characterization Methods (Griffin and Watson, 2002a; 2002b)

Method	Study Findings
3-D High Resolution Seismic Survey A geophysical survey was performed to image subsurface structure and stratigraphy in an attempt to delineate DNAPL migration pathways and trapping structures.	"The seismic survey was successful in identifying small-scale structural features in the subsurface, as well as fracture systems within unconsolidated strata. However, little if any correlation between DNAPL occurrence and structural features was apparent at this study site. Additionally, instantaneous attribute analysis of the seismic data provided no obvious evidence of seismic signal attenuation in confirmed DNAPL zones."
Rotasonic Coring and Hydrophobic Dye Reactive Strip Testing Select sonic drilling core samples were extruded into plastic core bags containing a 3-inch wide strip of a reactive liner material that was impregnated with hydrophobic Sudan IV dye to turn bright red where contacted by organic NAPL.	"DNAPL was confirmed using the Flute liner in several locations; however, liner discoloration associated with handling and contact with the plastic core bags, as well as the less dramatic reaction associated with Freon 113 (compared to TCE) often made interpretation difficult. Based on this study, substantial staining of the reactive liner material provides positive confirmation of NAPL; however, the absence of staining does not provide adequate assurance that NAPL is not present; particularly in residual quantities."
OVA Screening of Soil Cores Direct OVA readings were taken within rotosonic core sample bags by cutting a small slice in the core bag, opening a space in the core, inserting the FID tip, and sealing the open slit with cupped hands.	"This method allowed for rapid screening of cores at roughly 2-ft intervals, focusing subsequent sample collection on impacted areas." "In general, OVA/FID readings exceeding about 3,000 parts per million by volume (ppmv) were associated with areas where other DNAPL confirmation occurred. However, a small number of sample locations exhibited OVA readings above 3,000 ppmv with no other indications of NAPL."
Sudan IV Hydrophobic Dye Shake Test and Centrifugation of Core Samples Soil samples from core with high OVA readings and hydrophobic dye strip reactions were subjected to a hydrophobic dye shake test and centrifugation.	"DNAPL separation was not identified in any of the centrifuged samples, either with or with the hydrophobic dye added."
UV Fluorescence Screening	"The presence of abundant shell fragments inhibited interpretation during this study and DNAPL product was not discernable by UV fluorescence, even when TCE and Freon 113 were added directly to the sample."
Membrane Interface Probe (MIP)	"The MIP provided rapid and near continuous delineation of heavily-impacted soils, optimizing selection of soil sample intervals. Subsequent soil analytical data in combination with the MIP records provided detailed delineation of the DNAPL area."
Chemical Partitioning Calculation Procedure Applied to VOC Analyses The total concentration of a contaminant detected in a soil sample was compared to the minimum concentration that would be expected in a sample containing DNAPL TCE or PCE based on the method described by Feenstra et al. (1991).	"Field laboratory analyses of soil samples were generally consistent with OVA/FID, Flute liner, and MIP results, with a few exceptions." "The MIP provided rapid and near continuous delineation of heavily-impacted soils, optimizing selection of soil sample intervals. Subsequent soil analytical data in combination with the MIP records provided detailed delineation of the DNAPL area."

Based on the documents listed above, a general strategy for characterizing fractured media can involve multiple steps and include data collection at multiple scales. Although the steps are presented in a linear fashion, characterization often proceeds in parallel using some of the same tools in multiple steps. Step 1 entails geological characterization, which can include large-scale approaches, such as outcrop mapping and fracture trace analysis, and local-scale approaches, such as use of surface geophysics, drilling and coring, and borehole geophysics (Appendix 8.A). For example, one approach involves rotosonic drilling to provide continuous core geologic information outside of the source area (to minimize the potential for cross-contamination).

Step 2 involves hydraulic characterization, which, as with geological characterization, should proceed outside the DNAPL source zone to minimize cross-contamination. If available, regional hydrogeologic information should be reviewed, including water table or potentiometric surface maps. On a more local scale, vertical head profiling (using isolation packers, cluster wells, and multilevel sampling ports) and hydraulic testing (via injection tests and pumping tests) may be conducted. Borehole flowmeter tests may be used to help identify fracture zones where groundwater is entering or leaving the borehole. Tracer tests also are used to estimate fracture connectivity and porosity (assuming Darcy's Law is valid). Porosity values also may be estimated from cores or possibly using geophysics (e.g., Lane et al., 1996). Borehole flowmeter and tracer tests and some hydraulic tests are performed at a local scale, and scaling up to a more regional scale should be performed with caution.

During Step 3, drilling and chemical characterization proceeds in source zones and downgradient. Vertical chemical profiling is performed by collecting water samples from specific vertical intervals, which may be isolated using packers in open boreholes, completing monitoring wells over specific intervals in well clusters, or installing multilevel well monitoring assemblies. A comparison of three multilevel well systems installed at a fractured rock site is presented in Box 8.2. NAPL FLUTe^{TM} liners may be used to locate zones containing DNAPL. Matrix diffusion effects can be evaluated by analyzing core samples to determine contaminant mass stored in the matrix (Parker et al., 1994, 1997; Sterling et al., 2005).

Box 8.2. Example of Multilevel Well Installation

Determining the three-dimensional characteristics of site hydrogeology and contamination can be costly using conventional single-screen wells. As a result, more often than not, site characterization is less than optimum due to cost constraints. Multilevel wells completed in a single borehole provide a cost-effective alternative to this site characterization dilemma. This example describes the use of three types of single-borehole multilevel wells (Westbay MP System®, Waterloo Multilevel System, and Water FLUTe^{TM}) that were installed at a site with chlorinated hydrocarbon DNAPLs in fractured sedimentary rock.

A Westbay polyvinyl chloride (PVC) MP38 (38 mm; 1.5 inches ID) system with 38 sampling/measurement ports and 29 pumping ports was installed to a depth of 450 feet (ft) (137 meters [m]). The ports are isolated with water-inflated packers. A submersible pump can be lowered down the central casing to the desired pumping port for well development, pumping tests, and interconnectivity tests. Pressure measurements and sampling are conducted with a special Westbay tool that is lowered down the casing to the desired port. The water sample is collected directly from the formation with no purging necessary.

A Water FLUTe^{TM} open tube multilevel system with nine sampling ports was installed to a depth of 300 ft (91 m). Hydrostatic pressure from water placed inside the nylon FLUTe liner forms the seal along the borehole wall and isolates the ports. Because of the shallow depth to water at this site ($<$5 ft [1.5 m]), a 15-ft (4.6 m) high scaffold was needed to provide enough head to evert the FLUTe and 6 ft (1.8 m) of permanent aboveground casing was required to maintain an adequate pressure head to keep the borehole sealed. Open nylon tubes (0.117 inches ID) extend from each FLUTe port to within 20 ft (6 m) of the ground surface. The upper 20 ft (6 m) is converted to 0.5-inch polyvinylidene fluoride (PVDF) tubing to facilitate collecting water samples with a peristaltic pump and water-level measurements. Because of the open tube design, purging is required but the narrow diameter tubing limits purging capability (400–1,000 mL before running dry).

A Waterloo Multilevel System with 13 ports was installed to a depth of 360 ft (110 m). The sampling ports are constructed of stainless steel and are connected to segments of 2-inch diameter schedule 80 PVC pipe. The ports are isolated with water-activated permanent packers in the lower 4-inch diameter portion of the borehole. The upper 3 ports are isolated with standard bentonite seals in the 6-inch diameter portion of the borehole. Open Teflon tubes (0.25 inches ID) extend from each port to the ground surface to facilitate collecting water samples with a peristaltic pump and water-level measurements. Purging is required prior to sample collection because of the open tube design.

The advantages of the Westbay system over the other two systems include (1) greater number of ports (limited only by borehole length) (2) no purging required, which reduces sampling time, and (3) versatility of pumping ports for well development and hydraulic testing. These advantages come with a higher system cost.

The number of ports possible with the FLUTe and the Waterloo systems are limited by the number of tubes that can fit inside the diameter of the riser. Both systems provide larger diameter options that increase the number of ports that can be installed. Both systems are open tube and require purging, which was a bigger limitation with the FLUTe system because of the narrow diameter tubes.

Various downhole geophysical and hydrophysical logging tools were used at all three boreholes prior to well installation to assist in the design of port and packer placements. During this process, safeguards were taken to reduce the potential for cross-contamination by minimizing the amount of time that a borehole was left open. Prior to well installation, a blank FLUTe liner was installed to seal each borehole and prevent contaminant movement up or down the borehole. Once the multilevel well was designed and fabricated, the blank FLUTe liner was removed and the multiport well installed.

Despite these safeguards, cross-contamination still occurred. One cause of cross-contamination was the open borehole condition (although limited) during downhole logging. Another cause of cross-contamination is related to the installation and removal of the blank FLUTe liner itself. As the liner is everted from the top down, water inside the borehole is forced down and out the most permeable pathways. The reverse occurs when the liner is removed. Depending on the borehole, the liner was everted and removed one or more times prior to well installation to accommodate different logging events.

The ability to rectify cross-contamination is greatest with the Westbay system, which included pumping ports for well development. The 0.25-inch diameter tubing in the Waterloo system allowed for enough purging with a peristaltic pump that eventually cross-contaminated ports could be cleaned up in that system. The narrow-diameter tubing (0.117 inches ID) in the FLUTe system significantly hampered any ability to purge cross-contaminated ports. Even after allowing the formation to flush itself for over a year, the ports in the FLUTe system still showed evidence of cross-contamination. It was suspected that VOC contaminants diffused through the tubing of a port sampling a highly contaminated zone and into the tubing of the other ports. Because of the limited purge capability of the FLUTe system, the purging efforts could not overcome the effects of this contaminant diffusion. The FLUTe multiport well was subsequently replaced with a Westbay multiport system in an adjacent borehole. The new multiport well detected no contaminants in the zones of suspected cross-contamination confirming the false positive contamination results being produced by the FLUTe multiport.

The final step involves data integration and interpretation. This includes assessing water quality data over space (e.g., plume maps) and time (e.g., concentration-time-series plots), which along with stratigraphic information (e.g., fracture spacing and orientation) and hydraulic head data, are used to refine the CSM. In complex fractured media, data interpretation can be challenging where different pieces of information may be internally inconsistent and analyzing hydraulic testing may be difficult, perhaps requiring numerical models. Drilling/coring will be more expensive than using direct-push probing techniques in overburden.

Consequently, less data likely will be available and the characterization will be more uncertain. An example of characterization at a fractured rock site and its relationship to remedial performance is given in Box 8.3.

Box 8.3. Characterization of Fractured Media (Davis et al., 2005; Lane et al., 1996; Thompson et al., 2004)

The former Loring Air Force Base is located in Limestone, Maine. The site is contaminated with VOCs, which have elevated concentrations indicative of DNAPL, primarily PCE. The site is an abandoned quarry in fractured limestone.

Characterization activities were initiated in 2001 (Davis et al., 2005). A total of 23 boreholes were drilled, ranging in depth from 75 to 150 ft (23 to 46 m). These borings were cored and logged, and rock chip samples were collected from fracture surfaces for determination of contaminant concentrations in the rock matrix. Additional characterization activities included discrete interval transmissivity testing and groundwater sampling, conventional borehole geophysical (caliper, fluid temperature and fluid resistivity) and acoustic televiewer (ATV) logging, and interconnectivity testing. The fluid resistivity plots appeared to show the greatest number of hydraulically active fractures; only occasionally were temperature anomalies noted that were not also shown in the resistivity data. ATV logs provided orientation of the fractures. The measurement of transmissivity was obtained using a modified slug test method combined with a straddle packer system designed to isolate specific sections of the borehole. To measure fracture interconnectivity and to determine which fractures conduct the majority of groundwater, hydraulic measurements were conducted where an isolated interval is pressurized in a borehole, and the response is observed in another borehole. The most efficient means by which to conduct these hydraulic tests is based on the pulse interference test method. This method is conducted using a constant pressure slug test in one hole and observing the response in another. Groundwater sampling also was conducted in the borehole. Sampling focused on more permeable zones that were isolated using a dual packer system over 10-ft intervals. Additional sampling made use of the rock chip sample results to focus on more contaminated zones. The potential for cross contamination was not evaluated, but given the amount of testing in open borehole, it likely occurred.

Water quality sampling results indicated a west-southwest trending dissolved-phase plume consistent with the general hydraulic gradient, where the highest concentrations were located on the eastern portion of the site. Based on the site characterization, three fracture sets were observed – bedding plane fractures, axial plane fractures, and regional joint fractures. The bedding plane fractures were the main control for groundwater flow. The fractures were more abundant and better connected near the surface. At depths between 55 to 70 ft (17 to 21 m), fractures were typically widely spaced (about 3 ft (1 m) apart) and fracture apertures were less than 0.1 inches. Some fractures also were observed to be filled to partly filled with calcite, which reduced fracture interconnectivity. In one study, 31 of 163 (about 19%) of the fractures were identified as capable of transmitting groundwater (Lane et al., 1996). The horizontal hydraulic gradient was 0.03, suggesting a low transmissivity. Transmissivity, based on slug tests, was estimated to be low, between about 2×10^{-7} to 2×10^{-4} square feet per second (ft^2/sec). The fracture porosity was estimated at about 1% (Lane et al., 1996); at the quarry, the porosity of the weathered rock matrix adjacent to fractures was estimated to be at least 3% (Thompson et al., 2004). Consequently, based on this characterization, this fractured limestone had a low yield and was not capable of transmitting much fluid. However, it was capable of transmitting a quantity of DNAPL sufficient to impact this site.

In spite of the low yield, steam enhanced remediation (SER) was applied at this site (Davis et al., 2005), focusing the injection on the higher transmissivity zones. During SER, 21 thermocouple strings were used to track temperature changes and electrical resistance tomography (ERT) was used to track steam displacing water. Early in the operations, it became apparent that steam injection rates were much lower than the design required due to low transmissivities in the injection intervals and due to sparsely spaced fractures. In an attempt to inject more steam, three extraction wells were converted to injection wells. After 50 days of steam injection, funding for the project ran out. The highest recorded temperature away from the injection wells was approximately 50 degrees Celsius (°C). Only a small amount of contaminant mass was extracted; the total mass of contaminants removed from vapor and groundwater was 16.23 pounds (lbs), including 11.12 lbs of VOCs, which is less than a gallon of PCE. It was concluded that (Davis, 2005, p. viii), “for highly complex, low permeability fractured sites with low interconnectivity, such as the Loring Quarry, steam injection may not be the best method for remediation.”

8.3.3 Risks of Contaminant Dragdown and Cross-Contamination

The risk of enlarging the zone of chemical contamination by use of invasive methods is an important consideration that must be evaluated during a site investigation. Migration of NAPL and dissolved contaminants due to characterization activities may (1) heighten the risk to receptors, (2) increase the difficulty and cost of site remediation and/or (3) generate misleading data, resulting in a flawed conceptual model and flawed assessments of risk and remedy (Cohen and Mercer, 1993; Sterling et al., 2005).

Drilling, well installation and related activities (e.g., geophysical logging and hydraulic testing) typically create the greatest risk of causing contaminant migration during site investigation. In the absence of adequate sampling and monitoring as drilling progresses, it is possible to drill through a DNAPL zone without detecting its presence. Regardless of whether an outside-in or inside-out approach is chosen, characterization should proceed from shallow depths to greater depths to reduce the risk of mobilizing contaminants deeper. An example step-down protocol using multiple telescoped isolation casings to determine the vertical extent of contamination beneath a wood-preserving site in Florida is described in Box 8.4.

Box 8.4. Example Protocol to Determine Vertical Extent of Contamination (Mercer et al., 2006)

This example involves determining DNAPL in the Hawthorn Group, which underlies the Surficial Aquifer where source areas were located at a wood-preserving site in Florida. To determine the potential vertical extent of contamination in the Hawthorn Group and Upper Floridan (UF) Aquifer, monitoring wells were installed. The first well in each source area was located using results from a Surficial Aquifer study. During drilling, continuous split-spoon soil samples were collected and examined for the presence of DNAPL. If no DNAPL was observed immediately below the Upper Hawthorn Clay, then it was concluded that DNAPL did not penetrate the clay at this location. However, because DNAPL may have penetrated the clay at other locations, the most likely zone where DNAPL may have accumulated was targeted, which is the lower part of the Upper Hawthorn Group (UHG) on top of the next clay layer. Therefore, drilling continued through an isolation casing set into the upper clay to the lower part of the UHG. If DNAPL was present there based on visual examination of the split-spoon soil sample, then the well was completed in the lower portion of the UHG. If no DNAPL was observed there, then the borehole was backfilled and the well completed in the upper portion of the UHG. Lower Hawthorn Group (LHG) wells only were drilled if DNAPL was observed in the lower portion of the UHG. The logic for well completion in the LHG was the same as that just described for the UHG. In addition, UF Aquifer wells were drilled to estimate potential impacts to this aquifer. As many as four isolation casings were used in each well to reduce the potential for causing cross-contamination.

Conditions which may result in downward DNAPL and dissolved contaminant migration include (1) an open borehole during drilling and testing prior to well installation, (2) an inadequately sealed well or borehole and (3) a well completion that spans a barrier layer and connects clean and dirty zones. To minimize the risk of inducing DNAPL migration as a result of drilling, site investigators should (1) avoid unnecessary drilling, particularly in the source zone, (2) minimize the time during which a boring is open, (3) minimize the length of hole which is open at any time, (4) use telescoped casing drilling techniques to isolate shallow contaminated zones from deeper zones, (5) carefully examine materials brought to the surface (looking for evidence of DNAPL pools and/or changes in lithology) as drilling progresses to avoid drilling through a barrier layer beneath, (6) decontaminate equipment and (7) take other precautions as appropriate at specific sites.

The risk of cross-contamination is particularly acute when drilling through contaminated zones in fractured rock. Sterling et al. (2005) showed that severe cross-contamination effects can persist for years in sedimentary rocks with high matrix porosity, even when the time period of open-hole conditions causing the cross-connection is small, due in part to the lingering effects of back-diffusion. Noting well development and purging prior to sampling may not provide an adequate solution to cross-contamination, Sterling et al. (2005) warn:

> “When drilling takes place in an area of suspected or known contamination, the chances for predicting what will happen in any particular borehole are minimal because so many factors influence the outcome. Therefore, a major objective in drilling protocols should be to reduce cross contamination effects by minimizing the time period of open-hole conditions. Another approach for reducing these effects is to inflate packers or a liner in the hole to prevent vertical flow when drilling or other open-hole activities, such as geophysical logging, are not in progress. This involves extra effort initially but saves considerable time and effort needed to purge the affected wells and reduces the uncertainty with interpretation of the natural site conditions on contaminant distribution prior to the system being disturbed.”

As reported in Box 8.2, despite taking such safeguards (as liner emplacement prior to well construction), cross-contamination is reduced, but not eliminated.

8.4 DATA INTERPRETATION

Data collection is usually very expensive. Therefore, it is important to pull as much information out of the data as possible. Tools (e.g., geographical information systems) are available to display and analyze data graphically (e.g., using bubble plots of concentrations and time-series plots). More detailed analysis may include flow and transport modeling. In addition, there are numerous data analysis methods and interpretations that can be made, some of which are discussed below. Another important aspect of data analysis is making sure that the data are representative and not caused by cross-contamination.

8.4.1 Interpretation of DNAPL Presence

Direct observation of DNAPL is difficult at many sites, hence the use of hydrophobic dye to enhance its detection. At residual saturation, DNAPL will not flow to a well and, depending on its appearance and distribution, it may be difficult to identify visually in soil and rock core. In addition, complex DNAPL architecture may lead to highly stratified dissolved-plume concentrations that can be difficult to differentiate. For these reasons, indirect methods are used to infer DNAPL presence, including (1) observation of contamination in hydraulically anomalous locations, (2) persistence of contamination and (3) elevated groundwater, soil-gas and soil concentrations.

Laboratory experiments show NAPL : water equilibrium (dissolved concentrations at aqueous solubility limit) at typical groundwater velocities of 10–100 cm/day flow. Groundwater concentrations at DNAPL sites, however, are typically less than 1% to less than 10% of the DNAPL aqueous solubility limit (mg/L) due to non-uniform NAPL distribution, mixing of groundwater in sampled wells and effective solubility (for DNAPL mixtures). Elevated concentration data that suggest DNAPL presence include: (1) dissolved concentrations greater than 1% of aqueous or effective solubility, (2) soil concentrations greater than 10,000 mg/kg (or exceeding a limit determined by site-specific partitioning calculations) and (3) organic vapor analyses greater than 100–1,000 ppm (Pankow and Cherry, 1996). Using analyses of soil chemistry along with estimates of soil porosity and partitioning parameters (e.g., f_{oc} and K_{oc}), equilibrium partitioning calculations can be made to determine if NAPL is present and to estimate its saturation and distribution between phases (Feenstra et al., 1991; Mott, 1995; Mariner et al., 1997; McCray and Cohen, 2003).

8.4.2 Source Strength

Source strength refers to the total DNAPL mass present and its rate of dissolution (i.e., the mass of contaminants released into groundwater per unit time). Estimates of DNAPL mass are usually highly uncertain and can be based on (1) soil concentrations from multiple borings where soil concentration data indicate DNAPL presence, (2) DNAPL thickness measurements in multiple wells and (3) PITT results (e.g., Jin et al., 1995). If DNAPL flows into a well, then the DNAPL elevation and thickness in the well can be determined and a DNAPL sample obtained for property determination (e.g., density, viscosity, composition, interfacial tension). Care must be taken on how to interpret measurements of DNAPL elevation and thickness in wells (Cohen and Mercer, 1993). Other invasive tools include borehole geophysics. Unfortunately, DNAPL is a poor target for geophysical methods, and they are unlikely to detect DNAPL (Kavanaugh et al., 2003). Residual DNAPL saturations may be estimated using a PITT by comparing the retardation of tracers that partition into the DNAPL (e.g., alcohols) to tracers that are not retarded (e.g., bromide). Advantages and limitations of PITT are listed in Appendix 8.A. Another way to estimate DNAPL saturation is the push-pull partitioning tracer test using naturally occurring radon-222 (Davis et al., 2003). The DNAPL dissolution rate depends on the local and variable groundwater flow rate (a function of the permeability distribution), DNAPL architecture and the effective solubility of the chemicals in the DNAPL.

8.4.3 Mass Flux

Mass flux is used to assess DNAPL impacts to groundwater; it provides an estimate of DNAPL source strength and mass loading. It also can be used as a metric to assess source remediation and is a key input to evaluate MNA, for which one needs to know (1) source strength (contaminant flux leaving the source), (2) natural attenuation rate and (3) remediation performance at a downgradient compliance point.

Three methods to measure mass flux are discussed in Appendix 8.A. These include (1) using water quality data from transects (multiple locations and depths) and groundwater velocity, (2) using sorptive permeable media in downgradient wells to intercept contaminated groundwater and release resident tracers (the passive flux meter method) and (3) plume capture by pumping (the integral pumping method).

8.4.4 Plume Longevity

At many DNAPL sites, the requirement for source zone treatment hinges, in part, on the question of plume longevity. If MNA alone is selected, how long will the DNAPL source continue to dissolve and feed the downgradient aqueous plume? If partial mass removal is conducted, how will that change plume longevity? In order to answer these questions, the source strength must be known, including the amount of DNAPL mass and its dissolution rate, the amount of sorbed mass and its desorption rate, the mass that is stored in fine-grained material, and the back-diffusion rate. Having these and other data, the only way to make plume longevity predictions is with the use of models, such as SEAM3D (Waddill and Widdowson, 2000).

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APPENDIX 8.A. DNAPL Site Characterization Methods (after USEPA 2004; Mercer and Cohen, 2003; Kram et al., 2001)[1]

Method	Uses/Advantages	Limitations
Desktop Review		
Review Site History Information • Chemical use, inventory, handling and disposal records • Site engineering drawings • Historic aerial photographs • Employee/witness interviews References: Newell and Ross (1992); Cohen and Mercer (1993); Pankow and Cherry (1996); ITRC (2003)	• Site investigation should begin with a review of site use/history information to assess chemical use, release, disposal and contamination • Information will help guide subsequent characterization work	• Requires field confirmation • Does not reveal adequate information regarding subsurface migration and fate
Literature Review		
• Geologic, hydrogeologic and soils reports • Prior site investigation reports	• Used to develop/refine CSM and guide characterization work	• Unlikely to provide adequate detailed information regarding site-specific conditions
Soil Gas Survey Methods		
Soil Gas Surveys – NAPL VOCs *Active grab sampling* – After driving a hollow probe with a porous tip to a target depth (e.g., using direct push, rotary hammer or other methods), a vacuum is applied to with draw soil gas. The gas is captured for VOC analysis in metal canisters, Tedlar bags or by a syringe needle from the vacuum hose for direct injection to a field GC. *Passive sampling* (e.g., Gore-Sorber® and Quadrel Enflux® samplers) – Involves shallow burial of a sorbent sampling device in a hole made using hand tools, retrieval after allowing days to weeks for soil gas to diffuse and sorb to the sampler, and laboratory chemical analysis. References: ASTM D5314-92 (2006); Marrin and Thompson (1987); Devitt et al. (1987); Marrin (1988); Marrin and Kerfoot (1988); Cohen and Mercer (1993); Rivett (1995); Pankow and Cherry (1996); USEPA (1997b); USEPA (1998a;b); Wolfe and Williams (2002); www.geoprobe.com	• Can provide indirect evidence of volatile NAPL presence in the vadose zone based on detection of very high concentrations (approaching saturated vapor concentrations) • Under certain conditions, this method also can be used to delineate shallow groundwater contamination • May be used to focus subsequent drilling/probing • May be used to help assess risk • Rapid	• Unlikely to be able to delineate NAPL and VOCs at depth below the water table due to limited volatilization • Potential misinterpretation due to heterogeneity • Active sampling not effective in fine-grained soil (clay and silt) • Older releases may have a limited signal due to prior contaminant volatilization, especially in hot dry areas • False negatives

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[1] References cited in Appendix 8.A are listed at the end of Chapter 8.

Method	Uses/Advantages	Limitations
Soil Gas Surveys – NAPL Derivatives Soil gas surveys can be used to infer NAPL presence based on the distribution of biodegradation products such as CH_4 in the subsurface. Reference: Marrin (1987)	• See above • CH_4 concentrations generated in NAPL-contaminated soil can be within the percent range and correlate directly with NAPL distribution	• Potential misinterpretation due to heterogeneity • Degradation products may not be concentrated at new releases
Soil Gas and Groundwater Surveys for Radon-222 Radon-222 is a naturally occurring, radioactive, inert isotope that occurs in soil gas and in groundwater as a dissolved gas. Part of the uranium-238 decay series, radon-222 has a half life of 3.8 days and is continuously generated by the decay of radium-226, which has a half life of 1600 years and is present in minerals and secondary mineral coatings. Due to its non-polarity, radon-222 partitions preferentially into a wide range of NAPLs relative to air and water. Thus, radon-222 concentrations in soil gas and groundwater tend to be anomalously low in the vicinity of NAPL contamination. References: Semprini et al. (1998); Semprini et al. (2000); Schubert et al. (2002); Davis et al. (2002); Davis et al. (2003); Hohener and Surbeck (2004)	• Provides indirect evidence of NAPL presence/absence • Sampling and analysis is relatively simple, fast, and easily combined with traditional soil gas and groundwater monitoring	• Potential misinterpretation due to subsurface heterogeneity • Specialized sampling and analysis procedures needed • May only be effective to help delineate NAPL at heavily contaminated sites with uniform spatial generation of Rn-222
Surface Geophysical Survey Methods		
Surface Geophysical Surveys – Overview Several surface geophysical survey methods have been widely used to enhance contamination site characterization and focus investigation activities. References: ASTM D6429-99 (2006); Zohdy et al. (1974); Benson et al. (1982); USACE (1995); USEPA (1997a); Reynolds (1997); USEPA (1993); ITRC (2000); USEPA (2000); Allen (2004); http://water.usgs.gov/ogw/bgas/full_biblio.html	• See below	• Geophysical interpretations are always subject to ambiguity and uncertainty • See below
Electrical Resistivity (ER) ER measurements are made by injecting a current into the earth through a pair of electrodes and measuring the resultant potential drop (voltages) from the earth at the second pair of electrodes. The current and	• Used to delineate stratigraphy, infer depth to water table, locate fractures and faults in rock, identify karst features, delineate buried waste and map conductive plumes	• Generally not applicable for direct detection of pre-existing DNAPL • Spatial variability and anomalies can be caused by several factors, thereby confounding interpretation

Method	Uses/Advantages	Limitations
potential electrodes are arranged in a linear array. ER generally decreases with increasing clay mineral content, water content, and water ionic strength. Measurement depth is typically 25% of the electrode spacing, which can be progressively increased (using multi-electrode arrays) to determine lateral variations in resistivity at a given depth of penetration. ER surveys include profiling with fixed electrode spacing, 1D sounding by increasing electrode spacing at a fixed location, and computer-controlled 2D and 3D imaging using multi-electrode arrays and an automatic electrode switching system to depths of several hundred feet. The development of multi-electrode resistivity data acquisition systems and inversion methods in the 1990s greatly increased the speed and cost-effectiveness of ER survey work. References: ASTM D6431-99(2005); Sauck (2000); Atekwana et al. (2001); Werkema et al. (2002); Atekwana et al. (2002); Atekwana et al. (2003); Atekwana et al. (2004); Werkema et al. (2004); Watson et al. (2005); www.agiusa.com; www.abem.se	• Can be used to map potential fluid migration pathways and DNAPL traps (e.g., depressions in the surface of a fine-grained capillary barrier) • Can help delineate highly-resistive NAPLs if present in sufficient extent • Aged hydrocarbon LNAPL contamination has been shown to produce low ER anomalies, apparently due to the release of ions from formation solids by reaction with organic acids or carbonic acids derived from biodegradation • Rapid survey method	• Difficult to distinguish geophysical signature of DNAPL from other lithologic and fluid variations • Resolution decreases significantly with depth
Frequency Domain Terrain Conductivity Electromagnetic (EM) Methods Terrain Conductivity EM systems use a transmitter that emits a sinusoidally varying current at a specific frequency to a transmitter coil, which in turn, creates a primary EM field at the ground surface. The time-varying primary magnetic field induces eddy current loops in the earth, which create a secondary magnetic field in the ground. Both fields are measured at the receiver, and the meter electronically separates the received signal into a component that is in-phase with the transmitted field and a second component that is 90 degrees out-of-phase (quadrature phase) with the transmitted field. The quadrature phase can be related directly to subsurface electrical conductivity. The in-phase signal is not directly related to	• Used to detect and map shallow, lateral changes in subsurface electrical conductivity • Can be used to detect and map conductive contaminant plumes • Can be used to map buried wastes, metal drums, tanks and metal utilities • Aged hydrocarbon LNAPL contamination has been shown to produce high conductivity anomalies apparently due to the release of ions from formation solids by reaction with organic or carbonic acids derived from biodegradation processes • Does not require ground contact to make measurements	• Interpretation is qualitative • Limited depth penetration • Limited vertical resolution • Generally not applicable for direct detection of pre-existing DNAPL • Affected by cultural features, such as buried utility lines, fences, radio transmitters and building foundations

Method	Uses/Advantages	Limitations
ground conductivity, but is sensitive for locating buried metal objects (e.g., steel drums and tanks). The depth range from which data can be obtained increases with the distance between the two coils and is greater when the coils are oriented planar to the ground than when they are oriented at right angles to the ground. Commonly used terrain conductivity meters include Geonics' EM-31 meter, which has an intercoil spacing of 3.66 m and can measure to 6 m, and Geonics' EM-34, which can use intercoil spacings of 10 m, 20 m, and 40 m to measure to 60 m. Continuous or station measurements are recorded, and vertical soundings can be made using the three EM-34 intercoil spacings (and two coil orientations). References: ASTM D6639-01; McNeill (1990); www.geonics.com	• Measurements are easy to make and data require little processing	
Very Low Frequency (VLF) EM VLF-EM survey instruments measure magnetic fields in long conductive bodies, such as water-filled fractures and ore dikes, that are induced into the earth by high-powered military radio transmitters (used for submarine navigation) broadcasting in the 15 to 30 kHz range. Station measurements are made on a grid to locate vertical or steeply inclined EC anomalies, which may include bedrock fracture zones, clay-filled sinkholes, buried wastes, etc. References: www.abem.se; www.geonics.com	• Most commonly used to map near-vertical bedrock fracture zones, conductive groundwater contamination, and mineralized zones • Simple, rapid, one-person operation • Reported investigation depth ranges from 30 to 250 feet	• Cannot detect DNAPL • Ability to detect features is limited by their orientation relative to military transmitters • Data interpretation may be ambiguous • Interference from buried metal pipes, power lines, etc.
Fixed Source Time Domain EM (TDEM) These methods use a receiver to measure the decay of secondary magnetic fields, which are induced by pulsing electrical current through a transmitter and governed by the electrical resistivity of subsurface. A square wave with a frequency on the order of 1–100 Hz is passed through a square loop of transmitter wire (1 to >1,000 feet per side) at the ground surface to establish a magnetic field in the subsurface. When the current is shut off (for an equivalent period), the	• Primarily used to determine depth and thickness of geologic strata • Can provide excellent lateral resolution using adjacent soundings • Can be used to detect and map conductive landfill leachate plumes, seepage from brine pits, saltwater intrusion and for mineral exploration • Requires less space than resistivity measurements to reach the same depth	• Generally not applicable for direct detection of DNAPL • Spatial variability and anomalies can be caused by several factors • Deep measurements require a large transmitter coil (1,000 feet per side) which may exceed accessible space • Susceptible to interference from nearby metal pipes, cables, fences, vehicles and induced noise from power lines

Method	Uses/Advantages	Limitations
collapse of the magnetic field induces a time-dependent voltage that is measured at a smaller receiver coil (placed at the center or just outside of the transmitter loop) and caused by variations in electrical conductivity with depth. The process is repeated to enhance resolution. The voltage-time data are inverted to estimate electrical conductivity versus depth. Investigation depth range is on the order of the transmitter coil size and can range from about 3 to 3,000 feet. References: ASTM D6820-02; Hoekstra et al. (1992); www.geonics.com		• Not effective for imaging shallow strata ($<$20 feet) • May fail to detect thin, resistive layers
Ground Penetrating Radar (GPR) Short pulses of high frequency electromagnetic waves are radiated into the subsurface from a transmitter. Wave propagation velocity is related to electrical properties of the subsurface. Upon meeting layers and objects with contrasting electrical impedances (due to changes in dielectric constant and electrical conductivity), the pulses are partly reflected back to a receiving antenna. Reflector depths are determined by measuring arrival times and amplitudes of successive reflected waves. The reflected signals are recorded as the unit is pulled across the ground and used to produce a continuous cross-sectional image, which can reveal features such as bedding, cementation, clay content, voids, fractures and man-made structures. Radar penetration depth is controlled by wave frequency and the electrical properties of subsurface materials. Conductive strata (e.g., clay and shale) have high attenuation rates that limit radar penetration to less than a few feet. Signals can penetrate to much greater depth ($>$100 feet) in resistive media such as dry sand or granite. References: ASTM D6432-99(2005); Brewster and Annan (1994); Brewster et al. (1995); Bermejo et al. (1997); Lane et al. (2000); USEPA (2000); www.sensoft.ca; www.geophysical.com	• Primarily used to obtain high resolution cross sections of shallow stratigraphy and to locate buried utilities or other objects and structures (e.g., tanks, drums, waste pits) • Can delineate the surface of the uppermost fine-grained capillary barrier layer along which DNAPL may flow or accumulate in depressions • Can reveal the water table • Can help locate NAPL if a high reflective contrast exists between NAPL and surrounding media, and sufficient NAPL is present • Rapid survey method	• Generally not applicable for direct detection of pre-existing DNAPL • Not useful to examine conditions in or below conductive strata (e.g., clayey soil and shale); thus depth of investigation may too shallow to be useful • Data acquisition may be slow in difficult terrain • Near surface artifacts and aboveground features may scatter transmitted energy, add noise to the received signal, and/or reduce penetration depth

Method	Uses/Advantages	Limitations
Magnetometers Magnetometers are used to measure the strength of the earth's magnetic field and locate buried ferrous metal objects (e.g., drums, pipelines, USTs, buried waste, etc.) that perturb the magnetic field. Surveys are typically conducted in parallel lines along a grid, with the separation between lines no greater than half the expected target depth. Magnetometers respond only to ferrous metals and their response is proportional to the mass of iron in the target. References: www.geometrics.com; www.gemsys.ca	• Can locate buried drums or tanks that may have contained NAPL (including in electrically conductive soils where GPR does not work) • Used to locate unexploded ordinance • Used to map soil and rock with magnetic contrasts and karst features • Rapid survey method	• Not applicable for direct detection of DNAPL • Effectiveness can be reduced by natural fluctuations in earth's magnetic field and by interference (noise) from iron debris, pipes, fences, buildings, and vehicles
Seismic Reflection Seismic reflection surveys measure the two-way travel time of seismic P waves from a ground surface energy source (such as a sledgehammer blow on a strike plate) down to geologic contacts where part of the seismic energy is reflected back to geophones and digital data recording systems (seismographs) at the surface. Reflections occur at subsurface acoustic horizons where there is a contrast in the density and velocity between two layers. Lines and grids of seismic source impacts and geophones are used, respectively, to perform 2D and 3D seismic reflection surveys. *Amplitude Versus Offset (AVO)* analysis involves comparing near and far offset tracks to see if there is an impedance change indicated by the amplitude of reflected P waves for angles of incidence $>30^{o}$. The field data are compared with modeled AVO responses to determine if there is deviation from the expected response that may result from NAPL presence. References: ASTM D7128-05; Adams et al. (1998); USEPA (1998c); NAVFAC (1999); Temples et al. (2001); Griffin and Watson (2002b); www.geometrics.com; www.abem.se	• Excellent tool for mapping subsurface stratigraphy, and potential preferential DNAPL flow pathways and traps • Used to provide high-resolution images of soil/rock strata as thin as a few feet in a depth range from ~20 to >1,000 feet • Unlike GPR, can be used to image strata below high conductivity media • Reflection anomalies might be used to detect NAPL if it is present in sufficiently large quantities	• During testing at three U.S. Navy demonstration sites, validation probing detected DNAPL in only 1 of 27 locations where seismic reflection surveying predicted its presence • Slower application rate than most geophysical methods • Requires extensive processing • Vertical seismic profiles need to be made in wells or boreholes to calibrate seismic data to depth • Generally not suitable for imaging very shallow strata
Seismic Refraction Seismic refraction is used to determine the P-wave velocity structure in the subsurface and the depths to layers with a significant change in P-wave	• Most often used to map overburden (unconsolidated material) thickness and bedrock topography where	• Not applicable for DNAPL detection • Generally limited to depths of <300 feet and resolution of 2 to 3 layers

Method	Uses/Advantages	Limitations
velocity (e.g., overburden to rock). Typically 12 to 24 geophones are deployed at intervals of 5 to 50 ft, in line with a seismic shot source. Lateral resolution is controlled by geophone spacing. A portion of the seismic waves generated by a shot on the surface propagate downward and undergo critical refraction in accord with Snell's Law at interfaces between materials of different seismic velocities. These seismic 'head' waves travel along an interface with the velocity of the underlying (faster) layer. Secondary waves emanating from head waves are returned to the surface at the critical angle of refraction (which depends on the ratio of layer velocities), detected by geophones, and recorded by a seismograph. Shots are typically made at and beyond both ends of the spread, and at intermediate positions, to acquire sufficient refracted wave travel time data at each geophone. Seismic velocities in each layer and depths to each layer are calculated using a horizontal layered earth model. References: ASTM D5777-00(2006); Haeni (1986); Haeni (1988); Taucher and Fuller (1994); Murray et al. (1999); www.geometrics.com; www.abem.se	there is a single overburden unit • Can also be used to measure landfill depth • Provides data to depths of 100 feet or more • Can resolve up to 3 or 4 layers • Used to assess rock strength, the degree of weathering of in the upper bedrock, rippability, and shallow fault/fracture zone presence • The seismic energy source can be as simple as an 8-pound sledgehammer	• Seismic velocity of layers must increase with depth (will not detect lower low velocity layers) • Will not detect thin layers • Survey line length (source to farthest geophone) may need to be 4 to 5 times the desired depth of investigation • Sensitive to acoustic noise and vibration • Deep measurements may require explosives to provide a greater source of energy
Sample Examination Methods to Detect NAPL		
Organic Vapor Analysis (OVA) for Screening Samples OVA measurements are made using a flame ionization detector (FID) and/or a photoionization detector (PID) to screen soil/rock samples for VOC contamination (and to monitor air quality). Soil core is typically screened every 6 to 12 inches by inserting an OVA probe tip into a freshly opened void space in the core and recording peak readings, or by measuring vapors in the headspace of sample jars or bags. Vapor concentrations emitted from a NAPL may be much less than the saturated vapor concentration of a pure chemical. Very high OVA readings (e.g., >1,000 ppmV) may suggest NAPL presence.	• Rapid and inexpensive • High concentrations of VOCs (>1000 ppm vapor) may suggest NAPL presence • Useful to focus sampling	• Readings sensitive to effective contaminant volatility, water content, sample temperature, and sample handling • Screening tool only, often used to help select soil subsamples for analysis

Method	Uses/Advantages	Limitations
References: Cohen et al. (1992); Feenstra and Cherry (1996); Griffin and Watson (2002a, 2002b)		
UV Fluorescence Inspection for NAPL Fluorescence refers to the spontaneous emission of visible light resulting from a concomitant movement of electrons from higher to lower energy states when excited by ultraviolet (UV) radiation. Samples and core can be inspected in a dark space under UV light (e.g., using a small portable UV light box) for fluorescence, which may indicate the presence of NAPL containing polyaromatic hydrocarbons (PAHs) or other commingled fluorophores. Fluorescent response depends on UV excitation wavelength. Known background soil and NAPL-contaminated samples should be checked for interference and site-specific NAPL response. References: Kram et al. (2001a,b); Kram and Keller (2003a,b); Kram and Keller (2004); www.ptsgeolabs.com	• Can illuminate NAPLs that fluoresce including those that contain PAHs (coal tar, creosote, and petroleum products) and those mixed with fluorescent impurities (e.g., oil and grease removed by solvent during degreasing, or humic compounds from natural organic matter) • Can provide detailed information on relationship between stratigraphy and fluorescent NAPL distribution • Can guide selection of subsamples for chemical or saturation analyses	• Chlorinated solvents generally do not fluoresce when exposed to ultraviolet-visible light unless commingled with sufficient fluorescent impurities • Indiscriminant • Interference from non-target fluorescent materials (such as shell fragments in coastal sediment) • Significant potential for false positives and false negatives
Hydrophobic Dye Shake Test to Detect NAPL Direct visual detection of NAPL in soil or water may be difficult where the NAPL is clear and colorless, present at low saturation or distributed heterogeneously. Hydrophobic dye can assist visual detection of NAPL. The test involves adding a very small amount of a hydrophobic dye (e.g., 2 mg), such as Sudan IV, soil (e.g., ~20 cm^3), and a small volume of clean water (~15 mL) in a sealed plastic or glass jar (e.g., a 40-mL vial), which is then capped and shaken by hand. Sudan IV is a reddish-brown powder that dyes organic fluids red upon contact, but is practically insoluble in water at ambient temperatures. If NAPL is present in sample (and contacts the dye), it will appear as red globules, a red meniscus, a red film, etc. Background and NAPL-contaminated samples should be examined to check for interference and site-specific response. A similar test can be made on water samples	• Fast, inexpensive, and direct method for identifying NAPL presence in soil or water samples • Capable of detecting clear, colorless NAPL at low saturations	• Potential for false negatives; can only detect NAPL if present in subsample examined • Visual contrast can be difficult to see in dark soil • Precaution should be taken to avoid complete evaporation of highly-volatile NAPL from sample • Like many solvent dyes, Sudan IV is an irritant and possible mutagen; skin and eye contact should be prevented

Method	Uses/Advantages	Limitations
by adding dye. Test kits with enhancements are available commercially. References: Cohen et al. (1992); Parker et al. (2003); www.oil-in-soil.com		
Using NAPL FLUTe^{TM} to Detect NAPL in Soil Cores The NAPL FLUTe^{TM} liner developed for downhole placement (see related entry) also can be used above ground to detect NAPL presence in core samples. The liner cover is a hydrophobic dye-striped tubular fabric that can be slipped over core extruded during sonic drilling. A tubular plastic core cover is then slipped over the NAPL FLUTe^{TM} liner, knotted at each end to contain fluid and vapor, and laid down (and/or rolled) so that the core presses against the liner. After allowing at least several minutes for contact between NAPL and the liner, the core covers are opened, the core is logged and the liner is inspected for stains indicative of NAPL presence. References: Griffin and Watson (2002a, 2002b); www.flut.com	• Relatively simple and direct detection of NAPL • Can provide detailed information on relationship between stratigraphy and contaminant distribution • Provides focus to core examination • Amenable to rapid documentation via photography	• Relatively ambiguous reaction to some NAPLs may be difficult to interpret • Possible color fading and/or non detection due to evaporation • Potential for false positives and false negatives • Wicking may exaggerate NAPL presence
Chemical Analysis of Soil and Equilibrium Partitioning Calculation Subsamples are taken as quickly as possible, to minimize VOC volatilization, from freshly exposed soils or undisturbed cores (after exposing an interior core section) using a dedicated or decontaminated small-diameter core sampler (e.g., the En Core® sampler). The sample is extruded into a pre-weighted glass VOA bottle, which may contain a known volume of HPLC-grade methanol for preservation and VOC extraction, and analyzed to determine chemical concentrations in the wet soil sample. Based on estimates of soil porosity and chemical partitioning properties, equilibrium partitioning calculations can be used to evaluate if NAPL is present, its saturation and chemical partitioning among soil, water and NAPL.	• Convenient method to assess NAPL presence and chemical partitioning using soil analysis data	• Method requires estimates of porosity and contaminant partitioning parameters (e.g., k_{oc} and f_{oc} data), which may be subject to significant uncertainty • Can only detect NAPL if present in subsample • Potential loss of volatiles during sampling

Method	Uses/Advantages	Limitations
References: Feenstra et al. (1991); Mott (1995); Mariner et al. (1997); McCray and Cohen (2003)		
Direct-Push Characterization Methods		
Direct Push (DP) Probing and Sampling Methods DP systems refer to equipment and methods used to perform subsurface investigations by driving, pushing and/or vibrating small-diameter hollow steel rods into the ground; and then sampling, sensing or testing subsurface media using a variety of attached and inserted tools and sensors. Information regarding widely-used DP systems (percussion probing with GeoProbe® equipment and Cone Penetrometer Testing) is presented below. References: ASTM D6001-05; ASTM D6282-98; ASTM D6724-04; ASTM D6725-04; ASTM D3441; ASTM D6067-96; USEPA (1997c); USEPA (2004); USEPA (2005a); McCall et al. (2005)	• Rapid stratigraphic logging and contaminant detection using sensors • Rapid depth-discrete sampling of soil, soil gas, and groundwater • Little investigation derived waste • Minimally invasive; effective grouting and sealing capabilities • Reduced potential for contaminant drag-down • Reduced cost and wide availability	• Penetration limited by gravel layers, cobbles, boulders, dense stiff soils, highly cemented soils and rock • DP can cause some smearing, which can affect water levels of hydraulic test results • Not suitable for constructing telescoped wells
Percussion Probing – GeoProbe® Direct-Push Methods Hydraulically-powered DP machines use a relatively small amount of vehicle weight combined with percussion to advance a steel rod and tools, typically less than 100 ft, into unconsolidated sediments. Available tooling includes: soil core, groundwater, and soil gas sampling tools; as well as equipment for performing hydraulic conductivity testing, Standard Penetration Tests, and direct imaging (e.g., Membrane Interface and Electrical Conductivity Probes). References: ASTM D6001-05; ASTM D6282-98; ASTM D6724-04; ASTM D6725-04; USEPA (1997c); USEPA (2004); USEPA (2005a); McCall et al. (2005); www.geoprobe.com	• Less expensive than CPT • More mobile and available than CPT • Well-developed soil gas, soil, and groundwater sampling tools/methods • Other sensors available for use include the LIF probe, MIP, electrical resistivity and conductivity probes, natural gamma logging tools and downhole cameras	• Difficult to penetrate hard dense soils • More restrictive depth limitation than CPT
Cone Penetration Testing (CPT) – 3 Channel Piezocone Hydraulic rams, supported by the reaction weight of a 10 to 40 ton truck, are used to push a narrow diameter (1.44 or 1.77 in) rod with a conical point	• Rapid, high resolution (to 2 cm), stratigraphic characterization tool capable of penetrating 200 to 500 ft/d • Typically applied to up to 300 ft	• Data need to be calibrated against conventionally logged borehole(s) • Penetration resistance limitations

Method	Uses/Advantages	Limitations
into the ground at a maximum steady rate of 2 cm/s. An instrumented cone probe measures penetration tip resistance, sleeve (side) friction and pore pressure. The tip resistance and friction values, which are measured using load cells, are then related to soil behavior type. Sandy soils have high tip resistance and low sleeve friction; clayey soils have low tip resistance and high sleeve friction. Pore pressure is measured using a pressure transducer connected to a ceramic screen mounted just above the cone tip. Pressure exerted on water by cone advancement dissipates more quickly in permeable media (e.g., sand) than in finer grained units. Hydraulic conductivity of tight media can be estimated *in situ* using the CPT pore pressure dissipation test. Penetration depth is measured using a linear displacement transducer. The soil behavior data are transmitted up-hole via cabling, typically recorded each second (providing a spatial resolution of 2 cm), and compiled to generate logs, which are interpreted to delineate stratigraphy and estimate hydraulic conductivity. References: ASTM D3441; ASTM D6067-96; Robertson and Campanella (1986); Chiang et al. (1992); Berzins (1993); Lutenegger and DeGroot (1995); Lunne et al. (1997); USEPA (1997c); McCall et al. (2005); http://www.vertek.ara-robotics.com/	• Inclinometer measurements can be used to indicate if rods are bending (and the push should be terminated) • Retraction grouting and/or grouting during advancement can be used to reduce risk of cross-contamination • Greater depth penetration than percussion probing methods • CPT tools can be used to sample soil, soil gas, and groundwater • Other sensors available for use with CPT include the LIF probe, MIP, electrical resistivity and conductivity probes, nuclear logging tools (including natural gamma), GeoVIS, seismic geophones, etc.	• Heavier trucks, which allow deeper penetration, are more difficult to maneuver off road • Cannot be used on steep slopes • Compared to Geoprobe, CPT is more expensive, less maneuverable and less available
Membrane Interface Probe (MIP) Developed by Geoprobe® Systems, the MIP is a screening tool that provides real-time, near-continuous, semi-quantitative data on VOCs extracted from soil as it is advanced using DP methods (typically at a rate of 1 ft per minute). The MIP is deployed in tandem with a soil conductivity (SC) tool, which uses a dipole arrangement to log electrical conductivity for stratigraphic interpretation. The MIP membrane (a semi-permeable thin film polymer impregnated into stainless steel screen) is seated in a steel plate that is heated to 100 to 120^o C.	• Widely available • Provides simultaneous log of VOCs and soil conductivity • Operates in vadose and saturated zones • Useful for delineating NAPL source zones • Rapid site screening (typically 150 to 300 ft per day)	• High detection limits • Qualitative analytical data • Designed for VOCs; cannot detect compounds with boiling points $>250^o$ F • Contaminant carryover can be high • Penetration resistance limitations • Shallow use (generally <60 ft) • Through tip, retraction grouting not available on standard Geoprobe unit

Method	Uses/Advantages	Limitations
Heating enhances the diffusion of VOCs through the membrane. The flow of gas or liquid, however, is resisted by the hydrophobic membrane. A clean, inert carrier gas sweeps through tubing attached behind the membrane and carries VOCs to gas phase detectors at the surface. Detectors used commonly include a PID for aromatic hydrocarbons, an electron capture detector (ECD) for halogenated compounds, and a FID for aliphatic hydrocarbons. Detection limits vary, but are on the order of 200 ppb for chlorinated compounds using an ECD, 1 ppm for BTEX compounds using a PID, and 1 ppm for BTEX and chlorinated compounds using a FID. Results are reported as detector response in microvolts (uV) and reflect relative total VOC concentrations. The MIP also records and graphs sample depth, soil conductivity, and temperature. References: Christy (1996); Griffin and Watson (2002a, 2002b); Myers et al. (2002); USEPA (2004); www.geoprobe.com		
Laser Induced Fluorescence (LIF) Probes Laser Induced Fluorescence (LIF) tools employ a laser to pulse excitation light down fiber optic cable within DP rods to a sapphire window located near the bottom of Cone Penetrometer (CPT) or Geoprobe rod string. The excitation light induces fluorescence of 2-ring and higher PAH compounds and/or other fluorophores located across the sapphire window. This fluorescent light is transmitted up-hole through a second cable to a surface detection system. Fluorescence intensity and spectral waveforms are recorded continuously in real time and interpreted to infer NAPL presence and distribution. LIF systems that have been deployed on CPT and/or Geoprobe units include: SCAPS, ROST^{TM}, UVOST^{TM}, and TarGOST^{TM}. An alternative type of downhole fluorescence probe is the	• Used for continuous logging/ detection of petroleum products (i.e., gasoline, diesel fuel, and jet fuel), coal tar, and creosote • Possible use for solvent NAPLs, commingled with fluorescent compounds • CPT/LIF provides concurrent delineation of stratigraphy and fluorescent contamination • Typical daily probing of 300 to 500 ft at 10 to 20 locations • LIF waveforms allow product identification and rejection of non-contaminant fluorescence • Reduced IDW and exposure to site contaminants	• Primarily applicable to PAHs; very limited use/experience at chlorinated solvent sites • Subject to interferences • NAPL has to be adjacent to sapphire window • Penetration resistance limitations • Limited availability

Method	Uses/Advantages	Limitations
Fuel Fluorescence Detector (FFD), which uses a downhole mercury lamp for its UV light source. See references for product information. References: ASTM D6187-97; USEPA (1998a; b); Kram et al. (2001b); USDOE (2002); Kram and Keller (2003a; b); Kram et al. (2003); www.dakotatechnologies.com; www.fugro.com; http://www.vertek.ara-robotics.com/		
Direct-Push Electrical Conductivity (EC) Logging Using DP methods (including Geoprobe® and CPT), a high-resolution measure of the apparent electrical conductivity of an interval of unconsolidated media is calculated as an imposed current is passed through it. Higher EC values generally correlate with fine-grained strata, and lower values indicate coarser sediments. References: Beck et al. (2000); Schulmeister et al. (2003); Sellwood et al. (2005); Wilson et al. (2005); Harrington and Hendry (2006); www.geoprobe.com	• Small electrode spacing (e.g., 0.02 m) allows the sensor to resolve stratigraphic units and sample a small outer radius (e.g., 5 to 10 cm) • Data collected every 15 cm • DP method (and grouting) limit potential for cross-contamination • Rapid stratigraphic characterization	• Penetration resistance limitations • Variations in EC caused by fluid saturation and chemistry can confound interpretation • Data should be calibrated against conventionally logged borehole(s)
Direct-Push Natural Gamma Logging Small diameter natural gamma logging tools have been developed for use with DP rigs. These include slim loggers that are lowered in an open borehole or DP rods after probing to a set depth, and a gamma sensor built into a standard cone penetrometer that measures cone resistance, sleeve friction, and gamma counts as it is pushed though overburden. Natural gamma logs can be used to delineate stratigraphy because clayey sediments emit higher gamma radiation than sands. References: USEPA (1997c); Viellenave and Fontana (1999); McCall et al. (2005)	• Rapid stratigraphic characterization • Unlike EC methods, natural gamma tools are not sensitive to water chemistry and saturation, thereby reducing log ambiguity	• Logging within steel rods reduces overall gamma radiation coming from the formation • Data should be calibrated against conventionally logged borehole(s)
CPT In-Situ Video Camera The GeoVIS probe, developed by the Navy and deployed using a CPT, is an *in situ*, downhole video microscope that can provide detailed imagery documenting soil characteristics and	• Can provide direct evidence of NAPL presence and distribution based on video image processing • Provides continuous, high-resolution view of soil with	• Unless NAPL is black or highly colored, it may be difficult to detect • Penetration resistance limitations

Method	Uses/Advantages	Limitations
NAPL distribution. The device illuminates the subsurface across a sapphire window on the side of the probe. Video signals from a miniature color CCD camera are returned to the surface, where they can be viewed in real time on a video monitor and documented on a video recorder. The standard GeoVIS optics system provides a viewing field of approximately 2 by 3 mm and a magnification factor of 100 when viewed on a standard 13-inch monitor. GeoVIS has been to characterize NAPL contaminants at Naval Air Station sites in California. Another version of a CPT-deployed downhole video camera is sold by ARA/Vertek. References: Lieberman (2001a; b); http://www.vertek.ara-robotics.com/	depth; can be used to identify geologic materials and delineate stratigraphy	• Slow rate of probe advancement (1 ft every 3 to 5 minutes) • Area viewed is small • Pressure or heat front may drive NAPL droplets away from window • Limited availability
Direct Push Hydraulic Conductivity (K) Testing *CPT piezocone measurements* of soil behavior can be used to infer soil type and estimate hydraulic conductivity (K) with depth. *CPT pore pressure dissipation tests* involve halting cone penetration and measuring pore pressure dissipation with time, which is used to estimate K. *Monitoring water injection rate and pressure* while advancing a groundwater profiler (to prevent screen clogging) provides a relative measure of K. *Constant drawdown pumping tests and slug tests* can be performed using small-diameter adaptations of conventional methods. References: ASTM D7242-06; Hinsby et al. (1992); Lunne et al. (1997); Cho et al. (2000); Butler et al. (2000, 2002, 2007); Pitkin and Rossi (2000); McCall et al. (2002); Sellwood et al. (2005); www.geoprobe.com	• Depth discrete data can be obtained at multiple depths and locations to rapidly delineate spatial variations in K in many unconsolidated formations • Eliminates the need for permanent wells and associated drilling, disposal of drill cuttings, well construction cost, and generation of large volume of development water • DP rig mobility allows work in difficult-to-reach areas	• Small test zone may not be representative • Inadequate well development can result in underestimation of K, particularly when driving an unshielded screen through silt and clay layers • Small diameter rods limit equipment and methods • Water added to prevent screen clogging can affect test interval water chemistry
Drilling		
Drilling Methods A variety of drilling methods (hollow-stem auger, sonic, and rotary methods) are commonly used for sampling and well construction in overburden and rock. Due to risks of		

Method	Uses/Advantages	Limitations
contaminant drag-down and cross-contamination, careful consideration should be given to selecting methods which allow for (1) high-quality sampling to help identify DNAPL presence and potential barrier layers, and (2) highly-controlled well construction and hole abandonment. Various strategies (e.g., outside-in approach, use of multiple isolation casings, use of drilling mud, etc.) can be employed to reduce contamination risks. References: ASTM D6286-98; Cohen and Mercer (1993); Sterling et al. (2005); www.frtr.gov		
Groundwater Quality Profiling		
Direct Push Groundwater Profiling Several DP probes and methods have been developed to provide depth-discrete groundwater samples that can be used for detailed characterization of contaminant distribution. For example, the Waterloo profiler can be used to collect very small volume groundwater samples from multiple depths at the same location without removing the sampling tool for decontamination between samples. The profiler has a stainless steel tip with circular screened ports that is pushed to the first sampling depth where groundwater can be extracted by pumping through tubing to the surface. As the profile is driven to the next sampling interval, distilled water is injected at a low rate to purge the tubing and reduce potential screen clogging. Purging and sampling then occurs by pumping from the second zone, and the process is repeated at the desired depths to the bottom of the push. Onsite lab analysis can optimize selection of sampling locations. Depth-discrete field techniques such as the Waterloo profiler are needed to delineate localized source zones that produce the bulk of contaminant mass flux and thereby facilitate remediation design. References: Pitkin et al. (1999); USEPA (2005a); Guilbeault et al. (2005); www.geoprobe.com	• Can collect multiple samples (at any spacing) with depth using peristaltic or pneumatic pumping methods, bailers, and other devices • Provides detailed concentration profiles that can be used for backtracking to NAPL source area • Pushing DP rods through soil generally wipes soil aside reducing potential for contaminant dragdown; however, it is unlikely that DNAPL or certain soils (such as sticky clays) would be completely wiped clean • No drill cuttings; little purge water • Can pump clean water out through screen during advancement to minimize clogging and dragdown of contaminants • Can develop probe screen	• Limited by lithology (clogging, turbidity, and lack of yield problematic in fine-grained sediments) and depth (depending on probing and sample collection methods) • Only provides a snapshot in time of water quality • Concentrations of metals and hydrophobic compounds tend to be biased high due to sample turbidity • Vertical hydraulic gradients can confound backtracking • Heterogeneity and dilution effects hinder backtracking delineation of DNAPL architecture • Penetration limitations

Method	Uses/Advantages	Limitations
Direct-Push Pre-Packed Well Installation DP wells are installed in unconsolidated media without first having to construct an open borehole as is done hollow-stem auger and other conventional drilling methods. A common installation method involves driving probe rods to the target depth, lowering a pre-pack screen well assembly into the rod string using threaded PVC riser pipe, retracting the outer rod to a point above the screen, and then emplacing a fine sand barrier over the pre-pack followed by granular bentonite or bentonite slurry in the annulus between the PVC riser and the outer steel drive rod to form a well seal. Small diameter Geoprobe® pre-pack screen uses 0.5-inch Schedule 80 PVC riser pipe installed in 2.125-inch OD probe rods. Larger diameter pre-pack screen uses 1.0-inch Schedule 40 PVC riser pipe installed in 3.25-inch OD probe rods. References: ASTM D6724-04; ASTM D6725-04; Kram et al. (2001c); ETSCP (2008); ITRC (2006a); www.geoprobe.com	• Monitoring studies show that groundwater samples taken from DP wells are comparable in quality to those obtained from conventionally-constructed wells • Minimal cutting wastes and less well development waste generated • Rapid and minimally intrusive installation • Less worker exposure to contamination • Cost savings	• Well penetration (depth) and diameter limitations • Lack of regulatory acceptance in many States • DP wells may be more likely to cause vertical cross-contamination if they are installed without using an outer casing and adequate grout seals • Potential for higher turbidity in wells with no filter pack or inadequate development
Multilevel Groundwater Monitoring Systems The *Westbay MP System®* uses modular installation of blank (PVC or steel) pipe in variable lengths, packers, couplings and valved ports to provide access to multiple isolated monitoring zones in one borehole. Portable, wireline tools are run in the casing to measure fluid pressure, collect water samples and perform tests. The *Solinst Waterloo*^{TM} *Multilevel System* uses multiple monitoring ports set in 2-in PVC casing, which are isolated in the hole by packers or alternating layers of sand and bentonite backfill. Each port has a single or dual stem that is connected to tubing, a pump, or a pressure transducer that runs to the surface. The *Solinst Continuous Multichannel Tubing (CMT*^{TM}*) System* uses flexible 1.6-in OD CMT HDPE tubing to monitor up to seven discrete zones via	• Provides detailed three-dimensional hydraulic head and water chemistry data, leading to improved site characterization, risk assessment and remediation • Dedicated sampling diminishes potential for cross-contamination • Small monitoring zones and tube sizes reduce pressure equilibration times and purge water volumes (reducing handling and disposal costs • Savings from drilling fewer holes • Potential for improved hydraulic seals compared with nested systems • Reduced site disturbance	• Can be more difficult to install than individual wells, requiring the use of specialist contractors • Fewer purging/sampling options may increase sampling time • Potential for cross-contamination prior to completing well construction • May be difficult to decommission/abandon

Method	Uses/Advantages	Limitations
intake ports cut into the tubing. Sandpacks and annular seals are emplaced by backfilling. A 1.1-in OD version can be installed using DP rigs to monitor up to three zones. The *Water FLUTe^{TM} System* uses a flexible impermeable liner fabric (2 – 20 in OD) to isolate up to >20 intervals for monitoring. Shipped preassembled in a coil, the system is reeled downhole and everted using water pressure, which also seals the liner against the hole wall. Samples are taken through tubing using gas pressure. Heads are measured using dedicated transducers or water-level probes. References: USEPA (1997d); Einarson and Cherry (2002); Keller (2004); Einarson (2005); www.solinst.com; www.flut.com; www.westbay.com		
Discrete-Interval Passive Groundwater Sampling Methods Other methods to sample groundwater from discrete intervals include use of nested wells with small screens, packers to isolate sample zones, low-flow procedures, and passive samplers – three types of which are discussed below. The *HydraSleeve^{TM}* grab sampler is used to retrieve groundwater from a discrete depth in a well for analysis of VOCs, SVOCs and metals without purging. It consists of a reusable weight attached to the bottom of a long lay-flat disposable polyethylene sample sleeve with a self-sealing valve. The valve opens when the device is quickly raised using a suspension cord and closes when the sampler is full. Samples are transferred to containers (e.g., 40-mL vials) at the surface. HydraSleeve^{TM} samplers have been made to retrieve from 80 to >4,000 mL and for use in wells as small as 1 inch diameter. The *Snap Sampler^{TM}* is a grab sampling device suitable for VOC, SVOC and metals analysis. It employs a cable to trigger release of a spring and close Teflon end caps on a double-opening 40 mL VOA vial or a	• Field testing has demonstrated reliability and efficacy of no-purge passive sampling methods • Reduces variability associated with inconsistent purging/pumping methods • Not susceptible to turbidity interference • Grab samplers allow analysis for all common analytes • Multiple samplers can be deployed in a single well for vertical profiling of contamination • Passive samplers, particularly Hydrasleeve^{TM} samplers and PDBs, can be easily deployed by one person • Eliminates purge water costs, reduces labor costs • Reduces disruption at well sites • Passive samplers can be left downhole from one sampling event to the next to minimize cost	• Relies on free movement of water through well screen or open hole • Vertical flow in well can confound data interpretation • Grab samplers should be left downhole in the sample interval for at least 24 hours prior to sampling to allow for re-equilibration • PDBs are not suitable for sampling polar VOCs (e.g., acetone, MTBE, MIBK and styrene), higher molecular weight compounds (e.g., SVOCs), metals, anions, field parameters (e.g., specific conductance), and other analytes that do not diffuse through polyethylene • Regulatory acceptance issues

Method	Uses/Advantages	Limitations
125 mL polyethylene bottle *in situ* without headspace vapor. Once retrieved from the well, standard screw caps and preservatives can be added to the sample container. Up to four samplers can be attached in series to one trigger cable. Snap Samplers^{TM} fit in 2-in or larger monitoring wells. *Polyethylene diffusion bag (PDB)* samplers rely on equilibrium diffusion of nonpolar VOCs downhole through a tubular polyethylene film that is initially filled with de-ionized water and sealed. PDB samplers are typically 18 to 24 inches long, 1.25 to 1.75 in in diameter, and provide 200 to 350 mL of sample. One or more samplers are set at desired depths in screened or open well intervals and left in place for at least two weeks. Upon retrieval, PDB samples, which are typically representative of adjacent well water quality during the last few days of deployment, are transferred to 40-mL VOA vials. Other discrete-interval sampler methods are described in the listed references. References: ASTM 6771-02; Puls and Barcelona (1996); Vroblesky (2001); Parsons (2005); ITRC (2006b); www.itrcweb.org; www.hydrasleeve.com; www.snapsampler.com; www.eonpro.com; www.caslab.com		
NAPL Profiling		
Measuring NAPL Thickness and Elevation in Wells If present, LNAPL will float on the water column and DNAPL will usually sink to the base of a well; thus measurement/sampling should carefully examine the air-fluid interface and extend to the well bottom. *Transparent, bottom-loading bailers* can be gently lowered to below the air-fluid interface and retrieved to measure LNAPL. To estimate DNAPL thickness, a *transparent, double check-valve bailer* can be lowered to the bottom of the well and withdrawn. Bailer length must exceed NAPL column height and a steel ball check	• Can provide direct evidence of NAPL presence • Can provide NAPL samples for property measurement • Can be compared to other data (e.g., boring logs) to refine the CSM • Can provide indication of remediation progress	• NAPL thickness and elevation in well may not correlate with that in formation • NAPL at residual saturation • Will not enter well, and the filter pack may resist NAPL entry • Conductive NAPL, emulsions, and viscous NAPL may produce spurious interface probe signals • Potential problems with interface probe decon • Accuracy using bailers is limited by several factors including difficulty in precise placement of bailer to

Method	Uses/Advantages	Limitations
valve must be used to ensure seating if the fluid density is >1.3 g/cm^3. *Other Methods* include use of hydrocarbon and water detection pastes, discrete-depth sampling devices, and measuring the length of DNAPL that stains a weighted cotton string lowered to the well bottom. References: Cohen and Mercer (1993); Pankow and Cherry (1996)		intersect NAPL-water interface.
Downhole NAPL FLUTe^{TM} Liner NAPL FLUTe^{TM} liners are composed of inflatable tubular membrane covered by a dye impregnated hydrophobic fabric that reacts upon contact with NAPL to produce an obvious stain. The liner can be deployed in open holes or through DP rods. In open holes, the tubular membrane is everted (outside cover in turned out) using air pressure, which also causes the hydrophobic cover to expand against the hole wall. Typically after one hour, the membrane is inverted (turned outside in) by pulling up on a removal tether so that the reactive cover does not contact the bore wall upon its retrieval. At the surface, the line is everted again and the locations of dye stains are measured to determine subsurface NAPL depths. Samples of the stained fabric can also be analyzed to determine NAPL composition. For deployment through DP rods, the liner is inserted through the rods with the hydrophobic cover out to the bottom of the cased hole. Upon rod withdrawal, the liner is filled with water to ensure that it expands flush against the hole wall. Liner retrieval and examination are the same as with the open hole method. References: www.geoprobe.com; www.flut.com	• Provides a continuous record of NAPL distribution with depth at borehole location • Can be deployed in variety of hole types, including through DP rods • Recommended for use as a confirmation tool after using MIP, rather than a NAPL exploration tool	• Potential for cross contamination when borehole is open (e.g., during liner retrieval) • Relatively ambiguous reaction to some NAPLs • Wicking may exaggerate NAPL presence • Potential for false positives and false negatives; can only detect NAPL in contact with reactive cover • Smearing of bore wall by DP drive may preclude contact of NAPL with liner • Use in rock may be difficult • Results may be sensitive to time in borehole
Partitioning Interwell Tracer Test (PITT)		
Partitioning Interwell Tracer Test (PITT) More than 50 PITTs have been used at contaminated sites to derive quantitative estimates of the saturation and volume of DNAPL in the subsurface. In most cases, these tests	• Can estimate DNAPL saturation and volume in tested zone • Can be used to assess remediation effectiveness • Provides alternative means of estimating NAPL volume	• Need to know DNAPL location to design test • Need sufficient hydraulic conductivity for tracer test • Need small enough source to allow adequate well spacing

Method	Uses/Advantages	Limitations
were performed to assess remediation performance. During a PITT, a suite of conservative and partitioning tracers injected via wells migrate with groundwater to extraction wells. Partitioning tracer velocities are retarded to various degrees depending on their affinity to partition to NAPL. Thus, tracer travel times, in conjunction with laboratory measurements of NAPL-water partitioning coefficients, are analyzed to estimate the saturation of NAPL in the inter-well zone swept during the test. Single-well push-pull tests have been proposed to characterize near-well NAPL presence, and gas-phase PITTs have been applied to estimate NAPL volume in the vadose zone. References: Jin et al. (1995); Jin et al. (1997); Annable et al. (1998); Nelson et al. (1999); Young et al. (1999); Mariner et al. (1999); Rao et al. (2000); Londergan et al. (2001); Dai et al. (2001); Meinardus et al. (2002); Brooks et al. (2002); Istok et al. (2002); Davis et al. (2002); Werner and Hohener (2002); Imhoff et al. (2003); Jalbert et al. (2003); Brusseau et al. (2003); Moreno-Barbero and Illangasekare (2006)	over relatively large areas, which typically relies on interpolation between point measurements • Extensive monitoring (e.g., multilevel samplers) and detailed data analysis can be used to evaluate the architecture of subsurface DNAPL	to conduct tracer test in reasonable time frame • Tracer partitioning to natural organic carbon can cause overestimation of NAPL • Nonequilibrium tracer partitioning can result in underestimation of NAPL • PITTs likely to underestimate NAPL present in pools • Tracers may bypass low permeability zones and underestimate NAPL • Multiple confounding factors can lead to large errors • Expensive, and may require recovery of tracers
Mass Flux Estimation Methods		
Mass Flux Calculation – General Several methods have been used to calculate the mass of dissolved contaminants moving with groundwater from an upgradient source zone through a defined subsurface area as a function of time. Mass flux determination using transect data, plume capture by pumping, passive flux meters are discussed below. Solute transport modeling can also be used to evaluate contaminant mass flux. Reference: Farhat et al. (2006)	• Mass flux estimates can be used to assess upgradient source areas, potential impacts on downgradient water supply wells or other receptors, natural attenuation of contaminant mass, and the effectiveness of remedial actions based on reductions in mass flux	• Requires understanding of groundwater flow field • Accuracy depends on density of sampling/measurement data • Cost increases with accuracy • Assessment confounded by heterogeneous hydrogeologic and contaminant conditions
Mass Flux Calculation – Orthogonal Transects Downgradient of a Source The most commonly used method for mass flux estimation involves multiplying contaminant concentration and groundwater flow rate data	• Provides snapshot of mass flux at time of sampling • Can be used to delineate contaminant distribution across the plume and infer contaminant architecture • Simple calculation	• See above

Method	Uses/Advantages	Limitations
derived from single- or multi-level monitoring wells, or DP profiles, installed along parallel transects that are oriented perpendicular to groundwater flow and downgradient from a source area. Flow rates can be calculated by measuring hydraulic heads, performing hydraulic conductivity tests, and/or conducting natural gradient tracer tests. The mass flux in each defined 'flow tube' is summed to estimate mass flux across a defined plane. References: Gradient/GeoTrans (1988); Semprini et al. (1995); Feenstra et al. (1996); King et al. (1999); Guilbeault et al. (2005)		
Mass Flux Calculation – Passive Mass Flux Meter The EnviroFlux Passive Flux Meter^{TM} (PFM) is designed to simultaneously measure contaminant and groundwater fluxes. It uses a sorptive permeable medium (a nylon mesh tube filled with sorbent/tracer mixture) that is placed in a borehole or monitoring well to passively intercept contaminated groundwater and release 'resident' tracers. After a specified residence time (typically 1 to 4 weeks) in the flow field, the sorbent/ tracer tube is retrieved for extraction and analysis. Detected contaminant masses are used to calculate time-averaged contaminant fluxes, and the residual tracer mass data are used to determine cumulative groundwater flux. By selecting appropriate sorbents, PFMs can be used for a wide variety of contaminants. For common organic contaminants, such as chlorinated solvents, activated carbon and a suite of different alcohols are used as the sorbent and tracers, respectively. Depth variations of groundwater and contaminant fluxes are measured by vertically segmenting sorbent/ tracer mixture in a well or borehole. Fluxes across a transect perpendicular to flow are measured by placing PFMs in multiple wells. References: Hatfield et al. (2004); Annable et al. (2005); www.enviroflux.com	• Simultaneous assessment of water and contaminant fluxes under natural gradient conditions • Time-averaged measurements are increasingly less sensitive to short-term fluctuations in groundwater flow and contaminant concentrations • Only two site visits required • Can be used to measure vertical variations in horizontal fluxes • Passive technique requires no electrical power or pumping • Precise prior knowledge about local aquifer hydraulic conductivities not required	• Limited application of this recently developed method • Each PFM interrogates a small volume of formation, thus multiple PFMs need to be deployed, and resultant data must be integrated to estimate mass flux across a plane • Competitive sorption or rate-limited sorption may affect the ability of the PFM to capture and retain contaminants • As with other methods, requires proper placement in the groundwater flow field • Method assumes horizontal flow

Method	Uses/Advantages	Limitations
Mass Flux Calculation – Plume Capture by Pumping (Integral Pumping Method) The mass flux from one or more pumping wells that fully capture a contaminant plume is calculated by measuring (and multiplying) pumping rates and contaminant concentrations in extracted groundwater. References: Ptak and Teutsch (2000); Bockelman et al. (2001); Einarson and Mackay (2001); Bayer-Raich et al. (2006)	• Can be applied using relatively few wells • Relatively few data requirements • Pumping integrates flow and concentration data, which may reduce uncertainties associated with point data	• Pumping may capture multiple ill-defined plumes, confounding interpretation • Potential handling and disposal of large volumes of groundwater • May cause undesirable plume migration • Must delineate capture zone
Borehole Logging Methods		
Borehole Logging Methods Significant advances have been made since the 1980s in the development and application of borehole logging tools for site characterization. However, drilling, logging, and other characterization activities at contamination sites can result in persistent cross-contamination, particularly in fractured rock, due to flow or dragdown of dissolved chemicals or NAPL, and the effects of matrix diffusion (Williams and Conger, 1990; Sterling et al., 2005). Such cross- contamination can impact drinking water quality and/or confound interpretation of chemistry data. A major objective in selecting drilling and testing protocols and locations should be to minimize the potential for cross-contamination. References: ASTM D5753-05; Keys (1990), USEPA (1993); USACE (1995); Keys (1997) http://water.usgs.gov/ogw/bgas/full_biblio.html; www.geologging.com; www.mountsopris.com; www.century-geo.com	• See below	• Geophysical interpretations are always subject to ambiguity and uncertainty • See below
Video Camera Video logs provide a fish-eye view of the borehole. High-end video systems are magnetically oriented and provide a 360^{o} color digital image of the borehole wall. References: Williams and Lane (1998)	• Used to inspect the condition of well casing and screens • Provides direct view of lithology, texture, structure, color, bedrock fractures, water levels and cascading water, and changes in water quality (chemical precipitates, suspended particles and gas bubbles) • May be able to observe NAPL	• Requires clear water • Open hole provides conduit for cross-contamination

Method	Uses/Advantages	Limitations
Acoustic Televiewer (ATV) ATVs provide continuous, magnetically oriented, 360°, photograph-like images of the acoustic reflectivity of a borehole wall. The tool records the travel time and amplitude of the reflected acoustic signal (a focused ultrasound beam) as separate image logs. Fractures reduce the reflected amplitude and often appear as dark sinusoidal traces on ATV images. The travel-time log is similar to a high-resolution 360° arm caliper; it shows diameter changes within open fractures and caved areas. ATV tools are typically 40 to 50 mm in diameter and 1.7 to 3.7 m long. Vertical image resolution varies from 1 to 7.5 mm, and logging speed is 1 to 3 m/min. Digital image data are transmitted uphole for display and analysis on a computer. References: Williams and Lane (1998); Williams and Johnson (2000); Williams and Johnson (2004)	• Provides oriented view of lithology, bedding features, foliation, structure, fractures and fracture infillings • Used to map fracture distribution, orientation (strike and dip) and size (aperture) in bedrock • Can be obtained from water or mud filled holes • In darker rocks, fractures readily apparent on ATV images can be difficult to distinguish from dark color zones on OTV images	• Not effective for very small fractures (<200 μm) • Iron staining and other chemical precipitation, NAPL and bacterial growth are readily apparent on OTV images, but not on ATV images • Relationship between lithology and structural features may not be clear • Open hole provides conduit for cross-contamination
Optical Televiewer (OTV) Housed in a transparent cylindrical window, OTV imaging systems use a ring of lights for borehole illumination, a charge-coupled device camera, and a conical or hyperbolic reflector (which focuses the camera on a 360° slice of borehole wall) to transmit a continuous, magnetically oriented, 360 ° optical image of the borehole wall uphole via cabling for display and analysis on a computer. OTV tools are typically 40 to 50 mm in diameter and 1.4 to 2.8 m long. The vertical and horizontal resolutions of OTV images are commonly 0.5, 1 and 2 mm and 180, 360 and 720 pixels per line data, respectively. Logging speed varies, but is typically ~1 m/min. Effective and integrated analysis of OTV and ATV images is performed using product software that displays their corresponding images side by side at the same scale and orientation. References: Williams and Johnson (2000); Williams and Johnson (2004)	• Provides oriented view of lithology, bedding features, foliation, structure, fractures, and fracture infillings • Used to map fracture distribution, orientation (strike and dip) and size (aperture) in bedrock • Iron staining and other chemical precipitation, NAPL, and bacterial growth are readily apparent on OTV images, but not on ATV images • Provides direct view of relationship between lithology and structural features, which is not always clear on ATV images • Less affected by clarity of borehole water than video camera	• Open hole provides conduit for cross-contamination • Unflushed drilling mud, chemical precipitates, bacterial growth, and other conditions that create turbid borehole water and/or coatings on the borehole wall negatively impact OTV image quality • In darker rocks, fractures readily apparent on ATV images can be difficult to distinguish from dark color zones on OTV images
Caliper Caliper logs record borehole diameter versus depth using mechanical arms (finger-type recommended).	• Measures borehole diameter • Useful to delineate fractures and borehole condition (i.e., caving)	• May not detect near-vertical fractures • Open hole provides conduit for cross-contamination

Method	Uses/Advantages	Limitations
A multi-arm tool is typically used so that hole diameter can be measured at multiple different chords simultaneously. References: ASTM D6167-97(2004)	- Facilitates analysis of other geophysical logs affected by diameter	
Electromagnetic (EM) Induction By transmitting an oscillating EM field (which induces alternating electric current the surrounding formation) and measuring voltages in receiver coils, this tool provides a measure of bulk electrical conductivity (EC) of the subsurface adjacent to the borehole. The radial depth of measurement depends on the transmitter-receiver configuration and EM signal frequency, but is typically on the order of 30 inches. References: ASTM D6726-01; Williams et al. (1993); www.geonics.com	- Measures bulk formation electrical conductivity in wet or dry boreholes or through plastic casing - Can be interpreted to infer distribution of conductive (clay) versus non-conductive soil (sand), permeable zones and porosity, and water salinity - Anomalous low EC could possibly result from large NAPL presence	- Variations in EC caused by fluid saturation and chemistry can confound stratigraphic interpretation - Open hole provides conduit for cross-contamination (but logging can be performed in a plastic liner , such as a blank FLUTe^{TM}, to reduce this risk)
Gamma-Gamma Probe Gamma-gamma logs record the response of media adjacent to a borehole to gamma radiation emitted from a logging tool source. The amount of radiation detected is inversely related to formation density. Formation porosity can be calculated using the gamma-gamma log if the formation bulk density is known.	- Provides measure of bulk density, porosity, and moisture content with vertical resolution to 1 cm - Can be used in cased (PVC or steel) and uncased holes - Can be used in saturated and unsaturated holes	- Cannot detect NAPL - Open hole provides conduit for cross-contamination (but logging can be performed inside a plastic liner , such as a blank FLUTe^{TM}, to reduce this risk)
Natural Gamma Probe Natural gamma logs record the amount of natural gamma radiation in counts per second detected as the probe is raised from the hole bottom at a steady rate of 5 to 10 ft per minute along the length of a borehole. The most significant natural sources of gamma radiation are potassium-40 and daughter products of uranium and thorium decay. Clayey sediments and shale-bearing rocks emit relatively high gamma radiation because they include weathering products of potassium feldspar and mica and preferentially sorb daughter products of thorium and uranium decay. References: ASTM D6167-97(2004); ASTM D6274-98(2004); Williams et al. (1993); www.geonics.com	- Used primarily to reveal the presence of clay and shale layers (i.e., DNAPL capillary barriers) - Fine-grained beds of clay and silt generally produce higher counts than sand and gravel - Can use in uncased and cased (PVC or steel) holes, the latter with limitations - Can be used in saturated and unsaturated holes	- Cannot detect NAPL - Quantitative interpretation in cased holes with grout and sandpack is not recommended due to signal attenuation - Open hole provides conduit for cross-contamination (but logging can be performed inside a plastic liner , such as a blank FLUTe^{TM}, to reduce this risk)

Method	Uses/Advantages	Limitations
Neutron Probe The neutron logging tool contains a radiation source (usually americium-241/beryllium) and single or dual He-3 detectors. Fast neutrons from the source are scattered and slowed, primarily by hydrogen in the formation, until they reach thermal energy levels and are absorbed. The rate at which neutrons are scattered back to the detectors is inversely proportional to the water content in the immediately adjacent formation. Other materials that slow He-3 neutrons include boron, cadmium, chlorine and hydrocarbons. References: ASTM D6727-01; Endres and Greenhouse (1996)	• Can provide estimates of moisture content in the vadose zone, total porosity in the saturated zone, and water table elevation • Detects neutron slowing that may due to NAPL presence • Can be used in cased (PVC or steel) and uncased holes • Can be used in saturated and unsaturated holes	• Very short radius of measurement (e.g., 6 to 12 in) • Radiation source requires special handling • Open hole provides conduit for cross-contamination (but logging can be performed in a plastic liner, such as a blank FLUTe^{TM}, to reduce this risk)
Borehole Radar Borehole radar reflection logging records the amplitude and transit time of reflected high-frequency EM waves using a pair of downhole transmitting and receiving antennas. The measurements are interpreted to identify the location and dip of fractures and lithologic changes, and to estimate the radial extent of these features beyond the borehole. Signal penetration increases with the electrical resistivity of the strata and water surrounding the hole, and may exceed 90 ft in resistive media (>500 ohm-meters). Radar measurements can be made in a single borehole or by cross-hole tomography. References: Lane et al. (1994); Williams and Lane (1998); Singha et al. (2000); Haeni et al. (2002); Johnson and Joesten (2005)	• Can be used to delineate fracture zones • Can be used to monitor movement of saline tracer through fracture zones • Can be used to monitor subsurface movement of non-conductive fluids (e.g., vegetable oil injection to stimulate bioremediation)	• Radial penetration is limited by electrically conductive media and radar system used • In electrically conductive rocks (e.g., shale or mudstone), or in formations containing saline water or mineralogic clay, EM waves may penetrate < 1 m • Open hole provides conduit for cross-contamination
Electrical Resistivity and Spontaneous Potential (SP) Classic electric logging includes simultaneous measurement of electrical resistivity and SP. *Electrical Resistivity* – Normal-resistivity logs record the ER of the borehole environment and surrounding strata and water, which are measured using variably-spaced potential electrodes on the logging probe. *Spontaneous Potential* – SP logs record voltages developed between the borehole fluid and fluids in strata adjacent to the sonde.	• Used to evaluate stratigraphy and water quality • Resistivity decreases with increasing clay mineral content, water-filled porosity, and ionic strength of water • High resistivity in porous sands may be caused by NAPL presence • Can be used to delineate fractured zones in competent rock	• Can only be performed in uncased holes filled with water or mud • Open hole provides conduit for cross-contamination

Method	Uses/Advantages	Limitations
Water Quality Logging Various multi-sensor instruments are available to simultaneously measure multiple water quality parameters (e.g., temperature, pressure, fluid conductivity, oxygen, pH, redox potential, nitrate, chloride, turbidity) and rapidly create continuous profiles of borehole water quality. References: www.in-situ.com; www.solinst.com; www.generaloceanics.com; www.idronaut.it	• Assists delineation of flow zones, contaminated groundwater and vertical flow in the borehole between zones of differing hydraulic head • Water flow zones are usually identified by distinct changes in quality (i.e., conductivity) • Vertical borehole flow is usually identified by detecting little or no gradient (i.e., conductivity) between a water-producing and receiving zones	• Vertical distribution of water quality can be confounded by diffusion, density-driven advection and complex hydrogeology • Open hole provides conduit for cross-contamination
Temperature Temperature logs provide a continuous record of fluid temperature with depth. Borehole flow between zones is indicated by temperature gradients that are less than the regional geothermal gradient, which is about 1 degree Fahrenheit per 100 ft of depth.	• Changes in temperature profile may be caused by changes in groundwater flow under ambient and pumping conditions • Useful to delineate water-bearing zones and identify vertical flow between zones of differing head	• Not useful in cased section • Open hole provides conduit for cross-contamination
Vertical Flowmeter Logging The velocity of vertical fluid flow in a borehole resulting from hydraulic gradients under ambient or pumping conditions is logged by trolling or making a series of stationary measurements. Logs can be made in fractured rock and unconsolidated sand and gravel aquifers. *Impeller (Spinner) Flowmeters* determine vertical flow velocity by measuring the rate at which a mechanical impeller revolves as water flows past its vanes. The typical measurement range is 5 to 200 ft/min. *Electromagnetic Flowmeters* measure the velocity of water flow through a hollow, cylindrical measurement section based on Faraday's law of induction. The typical measurement range is 0.5 to 250 ft/min. *Heat-Pulse Flowmeters* can measure very low flow rates. Electric current applied to a heating element warms well water. Flow direction and velocity are determined by measuring the time it takes for the greatest temperature change to be detected at the	• Under ambient conditions, flowmeter logging can help delineate transmissive fractures and other permeable zones, the rate and direction of vertical flow, and flows causing cross-contamination • Under pumped conditions, flow measurements can be used to develop K profiles and determine fracture interconnections within and between wells (cross-hole methods) • Provide a direct measure of where water enters a well during pumping • Useful in interpreting fluid conductivity logs and borehole water quality data • Useful to design discrete interval hydraulic tests and well construction to limit cross-contamination	• Open hole provides conduit for cross-contamination • Operational problems can limit utility (e.g., resulting from insufficient time to regain quiescent conditions after meter movement, coatings on electrodes, presence of gas or debris in well, etc.)

Method	Uses/Advantages	Limitations
thermisters. The typical measurement range is 0.5 to 20 ft/min. References: Molz et al. (1989); Young and Pearson (1995); Boman et al. (1997); Paillet (1998); Williams and Lane (1998); Young et al. (1998); Paillet (2000); Paillet and Reese (2000); Paillet (2001); Williams and Paillet (2002); Paillet (2004); Newhouse et al. (2005)		
Tomographic Methods Tomographic geophysical methods (e.g., using radar, seismic and electrical methods) involve sending signals between transmitter and receiver antenna arrays in different wells, or between wells and the ground surface. Acquired data is processed to produce two and three dimensional visualizations of subsurface geophysical properties, which are interpreted to relate to hydrogeologic and/or fluid conditions. Using cross-hole methods, signal paths are one-way and typically much shorter than in a conventional surface geophysical survey. Shorter signal paths sample smaller volumes of subsurface material and provide higher resolution with less signal loss. References: USDOE (2000a; b; c); Davis et al. (2005)	• Tomographic methods can produce high-resolution images of stratigraphy, fractures, and possibly large NAPL pools (if present) • Can be used to delineate fracture zones between wells • Electrical Resistivity Tomography (ERT) can be used to monitor heating progress of steam injection and other thermal remediation methods	• Generally not successful in locating subsurface DNAPL • Tomographic images may be inaccurate due to many factors (signal wavelength, data noise, source and receiver geometry, and data processing artifacts) • Resolution varies spatially due to data acquisition geometry • Open holes provides conduit for cross-contamination
Measuring NAPL and Media Properties		
Measurement of NAPL Properties *Chemical Composition*, determined by analytical methods (e.g., GC/MS), is used for effective solubility calculations, evaluating fate and transport of NAPL constituents, and to assess risk. *Density* (mass per unit volume), typically measured using a pycnometer or hydrometer, is used to assess DNAPL mobility and for pool height calculations. V*iscosity*, which is used to assess DNAPL mobility, can be measured using a rotational viscometer, falling ball viscometer, glass capillary viscometer, or viscosity cup. *NAPL-Water Interfacial Tension* (the strength of the film separating two immiscible fluids) can be measured	• Need to understand NAPL and media properties to assess migration, distribution, and remedial alternatives • Property values needed for modeling NAPL movement and remediation • Properties of subsurface NAPL may differ greatly from pure products due to release of off-spec material, mixtures, and weathering, so textbook values of NAPL properties may be unreliable	• May be difficult to obtain NAPL samples at many sites • Samples tested may not be representative

Method	Uses/Advantages	Limitations
using the du Nuoy ring, capillary rise, or drop weight methods; it is used to assess capillary forces and pool heights. *Wettability* (preferential spreading of one fluid over solid surfaces in a multiphase system) is determined by contact angle measurement, capillary pressure-saturation, bottle tests and adhesion tests. It is used to assess mobility, capillary forces, and for pool height calculations. *Capillary Pressure and Relative Permeability versus Saturation Curves*, used to assess mobility, can be developed from flow and pressure measurements made in a test cell using representative samples of porous media and fluids. *Organic Carbon Partition Coefficient*, used to assess transport and sorption of dissolved NAPL contaminants, is usually estimated from published data. *Contaminant Half Life* is highly site-specific and is usually determined by analysis of field data and/or model calibration. References: Amott (1959); Bear (1972); Corey (1986); Honarpour et al. (1986); Kueper and Frind (1991); Cohen and Mercer (1993); Powers et al. (1996); Keuper et al. (2003)		

CHAPTER 9

REMEDIAL TECHNOLOGY SELECTION FOR CHLORINATED SOLVENT PLUMES

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9.1 INTRODUCTION

The number of technology options for chlorinated aliphatic hydrocarbons (CAHs) has increased significantly over the last 20 years. Initially, pump-and-treat was the *de facto* presumptive remedy, and extraction systems were installed at the overwhelming majority of sites. Pump-and-treat can be an effective mass removal technology and has been used successfully in several cases. However, under most conditions, these systems primarily provide hydraulic control and plume containment (USEPA, 1999; NRC, 1994). Further, pump-and-treat systems require continued operation and maintenance for long time periods, often at a considerable annual cost.

Remediation professionals were therefore motivated to develop and refine several technologies to treat contaminants in place (NRC, 1997). For example, the Department of Defense (DoD) made a concerted effort to develop and deploy innovative *in situ* technologies to replace pump-and-treat systems at CAH-contaminated sites (DoD, 1998), and they have made considerable progress in reducing both the total costs and time required for site restoration (DoD, 2005; GAO, 2005). A similar trend has been seen nationwide. For example, the number of Records of Decision (RODs) selecting *in situ* treatment as at least part of an overall remedy has steadily increased over time, as the number selecting pump-and-treat, either alone or in combination with other technologies, has steadily declined (USEPA, 2007; see Figure 9.1).

The experience from demonstrations and field-scale cleanups has shown that *in situ* technologies can work, and can reduce costs considerably. The experience also has led to refinement and evolution of technologies, so that there can be several options available for applying a technology such as *in situ* bioremediation, for example. Practitioners also have gained a better understanding of which technologies, and technology options, are most suited to specific site conditions.

Remedy selection occurs within a regulatory context, in which protection of human health and the environment must be assured. The process also includes defined criteria for evaluating alternative remedies, including cost, permanence of the remedy and time of restoration (e.g., Comprehensive Environmental Response, Compensation, and Liability Act [CERCLA] guidance). However, there is flexibility in the process because there are numerous technical and non-technical factors that can be important to the decision making process. It is therefore necessary to consider the ability of different remedial approaches to meet a variety of remedial action objectives, depending on the site and management factors involved at a given site.

The relatively large number of remedial approaches that have been developed for CAH plumes can make it difficult to select and design the appropriate technology for a given site. This chapter is designed to provide an overview of the available technologies and options, and

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initial guidance to help in the technology selection process. The complex set of site and management factors that impact the decision process make any simple and straightforward guidance impossible. Yet this initial guidance is intended to help identify the critical factors influencing the selection process, and the relative strengths and limitations of different remedial technologies.

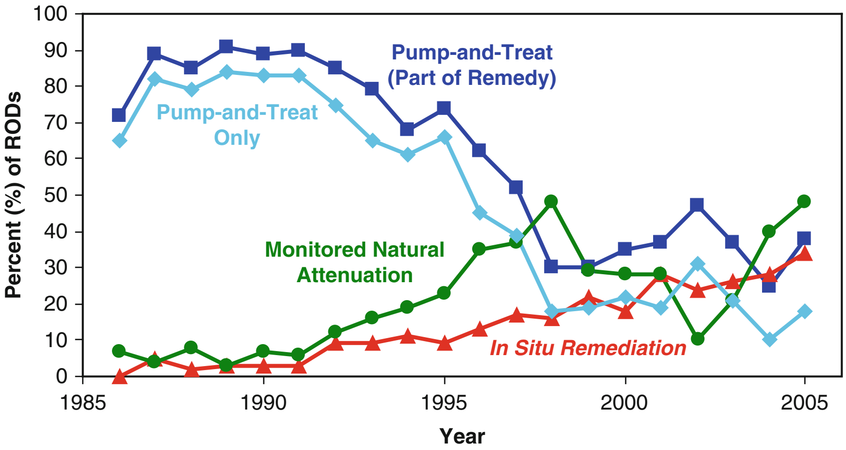

Figure 9.1. Trends in remedy selection for groundwater treatment at Superfund sites (1986–2005). Data include RODs identifying pump-and-treat remediation only, as well as RODs with pump-and-treat as part of a combined remedy. Modified from USEPA, 2007.

9.2 TECHNOLOGY SELECTION PROCESS

This chapter provides a streamlined, screening-level evaluation, intended to identify the most promising technologies and to illustrate the impacts of various decision criteria on the selection process. Figure 9.2 illustrates the overall approach, which is designed to be consistent with the increasing emphasis on streamlining the remediation process (e.g., NFESC, 2001). More detailed evaluations will be needed in most cases, because there are numerous options for implementing most of these technologies. Many of these options are discussed in the following sections, but a detailed evaluation of these options is beyond the scope of this chapter.

The first step is selecting a technology is to develop an adequate Conceptual Site Model (CSM) and Remedial Action Objectives (RAOs). In essence, these steps involve diagnosis (defining the problem) and setting realistic goals for treatment. For *in situ* technologies, whose performance and costs can be highly sensitive to site constraints, the CSM often needs to be more detailed than for more robust technologies. Similarly, RAOs need to be developed with care, especially for *in situ* technologies; it is often difficult to select and design an appropriate technology unless there is consensus on clear expectations for treatment and the results that would allow turning off the treatment system.

The CSM is a summary of conditions at a site that identifies the type and location of all potential sources of contamination; contaminant fate and transport; and how and where people, plants or animals may be exposed to the contamination. For *in situ* treatment, it is generally helpful to have a three-dimensional model of the subsurface and contaminant distribution, hydrogeological conditions (including significant temporal and spatial variations and heterogeneities), estimates of natural attenuation, geochemical conditions that can impact biological or chemical treatment, surface and subsurface features that could affect access or reagent delivery, and identification of significant data gaps (Mayer and Greenberg, 2005). The CSM should be constantly updated throughout the characterization and remediation process, but it is critical to have a clear picture of the current conditions before starting the technology selection process.

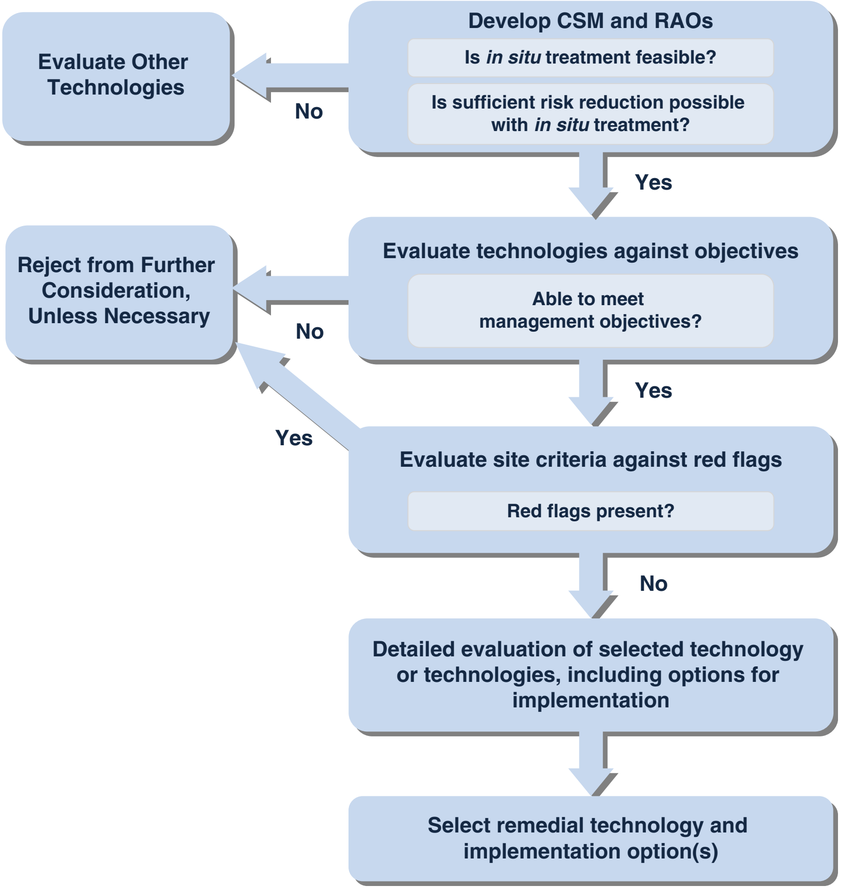

Figure 9.2. Schematic of screening-level evaluation process

RAOs are often thought of as “absolute objectives” such as attaining cleanup levels or protecting human health and the environment. However, for CAHs in groundwater, the RAOs may be less ambitious, such as reducing concentrations to levels that can be managed by monitored natural attenuation (MNA), preventing off-site downgradient movement of contaminants, or shutting off a pump-and-treat system. Often, the objectives for one action need to be viewed as part of an integrated remediation approach using several technologies in different places or times, with technology-specific RAOs. Carefully defining what is wanted from a technology often helps both in selecting the most appropriate approach as well as in stopping a remedial action when it is no longer cost effective.

After the CSM and RAOs are clearly defined, the next step in the selection process is to assess the ability of different candidate technologies to meet the primary management goals for the site, and to then identify whether there are serious site constraints (“red flags”) that could make a particular technology infeasible or prohibitively difficult or costly. These steps are discussed in more detail, after providing brief descriptions of the available *in situ* technologies.

9.3 *IN SITU* REMEDIATION

The following sections describe the primary *in situ* technologies available for treatment of CAH plumes, along with their key advantages and limitations. However, all *in situ* approaches share some advantages and limitations that need to be recognized early in the selection process. These are described below, before the sections focusing on individual technologies.

9.3.1 Advantages and Limitations

In situ treatment has many advantages, notably reduced costs and time for cleanup as compared to pump-and-treat. *In situ* treatment also does not require disruption of ongoing activities at a site in most cases and needs little or no aboveground infrastructure. Finally, *in situ* treatment generates few if any waste materials that will require disposal or treatment.

There are several limitations common to most if not all *in situ* technologies. The performance of virtually all of these technologies is strongly dependent on the degree of mixing possible within the subsurface. This means that permeability, the degree of heterogeneity within the subsurface, and the groundwater velocity will impact the ability to distribute materials within the aquifer, and therefore the efficacy of treatment. These site conditions can also impact the costs for *in situ* treatment because adequate treatment may require use of active recirculation systems to deliver materials, or numerous closely spaced injection points to ensure adequate distribution.

In situ treatment also often relies on establishing barriers to stop further downgradient migration of contaminants. Installing any barrier is generally limited to depths of less than 15 meters (m) (50 feet [ft]), and if there is no competent material at the base of the treatment zone, underflow can become a serious concern. Further, the “clean front” downgradient from an *in situ* barrier can move much more slowly than expected. Regulatory requirements and restrictions on injection of materials into the subsurface, and any potential detrimental effects on groundwater quality, can also impact the use of many *in situ* treatment technologies.

Finally, *in situ* treatment can be infeasible or excessively expensive if contamination extends too deep to allow delivery of remedial agents, or if contaminants are located in inaccessible areas. *In situ* treatment also can be more difficult, or in some cases impossible, if surface structures impede access or limit the ability to inject materials or install monitoring points. There is also an inherent degree of uncertainty involved with any *in situ* treatment. The key uncertainties include the actual extent and distribution of contamination, the ability to achieve adequate contact between contaminants and reagents, and the time required for treatment to acceptable levels.

9.3.2 *In Situ* Technologies

The primary *in situ* technologies used are listed below, classified by the dominant mechanisms responsible for treatment. Physical or hydraulic containment technologies have been excluded from this discussion, as have capping and stabilization/solidification techniques. The *in situ* technologies discussed include:

- Biological Treatment
  - Enhanced reductive dechlorination
  - Aerobic cometabolism
  - Phytoremediation
  - Monitored natural attenuation

- Chemical Treatment
  - Chemical oxidation
  - Chemical reduction (injection or barrier)
  - Electrochemical reduction
- Physical Treatment
  - Air sparging

Figure 9.3 provides a general indication of the maturity and level of use of these technologies, based on data from Superfund sites contaminated with halogenated volatile organics (USEPA, 2007). Air sparging is the most developed and most used technology for *in situ* groundwater treatment at these sites, though bioremediation and chemical treatment are also used at a significant number of sites despite being less mature. In this analysis, chemical treatment refers primarily to chemical oxidation, while all of the permeable reactive barriers are zero-valent iron (ZVI) walls, which are based primarily on chemical reduction.

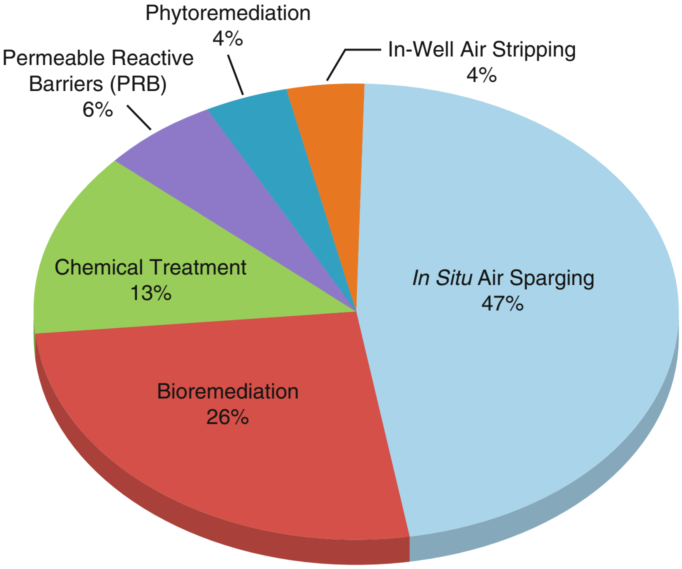

Figure 9.3. Remedial technologies used at Superfund sites contaminated with “halogenated volatile organics” (1986–2002). Total number of sites = 90. Data from USEPA, 2007.

The use of these technologies within the DoD is indicated by the current number of remedial systems for solvent only sites in operation by the U.S. Air Force (Figure 9.4). Pump-and-treat systems are still in operation at almost half the sites, but the results also reflect the rapid adoption of innovative technologies, particularly MNA. In contrast to the Superfund experience, *in situ* air sparging rarely has been used at U.S. Air Force sites.

The following sections briefly describe these general technologies, the options available for implementing them, and their advantages and limitations. The focus is on summarizing those aspects of the technologies that impact their suitability for specific site conditions and decision factors. Table 9.1 summarizes the key advantages and limitations for each of these technologies.

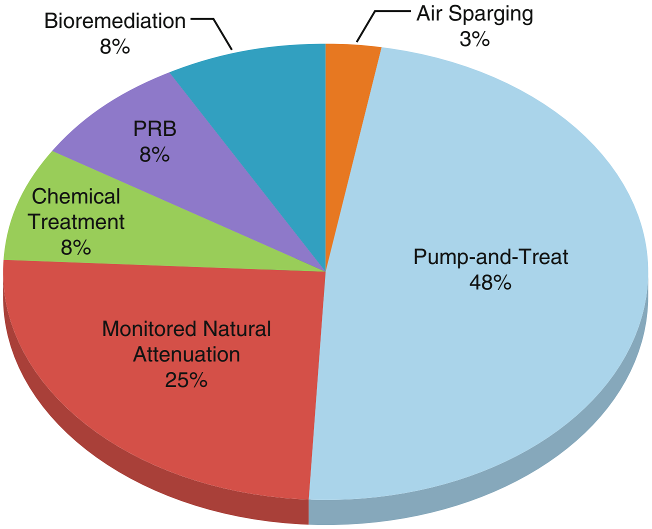

Figure 9.4. Remediation systems used for all solvent-only sites by the U.S. Air Force. Results do not include mixed solvent-fuel sites, or data for primarily source treatment technologies such as thermal treatment and dual-phase extraction, as well as 10 systems labeled "other." Total number of systems = 120. Data courtesy of John Gillespie, Air Force Center for Engineering and the Environment, Brooks City-Base, TX, USA (updated February 2006).

Table 9.1. Summary of the Advantages and Limitations of the Major *In Situ* Groundwater Remediation Technologies

Technology	Advantages	Limitations
Biological		
Enhanced Reductive Dechlorination (ERD)	– Moderate cost – Complete destruction possible – Flexible – numerous site adaptations possible – Effective for several cocontaminants – Compatible with other technologies	– Possible accumulation of toxic intermediates – Possible harmful volatile emissions – Sensitive to geochemistry and hydrogeology – Possible degradation of water quality – Relatively slow treatment
Aerobic Cometabolism	– Complete destruction possible – Few byproducts of concern	– Cometabolites often of environmental concern – Difficult process to control under field conditions – Sensitive to geochemistry and hydrogeology – Intermediates toxic to degrader organisms – Very limited field-scale experience

(*continued*)

Table 9.1. (continued)

Technology	Advantages	Limitations
Phytoremediation	– Low cost – High public acceptability – Little impact on water quality parameters – May include contaminant destruction	– Depth and climate restrictions – Relatively slow process – Subject to seasonal fluctuations – May require large land area for treatment/capture – Volatile emissions possible
Monitored Natural Attenuation	– Low capital cost – Non-intrusive – Compatible with other technologies	– Very slow removal rates – Sustainability difficult to predict – Long-term monitoring can be costly – Extensive evaluation needed – Possible accumulation of toxic metabolites – Rarely acceptable without source treatment
Chemical		
In Situ Chemical Oxidation	– Moderate cost (for high-concentration areas) – Rapid treatment – Complete destruction possible – Compatible with bioremediation	– High cost for dilute plumes – Short oxidant lifetimes – Health and safety threats – Not effective for low permeability zones – Rebound commonly observed – Oxidants may be consumed by other materials
In Situ Chemical Reduction	– Moderate cost (for ZVI barriers) – Compatible with other technologies, such as ERD – Lifetimes appear to be cost effective at many sites – Can degrade many cocontaminants	– Passivation can be rapid at some sites – Potential short circuiting or flow-around – Slow downgradient clean front migration
Electrochemical Reduction	– Moderate cost – Low power requirements – Flexible operation (reversals between electrodes) – Can potentially degrade most cocontaminants	– Relatively immature technology – Depth limitations – May not be feasible at sites with high total dissolved solids (TDS)
Physical		
In Situ Air Sparging	– Low to moderate cost (depends on vapor treatment) – Relatively easy to design and install	– Not effective for low permeability zones – Poor performance in heterogeneous or stratified aquifers – Not feasible for deep or thick aquifers – Not effective if dense nonaqueous phase liquid (DNAPL) present

9.4 BIOLOGICAL TREATMENT

The daunting diversity of remedial approaches is clear when considering "biological" treatment options. Microorganisms can degrade chlorinated solvents by several mechanisms, including aerobic oxidation, anaerobic reductive dechlorination, cometabolic biodegradation and possibly anaerobic oxidation. Plants also can absorb and in some cases degrade chlorinated solvents, leading to phytoremediation strategies. Finally, microbial processes also can be used in conjunction with abiotic processes.

Most of these processes have been exploited to develop a wide variety of *in situ* bioremediation approaches. Further, these processes may also occur under favorable conditions without active management, leading to the development and adoption of MNA as a remediation strategy at many sites. The following sections describe the predominant approaches used.

9.4.1 Enhanced Reductive Dechlorination

By far the most commonly used form of *in situ* bioremediation for chlorinated solvents has been some variation of enhanced reductive dechlorination (ERD), which takes advantage of the ability of select bacteria to dehalogenate many CAHs under strongly anaerobic conditions (Vogel and McCarty, 1985; Tiedje and Mohn, 1992). *In situ* bioremediation is the predominant approach for several reasons: (1) some compounds, notably perchloroethene (PCE), only can be degraded anaerobically (McCarty, 1994), (2) it has proven relatively easy to implement and control under field conditions, (3) it is a highly flexible technology and (4) it is a relatively inexpensive technology.

Various names have been used to describe the technology, including Enhanced Anaerobic Bioremediation, Enhanced *In Situ* Bioremediation, and Anaerobic Reductive Dechlorination. ERD has the advantage that it describes the fundamental process and the fact that it is being deliberately stimulated. However, other important biological and abiotic processes affecting the fate of the contaminants also may be occurring as a result of the effort to stimulate reductive dechlorination (Kennedy et al., 2006; AFCEE et al., 2008).

ERD involves delivery of an organic substrate into the subsurface in order to stimulate microbial growth and activity by creating an anaerobic groundwater treatment zone and generating hydrogen through fermentation reactions. This substrate addition creates conditions conducive to the anaerobic biodegradation of CAHs through the process of reductive dechlorination, in which hydrogen serves as the electron donor to sequentially replace chlorines with hydrogen atoms, eventually producing ethene.

Fundamental research on the microbiology has shown that several types of organisms can be involved, and redox status, the nature and concentrations of electron donors and hydrogen availability are key control parameters (AFCEE et al., 2008). Apparently a limited number of organisms are capable of complete dechlorination to ethene, and these may not be ubiquitous (Fennell et al., 2001; Hendrickson et al., 2002). The organisms use hydrogen as the electron donor and several CAHs as electron acceptors, resulting in sequential dechlorination (e.g., PCE to trichloroethene [TCE] to *cis*-1,2-dichloroethene [*cis*-DCE] to vinyl chloride [VC] to ethene and ethane). The hydrogen can be produced during the fermentation of several organic substrates.

One area of concern has been the observations that *cis*-DCE and VC can accumulate in some plumes because they are degraded more slowly than the parent compounds. Reasons for this accumulation are not fully known, and the mechanisms for *cis*-DCE and VC removal are not entirely clear (e.g., Bradley and Chapelle, 1996). In some cases, bioaugmentation with cultures containing specific *Dehalococcoides ethenogenes* strains can overcome this limitation, or reduce the lag time before the onset of complete dechlorination (ESTCP, 2005). Bioaugmentation has been proven to be successful during several controlled field-scale demonstrations (Major et al., 2002; Lendvay et al., 2003)

Numerous electron donor sources have been developed and used. Gases, solids, viscous fluids, oils and water soluble donors all have been used with success. Hydrogen can be directly sparged into the subsurface (Hughes et al., 1997), but this has not proven to be commercially successful, at least partly because of safety concerns. Slow- or controlled-release substrates have been developed, including polymerized lactic acid (Hydrogen Release Compound [HRC®]), and natural slow-release sources such as chitin have been used (Koenigsberg and Sandefur, 1999). Other natural organic materials also have been used, including soluble carbohydrates such as molasses, whey, mulch, chitin and compost (ARCADIS, 2002; AFCEE, 2004). Vegetable oil has been used at several DoD sites, generally as an emulsified solution to improve distribution (Borden and Lee, 2002). Different substrates also have been combined to provide customized formulations of slow- and rapid-release donor sources.

Partly because so many electron donors can be used successfully, ERD can be implemented in many different ways. "Biobarriers" can be established by injecting donors along a transect (Koenigsberg and Sandefur, 1999), or "biowalls" can be built by filling trenches with organic materials such as mulch (Aziz et al., 2001). One-time applications of long term sources such as HRC® or vegetable oil may be made, or repeated applications of high strength, soluble materials such as lactate (AFCEE, 2004). Combinations of these approaches are possible, and ERD also may be combined with other technologies.

The rapid evolution and widespread use of ERD, along with the confusing variety of possible applications, has led to the development of guidance documents that can aid in the selection, design and monitoring of these systems. Notably, the Interstate Technology & Regulatory Council published a technical and regulatory guidance document (ITRC, 1998) to foster the development and adoption of the technology, and the Air Force Center for Engineering and the Environment (AFCEE; previously the Air Force Center for Environmental Excellence) and the Environmental Security Technology Certification Program (ESTCP) published a more recent "Principles and Practices" manual (AFCEE, 2004).

Advantages of ERD include potentially complete mineralization of the contaminants *in situ* with little impact on infrastructure and relatively low cost compared to other active engineered remedial systems. ERD can also result in effective treatment of other contaminants, such as chromate and perchlorate, and can be used with other technologies in treatment trains or synergistic treatment systems (e.g., Mravik et al., 2003; Quinn et al., 2005). Finally, ERD is a highly flexible technology, and can be tailored to site conditions and optimized over time as results become available.

The potential limitations of ERD result from the profound changes it can cause in the subsurface environment, and the difficulties that can be caused by hydrogeological, geochemical and biological conditions. Site-specific limitations may include low permeability, a high degree of heterogeneity and geochemical constraints such as pH or competing electron acceptors (e.g., dissolved oxygen [DO], nitrate, or sulfate).

A common important limitation is the allowable timeframe for remediation, because ERD is a relatively slow technology. At some sites, dechlorination is not complete, and temporary or long lasting stalling at *cis*-DCE or VC can be an important limitation. Finally, secondary degradation of groundwater quality may occur (e.g., solubilization of metals such as iron, manganese and arsenic), acidification can become a serious problem or undesirable fermentation products may accumulate (e.g., ketones, methane or hydrogen sulfide).

9.4.2 Aerobic Cometabolism

Aerobic cometabolism of TCE and derivatives has been known for several years (Wilson and Wilson, 1985; Oldenhuis et al., 1989; Wacket and Gibson, 1988). A wide variety of cometabolites can support TCE biodegradation. Propane (Semprini, 1997), methane (Hazen et al., 1994), phenol (Hopkins et al., 1993) and toluene (McCarty et al., 1998) have all been used in field demonstrations. The technology relies on stimulating the production of oxygenase enzymes by organisms capable of growing on the cometabolite compound. These oxygenases (e.g., methane monoxygenase or toluene dioxygenase) can fortuitously degrade TCE.

Unfortunately, the problems involved in controlling cometabolic reactions *in situ* have proven difficult to overcome. These problems include the fact that the byproducts of TCE cometabolism can be fatal to the microbes responsible for biodegradation, the cometabolite itself may inhibit TCE destruction and effective mixing of oxygen, organisms and cometabolites can be challenging.

In practice, cometabolism can be used to establish an *in situ* barrier by recirculating fluids containing the cometabolite and oxygen source. The field demonstration at Edwards Air Force Base, California, took advantage of separate layers within the subsurface to establish such a fluid recirculating system (McCarty et al., 1998). Direct injection of air and gaseous cometabolites such as propane or methane also has been tested (Hazen et al., 1994), generally using a pulsed operation to first grow the TCE degraders on the cometabolite, and then allowing cometabolite concentrations to decrease, in order to enhance TCE degradation.

Like other bioremediation technologies, aerobic cometabolism can result in complete destruction of the contaminants, at relatively low cost. The primary advantage of this approach is that it is not necessary to force the aquifer to become anaerobic, which may be difficult at a site with a high influx of electron acceptors. There are also fewer byproducts of potential concern than during anaerobic treatment.

The limitations are generally similar to ERD (adequate permeability, accessible treatment zone, favorable pH). However, the ability to balance the substrate and oxygen levels is a technology specific issue. Oxygen and the cometabolic substrate must be supplied, to maximize degradation rates without driving the system anaerobic or poisoning the organisms responsible for degradation (e.g., Alvarez-Cohen and McCarty, 1991).

9.4.3 Phytoremediation

Phytoremediation also can be an effective bioremediation technology for CAHs and other contaminants in soil and groundwater (USEPA, 2000; Schnoor et al., 1995). Phytoremediation is actually a suite of technologies, involving several different plants and variations, as well as several different processes. Shrubs, trees or wetland plants may be used, and the plants may extract, sequester, transform, degrade or transpire the contaminants (McCutcheon and Schnoor, 2003).

Plant uptake of water and contaminants (phytoextraction) can be used for hydraulic control of impacted plumes (Eberts et al., 1999) or reduction in the concentrations downgradient. The extracted contaminants may be transferred to the atmosphere with partial or no degradation, a process called phytovolatilization (McCutcheon and Schnoor, 2003). However, some plants can also absorb and metabolize (phytodegrade) the chlorinated solvents (Schnoor, 1997; Newman et al., 1997). Further, some plants can enhance the microbial degradation of CAHs in their rhizospheres (Lee et al., 2000; Godsy et al., 2003).

Although multiple processes may be involved, and the fate of contaminants during treatment is not always well understood (Eberts et al., 2003), it is clear that phytoremediation can be effective given the right conditions. Several projects have demonstrated that successful containment and treatment of CAH plumes is possible, though results from some field demonstrations have been disappointing (e.g., USEPA, 2003). However, there have been relatively few full-scale applications, partly because the right conditions are not commonly found. These conditions include shallow contamination, favorable climate and adequate space (Chappell, 1998).

Phytoremediation has the advantages of low cost, high public acceptance and little secondary waste production. Its limitations include depth, contamination and climate restrictions, as well as the potential for transfer of contaminants from soil and groundwater into the food chain or the atmosphere. It is also a relatively slow process and subject to seasonal variations, so that often many plants spread over a large area will be needed for adequate groundwater capture and treatment. Finally, until the technology is more mature and controlled field demonstrations demonstrate it can be reliable, many practitioners will not have confidence in phytoremediation.

9.4.4 Monitored Natural Attenuation

Monitored natural attenuation is based on the recognition that natural processes can reduce the concentration, toxicity and mobility of contaminants, unaided by deliberate human intervention. Although many of the chlorinated solvents were long considered recalcitrant in the subsurface, it has become clear that natural processes can effectively attenuate and destroy CAHs (e.g., Wilson et al., 1994). These processes may be physical and chemical as well as biological, but MNA is grouped with biological technologies in this chapter because contaminant destruction is often a key issue for the demonstration and acceptance of MNA for chlorinated solvents, and that destruction is primarily due to biological mechanisms (Weidemeier et al., 1998).

MNA is often considered to be too slow to provide effective containment at most chlorinated solvent sites without prior aggressive treatment, particularly when residual DNAPL is present. In fact, the draft U.S. Environmental Protection Agency (USEPA) directive on the use of MNA (USEPA, 1998) states that "typically [MNA] will be used in conjunction with active remediation measures" and "removal, treatment or containment of NAPLs [nonaqueous phase liquids] may be necessary for MNA to be a viable remedial option or to decrease the time needed for natural processes to attain site-specific remediation objectives."

However, MNA has become increasingly used, with about 60% of MNA projects in one survey combined with source treatment, and 40% as a stand alone remedy (McGuire et al., 2003). Evidence suggests that some form of natural attenuation occurs at many sites, and that in many cases it can be protective. Although biological reductive dechlorination is usually the key process relied upon in selecting MNA, other biological process, including anaerobic oxidation (Bradley and Chapelle, 1996) and aerobic cometabolism (Sorenson et al., 2000) may also contribute under the right conditions. In addition, abiotic reduction can destroy CAHs *in situ* and can be an important natural attenuation process (Ferrey et al., 2004).

The primary advantage of MNA is its relatively low cost. Although it can be more expensive than anticipated, especially when life cycle costs are considered, it requires little labor and the lack of active management limits costs. It is minimally intrusive, and there is little disruption of ongoing operations. It can be used on all or some of a site, and can be used in conjunction with most of the more aggressive technologies. Finally, MNA is generally viewed favorably by both the public and regulators, so long as protection and management of risks can be ensured.

The primary limitation of MNA is that it is a relatively slow process. It can be difficult to predict the conditions under which MNA can be effective, or to determine how much aggressive treatment will be sufficient for MNA to be protective afterwards. Existing protocols (USEPA, 1998; Weidemeier et al., 1998) can require extensive evaluation and monitoring to determine if MNA can be used, and monitoring costs can continue for a long time. Partial degradation to more toxic intermediates (e.g., accumulation of *cis*-DCE and/or VC from TCE reduction) may be a concern as well, particularly if volatilization to indoor air is a potential issue. The long times that MNA can require may not be acceptable, and the long-term sustainability of MNA is also a potential concern (e.g., native electron donors may be depleted over time).

9.5 CHEMICAL TREATMENT

Chemical treatment includes technologies based on both *in situ* oxidation and *in situ* reduction. A wide range of reagents and techniques have been used to chemically treat CAHs. The following sections describe the major approaches taken, the variations that have been used commercially, and the advantages and limitations of each.

9.5.1 *In Situ* Chemical Oxidation

In situ chemical oxidation (ISCO) is capable of completely destroying chlorinated solvents (e.g., Gates and Siegrist, 1995) and has been widely used over the last decade. However, it is more commonly used for source treatment than for the dissolved phase (Siegrist et al., 2001). Oxidants are expensive and relatively short lived, so they usually are not suitable for use in barriers or treatment of low concentrations of contaminants within the plume. However, there have been cases where ISCO has been used for treatment of the dissolved phase, particularly in conjunction with source treatment (ESTCP, 1999).

ISCO involves injection of strong oxidants into the contaminated subsurface, in some cases with other chemicals that function as catalysts or pH adjusters (ITRC, 2005). The oxidants chemically break down CAHs upon contact, producing a wide range of often uncharacterized intermediates and innocuous end products (carbon dioxide, chloride and water). Several oxidants have been tried, but most commercial applications have used either hydrogen peroxide or permanganate in the saturated zone. However, there is increasing interest in other oxidants, such as persulfate and percarbonate (Watts and Teel, 2006).

The potential benefits from ISCO include *in situ* contaminant destruction, relatively low cost, reliability and simplicity (as compared to *in situ* biological treatment). The primary advantages of ISCO have been the low reagent costs and the potential for rapid treatment, potentially hastening site redevelopment or the transition to passive technologies.

ISCO has several limitations, including the potential threat to the health and safety of workers (ITRC, 2005). Strong oxidants are corrosive and potentially explosive. The design and operation of any ISCO system must take into account the hazards of the chemicals and the potential for vigorous uncontrolled reactions in the subsurface. Furthermore, because of the reactivity of the oxidants, there is potential for gas and heat evolution, which may cause significant changes in the distribution of contaminants within the subsurface (e.g., Watts et al., 2005).

Other limitations arise from the need for contact between oxidants and contaminants. Subsurface heterogeneities, preferential flow paths and poor mixing can result in extensive pockets of untreated contaminants (Siegrist et al., 2001). Slow diffusion of contaminants from inaccessible areas is one likely cause of the frequently observed rebound in aqueous concentrations after ISCO treatment (ESTCP, 1999; McGuire et al., 2003). Further, the reagents can be consumed by other oxidizable substrates (e.g., natural organic compounds or dissolved iron), limiting the efficiency of ISCO treatment. Finally, there is some potential for adverse impacts, such as increases in manganese concentrations and precipitation of manganese oxide after permanganate use (Crimi and Siegrist, 2004; Nelson et al., 2001).

9.5.2 *In Situ* Chemical Reduction

Chemical reduction of halogenated contaminants, including CAHs, can occur by contact with either reduced metals (Sweeney and Fisher, 1972; Reynolds et al., 1990) or metallic catalysts in the presence of hydrogen (Lowry and Reinhard, 1999). Rapid abiotic dechlorination of chloroethenes by ZVI was demonstrated in the early 1990s (Gillham and O'Hannesin, 1994). More recently, researchers have demonstrated that forms of reduced iron that are more common in the subsurface (such as FeS) can reduce CAHs (Butler and Hayes, 1999). This process, potentially mediated by naturally occurring electron shuttles (Lovley et al., 1999), can serve as the basis for MNA remedies, as noted earlier. It also may be exploited in more active remediation approaches.

The most common applications of *in situ* chemical reduction (ISCR) have involved installing PRBs, generally as trenches filled with ZVI (O'Hannesin and Gillham, 1998). Iron particles also can be injected into the subsurface to create reactive barriers or to treat plumes and sources directly (e.g., Cantrell et al., 1997). ZVI walls have been installed at numerous sites over the last decade and can work well when properly designed and constructed (Battelle, 2003).

Palladium catalysts installed in wells have been tested (McNab et al., 2000), and other forms of iron have been used, including nanoscale ZVI formulations (Elliott and Zhang, 2001; Zhang, 2003), bimetallic particles (Zhang et al., 1998) and ZVI mixed with emulsified oil (Quinn et al., 2005). The Biogeochemical Reductive Dechlorination (BiRD) technology also relies on chemical reduction, but uses biological activities to reduce native iron, that can then mediate CAH reduction (Kennedy et al., 2006).

The primary advantage of ZVI barriers is the passive nature of operation, which results in low labor and energy costs and potentially low life cycle costs. Other advantages include the lack of aboveground infrastructure that can interfere with ongoing operations, and the ability to reduce many dissolved contaminants, including common co-contaminants at DoD sites, such as perchlorate and ordnance compounds.

The main limitation of ZVI barriers is the potentially high installation costs, particularly if a significant quantity of ZVI is needed or the barrier must be installed to a significant depth or in difficult site conditions. There are concerns over the potential for short circuiting and fouling of ZVI barriers, as for any PRB approach. Finally, the actual longevity of PRBs under field conditions is not known, and the barrier may need to be replenished or replaced as the ZVI is oxidized or passivated (e.g., Agrawal et al., 2002; Farrell et al., 2000). However, the results from studies of existing ZVI barriers suggest the effective lifetimes may be well over 10 years in most cases (Battelle, 2003). It also should be noted that the appearance of a "clean front" downgradient of the PRBs has often not been observed, or was detected only after a delay of several years, at most of the sites surveyed. This result may reflect hydraulic problems such as short circuiting, but it may also indicate that recovery of plumes downgradient of a barrier will be a slow process (Gavaskar et al., 2005).

Other ISCR barriers generally share these advantages and limitations, although there are some technology-specific issues, including:

- **Nanoscale Iron**: The small size of nanoscale particles means they have large surface areas, and therefore high reactivities (Johnson et al., 1996), and also can be distributed more thoroughly within the subsurface. However, the cost for nanoscale iron is still much higher than for microscale forms, and their high reactivity can result in relatively short effective lifetimes, so nanoscale iron has been used primarily for source zone remediation.
- **Palladium**: Catalysis by palladium offers the advantage that the catalyst is not depleted and reaction rates are rapid. However, palladium is relatively costly, and cannot be widely distributed in the subsurface, so it must be contained within a treatment well. The operations and maintenance (O&M) needed to ensure consistent performance has also proven difficult under field conditions.

9.5.3 Electrochemical Reduction

The reduction of chloroethenes also can be accomplished by using electricity to drive the reaction (Sale and Gilbert, 2002). In practice, a panel of closely spaced electrodes is inserted into the subsurface perpendicular to the groundwater flow to create an “electron barrier.” Applying an electrical potential to the electrodes causes oxidizing conditions to develop at the positive electrode and reducing conditions at the negative electrode. The technique has been tested at field-scale, and CAH flux reductions of 90 to 95% were measured across a prototype electrically induced redox barrier (e-barrier) (Sale et al., 2005).

Promising aspects of the e-barrier technology include (1) no chemicals are introduced, (2) electrical power costs are low, (3) the potential at electrodes can be reversed or shifted to remove inorganic precipitates and (4) a wide range of contaminants can be treated because the process involves inducing both oxidizing and reducing conditions.

However, the e-barrier is still a developing technology, and the limited testing done so far suggests the costs are similar to those for other, more established approaches. e-barriers generally will be limited to shallow sites and may not be feasible in groundwater with high levels of total dissolved solids because of excessive scale formation.

9.6 PHYSICAL TREATMENT

In situ physical treatment technologies are designed to maximize removal. Only one such technology is included here, *in situ* air sparging. Multi-phase extraction is sometimes considered an *in situ* technology. However, it is not discussed in this chapter because it is primarily an extraction technology and it is used almost entirely for source removal and not for plume remediation.

9.6.1 *In Situ* Air Sparging

In situ air sparging (IAS) is a process in which air is injected directly into the saturated subsurface to volatilize contaminants from the liquid phase to the vapor phase, effectively stripping them from the saturated subsurface and into the vadose zone. Vapor phase contaminants may be treated within the vadose zone or migrate through it to the atmosphere, but they are most commonly extracted from the vadose zone, using soil vapor extraction (SVE) systems. For the purposes of this chapter, in-well air stripping is considered as a variation of IAS.

IAS has been most commonly used for petroleum contaminated sites, often with the intent of stimulating aerobic biodegradation (biosparging) as well as *in situ* air stripping. However, biodegradation plays a small role in contaminant removal with air sparging of CAHs, except in the few cases in which a cometabolite such as propane has been coinjected with air. Nevertheless, IAS has been the technology selected at approximately half of all Superfund sites with groundwater contaminated with halogenated volatile organics (USEPA, 2007; see Figure 9.2).

The advantages of IAS include that it is relatively low cost, it is easy to install and non-intrusive, and it can enhance the performance of existing SVE systems designed to remove CAHs from the vadose zone. IAS has been used successfully for source depletion at CAH sites (particularly when there is little or no DNAPL present), as well as for containment and remediation of dissolved phase plumes, either in barrier configurations or for plume wide treatment (NFESC, 2005). It is most applicable for homogeneous sites with moderate to high permeabilities (Leeson et al., 2000, 2002).

IAS has several limitations, largely resulting from difficulties in effective delivery and mixing within the subsurface. It is not recommended for areas with free product (as it may cause further spreading) or in groundwater in a confined aquifer. It may work poorly in stratified materials or at sites with high groundwater flow rates. Significant channeling can develop within the subsurface, or a large portion of the air can flow through existing preferential flow paths, resulting in poor contact with contaminants and lower percent removal. It is more difficult and costly at deep sites and those with thick contaminated zones.

9.7 DECISION GUIDELINES

It is not realistic or desirable to develop prescriptive guidance in this chapter. There are simply too many technology variations, decision drivers and site constraints to consider. Instead, this chapter will focus on red flags and problematic conditions for the technologies, and an evaluation of the ability of each technology to meet different management objectives for plume treatment.

The typical approach to developing a site-wide remediation strategy starts with the lowest-cost, most passive approach first (generally MNA), and an evaluation of where and when it can be used. Almost every site will use MNA for at least part of the site, for some period of time, so it is wise to evaluate its potential applicability. Such an evaluation can help develop remedial goals for more aggressive technologies. If MNA alone is not sufficiently protective across the entire site, without prior treatment, a subset of the available technologies is then evaluated.

The primary objective of such evaluations is to ensure adequate protection and compliance with regulatory requirements. However, there are several other factors to consider in the decision process. Management objectives will favor or preclude some *in situ* technologies. Site conditions can also impact the technology selected, with some technologies being particularly sensitive to some conditions but not others. While technologies often can be engineered to perform effectively at challenging sites, each technology has its own "red flags" — conditions that make a given technology infeasible, or at least considerably more difficult or expensive.

The following sections summarize the major technologies used for plume treatment according to their abilities to meet differing management objectives, and the most common site-specific constraints on their performance. The intent is to provide useful initial guidance, addressing the key decision criteria in a streamlined and pragmatic fashion. These criteria are depicted in Figure 9.5, and are similar to the factors defined by the USEPA for consideration in remedy selection (the nine "balancing criteria"), as well as to the macrocriteria and associated criteria used in more sophisticated decision support tools (Critto et al., 2006).

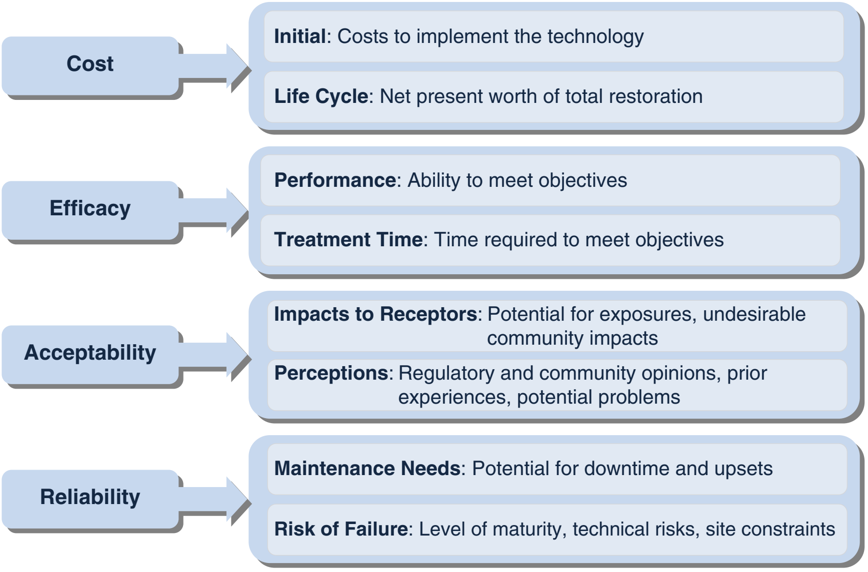

Figure 9.5. Macrocriteria and associated evaluation criteria used to compare remediation technologies

9.7.1 Ability to Meet Management Objectives

In many cases, minimizing cost is the primary decision driver. However, other factors are generally also important, and in many cases are more important than costs. Even though cost efficiency seems to be a clear goal, it may be more complicated in some cases because minimizing the costs for implementing a technology may not lead to the same decisions as minimizing overall life cycle costs for plume restoration.

Besides directly minimizing costs, other (often related) objectives include reducing the time of restoration, minimizing downtime and other reliability issues, and ensuring regulatory and community acceptance. Other goals that are not explicitly addressed in this screening evaluation but that may be important in some cases include minimizing interference with site activities and preventing undesirable side effects such as degradation of secondary water quality parameters.

The most commonly used *in situ* technologies have been compared for their abilities to achieve the key management objectives (Table 9.2). There could be considerable range within some of these relative rankings, depending on the specific conditions. However, these are intended only as screening-level comparisons designed to focus on the key attributes and constraints of each of the major technologies currently being used for full-scale cleanups.

9.7.1.1 Costs

If reducing initial implementation cost is the primary goal, MNA is generally the least costly option if it is appropriate for a site. Phytoremediation is also inexpensive to implement, particularly if deployed as a barrier to downgradient migration. ERD, ISCR and IAS all involve upfront costs for materials and injections, so all are considered moderate when used as barriers and all have a low ability to minimize initial costs when used for plume-wide restoration. ISCO is not commercially used for barriers and has probably the greatest initial cost of all of the technologies when used for plume restoration.

Table 9.2. Comparisons of Ability of the Most Common *In Situ* Technologies to Meet Key Management Objectives

Technology	Relative Ability to Meet Objective				
	Reduce Cost (Initial)	Reduce Cost (Life Cycle)	Rapid Treatment	Reliability	Public Acceptance
ERD (Barrier)	High	Moderate	Moderate	Moderate	Moderate
ERD (Plume)	Moderate	Moderate	Moderate	Moderate	Moderate
Phyto (Barrier)	High	High	Low	Moderate	High
Phyto (Plume)	High	High	Low	Low	High
MNA	High	High	Low	Moderate	Moderate
ISCR (PRB)	Moderate	Moderate	High	Moderate	High
ISCR (Plume)	Low	Low	Moderate	Moderate	Moderate
ISCO (Plume)[1]	Low	Low	Moderate	Moderate	Moderate
IAS (Barrier)	Moderate	Moderate	High	High	Moderate
IAS (Plume)	Low	Low	Moderate	Moderate	Moderate

[1] *In situ* chemical oxidation (ISCO) is not used as a barrier but may be used for plume treatment.
Relative rankings intended for screening-level comparisons. Site conditions may modify these rankings.

The rankings for long-term costs are similar. MNA generally has the lowest life cycle cost, when net present values are calculated. However, it is important to realize that the total monitoring cost can be considerable for sites where natural attenuation could require centuries. Phytoremediation also generally has a low life cycle cost. The life cycle costs are generally highest for *in situ* chemical treatments when used for plume wide restoration, because of the relatively high reagent costs and the inefficiency of using these technologies for low CAH concentrations. ERD and IAS are often more cost effective, unless the total electron donor demand is high (for ERD), or air injection wells are expensive to install and operate.

9.7.1.2 Speed

Speed also can be a complex goal. It could be interpreted as time needed to deploy the technology, or time needed for complete restoration of the plume. These criteria would modify the rankings presented in Table 9.2. However, for this discussion, speed refers to the most common and realistic management objective for *in situ* treatment: minimizing the time required to complete the treatment and meet the RAOs. These RAOs may be to achieve site closure, but more commonly they are to transition to more passive management (e.g., to initiate MNA or to turn off an existing pump-and-treat system) or to proceed with site development.

The biological technologies are not as fast as the chemical or physical treatments. Of the former, phytoremediation is a particularly slow process and ERD is generally more rapid. MNA is considered the slowest, generally because meeting its objective of closure can take a very long time. Installing a chemical or physical barrier is generally the choice for those wanting to move as quickly as possible into passive management. If a barrier alone is not sufficient to meet site goals, all of the other technology options will take longer to remediate the entire plume (although again, the biological technologies generally require the most time).

9.7.1.3 Reliability

Reliability refers to minimizing the need for optimization, maintenance or modifications due to performance shortfalls. ERD can require intermittent O&M, and there are often reliability concerns related to the potential for incomplete degradation, and resulting accumulation of more toxic byproducts. Phytoremediation can have reliability issues resulting from seasonal and year-to-year fluctuations in growth, water uptake and contaminant capture, although these usually can be addressed by over designing the treatment system. MNA is considered moderate because of concerns about the long-term sustainability of the remedy and because the lack of precision in the available predictive models often means that considerable monitoring may be needed to demonstrate reliability.

IAS is considered the most reliable, particularly when used as a barrier. However, there are still performance concerns with IAS in difficult hydrogeological conditions, and IAS systems require continued routine O&M. However, because of the ongoing O&M, there is less chance for failure or poor performance. Of course, if the systems are left unattended (which happens far more commonly than it should), reliability may be low.

The chemical treatments have had reliability issues. Rebound post-treatment is common for ISCO, for example. PRBs constructed with ZVI have had several reported hydraulic problems, and reductions in downgradient concentrations often have been slower than expected. However, PRBs that are designed and constructed well have been demonstrated to be reliable for over 10 years.

9.7.1.4 Public Acceptance

Acceptance of *in situ* technologies by regulators and communities generally has been high, despite initial skepticism. Typical issues that can cause difficulties are a perception of “doing nothing” or not doing whatever it takes to restore the site to pristine conditions. However, these initial objections usually can be addressed through education and negotiation. These public acceptance rankings address the technology-specific issues assuming *in situ* remediation in general is acceptable.

For ERD, the greatest barrier to acceptance has been the potential for accumulation of toxic byproducts, particularly if there is any potential for exposure to vapor emissions. The potential for impacts to downgradient water quality (increased dissolved metals, for example) may also raise concerns.

Phytoremediation generally has broad support and is perceived as “green” so long as adequate protection can be demonstrated. The potential issues affecting acceptance include emissions of contaminants to the atmosphere via evapotranspiration or accumulation in litter. Demonstrating degradation within the plants usually alleviates these concerns.

MNA usually has support, so long as the sources have been addressed and protection of potential receptors has been ensured. However, there is often a high hurdle to acceptance, requiring extensive testing, modeling and formulation of contingency plans.

Permeable reactive barriers generally raise few regulatory and community concerns. They are perceived as aggressive approaches to stopping plume migration and have few secondary impacts. Chemical treatment of plumes raises some issues related to rebound or occasionally negative impacts to water quality (e.g., dissolved and/or precipitated manganese from permanganate).

Air sparging generally has broad support, given the amount of successful use at numerous sites. The largest potential concern is vapor emissions, either because of plans for direct volatilization to the atmosphere without treatment, or because of proximity to occupied buildings. IAS also requires some aboveground facilities, for treatment and/or air injection, although these facilities are generally not obtrusive or objectionable. Finally, there may be regulatory concerns resulting from the potential for IAS to cause contaminants to migrate in the subsurface.

9.7.1.5 Sustainability

Although it is not included in Table 9.2, there is increasing interest in incorporating sustainability as one of the criteria for selecting remediation technologies (Vik et al., 2001). However, it is difficult to define or measure sustainability, and remediation may occur within a larger context that has its own sustainability impacts, such as brownfields redevelopment. Nevertheless, it seems likely that virtually all activities will increasingly be influenced by the need to ensure sustainability; in particular, environmental activities such as remediation will have to address sustainability (Pollard et al., 2004).

Sustainability evaluations of different remediation technologies can encompass environmental, economic and social issues (Dunmade, 2004). The factors most likely to be part of any sustainability assessment include environmental issues, particularly greenhouse gas (GHG) emissions, energy use, and use of water and other resources. Economic issues include the efficient use of resources to manage risks, assessment of the future benefits of remediation compared to the costs, as well as the impacts of remediation on the broader economy. The social issues include impacts on human health, noise and traffic.

In terms of environmental impacts, *in situ* technologies rank favorably in many areas. Wastes are generally destroyed and not simply transferred, and there is relatively little use of resources and energy. In terms of GHG emissions, the emissions rarely have been quantified, but they should be relatively low for most *in situ* technologies. In fact some technologies, notably phytoremediation, may result in carbon dioxide uptake from the atmosphere and offer the potential for mitigation credits. Addition of large amounts of fermentable material may lead to methane generation and release, and chemical treatment, particularly chemical oxidation, may lead to carbon dioxide emissions.

Remediation technologies that leave contaminants in place, such as MNA, raise other sustainability concerns. Will changing environmental conditions, including changes in climate, geochemistry or land use, impact the protectiveness of a remedy? Some of the potential changes that could impact remediation systems include rising or falling water tables, changes in groundwater extraction rates or flow directions, or even the effects of more severe storms or altered weather patterns.

9.7.2 Problematic Site Conditions

While it is not desirable or feasible to provide prescriptive technology selection criteria based on site characteristics, one can identify "red flags" (e.g., conditions that make the technology difficult to use and that should alert site managers that a thorough evaluation is needed). This approach is similar to that taken in the technology selection guidance provided in the "Principles and Practices of Enhanced Anaerobic Bioremediation" (AFCEE, 2004). These red flags have been summarized for each of the major technologies in Table 9.3.

A red flag does not necessarily mean a technology should be excluded. These are intended to be more like contraindications in the selection of a medical treatment. Just as in medicine, some contraindications are absolute (they make a particular treatment absolutely inadvisable), but in many cases they should be considered relative (they make a technology somewhat

Table 9.3. Problematic Site Conditions ("Red Flags") for the *In Situ* Technologies Most Commonly Used to Remediate CAH Plumes

Site Characteristic	ERD	Phyto-remediation	MNA	ISCR	ISCO	IAS
DNAPL Presence	Pooled DNAPL	Pooled DNAPL	Pooled or residual DNAPL	Little effect	Little effect	Pooled DNAPL
Plume Size	>4 hectares (10 acres)	>4 hectares (10 acres)	Expanding, or receptors impacted	>4 hectares (10 acres)	Large areas with low CAH concentrations	>4 hectares (10 acres)
Site Infrastructure	Potential for vapor intrusion or for high methane levels	Surface or subsurface obstructions	Little effect	Potential for vapor intrusion	Potential for vapor intrusion	Surface obstructions
Depth to Contaminated Groundwater	>11 m (35 ft) ("biowall") >30 m (100 ft) (plume)	>6 m (20 ft)	Little effect	>11 m (35 ft) permeable reactive barrier (PRB)	>30 m (100 ft)	>15 m (50 ft)
Saturated Thickness	>15 m (50 ft)	>3 m (10 ft)	Little effect	>15 m (50 ft) (total depth below ground surface)	>15 m (50 ft)	>6 m (20 ft)
Hydraulic Conductivity	<3.5 x 10^{-6} cm/sec (0.01 ft/day)	<3.5 x 10^{-6} cm/sec (0.01 ft/day)	Little effect	<3.5 x 10^{-6} cm/sec (0.01 ft/day)	<3.5 x 10^{-6} cm/sec (0.01 ft/day)	<3.5 x 10^{-6} cm/sec (0.01 ft/day)
Groundwater Velocity	<3 m/yr (10 ft/yr) or >3 m/day (10 ft/day)	>0.3m/day (1 ft/day)	Contaminant transport > attenuation rate	>3 m/day (10 ft/day)	Little effect	>3 m/day (10 ft/day)
Other	No detected biodegradation metabolites / pH <5.0 or >9.0 SO_4 > 5,000 mg/L	Overlying soils infertile or impermeable/ adverse climate	Remaining untreated source / unacceptable risk or restoration time frame	High sulfate, alkalinity or total dissolved solids / no lower confining layer	High total organic carbon, sulfides, or natural oxidant demand	Overlying soils with low permeability or preferential flow paths

Note: cm/sec - centimeters per second; mg/L - milligrams per liter.

inadvisable, but do not rule it out). Comparing these problematic conditions with those existing at a specific site can be helpful during the technology screening process.

9.7.2.1 Biological Treatment

For ERD, perhaps the most common red flags include the presence of pooled DNAPL, and current or potential vapor intrusion into occupied buildings. Many plumes are also simply too large to treat cost effectively with aggressive bioremediation, or too deep for an installed reactive barrier, or so-called biowall. Bioremediation is difficult in impermeable subsurface materials, and can be very difficult in rapidly moving aquifers because the effective residence time in the treatment zone is too low for complete remediation.

With respect to *in situ* plume containment or treatment, the lower depth to water (30 m [100 ft]) and maximum saturated thickness (15 m [50 ft]) are somewhat arbitrary. However, these values were used for all technologies, unless there was a reason to choose a different value, to reflect the common limitation that aggressive treatment of any site becomes significantly more difficult and costly at greater depths or thicknesses. The 4-hectare (10-acre) plume size limit (from AFCEE, 2004) is also not an absolute contraindication, only a reflection of the difficulty and expense involved in injecting remedial agents over a large area.

Phytoremediation has its own unique red flags related to the ability to grow the needed plants and the limitations of plants as remedial agents. Roots generally cannot tolerate or effectively treat areas with accumulated DNAPL, and they cannot grow through impermeable soils or to great depths.

MNA is applicable to a wide variety of site conditions, so long as the data indicate the risks are controlled and restoration will occur in a reasonable timeframe. Because it is relatively inexpensive and total removal is often not technically achievable, MNA is generally at least part of an overall site remediation strategy and is often the sole technology used (McGuire et al., 2003).

9.7.2.2 Chemical Treatment

ISCR, when used for plume remediation, is for most purposes limited to permeable reactive barrier applications in which ZVI can be placed in trenches or injected with adequate distribution. This limitation means that ISCR is practically limited to about an 11 m (35 ft) depth to water (approximately the maximum depth for relatively simple trench installation), and a total treatment depth of not more than about 15 m (50 ft) total.

ISCR is also not appropriate for direct treatment of low-permeability zones, but PRBs can be placed in most materials, unless the groundwater velocity is too rapid for effective treatment. PRBs also are not usually appropriate for geochemical conditions that will cause significant scaling or passivation or hydrogeologic conditions that lead to short circuiting or bypassing (e.g., lack of a lower confining barrier to groundwater flow).

ISCO is not often used for plume treatment or containment because it is too inefficient (and therefore too costly) to treat low concentration areas. It is difficult to distribute oxidizing compounds into low-permeability zones, and significant natural oxidizing demand can make treatment costly.

9.7.2.3 Physical Treatment

IAS is not appropriate at sites with significant pooled DNAPL, or in confined aquifers, or at highly stratified sites. It is an increasingly difficult technology to use as the depth of air injection wells increases and as the volume of subsurface needing treatment increases. It also may be difficult to get effective stripping of CAHs if the groundwater is moving rapidly through the treatment zone.

9.8 SUMMARY

This chapter is not meant as detailed guidance to selecting the appropriate *in situ* technology for any given site. Rather, it is intended to provide a framework for decision-making, as well as information and resources helpful for making decisions. In environmental restoration, there are rarely perfect alternatives or easy decisions because there are too many complex and interacting factors affecting the process. Nevertheless, this guidance can provide a useful starting point, allowing site managers and remediation professionals to focus on the most promising approaches quickly.

Finally, it is important to remember that most *in situ* technologies are very flexible, and are still evolving rapidly. Managers can often design and operate these technologies to overcome the constraints posed by a given site. However, understanding the site conditions, the site objectives and the technologies available as well as possible will help prevent perceived failures and ensure that the remedial goals are met as cost effectively as possible.

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CHAPTER 10

BIOREMEDIATION OF CHLORINATED SOLVENT PLUMES

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10.1 INTRODUCTION

The following sections summarize the major topics involved in *in situ* bioremediation of soluble phase (dissolved) chlorinated solvents in groundwater. This introduction is designed to provide some context for the following chapters and an overview of the development of *in situ* bioremediation for chlorinated solvents.

This chapter is principally concerned with the microbial remediation of chlorinated ethenes because these contaminants are particularly prevalent and problematic, especially at Department of Defense (DoD) sites. The focus is primarily on the use of reductive dechlorination, or chlororespiration—an anaerobic process that results in the sequential dechlorination of the chlorinated aliphatic hydrocarbons (CAHs), ultimately producing innocuous end products. This process has become important for the commercial success of engineered or intrinsic biodegradation to treat chlorinated ethenes in groundwater.

10.1.1 What is *In Situ* Bioremediation?

Bioremediation is the use of organisms, restricted here to microorganisms, to convert contaminants to less harmful compounds in order to clean up contaminated sites. It may just involve monitoring intrinsic biodegradation, or it may include deliberately altering the subsurface environment to enhance the desired biological processes. Such enhancement generally involves adding nutrients or energy sources to increase the activity of the organisms already present in the subsurface, but in some cases it may also involve adding selected organisms to improve the biodegradation capacity or its rate.

Bioremediation is possible only because organisms have developed such an impressive ability to survive under a wide variety of conditions. Although scientists in the past assumed that the subsurface and groundwaters below the soil profile were near sterile, in fact, the genetic diversity, physiological versatility and sheer numbers of microorganisms naturally present in the environment are overwhelming. Groundwaters may have 1 million (10^6) total recoverable cells in each milliliter (mL), though numbers in the range of 10^4/mL are more common (Hirsch and Rades-Rohkohl, 1988). Furthermore, perhaps only 1–10% of the total cells present are recoverable (Wilson et al., 1983; Amann et al., 1995). The vast majority of the cells are not in the groundwater but are attached to the subsurface solids (Thomas et al., 1987). The biological diversity of these subsurface microbial communities is staggering—researchers continue to find surprising capabilities among the virtually innumerable species and strains of microbes present throughout the environment (e.g., Pace, 1997; Rondon et al., 1999; Janssen et al., 2005).

One result of this biological potential is that most organic contaminants, and many inorganic contaminants, can be biodegraded or biotransformed by the indigenous organisms,

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often at rates that are sufficient to control the risks of exposure. When the rates are not sufficient, practitioners have developed the ability to supply the ingredients needed to enhance the rates. To use this approach, it is necessary to fully understand the requirements and limitations of the microbes responsible for biodegradation (based on their physiology and, to some extent, their ecology) as well as the methods for effectively delivering rate-increasing amendments to the subsurface, which is often a very technically challenging task (Kitanidis and McCarty, 2010).

In the case of CAHs, the ability to understand and enhance their biodegradation has not been straightforward. For one thing, these compounds are relatively oxidized (particularly perchloroethene [PCE] and trichloroethene [TCE]), and bioremediation was started with a focus on the aerobic oxidation of reduced contaminants such as petroleum hydrocarbons (Thomas and Ward, 1989). Aerobic oxidation can be mediated by a wide variety of microbes naturally present in the subsurface, although their activity is generally limited by oxygen—and sometimes nitrogen and phosphorus—availability, so delivery of oxygen and inorganic nutrients was the primary focus (Norris, 1994). However, more oxidized contaminants are more easily transformed by reduction, which is favored under anaerobic conditions. For many reasons, including the complexity of the anaerobic environment, the technical difficulties of working with anaerobes and the initially greater public concern over petroleum contamination, the scientific understanding and deliberate use of anaerobic microbiology for *in situ* bioremediation has been slower to develop.

Another reason that it took longer to develop enhanced anaerobic bioremediation for chlorinated solvents is that the virtual presumptive remedy for these contaminants was to pump and treat the groundwater. The recalcitrance of these compounds, and the resulting large dissolved-phase plumes, resulted in a rapid effort to hydraulically contain the plumes. As a result, there was relatively little motivation to test unproven innovative technologies until the limitations and seemingly never-ending costs associated with these pump-and-treat systems became apparent (NRC, 1994).

Finally, the early approaches to bioremediation of the most prevalent chlorinated solvent, TCE, focused on the promising aerobic cometabolic approach. Although there have been applications to both intrinsic and engineered *in situ* bioremediation and there is still ongoing research (Sorenson et al., 2000; Hopkins and McCarty, 1995 Kim et al., 2006), it has had little commercial use, in part because the process can be difficult to control in the field and there is no known competitive advantage to the microbes to use aerobic cometabolism for CAH degradation. This focus may have delayed the development of enhanced *in situ* anaerobic bioremediation, but once the latter technology was demonstrated, its adoption was extraordinarily rapid. Once anaerobic biodegradation of chlorinated solvents was recognized as a widespread naturally occurring process, given favorable conditions, the acceptance of monitored natural attenuation (MNA) of CAHs was also very rapid.

10.1.2 Why Use *In Situ* Bioremediation?

The primary driver behind the rapid adoption of anaerobic reductive dechlorination for chlorinated solvents has been cost reduction. As noted earlier, the limitations of pump-and-treat became obvious in the early 1990s (Travis and Doty, 1990). There was widespread interest in using *in situ* remedies to replace or lessen the use of pump-and-treat systems and thereby lower the long-term costs for managing these sites (NRC, 1994; DoD, 1998). In response, organizations such as the DoD's Strategic Environmental Research and Development Program (SERDP) and the DoD Service laboratories (Army, Navy and Air Force) committed significant funds to developing and testing innovative *in situ* remediation technologies.

There are several competing *in situ* technologies for containing and treating contaminated groundwater, including chemical oxidation and reduction, phytoremediation and air sparging, and all have their place in the remediation toolbox. The success of bioremediation is largely based on the fact that bacteria will literally work for food, and the food can often be inexpensive materials such as compost or vegetable oil (e.g., Long and Borden, 2006). Energetically, these materials serve as electron donor (and carbon) sources. Fermentation ultimately produces hydrogen, which the microbes responsible for reductive dechlorination of CAHs use as the source for electrons to reduce the CAHs, while using another fermentation product, acetate, as a carbon source. They derive energy from the reduction of the CAH, which serves as the electron acceptor in this paired reduction/oxidation reaction (e.g., Holliger et al., 1993).

In situ bioremediation also has found rapid acceptance because it can result in complete conversion to non-toxic products: ethene, ethane, methane and carbon dioxide. Historically, a major drawback has been that reductive dechlorination of PCE proceeds through sequential production of less chlorinated intermediates (TCE, *cis*-1,2-dichloroethene [*cis*-DCE], some *trans*-1,2-dichloroethene [*trans*-DCE], and vinyl chloride [VC]), and an apparent accumulation of the more toxic DCE and VC intermediates often occurs (Wiedemeier et al., 1999). However, given the right environmental conditions and subsurface microbial community, these intermediates can eventually be degraded as well (e.g., DeBruin et al., 1992).

In situ bioremediation also has proven to be a remarkably flexible technology. It has been implemented in many environments, in a wide variety of ways. Several electron donor sources have been successfully used, including soluble, semi-soluble and solid substances (AFCEE, 2004). Several methods of delivering and mixing amendments have been employed, and the flexibility of bioremediation has made it possible to use it in combination with several other technologies. It is also possible to biodegrade or biotransform many common co-contaminants, such as perchlorate, RDX (cyclotrimethlyenetrinitramine), and some metals, under anaerobic conditions (e.g., Logan, 2001; Regan and Crawford, 1994).

10.1.3 Why Not Use *In Situ* Bioremediation?

Any remediation technology has limitations, and reductive dechlorination has several that must be recognized (AFCEE, 2004). One of the more important limitations is that it cannot be used at all sites. Site-specific factors that make the distribution of amendments difficult, such as low permeability or highly heterogeneous conditions, can limit its applicability. Fractured bedrock sites may be difficult to treat effectively. Very deep contamination or very high concentrations (e.g., "pools" of free-phase product) may also pose problems. Sites with high influxes of alternative electron acceptors (e.g., relatively rapid groundwater flows with high sulfate concentrations) may also be difficult to treat because of the high electron-donor demand.

Another important limitation is that *in situ* bioremediation using anaerobic reductive dechlorination is a relatively slow approach, compared to thermal or chemical technologies, and a prolonged period of monitoring and operation may be needed. Responsible parties often place a high priority on rapid implementation (for example, when some remediation is required prior to a property transfer), and *in situ* bioremediation can require months to years to implement.

Another common objection is that adding large amounts of fermentable organic material to an aquifer can have undesirable side effects. Converting the subsurface into a highly anaerobic, carbon-rich environment can cause deterioration of water quality, notably the mobilization of some metals, such as arsenic and iron, that become more soluble under conditions of low oxidation-reduction potential (e.g., McLean et al., 2006). Noxious gases produced during fermentation (e.g., methane or hydrogen sulfide) can accumulate in the subsurface or in structures. There also has been some concern about gas blockage of aquifer pore space at particularly high rates of electron donor addition (Yang and McCarty, 2002).

Finally, the potential for incomplete biodegradation has been a source of some concern. As noted before, reductive dechlorination can "stall" at VC, resulting in greater risks of groundwater ingestion or indoor air exposures (Wiedemeier et al., 1999; McGuire et al., 2004). This stall may be the result of insufficient numbers of the needed microorganisms or geochemical conditions that limit the desired activities; however, it also may be simply a kinetic effect (the rates of reduction of the more oxidized PCE and TCE compounds are faster than those for the reduction of DCE or VC). Whatever the cause, temporary or sustained accumulation of the intermediates is commonly observed and requires careful monitoring and contingency plans because it can raise public concerns regarding the use of this technology.

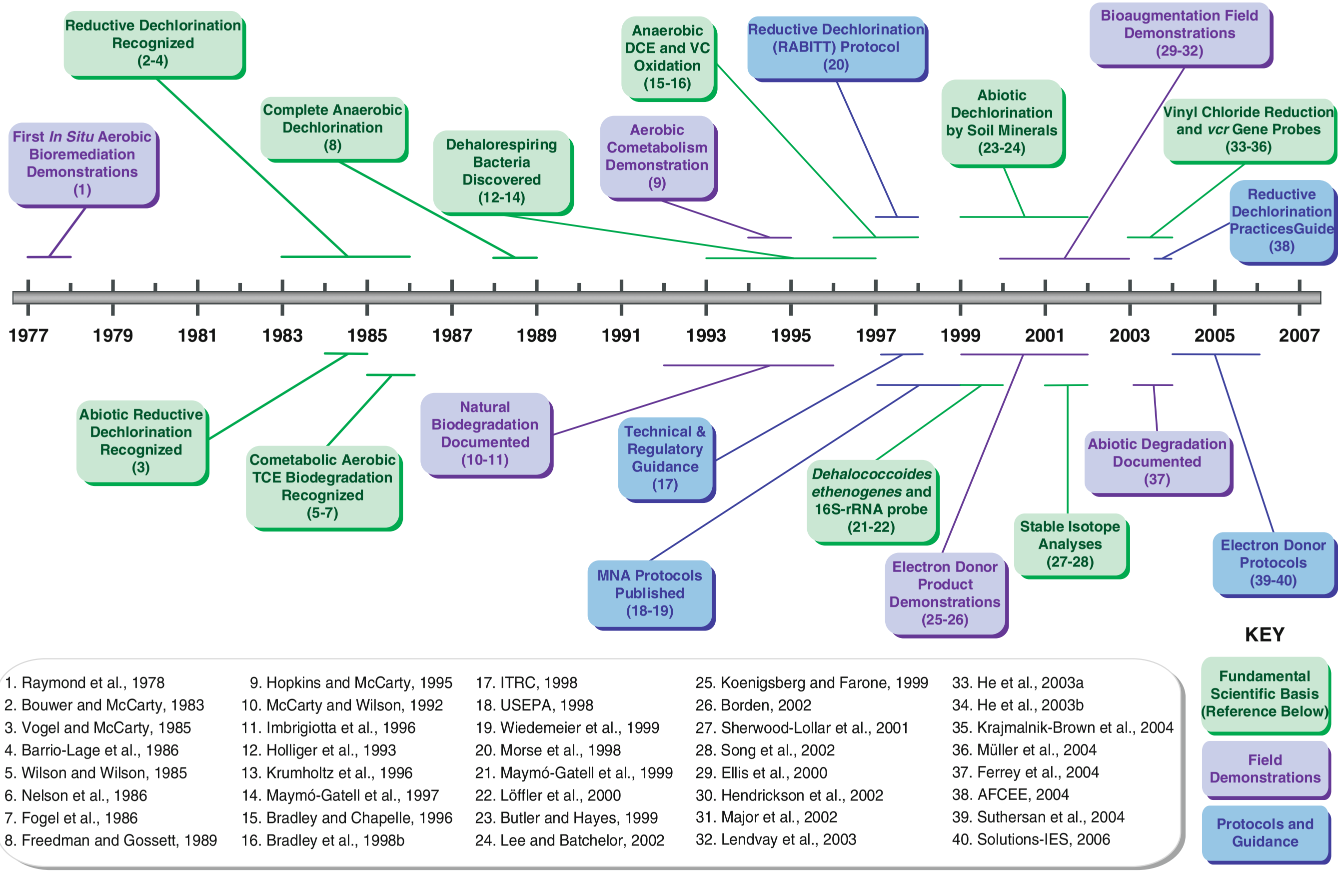
10.2 A BRIEF HISTORY

The development of *in situ* reductive dechlorination of chlorinated solvents is a fascinating story. The highly chlorinated ethenes (PCE and TCE) were used for decades by the DoD and many private sector industries as solvents and degreasers (see Chapter 1 of this volume). However, the very properties that made them useful to industry also made them among the most widespread and costly contaminants in groundwater. They also proved to be recalcitrant to biodegradation under most conditions. Considerable research and ingenuity over the past two decades have helped us understand how these contaminants can be biodegraded safely and cost-effectively, considerably reducing both the costs for cleanup and the continuing risks to human health and the environment.

In situ bioremediation of chlorinated solvents has progressed from basic laboratory discoveries to a mature technology in roughly 20 years. Along the way, new applications and understandings have led to refinements, and these refinements are still continuing. Figure 10.1 provides a timeline indicating the major developments, with some key references. It is not intended to be a complete history but to illustrate the major trends and often overlapping developments. Some of these developments are identified below:

- Recognition of the ability of anaerobic organisms to completely dechlorinate CAHs and discovery of some of the responsible organisms.
- Recognition that natural biodegradation could occur at rates adequate to control the risks of CAHs in groundwater.
- Understanding that the organisms responsible for efficient and complete dechlorination were not ubiquitous but could be successfully added to improve the performance of *in situ* reductive dechlorination systems.
- Development of methods to cost effectively formulate and supply electron donors.
- Recognition of the potential role of abiotic processes in natural and enhanced attenuation.
- Development of tests, protocols and tools to monitor and predict performance.

In situ bioremediation was first used by Raymond and co-workers at Sun Oil Co. to treat fuel contamination (Raymond et al., 1978). The use of aerobic processes has continued to the present day, and has been widely accepted since the late 1980s (Thomas and Ward, 1989). The



1. Raymond et al., 1978
2. Bouwer and McCarty, 1983
3. Vogel and McCarty, 1985
4. Barrio-Lage et al., 1986
5. Wilson and Wilson, 1985
6. Nelson et al., 1986
7. Fogel et al., 1986
8. Freedman and Gossett, 1989
9. Hopkins and McCarty, 1995
10. McCarty and Wilson, 1992
11. Imbrigiotta et al., 1996
12. Holliger et al., 1993
13. Krumholtz et al., 1996
14. Maymó-Gatell et al., 1997
15. Bradley and Chapelle, 1996
16. Bradley et al., 1998b
17. ITRC, 1998
18. USEPA, 1998
19. Wiedemeier et al., 1999
20. Morse et al., 1998
21. Maymó-Gatell et al., 1999
22. Löffler et al., 2000
23. Butler and Hayes, 1999
24. Lee and Batchelor, 2002
25. Koenigsberg and Farone, 1999
26. Borden, 2002
27. Sherwood-Lollar et al., 2001
28. Song et al., 2002
29. Ellis et al., 2000
30. Hendrickson et al., 2002
31. Major et al., 2002
32. Lendvay et al., 2003
33. He et al., 2003a
34. He et al., 2003b
35. Krajmalnik-Brown et al., 2004
36. Müller et al., 2004
37. Ferrey et al., 2004
38. AFCEE, 2004
39. Suthersan et al., 2004
40. Solutions-IES, 2006

Figure 10.1. Timeline illustrating key events in the development of *in situ* anaerobic bioremediation of chlorinated ethenes

lessons learned from the development and demonstration of aerobic *in situ* bioremediation have been valuable and have been adapted to the task of enhancing and monitoring the anaerobic biodegradation of CAHs.

The ability of anaerobic bacteria to partially degrade PCE and TCE was recognized in the mid-1980s (Bouwer and McCarty, 1983). However, the original research suggested that anaerobic biodegradation did not proceed past VC, a major limitation since VC is more toxic than the parent compounds. There was therefore interest in combining anaerobic treatment with aerobic polishing to allow complete biological treatment (e.g., Fogel et al., 1986).

The ability of aerobic bacteria to completely biodegrade some chlorinated solvents (notably TCE, but not PCE) was demonstrated in the mid 1980s (Wilson and Wilson, 1985; Nelson et al., 1986). These bacteria were able to degrade TCE by a process of aerobic cometabolism. In cometabolism, organisms use other carbon and energy sources—in this case the cometabolites include toluene, methane and propane—and fortuitously degrade chlorinated solvents by the same enzymes (monooxygenases or dioxygenases) (Strand and Shippert, 1986; Bielefeldt et al., 1995). However, aerobic cometabolism has proven to be difficult, but not impossible, to implement *in situ*. Despite considerable research, the field-scale use of this approach has been rare (Hopkins and McCarty, 1995; Goltz et al., 2005; Semprini, 1997; Kim et al., 2006).

The continuing research on anaerobic reductive dechlorination laid the groundwork for the development and rapid adoption of engineered and intrinsic bioremediation. Four findings in particular were important to the eventual success of these technologies.

- The discovery that some organisms could use CAH reduction for energy (Holliger et al., 1993), which allows more rapid and efficient biodegradation.
- The recognition that DCE and VC could be completely degraded under a variety of redox conditions (Freedman and Gossett, 1989; DeBruin et al., 1992; Hartmans and DeBont, 1992; Bradley and Chapelle, 1996; Lovley et al., 1996; Bradley et al., 1998a, 1998b).
- Elucidation of the role of hydrogen in the reductive transformation process, showing that hydrogen is the ultimate electron donor and that dechlorinating bacteria can access the hydrogen at lower concentrations than competing hydrogen users, such as methanogenic bacteria (Adrian et al., 2000; Maymó-Gatell et al., 1999; Smidt and deVos, 2004).
- The discovery of *Dehalococcoides* strains that could degrade all of the chlorinated ethenes completely to innocuous products (Maymó-Gatell et al., 1997; He et al., 2003a), and the observation that complete biodegradation occurred only at sites where *Dehalococcoides* was detectable (Hendrickson et al., 2002).

The biggest deterrent to *in situ* reductive dechlorination has been the potential for partial dechlorination, resulting in accumulation of *cis*-DCE and VC. The realization that complete dechlorination could be achieved, in the laboratory (Freedman and Gossett, 1989) and in the field (Major et al., 1991), stimulated the development of the technology, but stalling at DCE or VC still occurs at many sites. Although there are many potential causes for this stalling (e.g., Wiedemeier et al., 1999), the increased understanding of the responsible organisms and their ecology has led to isolation of several mixed cultures that have been successfully used for bioaugmentation (Ellis et al., 2000; Major et al., 2002; Lendvay et al., 2003; ESTCP, 2005). There are now several proven bioaugmentation cultures that can be used to overcome DCE or VC stalling at sites or to hasten the onset of complete degradation and/or increase the overall biodegradation rates (ESTCP, 2005).

The work on *Dehalococcoides ethenogenes* has shown that not all strains have similar degradation capabilities. The first strain discovered, Strain 195, can obtain energy from all steps in the sequential reductive dechlorination process except VC reduction and can degrade VC only by the slower and less certain process of anaerobic cometabolism (Maymó-Gatell et al., 1999). However, other strains have shown the ability to completely dechlorinate lesser-chlorinated ethenes and to obtain energy from even the VC reduction step (Duhamel et al., 2004; Cupples et al., 2003; He et al., 2003b; Löffler et al., 2000). These findings have increased the ability to characterize and monitor sites for reductive dechlorination potential and to implement both biostimulation and bioaugmentation remedies with greater confidence.

As the fundamental understanding and confidence in the process of reductive dechlorination increased, researchers recognized that natural biodegradation could be sufficiently protective under favorable conditions to manage the risks of CAHs in groundwater (e.g., Imbrigiotta et al., 1996). Protocols were developed by the U.S. Environmental Protection Agency (USEPA) and others to allow MNA at appropriate sites (USEPA, 1998; Wiedemeier et al., 1999). The acceptance of MNA at CAH sites has been rapid, partly because many of these sites cannot practically be cleaned up to regulatory standards through alternative, more intensive technologies (Stroo et al., 2003). The commonly used strategy of source treatment combined with MNA for the residuals and dissolved-phase contaminants has allowed many cleanups to progress beyond long-term hydraulic containment.

Commercial vendors realized there was a market for products designed to enhance reductive dechlorination, and several products have been developed (Suthersan et al., 2004; Borden, 2002; Koenigsberg and Farone, 1999). These products range from soluble substrates added frequently at relatively high concentrations, to semi-soluble and longer-lasting materials, to solid slow-release materials. A variety of organic wastes and inexpensive materials also has been used, and commercial formulations combining different types of electron donor sources have been developed. Each has its strengths and limitations, but careful field testing has shown that the process can be effective for plume treatment or containment using a wide variety of electron donor sources (AFCEE, 2004).

There have been several recent innovations that have the potential to improve chlorinated solvent bioremediation. One such innovation is the development of molecular biological tools (MBTs) and stable isotope analyses to assist in characterizing and monitoring sites (discussed in Section 10.3). In addition, the understanding of abiotic reactions involving chlorinated solvents has also increased (Butler and Hayes, 1999; McCormick and Adriens, 2003). It has become clear that abiotic reactions can contribute to natural and enhanced attenuation of these contaminants under reducing conditions (Ferrey et al., 2004). Modeling tools have also improved the ability to predict and evaluate natural and enhanced attenuation (e.g., Chapelle et al., 2003).

Further innovations seem likely as well. For example, the recent sequencing of the genome of several *D. ethenogenes* strains, beginning with Strain 195 (Seshadri et al., 2005) may lead to new molecular biological tools and insights. The anaerobic environment is complex and relatively unknown, and we have much to learn that could improve anaerobic *in situ* bioremediation (Lovley and Coates, 2000). Aerobic biodegradation may also play an important role. There have been several reports of aerobic biodegradation of DCE and VC by isolated bacteria (Verce et al., 2000; Coleman et al., 2002), and recent research suggests that aerobic oxidation of VC, and perhaps DCE, may occur at extremely low oxygen levels (Gossett, 2010). Organisms such as these may be useful for bioaugmentation at the aerobic fringes of sites if these metabolites have not been completely degraded within the anaerobic area of a site. Furthermore, aerobic cometabolism may be playing a larger role than previously believed in attenuating chlorinated solvents in aerobic plumes, although it may be difficult to detect (Erwin et al., 2005).

10.3 MOLECULAR BIOLOGICAL TOOLS

One area worthy of mention is the rapid advance in the use of MBTs to better characterize the biological potential at sites and to monitor bioremediation. Advances in molecular biology have had a profound effect on the understanding of biologically based remedial processes and MBTs are used extensively in research and development. Although their use in the operational cleanup community remains limited at present, there is tremendous potential for use of these technologies to improve the design, implementation, field performance and monitoring of remediation technologies (Lovley, 2003; Stroo et al., 2006).

MBTs are defined as tools that target biomarkers—specific nucleic acid sequences, peptides, proteins or lipids—to provide information about organisms and processes relevant to the assessment or remediation of contaminants. MBTs have the potential to provide rapid and reliable measures for both a second and third line of evidence for natural attenuation and *in situ* bioremediation: evidence that indigenous microorganisms have the potential to transform or degrade contaminants and evidence that transformation or degradation is occurring in the field (NRC, 2000; Smets and Pritchard, 2003; USEPA, 1998).

A recent SERDP expert panel (SERDP, 2005) identified the primary reasons that, to date, MBTs have not been more widely used, as well as the most promising research and development needs. Six barriers to field implementation were identified by the panel: subsurface sampling difficulties, insufficient knowledge regarding key biomarkers, limited decision-making impact, limited ability to develop rate information, insufficient confidence in results and limited commercial interest at present. In particular, the ability to use MBTs to quantitatively estimate the rates of biodegradation under field conditions would be of great value and would greatly increase the use of these tools.

Despite these barriers, progress continues to be rapid. Some of the significant advances affecting the bioremediation of chlorinated solvent plumes are listed below:

- Development of methods, particularly polymerase chain reaction (PCR) methods, to both identify and quantify the presence of specific deoxyribonucleic acid (DNA) sequences, such as the 16S ribosomal DNA of *Dehalococcoides* (Löffler et al., 2000).
- Sequencing of the *D. ethenogenes* genome (Seshadri et al., 2005).
- Discovery of probes for trichloroethene reductase (*tceA*) and vinyl chloride reductase genes (*vcrA* and *bvcA*), allowing direct measurement of the potential for TCE dechlorination and for complete dechlorination to ethene (Krajmalnik-Brown et al., 2004; Magnuson et al., 2000; Müller et al., 2004).
- Development of compound-specific stable isotope analysis to monitor chlorinated solvent biodegradation (Hunkeler and Aravena, 2000; Hunkeler et al., 2008).
- Development of enzyme probes to detect oxygenase enzymes capable of aerobic degradation of some solvents (Erwin et al., 2005).

In addition to PCR, common MBTs used to evaluate sites include phospholipid fatty acid analysis (PLFA), denaturing gradient gel electrophoresis (DGGE) and terminal restriction fragment length polymorphism (T-RFLP) (Stroo et al., 2006). PLFA was the first MBT to be commercialized for environmental applications, and it has been widely used at field sites. PLFA can provide high-level, qualitative information about overall community structure and microbial "health", and quantitative information about the biomass present. DGGE often has been applied at field sites to identify specific organisms, such as dechlorinators. DGGE also has been widely used, most often to evaluate microbial diversity, because it can distinguish closely related species or even strains within a species. T-RFLP is also useful for screening microbial diversity, because it facilitates differentiation of a large number of community members. The use of all of these tools has declined with the development and commercialization of quantitative PCR.

There are promising areas for future MBT applications (SERDP, 2005). For example, fluorescence *in situ* hybridization could allow direct detection and quantification of a specific organism of interest by staining organisms carrying certain genes. Quantification of messenger ribonucleic acid (RNA) (mRNA) levels would be of value because mRNA reflects not just the potential for producing enzymes of interest but also the amount being expressed (i.e., used for protein formation) at a given time (Johnson et al., 2005). Proteomics, the direct measurement of specific proteins (such as dechlorinase enzymes), could provide the most direct data on biodegradation rates or specific metabolic activities (Werner et al., 2009), but significant research is still needed before commercial use is possible.

10.4 USE OF *IN SITU* ANAEROBIC BIOREMEDIATION

The use of *in situ* reductive dechlorination is hard to assess, partly because it has been increasing so rapidly. *In situ* bioremediation in general has become widely accepted for many contaminants and site conditions; in particular, the use of MNA has become very common. For example, a 2001 survey of Leaking Underground Storage Tank (LUST) sites, which are primarily petroleum-contaminated sites, found that *in situ* bioremediation was used at 9% of the sites with groundwater contamination, and MNA was used at 67% (Kostecki and Nascarella, 2003).

The use of *in situ* anaerobic bioremediation for chlorinated solvent sites has also become widespread. Of the 90 Superfund sites with groundwater contamination by “halogenated organic volatiles”, 26% had used *in situ* bioremediation (USEPA, 2004), second only to the use of *in situ* air sparging (at 47% of the sites). A recent survey by the U.S. Air Force indicated that active *in situ* bioremediation systems were in place at approximately 8% of all “solvent-only” contaminated groundwater sites, while MNA was in place at 25%. However, use is likely to continue expanding, because pump-and-treat systems were in place at almost half of the sites, and much of the motivation to use *in situ* technologies has been to replace pump-and-treat systems (GAO, 2005).

MNA in particular seems likely to become even more common at chlorinated solvent sites. A recent expert survey examined 191 sites and concluded that MNA could be a possible sole remedy or remedy component for 75% of the sites (McGuire et al., 2004). In the same report, a survey of 45 sites currently undergoing MNA showed that anaerobic biodegradation was the primary attenuation mechanism at over 70% of the sites. However, of those 45 sites, MNA was the sole remedy at only 21% of the sites and was usually used in conjunction with active treatment either for portions of the site or after some active treatment was first completed.

It can be difficult to separate the use of *in situ* bioremediation for dissolved phase CAHs and its use for source depletion or containment. Recent findings have shown that bioremediation of DNAPL source zones is possible, and its use for source control is rapidly increasing as well (Adamson et al., 2003; ITRC, 2005). There is a lot of interest in combining technologies for efficient site-wide remediation strategies, and *in situ* bioremediation is well suited to such combined remedies (SERDP, 2006).

Anaerobic *in situ* bioremediation can actually be used for several purposes at a site, often at the same time (Figure 10.2). It can be used to contain a contaminant plume (in biobarriers formed by injecting electron donor sources into the aquifer, or in “biowalls”—trenches filled with organic materials), to remediate the entire plume, to remove the contaminant sources, or to contain those sources. It can be applied passively by one-time, or infrequent, injections of slow-release donor sources, or it can be applied in a much more active manner, with frequent (weekly to monthly) injections and/or recirculation of groundwater to enhance the distribution of amendments (AFCEE, 2004).

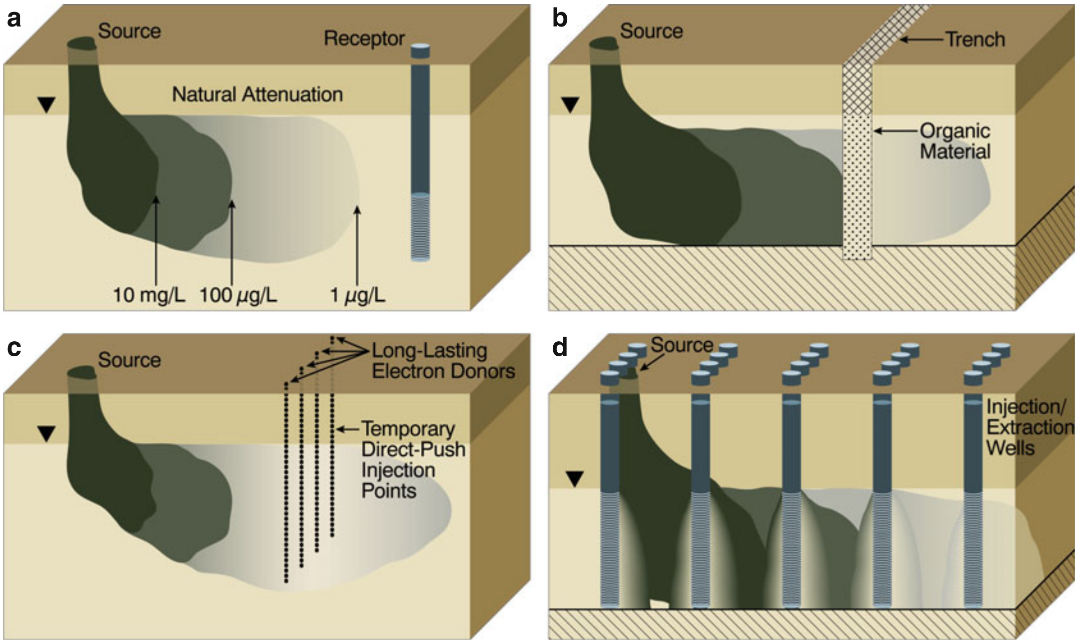


Figure 10.2. Conceptual diagrams of methods for implementing *in situ* anaerobic bioremediation for chlorinated solvents: (a) monitored natural attenuation; (b) plume containment by installation of a biowall; (c) plume containment by use of direct-push points (or wells) to inject long-lasting (3–5 years) electron donor sources such as HRC™ or vegetable oils; (d) plume and source remediation by installing rows of injection points, or paired rows of injection and extraction wells to recirculate groundwater and enhance distribution of amendments.

10.5 SUMMARY

In situ anaerobic bioremediation of chlorinated ethenes has progressed rapidly into one of the most commonly used remediation technologies, largely because it is relatively inexpensive and can be tailored to a wide variety of site conditions. Considerable ingenuity has been applied to its development, and applications have followed closely behind new research findings and scientific understanding. The use of natural and enhanced attenuation has resulted in significant savings for the DoD and other responsible parties and has allowed costly and inefficient pump-and-treat systems to be replaced at many sites. The future prospects for these technologies are bright, as continued innovation leads to improvements in the ability to monitor and predict performance, as well as to apply the technology to more challenging sites.

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CHAPTER 11

MONITORED NATURAL ATTENUATION OF CHLORINATED SOLVENT PLUMES

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11.1 SYNOPSIS OF THE TECHNOLOGY

As specified by the U.S. Environmental Protection Agency (USEPA, 1999), the term "monitored natural attenuation ... refers to the reliance on natural attenuation processes ... to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The 'natural attenuation processes' that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These *in situ* processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants. When relying on natural attenuation processes for site remediation, EPA [U.S. Environmental Protection Agency] prefers those processes that degrade or destroy contaminants."

If the goal for a site is to clean up the contamination and restore the site to an acceptable condition, then monitored natural attenuation (MNA) is a remedy just like any other remedy for cleanup such as pump-and-treat or *in situ* enhanced bioremediation. If the goal is risk management by containing the contamination on site, again MNA is a remedy like any other remedy, such as slurry walls, passive reactive barriers, or capping.

The important difference between MNA and other "active" remedies is the fact that the processes responsible for remediation through natural attenuation are preexisting at the site. Instead of the remedy being designed and implemented, the processes responsible for the remedy are recognized and defined through appropriate site characterization. Because the mix and relative contributions of different processes are different at every site, every MNA remedy is unique. However, most decisions to implement MNA at a site follow a common framework. Through site characterization, lines of evidence are developed that document the contribution of the various processes that contribute to MNA. As specified by USEPA (1999), the lines of evidence are as follows:

(1) Historical groundwater and/or soil chemistry data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points.

(2) Hydrogeologic and geochemical data that can be used to demonstrate indirectly the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to required levels.

(3) Data from field or microcosm studies (conducted in or with actual contaminated site media) which directly demonstrate the occurrence of a particular natural attenuation

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process at the site and its ability to degrade the contaminants of concern (typically used to demonstrate biological degradation processes only).

Unless the USEPA or the overseeing regulatory authority determines that historical data (Number 1 above) are of sufficient quality and duration to support a decision to use MNA, data characterizing the nature and rates of natural attenuation processes at the site (Number 2 above) should be provided. Where the latter are also inadequate or inconclusive, data from microcosm studies (Number 3 above) also may be necessary.

The Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water (USEPA Protocol) (Wiedemeier et al., 1998) offers technical recommendations for developing lines of evidence in support of MNA for chlorinated solvents. The USEPA Protocol is readily available; it has been widely used at hazardous waste sites (McGuire et al., 2004), and in general is well understood by practitioners in the field of environmental restoration. Explicit guidance on the design of monitoring systems for natural attenuation is provided in Pope et al. (2004). These recommendations are comprehensive and will not be repeated here.

USEPA guidance and technical recommendations have been used successfully to implement MNA at a number of sites. In the author's experience, successful proposals to use MNA have a number of common features. First, they demonstrate an understanding of the flow of groundwater from the source areas to potential receptors. This knowledge is necessary to provide confidence that there are an adequate number of monitoring wells, and that the wells are in the right places, as well as confidence that the potential risks are adequately controlled. Second, they have a monitoring record that demonstrates a substantial reduction in contaminant concentration over the monitoring period at a level of statistical confidence that is acceptable to the appropriate regulatory authority. Often the monitoring record extends over a decade or more, and shows reductions in contaminant concentrations of an order of magnitude or more. Third, the monitoring record includes geochemical and microbiological parameters that document that the groundwater is an appropriate habitat for anaerobic or aerobic bacteria that can degrade chlorinated solvents to harmless materials. Finally, successful proposals often make a comparison between the spatial distribution of concentrations of the contaminants and their transformation products to the distribution that would be expected if the contaminants were not being degraded. This is commonly done by simulating the transport and fate of the contaminants using mathematical models.

Successful decisions to implement MNA as a remedy also have common features. First, the rate of attenuation seen in the site characterization data is borne out in the periodic review of the long term monitoring data. Second, the apparent "footprint" of the plume retreats back toward the source with each period of review. Third, the rate of attenuation of concentration over time in monitoring wells is at least 0.2 per year. If the rate is any slower, it is very difficult to see improvement at the end of the review period with any reasonable level of statistical confidence. Finally, in the author's experience, successful implementation of MNA almost always incorporates control of the source to prevent further contamination of groundwater, through remediation and/or containment of the source.

Monitored natural attenuation at a particular site is discovered, described and documented, but it is not designed as an active remedy would be. It is a matter of seeing and understanding what is already there, and then being able to share that quantitative understanding of the behavior of the contaminants with others. That process of discovery, description, and documentation is described in detail in Wiedemeier et al. (1998) and Pope et al. (2004), and will be briefly illustrated with a case study in Section 11.2.

Since the USEPA Protocol was issued, there have been three substantive advances in the state of knowledge about natural attenuation of chlorinated solvents in groundwater. These will be discussed in the remainder of this chapter. The first advance is the application of molecular biological tools, in particular assays based on the polymerase chain reaction, to recognize the presence in groundwater of *Dehalococcoides* species. These are the only organisms known to carry out reductive dechlorination of *cis*-dichloroethene (*cis*-DCE) and vinyl chloride (VC). The second advance discussed is the development of a statistical model to predict the presence of *Dehalococcoides* organisms in groundwater from the concentrations of nitrate plus nitrite nitrogen, the concentrations of methane, and the oxidation-reduction potential (ORP). Finally, this chapter will describe the recent developments in compound-specific analysis of stable isotopes to recognize and evaluate the extent of the natural biodegradation of chlorinated solvents.

11.2 CASE STUDY AT THE TWIN CITIES ARMY AMMUNITION PLANT

Disposal of waste solvents containing trichloroethene (TCE) and 1,1,1-trichloroethane (1,1,1-TCA) at the Twin Cities Army Ammunition Plant (TCAAP) in Minnesota created a plume of groundwater contamination. In 1981, solvents were discovered in groundwater wells beyond the TCAAP boundary, including the city of New Brighton's municipal water supply. In 1983 the site was placed on the federal National Priorities List (NPL). For purposes of the regulatory enforcement action, the plume was divided into a North Plume and a South Plume (Figure 11.1). The projected date for all remedies to be in place is 2008. A date of 2040 is projected for the completion of groundwater restoration. The site is scheduled to be delisted from the NPL in 2040 (MPCA, 2009).

A short history of the site is provided by a USEPA fact sheet (USEPA, 2007). Records of decision (RODs) for Operable Unit (OU) 1, which is the North Plume of contaminated groundwater that has migrated off the TCAAP, and Operable Unit 3, which is the smaller South Plume, were signed in 1992 and 1993. The remedies selected for the North Plume and the South Plume include pumping of the plumes to prevent further migration, treatment of the pumped water with granular activated carbon, discharge of the treated water to the New Brighton municipal distribution system, the provision of alternate water supplies to affected users of private wells, and drilling advisories and monitoring of the impacted aquifer. The OU-1 and OU-3 RODs provide for containment pump-and-treat systems comprised of wells that serve the dual purposes of containment and municipal water supply for the city of New Brighton. The OU-3 system was in full operation in 1994, and the OU-1 system was completed in 2000. As part of the remedy, a permanent granular activated carbon (GAC) water treatment system was installed for the city of New Brighton, completed in June 1990, and a GAC treatment system was installed for the village of St. Anthony, completed in 1991. Soil vapor extraction (SVE) systems were installed at two areas on the TCAAP in 1986. The systems have removed over 100,000 kilograms (kg) of volatile organic compounds (VOCs) from soils. A shallow groundwater pump-and-treat system was installed in source areas of the plumes in 1988 and in 1994. Beginning in 1988, a series of wells were installed to capture contaminated groundwater at the TCAAP boundary. The system of wells has removed approximately 70,000 kg of VOCs from the deep groundwater.

A maximum of 12,100 kg of chlorinated organic compounds was recovered in 1991 (Figure 11.2). Over time, the recovery of chlorinated organic compounds has declined; 1,200 kg of chlorinated organic compounds was recovered in 2005.

On the TCAAP there are a series of aquifers (Figure 11.3). The water table aquifer, which is composed of unconsolidated glacial sands, is termed the Hillside Sand Aquifer or Aquifer

Unit 3. Below the Hillside Sand Aquifer is an aquifer in fractured rock of the Prairie du Chien and Jordan Sandstone formations. This aquifer is called Aquifer Unit 4. The natural flow of groundwater carried the plume to the West and to the South toward the Mississippi River (Figure 11.1). The contaminated private wells immediately downgradient of the TCAAP produce water from the Hillside Sand Aquifer (Unit 3). The Hillside Sand Aquifer pinches out west of the TCAAP and private wells further to the west and southwest of TCAAP produce water from the Prairie du Chien group and the Jordan Sandstone (Aquifer Unit 4).

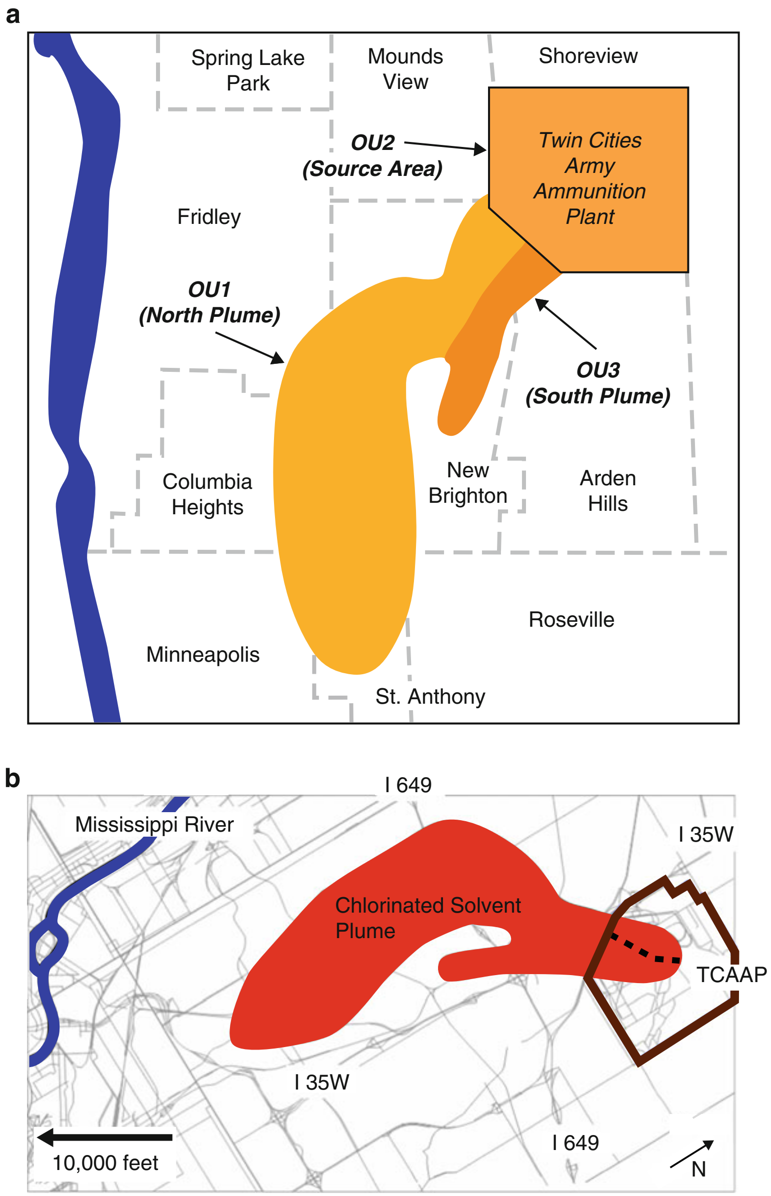

Figure 11.1. Distribution of chlorinated solvent contamination in groundwater at the New Brighton/Arden Hills/TCAAP (U.S. Army) NPL site. Part a from MPCA, 2009; Part b copied from Wilson et al., 2001.

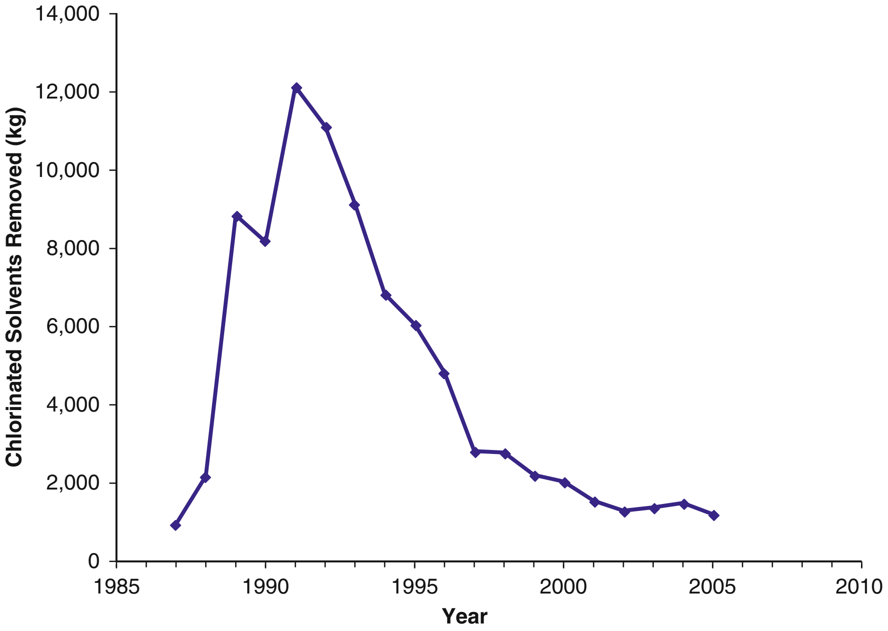

Figure 11.2. Recovery of chlorinated organic compounds by the pump-and-treat system at the TCAAP in each year of operation (prepared from data provided in TCAAP, 2006).

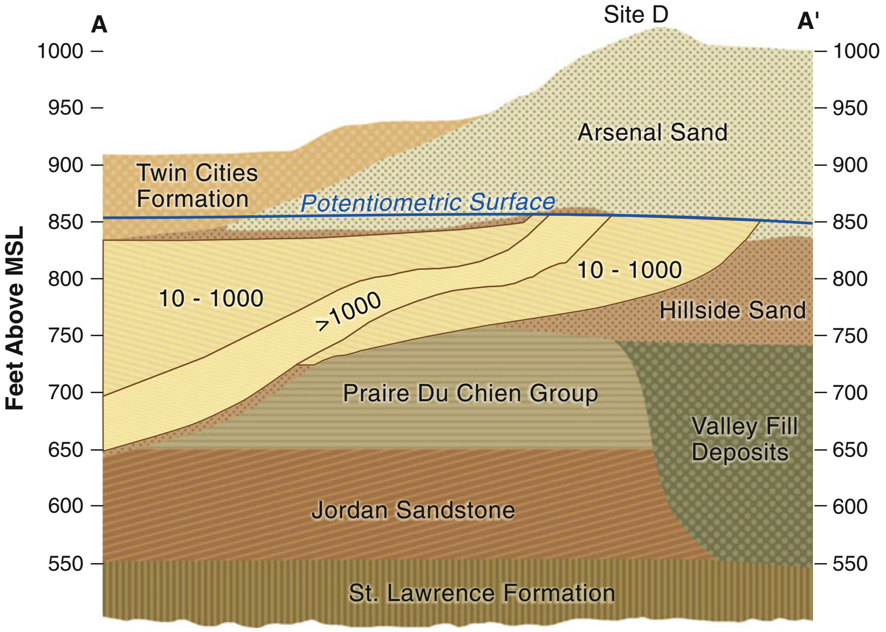

Figure 11.3. Geological cross section at the TCAAP showing the relationship between the origin of the plume of chlorinated solvents and the important aquifer units. The section A' to A is oriented along the dashed line in Panel B of Figure 11.1, extending from Northeast to Southwest. Values in Figure 11.3 are concentrations of total chlorinated organic compounds (micrograms per liter [µg/L]). Redrawn from Wilson et al., 2001.

The plume of chlorinated solvents failed to reach a maximum distribution that was projected using a groundwater transport and fate model. The assumption had been that there was no degradation of TCE in the aquifer. This was taken as evidence that natural biodegradation processes were contributing to natural attenuation in the groundwater. The chlorinated solvent plume was selected by staff of the MPCA for a "Beta Test" of the USEPA Protocol (Wiedemeier et al., 1998). The results of the "Beta test" are reported in Wilson et al. (2001).

Figure 11.4 presents the distribution of total chlorinated organic compounds in wells screened in the upper portion of Aquifer Unit 3 in 1998. The North Plume extended approximately 5,000 ft (1,500 meters [m]) southwest of the boundary of the TCAAP, and the South Plume extended approximately 1,000 ft (300 m) southwest of the boundary. On the TCAAP, concentrations of chlorinated solvents exceeded 1,000 μg/L.

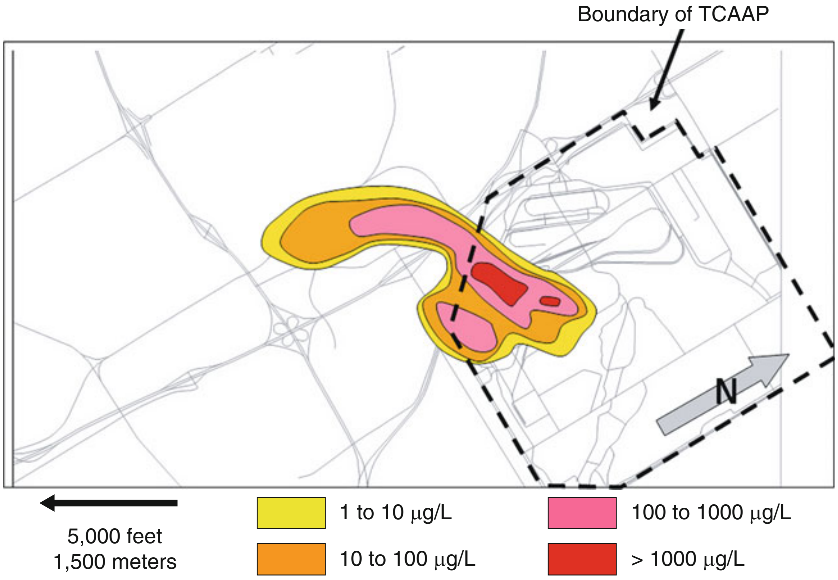

Figure 11.4. Distribution of chlorinated volatile organic compounds (CVOCs) in groundwater in the upper portion of Aquifer Unit 3 (unconsolidated sand) in 1998, at the time an evaluation of monitored natural attenuation of the contaminant plume began (redrawn from TCAAP, 1999).

After seven years, the plume as sampled by wells in the upper portion of Aquifer Unit 3 had extended an additional 1,000 ft (300 m) (compare Figures 11.4 and 11.5). Wilson et al. (2001) calibrated BIOSCREEN to the North Plume in Aquifer Unit 3. The estimated seepage velocity in the calibration was 931 ft per year (284 m per year). The plume should have extended an additional 6,500 ft (1980 m). After seven years water in all the wells screened in the upper portion of Aquifer Unit 3 had total concentrations of chlorinated organic compounds less than 1,000 μg/L.

Figures 11.6 and 11.7 compare the distribution of chlorinated organic compounds in groundwater in the lower portion of Aquifer Unit 3. In 1998, contamination in the lower portion of Aquifer Unit 3 extended approximately 1,000 ft (300 m) further downgradient compared to the upper portion of Aquifer Unit 3 (compare Figures 11.6 and 11.7). After seven years, there was no noticeable change in the distribution of contamination in the North Plume in the lower portion of Aquifer Unit 3; however there was a significant reduction in the concentrations in the South Plume (compare Figures 11.6 and 11.7). In this time interval, groundwater would have been expected to move 6,500 ft (1980 m).

The distribution of chlorinated organic compounds in the deep fractured rock aquifer is presented in Figures 11.8 and 11.9. This is the aquifer that is used for water supply by the municipalities to the west and south of the TCAAP. In seven years, there was very little change in the distribution of chlorinated solvents in the range of 1 to 10 µg/L, or in the range of 10 to 100 µg/L. There was a major reduction in the volume of groundwater containing concentrations between 100 and 1,000 µg/L. Wilson et al. (2001) calibrated BIOSCREEN to the North Plume in Aquifer Unit 4. The estimated seepage velocity in the calibration was 1,589 ft per year (484 m per year). In seven years, groundwater in the plume would have moved approximately 10,000 ft (3,000 m per year).

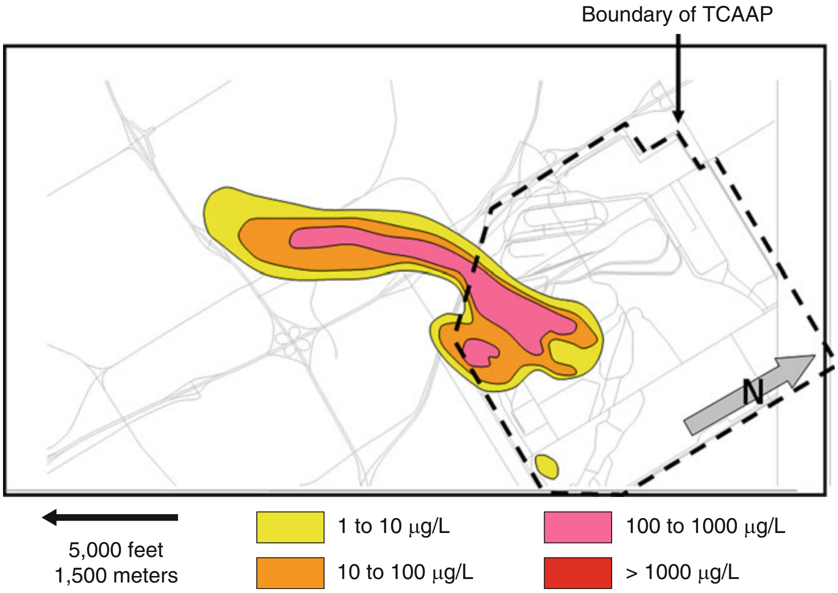

Figure 11.5. **Distribution of CVOCs in groundwater in the upper portion of Aquifer Unit 3 (unconsolidated sand) in 2005, seven years into a period of long term monitoring of natural attenuation of the contaminant plume (redrawn from TCAAP, 2006).**

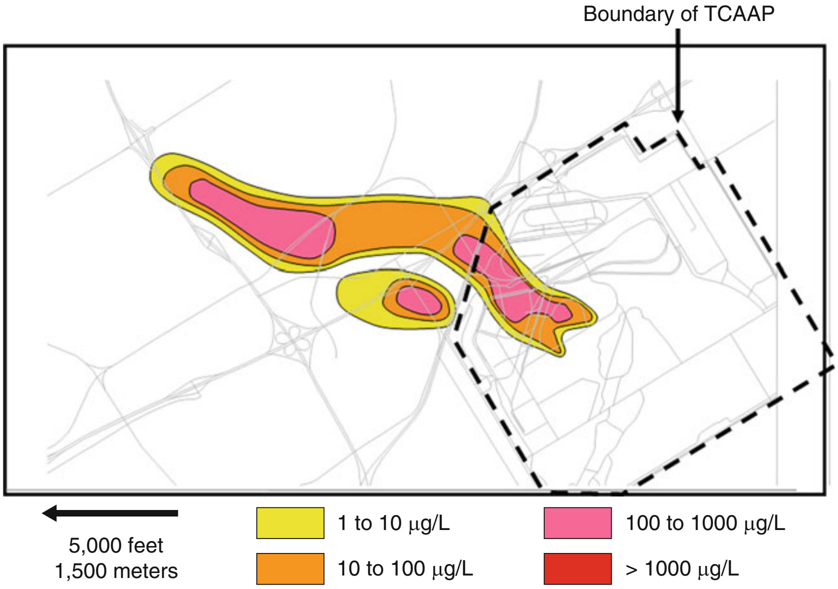

Figure 11.6. **Distribution of CVOCs in groundwater in the lower portion of Aquifer Unit 3 (unconsolidated sand) in 1998, at the time an evaluation of monitored natural attenuation of the contaminant plume began (plume redrawn from TCAAP, 1999).**

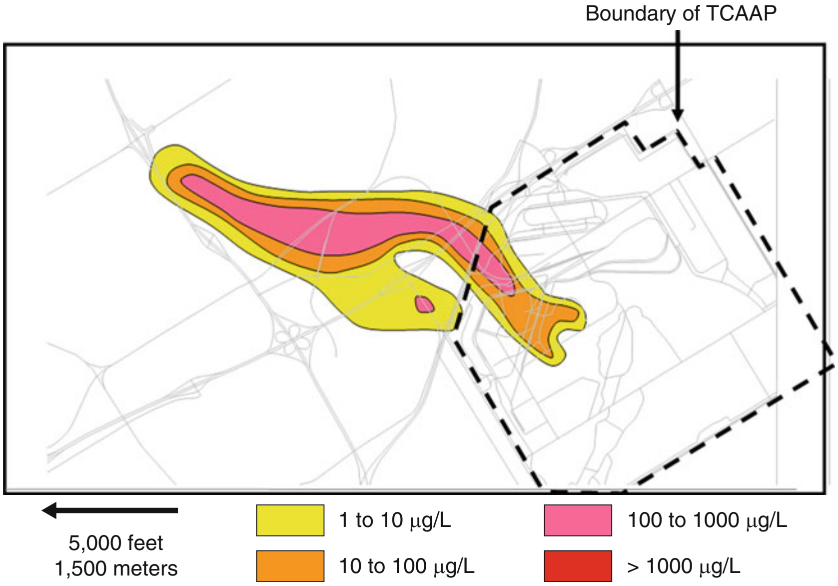

Figure 11.7. Distribution of CVOCs in groundwater in the lower portion of Aquifer Unit 3 (unconsolidated sand) in 2005, seven years into a period of long term monitoring of natural attenuation of the contaminant plume (redrawn from TCAAP, 2006).

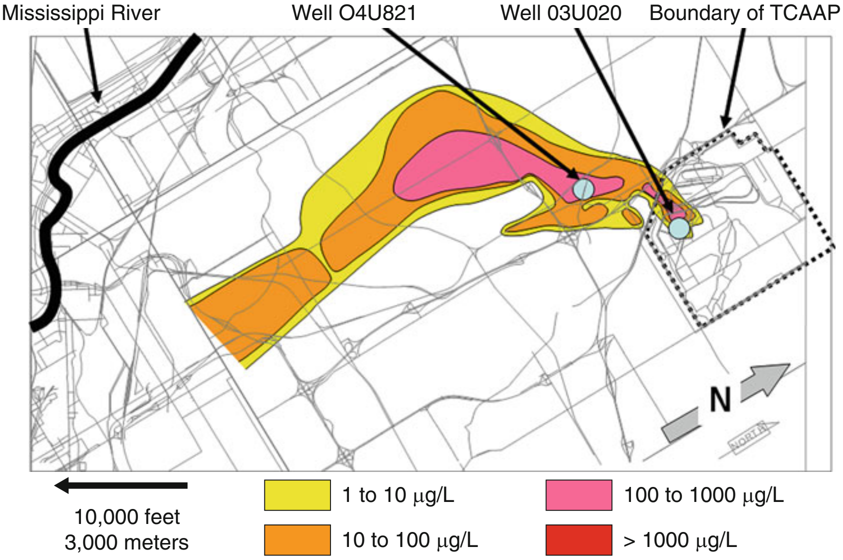

Figure 11.8. Distribution of CVOCs in groundwater in the upper portion of Aquifer Unit 4 (fractured bedrock) in 1998, at the time an evaluation of monitored natural attenuation of the contaminant plume began (plume redrawn from TCAAP, 1999).

Figure 11.8 presents the location of monitoring well 04U821, which is located in the center of the most contaminated area in the upper portion of Aquifer Unit 4, downgradient of the TCAAP. Figure 11.10 compares the rate of attenuation in concentration of TCE in monitoring well 04U821 over time. There is a general downward trend in concentration. The concentration fell from 950 µg/L in November 1987 to 140 µg/L in March 1994. The data set will be used to illustrate an approach to evaluate the progress of natural attenuation used as a remedy. For purposes of illustration, these data will be considered to be the site characterization data used in part to justify the selection of MNA as a remedy. The first order rate of attenuation in concentration of TCE in monitoring well 04U821 is 0.31 per year. The one-tailed 95% confidence interval on that rate is 0.25 per year. The rates were calculated using the procedures in Newell et al. (2002) and Wilson et al. (2005).

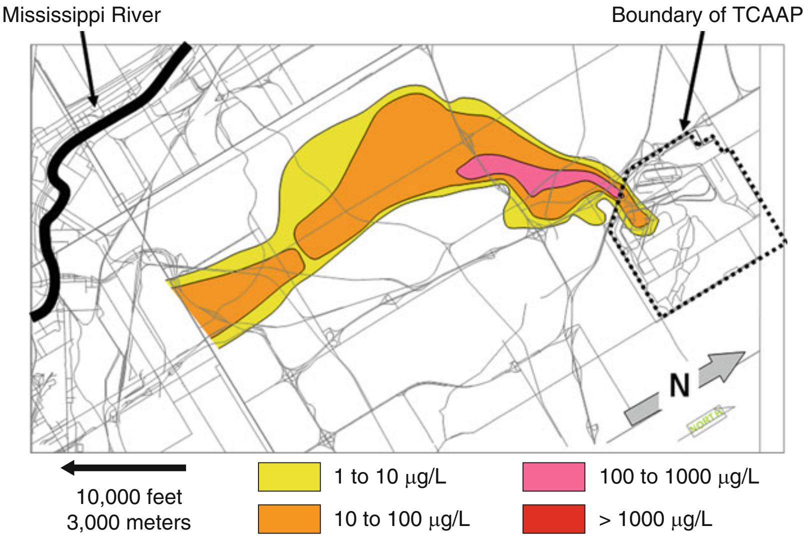

Figure 11.9. Distribution of CVOCs in groundwater in the upper portion of Aquifer Unit 4 (fractured bedrock) in 2005, seven years into a period of long term monitoring of natural attenuation of the contaminant plume (redrawn from TCAAP, 2006).

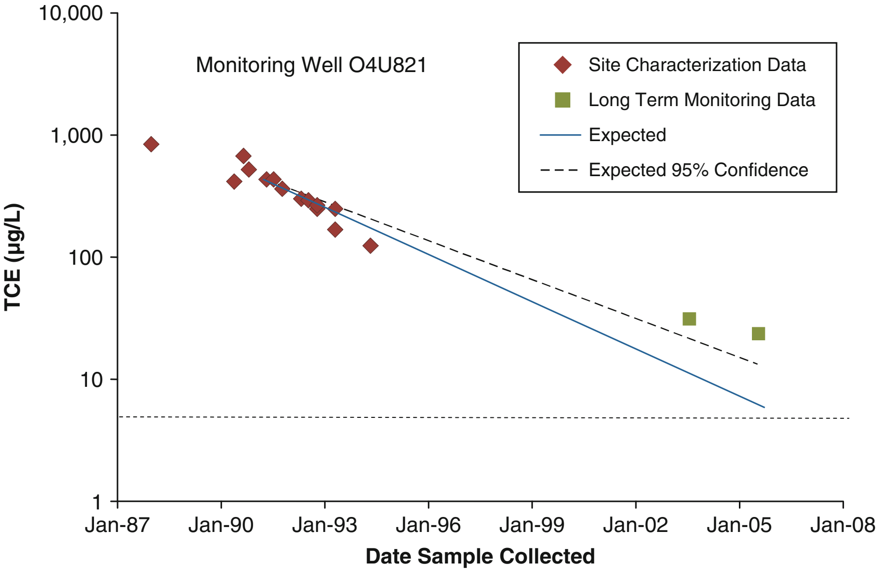

Figure 11.10. Attenuation in concentrations of TCE over time in monitoring well 04U821, screened in the Prairie Du Chien Group at a depth of 98 to 103 ft (30 to 31 m) below the water table. The expected concentrations are projected based on the site characterization data only. Prepared from data provided in TCAAP, 2006.

In the solid and dashed lines in Figure 11.10, the rate of attenuation and the rate of attenuation significant at 95% confidence are projected from the median data point in the site characterization data. At the average rate of attenuation, the concentration of TCE would be expected to reach the maximum contaminant level (MCL) for TCE in 2006 (the MCL is 5 µg/L, see horizontal dotted line in Figure 11.10). A long term monitoring sample collected in June 2003 reported 33 µg/L, and a sample collected in June 2005 reported 25 µg/L. The extent of attenuation is less than expected at 95% confidence. Although the concentrations are lower than the lowest concentration in the site characterization data, the rate of attenuation has slowed in water collected from monitoring well 04U821.

An appropriate response would be to calculate a new rate constant for the entire monitoring interval, including the long term monitoring data, and compare the new projection of the time expected to reach the MCL to the expectations for performance of MNA at the site. This was done in data presented in Figure 11.11. The regression to estimate the rate constants included the site characterization data and the two values from the long term monitoring data. In this expanded data set, the average first order rate of attenuation was 0.21 per year, and the rate significant at 95% confidence was 0.19 per year. The groundwater is expected to be cleaned up by 2040 (MPCA, 2009). The average rate of attenuation could be expected to meet the MCL by 2012, and the rate significant at 95% confidence by 2015. Although the rate has slowed, the rate of attenuation is still on track to meet the cleanup goal. Obviously, continued monitoring is necessary to determine if the current rate will be sustained, or whether the rate will decrease even further.

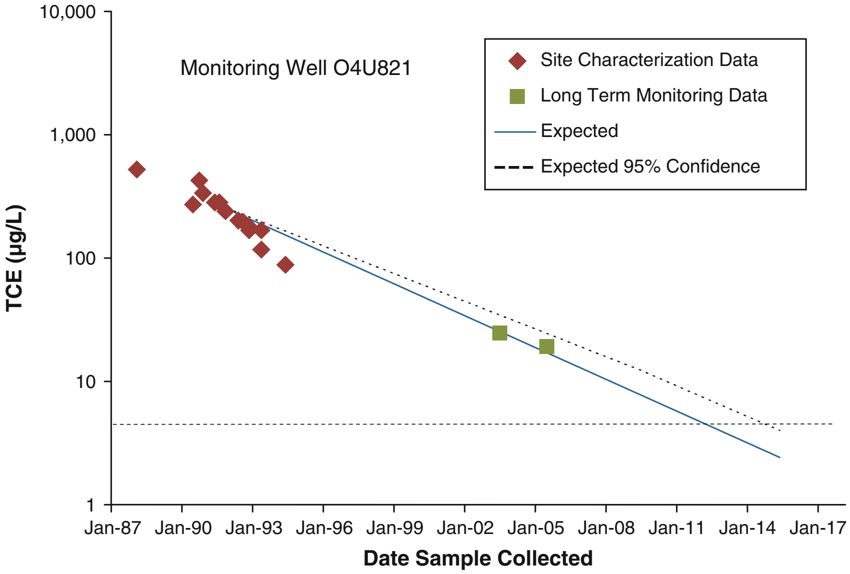

Figure 11.11. Attenuation in concentrations of TCE over time in monitoring well 04U821. The expected concentrations are projected based on the site characterization data and long term monitoring data. Prepared from data provided in TCAAP, 2006.

The approach was also applied to a second monitoring well in Aquifer Unit 4 on the TCAAP. The location of monitoring well 04U020 is presented in Figure 11.8, and the rate of attenuation in concentration over time is presented in Figure 11.12. The first order rate of attenuation in the site characterization data was 0.60 per year, and the rate significant at 95% confidence is 0.48 per year. As was the case with monitoring well 04U821, the concentrations in the long term monitoring data fell above the expected concentrations, indicating that at 95% confidence, the rate of attenuation of TCE in the well had slowed over the time interval between the site characterization data and the long term monitoring data. However, the long term monitoring data were below the MCL. Substantial concentrations of TCE remain in Aquifer Unit 3 at the location of monitoring well 04U020. However, the combined benefits of pump-and-treat and natural attenuation had restored the deeper groundwater in Aquifer Unit 4.

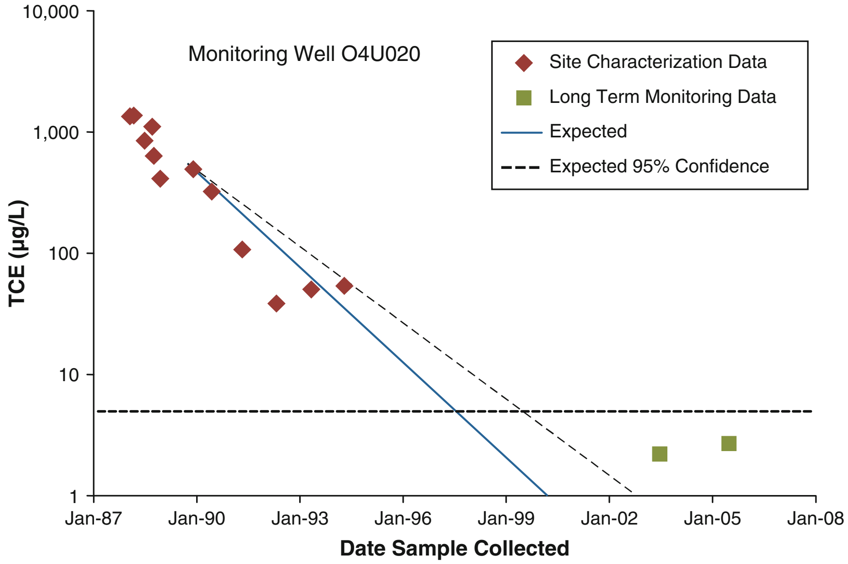

Figure 11.12. Attenuation in concentrations of TCE over time in monitoring well 04U020, screened in the Jordan Sandstone from 147 to 157 ft (45 to 48 m) below the water table (prepared from data provided in TCAAP, 2006).

For some years, the concentrations of VOCs in monitoring wells in the South Plume have been below detection. In 2001, the U.S. Army ceased pumping the OU-3 pump-and-treat systems (MPCA, 2009). The ROD for Operable Unit 3 has been amended to make the shutdown permanent (USEPA, 2007).

Natural attenuation in the TCAAP chlorinated solvent plume has been successful for a number of reasons. First, the U.S. Army used pumping to prevent further contamination of the aquifer downgradient of the TCAAP. Once further contamination was prevented, the natural mechanisms for attenuation of concentrations of TCE could control the distribution of TCE. Second, there was a process for degradation of the primary reduction products of TCE, in particular 1,1-DCE and *cis*-DCE, that could remove 1,1-DCE and *cis*-DCE as rapidly as they were produced from biological reductive dechlorination of TCE. This mechanism was associated with non-biological degradation of *cis*-DCE and 1,1-DCE by the mineral magnetite that naturally occurred in the aquifer matrix (Ferrey et al., 2004). Third, the rates of removal of TCE and its degradation products were fast enough to be easily documented with statistical significance over a ten-year interval of site characterization, and the rates of removal were fast enough to meet the cleanup goals within the specified time interval. Finally, the initial site characterization was designed to understand the behavior of the plume in three spatial dimensions, as well as the dimension of time. This made it possible to forecast the future behavior of the plume, and to compare the response of remedial actions to the forecast.

11.3 USE OF MOLECULAR BIOLOGICAL TOOLS

The Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) of the U.S. Department of Defense (DoD) organized a workshop to evaluate the application of molecular biological tools to environmental remediation. The report of the workshop is a useful summary of the current state of practice (SERDP, 2005). The workshop identified the need to compare the results from molecular biological tools used to estimate the density of active organisms to the achieved rate of biodegradation at field scale.

When the USEPA Protocol was written in the middle 1990s, it understandably focused on guidelines to recognize and identify anaerobic biological sequential reductive dechlorination. Abiotic chemical reactions capable of degrading chloroethenes were not yet recognized. However, it was known that physical mechanisms such as sorption could not have a significant impact on attenuation rates, particularly when the chlorinated solvent concentrations were often several orders of magnitude higher than the designated cleanup levels (MCLs). The authors of the USEPA Protocol reasoned that if MNA were to be useful for field-scale plumes, perchloroethene (PCE) and TCE must be removed by anaerobic biodegradation. At the time, little was known of the agents of anaerobic biological degradation of PCE and TCE in groundwater, and as a consequence, the USEPA Protocol relied heavily on a lines-of-evidence approach that associated biological reductive dechlorination with geochemical parameters in the groundwater. Engineering judgment was used to assign a weighting factor to various geochemical parameters, and the weights were summed to get a score for a particular monitoring well.

The scoring system was criticized by the Committee on Intrinsic Remediation of the National Research Council (NRC, 2000), and the Committee recommended that the scoring system should not be used to evaluate the prospects for MNA. Since the publication of the USEPA Protocol, it has become apparent that various strains of *Dehalococcoides* are responsible for complete biodegradation of PCE and TCE in contaminated plumes (Fennell et al., 2001; Maymó-Gatell et al., 1997; Maymó-Gatell et al., 2001; He et al., 2003a, 2003b). An assay is now available that can be used to recognize deoxyribonucleic acid (DNA) in the 16S recombinant ribonucleic acid (rRNA) gene of *Dehalococcoides* species (Löffler et al., 2000; Fennell et al., 2001; Hendrickson et al., 2002; He et al., 2003a, 2003b).

Löffler et al. (2000) were the first to publish a polymerase chain reaction (PCR) assay for the density of *Dehalococcoides* bacteria. The primers of the PCR assay were designed based on the 16S rRNA sequence of *Dehalococcoides* sp. strain FL2, which is closely related to *Dehalococcoides ethenogenes* (96.9% sequence similarity). The PCR approach was used to detect *Dehalococcoides* populations in aquifer sediments, and the results were confirmed by microcosm studies.

Fennell et al. (2001) designed a *Dehalococcoides* primer set based on the 16S rRNA gene of *Dehalococcoides* ethenogenes strain 195 and used it for the detection of *Dehalococcoides* at a TCE-contaminated site. Hendrickson et al. (2002) developed a PCR assay to conduct an extensive survey for the presence of *Dehalococcoides* at multiple chlorinated ethene-contaminated sites. The PCR assay was applied to groundwater samples and soil samples collected from 24 sites. Positive results were obtained at 21 sites where chlorinated ethenes had been completely dechlorinated to ethene.

All of these studies used a direct PCR technique which uses gel electrophoresis to detect the amplified gene product. This direct PCR is a qualitative or semi-quantitative method. More recently, real-time PCR (RT-PCR) has been developed to precisely measure the density of the *Dehalococcoides* gene copies (Lendvay et al., 2003; He et al., 2003a, 2003b). RT-PCR makes use of the same principles of gene amplification as standard PCR. In RT-PCR amplification, the primer targeting the 16S rRNA gene sequences of *Dehalococcoides* is labelled with a fluorescent dye. The accumulation of the replicated DNA by the instrument during each cycle of the polymerase chain reaction is determined by the fluorescence of the amplified DNA. The number of cycles required to accumulate enough amplified DNA to attain a "threshold" level of fluorescence is used to quantitatively determine the initial concentration of DNA.

Unfortunately, not all strains of *Dehalococcoides* can completely dechlorinate PCE or TCE to ethene or ethane, and the presence of *Dehalococcoides* DNA does not guarantee that biological reductive dechlorination will occur in an aquifer (Adrian et al., 2000; Duhamel et al., 2002; Fennell et al. 2001; He et al., 2003a, 2003b). One alternative is to create primers for the genes for the dehalogenase enzymes that actually carry out the transformation of TCE or VC to ethene. Ritalahti et al. (2006) used a combined approach with PCR assays for three reductase genes and a PCR assay for the 16S rRNA *of Dehalococcoides*. A second alternative would be to establish a benchmark for the predictive power of the 16S rRNA assay by conducting a survey of the distribution of the gene for 16S rRNA in *Dehalococcoides* in field scale plumes, and compare the distribution to the achieved field scale rates of reductive dechlorination.

11.4 CORRESPONDENCE BETWEEN PCR ASSAYS FOR 16S rRNA IN *DEHALOCOCCOIDES* AND RATES OF NATURAL ATTENUATION

Recently Lu et al. (2006a, 2006c) compared PCR assays for 16S rRNA in *Dehalococcoides* and rates of attenuation in eight groundwater plumes at seven locations. They estimated the density of *Dehalococcoides* gene copies in groundwater using a commercially available assay based on quantitative RT-PCR. They used the computer application BIOCHLOR (Aziz et al., 2000) to extract the rates of natural attenuation of *cis*-DCE and VC in the groundwater plumes from the long term monitoring data at the sites. Different rate constants were inserted into BIOCHLOR until the projection of the application best matched the field data from the sites. Candidate first order rate constants for biodegradation were 0.01 per year, 0.03 per year, 0.1 per year, 0.3 per year, 1.0 per year, 3.0 per year and 10 per year. When the rate constants varied from each other by a factor of three, one calibration was always a better fit than the other calibrations. PCE was calibrated first, then TCE, then DCE, then VC.

Six of the sites formed conventional plumes, with the highest concentrations of contaminants in the source area, and lower concentrations along the flow path in the aquifer, away from the source area. These sites were: the Western Processing Site at Kent, Washington; Landfill Number 3 (LF3) and Fire Training Area Number 2 (FTA2) at Tinker Air Force Base (AFB), Oklahoma; the North Beach Site at the U.S. Coast Guard (USCG) Support Center in Elizabeth City, North Carolina; Spill Site Number 17 (SS-17) at Altus AFB, Oklahoma; the Target Area 1 Site at Dover AFB, Delaware.

The plume at the Western Processing Site was extracted with a pump-and-treat system from September 1988 through April 2000. The plume at site LF3 has been extracted by a pump-and-treat system since early 1999. The plume at site SS-17 has been extracted with a two-phase vacuum extraction system since September 1996. At the North Beach Landfill Site, the source was removed in 1999. There are no engineered remediation actions at the other sites. To avoid errors in fitting rate constants for natural attenuation, the rate constants were fit to data that were collected prior to initiation of any engineered remedies.

Table 11.1 compares the concentrations of chlorinated organic compounds in groundwater, the calibrated rates of reductive dechlorination, and the density of *Dehalococcoides* DNA in water from monitoring wells at the six sites with conventional plumes. The contamination at the Western Processing Site in Kent, Washington was originally PCE and TCE. After the source area was contained by a slurry wall, all of the PCE and TCE in the plume was degraded to *cis*-DCE. Then over a period of years, the *cis*-DCE was sequentially degraded to VC and ethene. The rates of degradation of *cis*-DCE and VC varied from 0.6 to 3 per year. When the plume was sampled in 2003 for the presence of *Dehalococcoides* DNA, very little *cis*-DCE or VC remained. In three of six wells at the site, the density of *Dehalococcoides* gene copies varied from 2.5×10^5 to 3.4×10^7 per liter. The situation in LF3 at Tinker AFB, OK was similar, although dechlorination was not as extensive. Both PCE and TCE were largely degraded, and the concentration of VC was roughly equivalent to the concentration of *cis*-DCE. The rates of dechlorination and the density of *Dehalococcoides* gene copies fell into a range similar to that at the Western Processing site.

At the North Beach site near Elizabeth City, NC, dechlorination was not as extensive as at the two previous sites; however, the rates of dechlorination, and the density of *Dehalococcoides* gene copies (in the one well where the DNA was detected) were similar to the two previous sites. Where *Dehalococcoides* DNA was detected, the achieved rates of dechlorination of *cis*-DCE and VC at field scale were in the range of 0.6 to 3 per year.

At the FTA2 sites at Tinker AFB, OK, and the SS-17 site at Altus AFB, OK, there was extensive dechlorination of PCE and TCE to *cis*-DCE, but limited degradation of *cis*-DCE to VC or ethene. Rates of dechlorination of *cis*-DCE and VC could not be extracted from the monitoring data, and *Dehalococcoides* DNA was not detected. At the Target Area 1 site at Dover AFB, DE, low rates of dechlorination could be extracted from the monitoring data when water samples were collected in 1997, but not in 2003 when samples were collected for assay of *Dehalococcoides* DNA. *Dehalococcoides* DNA was detected by a direct PCR assay, but not by the quantitative RT-PCR assay.

At three of the six sites with conventional plumes, the presence of *Dehalococcoides* DNA in at least one well in the plume was associated with rates of dechlorination of *cis*-DCE and VC in the range of 0.3 to 3 per year. In the three plumes with no discernable dechlorination of *cis*-DCE or VC, *Dehalococcoides* DNA was not detected.

Two sites at the former England AFB, LA were in an aquifer with no discernable net direction of groundwater flow. As a result the distribution of contaminants formed a "bull's eye" around the source, instead of a conventional plume. Table 11.2 compares the concentrations of chlorinated organic compounds, the rate of attenuation in concentration of the chlorinated organic compounds over time in particular wells, and the density of *Dehalococcoides* DNA in groundwater from the wells. Area 800 exhibits limited dechlorination to VC, while Area 2500 exhibits extensive dechlorination to VC. In Area 2500, with extensive dechlorination to produce VC, the concentration of *Dehalococcoides* gene copies was similar to the concentration in the conventional plumes, in the range of 5×10^5 to 4×10^6 per liter. However, in two of the three wells in Area 2500, concentrations of VC increased over time instead of decreasing, and in one well, concentrations of both *cis*-DCE and VC increased over time, although there was no detectable TCE in the groundwater. *Dehalococcoides* DNA was also detected in a well in Area 800, which exhibited limited accumulation of VC. However, *Dehalococcoides* DNA was not detected in a second well with rates of attenuation of *cis*-DCE and VC in the range of 1 to 3 per year, and *Dehalococcoides* DNA was not detected in two other wells where the concentrations of *cis*-DCE and VC were increasing.

The PCR assay provided little information that could be used to interpret changes in concentrations of chlorinated organic compounds over time in monitoring wells in these "bull's eye" plumes. Presumably, the concentration trends were controlled more by recruitment of contamination from the source area of contamination than by attenuation of the contamination through biological degradation in the groundwater.

Table 11.1. Relationship between the Concentrations of Chlorinated Ethenes in Groundwater, their Apparent Rates of Dechlorination Along an Inferred Flow Path in the Aquifer, and the Density of *Dehalococcoides* Bacteria

Facility and Location	Date	PCE	TCE	*cis*-DCE	VC	Ethene	PCE	TCE	*cis*-DCE	VC	*Dehalococcoides* DNA		
		Concentration near source (µg/L)					First order rate of dechlorination (per year)				Wells where detected	Gene copies per liter	
												Min	Max
Western Processing Kent, WA	1988	—	—	10000	460	—	—	—	0.6	3	—	—	—
	1999	—	—	26	44	—	—	—	0.6	1	—	—	—
	4/2003	—	—	0.34	1.59	6	—	—	—	—	3 of 6	2.5×10^{5}	3.4×10^{7}
LF3 (landfill) Tinker AFB, OK	9/1997	5.3	97	38000	23000	—	—	—	1	3	—	—	—
	11/2002	8	28	28400	20400	5.3	—	—	1	3	4 of 4	6.7×10^{5}	2.0×10^{8}
North Beach, USCG Support Center, Elizabeth City, NC	1997	2000	105	74	30.8	—	0.1	1	0.3	1	—	—	—
	10/2002	561	52	25	<1	<1	0.1	1	0.3	1	1 of 4	—	1.8×10^{5}
FTA2 (fire training) Tinker AFB, OK	8/1997	6.1	9440	1200	1.7	—	—	0.1	—	—	—	—	—
	11/2002	7.5	9330	977	2.9	1.7	—	0.3	—	—	—	—	Not Detect
SS17 Site Altus AFB, OK	3/2003	38.5	8160	264	4.28	3.0	—	0.01	—	—	—	—	Not Detect
Target Area 1 (Lower Plume) Dover AFB, DE	7/1997	680	2400	560	<1	<1	0.1	0.1	0.1	0.3	—	—	—
	4/2003	273	2630	7360	4.9	<1	—	—	—	—	—	—	Not Detect

Table 11.2. Relationship between the Apparent Rates of Dechlorination over Time and the Detection of Bacterial DNA and *Dehalococcoides* DNA in Water Samples from Monitoring Wells at England AFB, Louisiana

Plume	Well	Time interval over which data collected	TCE	*cis*-DCE	Vinyl Chloride	Ethene	TCE	*cis*-DCE	Vinyl Chloride	*Dehalococcoides* DNA
			Concentration near source ($\mu g/L$)				Rate of Dechlorination (per year)			Cell Density (cells/L)
Area 2500 exhibits extensive dechlorination to vinyl chloride.										
Area 2500	A39L011PZ	9/1997 4/2003	<1	<1	102	0.02	No TCE	1	VC↑	4.0×10^6
Area 2500	A39L010PZ	6/1997 4/2003	<1	<1	95.5	0.895		0.3	0.3	1.2×10^6
Area 2500	Well #23	5/2000 4/2003	<1	92	60.6	<1		*cis*-DCE ↑	VC↑	4.8×10^5
Area 800 exhibits limited dechlorination to vinyl chloride.										
Area 800	A39L009PZ	6/1997 4/2003	20.8	52.6	5.21	<1	0.1	0.1	1	6.7×10^5
Area 800	SS45L001MW	6/1997 4/2003	249	126	4.46	0.02	0.1	1	3	Not Detected
Area 800	Well #17	3/1999 4/2003	20.5	30.1	3.88	<1	TCE ↑	*cis*-DCE ↑	VC↑	Not Detected
Area 800	Well #19	3/1999 4/2003	<1	<1	3.85	<1	No TCE	No *cis*-DCE	VC↑	Not Detected

It is tempting to suppose that there was a quantitative relationship between the density of *Dehalococcoides* cells in groundwater produced from monitoring wells and the rate of biological reductive dechlorination. Figure 11.13 makes this comparison. The open symbols in the figure are data from monitoring wells. Notice the wide variation in density for a narrow variation in rate constants. Densities that varied over four orders of magnitude produced rate constants for degradation of *cis*-DCE or VC that were near 1 per year.

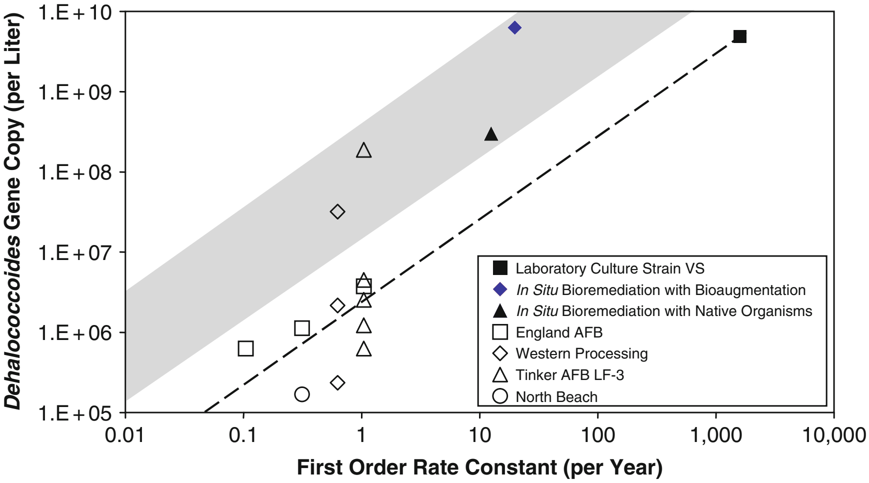

Figure 11.13. Relationship between the density of *Dehalococcoides* gene copies in water and the achieved first order rate of dechlorination of either PCE, TCE, *cis*-DCE or VC at field scale (redrawn from Lu et al., 2006a).

The filled symbols are taken from studies in the literature. Cupples et al. (2004) reported the kinetics of *cis*-DCE biotransformation by a laboratory culture of *Dehalococcoides* strain VS that was growing at 20 degrees Celsius (°C) with optimal concentrations of molecular hydrogen. The first order rate of *cis*-DCE transformation in the culture was calculated by dividing the reported maximum rate of transformation of *cis*-DCE by the reported half saturation constant for *cis*-DCE transformation. The solid square in Figure 11.13 is the calculated first order rate of transformation of *cis*-DCE at the reported cell density in the culture.

If the concentration of chlorinated organic compound in the field is less than one third of the half saturation constant, and the density of organism does not change over time, the attained rate of dechlorination should be directly proportional to the density of active organisms. The dotted line in Figure 11.13 extrapolates the performance of the laboratory culture to cell densities that were attained in monitoring wells at the study sites. A number of the field comparisons lie along the dotted line, suggesting that *Dehalococcoides* cells in groundwater in the aquifer at the field sites performed as well or better than the culture growing under optimal conditions in the laboratory. Several of the comparisons lie far below the line, suggesting that a much lower density of cells in the aquifer could attain the same rate of dechlorination that would be expected based on the performance of the culture in the laboratory.

Lendvay et al. (2003) compared the density of *Dehalococcoides* DNA in sediment as measured by the quantitative RT-PCR to the removal of *cis*-DCE during *in situ* bioremediation of a PCE plume. They determined the total density of *Dehalococcoides* cells in the aquifer, not just the density in the groundwater. Lu et al. (2006a) evaluated the data of Lendvay et al. (2003) to extract rate constants for dechlorination of *cis*-DCE in the demonstration plots. The filled triangle and filled diamond in Figure 11.13 express the data from the bioremediation demonstrations as if all the *Dehalococcoides* cells in the aquifer were free floating in the groundwater. The gray shape in Figure 11.13 bounds and extrapolates the performance of native and augmented strains of *Dehalococcoides* at field scale. Two of the comparisons from the plumes undergoing natural attenuation actually match the performance of the bioremediation field demonstration. All the other comparisons lie considerably below the gray shape, suggesting that *Dehalococcoides* cells in the plumes were much more effective than *Dehalococcoides* cells in the bioremediation demonstration.

It is possible, but not plausible, that the strains of *Dehalococcoides* at the natural attenuation study sites were more effective than the laboratory culture or the strains in the bioremediation demonstrations. A more likely explanation is that the *Dehalococcoides* cells in the aquifer were attached to solids, and were not sampled efficiently by collecting water from a monitoring well (Lu et al., 2006a, Thomas et al., 1987). If PCR assays or other molecular biological tools are to be used to estimate rates of natural biodegradation of chlorinated organic compounds in groundwater, it will probably be necessary to extract DNA from core samples, as was done by Lendvay et al. (2003). However, the PCR assays provided a good qualitative prediction of useful rates of reductive dechlorination.

Although there is a possibility that the PCR assay for DNA that codes for 16S rRNA will recognize DNA from stains of *Dehalococcoides* that cannot dechlorinate *cis*-DCE or VC, there was no evidence in the survey conducted by Lu et al. (2006a, 2006c) that this was a problem. *Dehalococcoides* DNA was not detected in three plumes where dechlorination was absent, or where the rate of dechlorination was too slow to contribute to MNA. In the three plumes where the rate of dechlorination was rapid enough to contribute to MNA, *Dehalococcoides* DNA was present in the groundwater at concentrations in the range of 10^5 to 10^8 gene copies per liter.

11.5 USE OF BIOGEOCHEMICAL PARAMETERS TO PREDICT THE PRESENCE OF *DEHALOCOCCOIDES* DNA

As mentioned earlier, the USEPA Protocol used a scoring system, based on professional judgment, to recognize sites where biological reductive dechlorination might contribute to MNA. The scoring system has been much criticized. To provide an alternative to the scoring system, Lu et al. (2006a, 2006b) compared the presence of *Dehalococcoides* DNA in groundwater from 45 monitoring wells in 15 separate plumes at 10 locations to the geochemical parameters in the groundwater. The direct PCR assay was used to recognize DNA in the 16S rRNA gene of *Dehalococcoides* species. The detection limit was in the range of 10^3 to 10^5 gene copies per liter. Geochemical parameters in the survey included dissolved oxygen, nitrate plus nitrite nitrogen, methane (CH_4), dissolved molecular hydrogen, iron (II), sulfate, total organic carbon, chloride, ORP, pH, temperature, and the total concentrations of benzene, toluene, ethylbenzene and xylenes.

Lu et al. (2006a, 2006b) evaluated each parameter in turn to determine whether the value of each particular parameter could predict the presence of *Dehalococcoides* DNA in groundwater. They compared the distribution of values for each parameter in water from the wells where *Dehalococcoides* DNA was detected to the distribution in water where *Dehalococcoides* DNA was not detected.

They used a two-sample Kolmogorov-Smirnov test to generate a probability (p) that there was a difference between the distribution of each parameter in wells where *Dehalococcoides* DNA was detected and the distribution in wells where *Dehalococcoides* DNA was not detected. To deal with the problem of multiple comparisons, they used the False Discovery Rate (FDR) developed by Benjamini and Hochberg (1995) to control the proportion of significant results that were type I errors (false positive). They were willing to accept a False Discovery Rate of 0.05 (that is, in every 20 significant results, the expected number of false positives is one). The distribution of the values of the concentration of nitrate plus nitrite-nitrogen, of ORP, and of the concentration of CH_4 was significantly different between the samples of groundwater where *Dehalococcoides* DNA was detected and the samples where *Dehalococcoides* DNA was not detected. There were no significant differences in the distribution of the values of all the other parameters at the specified FDR controlling level.

Lu et al. (2006a) and Lu et al. (2006b) used the data set to develop a statistical model for the probability of *Dehalococcoides* DNA in groundwater based on values for ORP, and concentrations of nitrate plus nitrite-nitrogen and methane. However, Lu et al. (2006a) and Lu et al. (2006b) developed the statistical model in two different ways. Lu et al. (2006b) used 30 of the 45 samples as the "training" set, and reserved the 15 samples as a "testing" set.

They used a logistic regression with a binary response to model the relationship. In the model, the response variable (Y) had two values: Y=1 for the presence of *Dehalococcoides* DNA and Y = 0 for the failure to detect *Dehalococcoides* DNA. The three biogeochemical parameters (ORP, CH_4, and nitrate plus nitrite-nitrogen) were the explanatory variables. The model was as follows:

$$\mathrm{logit}(p) = \log\left(\frac{p}{1-p}\right) = -0.397 - 0.006 \times ORP + 0.126 \times CH_4 - 0.098 \times NO_3^{-1} \text{ plus } NO_2^{-1} - N \quad \text{(Eq. 11.1)}$$

where p is the probability of the presence of *Dehalococcoides* DNA, ORP is the value of oxidation reduction potential against a silver/silver chloride reference electrode in millivolts, CH_4 is the concentration of methane in milligrams per liter (mg/L), and NO_3^{-1} plus NO_2^{-1}-N is the concentration of nitrate plus nitrite nitrogen in mg/L.

When the predicted probability was compared to the actual detection of *Dehalococcoides* DNA in the "testing" set, and a probability equal to or greater than 0.5 was taken as a prediction that *Dehalococcoides* DNA was present, the equation was accurate 66.7% of the time for the presence of *Dehalococcoides* DNA, and 100% of the time for the absence of *Dehalococcoides* DNA. When the predictions were compared for the "training" set, the equation was accurate 81.1% of the time for the presence of *Dehalococcoides* DNA and 89.5% of the time for the absence of *Dehalococcoides* DNA.

Lu et al. (2006a) used all 45 sets of data to develop the statistical model. The equation developed was as follows:

$$\mathrm{logit}(p) = \log\left(\frac{p}{1-p}\right) = -0.1370 - 0.0050 \times ORP + 0.1328 \times CH_4 - 0.0468 \times NO_3^{-1} \text{ plus } NO_2^{-1} - N \quad \text{(Eq. 11.2)}$$

where values for ORP, nitrate plus nitrite-nitrogen, and methane are as before.

Either equation can be used to estimate a probability that *Dehalococcoides* DNA will be found in groundwater from a monitoring well. Either equation is superior to the screening system in the USEPA Protocol because the equations, and the data used to develop the statistical model, are documented. The equation in Lu et al. (2006b) has the advantage that it has gone through a process of validation. The equation of Lu et al. (2006a) has the advantage that it is built on a larger database, and has more degrees of freedom.

Neither equation is intended as a substitute for a PCR assay for *Dehalococcoides* DNA. However, the equation can be used to screen monitoring wells to identify the wells where the geochemical parameters would justify the cost of an assay for *Dehalococcoides* DNA. The equations also can be used to calibrate computer models of natural attenuation that include natural anaerobic biodegradation. Most sites will have more extensive data sets for geochemical parameters than for distribution of *Dehalococcoides* DNA. Rate constants for anaerobic biodegradation should not be assigned to cells in the model where the geochemical parameters indicate a low probability that *Dehalococcoides* organisms are present.

11.6 USE OF STABLE ISOTOPES TO RECOGNIZE NATURAL BIODEGRADATION

Since the release of the USEPA Protocol for evaluation of natural attenuation of chlorinated solvents, a new technique has been developed to evaluate the extent of biodegradation at field scale (Dempster et al., 1997). The technique is based on the fractionation of the stable carbon isotopes in the chlorinated hydrocarbon during the course of its degradation. The fractionation of the stable carbon isotopes of the chlorinated solvents can provide an unequivocal indication of natural biodegradation.

There are two stable isotopes of carbon: carbon-12 (^{12}C) and carbon-13 (^{13}C). Approximately 1% of the carbon on Earth is ^{13}C. During anaerobic reductive dechlorination, molecules composed entirely with ^{12}C are metabolized more rapidly than molecules with at least one ^{13}C atom (Meckenstock et al., 2004; Schmidt et al., 2004). This discrimination against the heavier isotope is called the kinetic isotope effect. As biodegradation proceeds, the remaining chlorinated organic compound contains a progressively greater proportion of the ^{13}C isotope. As a consequence, the extent of biodegradation can be determined from the change in the ratio of stable isotopes in the chlorinated compound.

Recent advances in analytical chemistry make it possible to determine the ratio of stable isotopes in organic compounds dissolved in a water sample at concentrations that are near regulatory standards (Schmidt et al., 2004). The chlorinated organic compound is separated from water by purge and trap or by solid phase microextraction, and then further separated by gas chromatography, and finally the ratio determined with an isotope ratio mass spectrometer. The effective minimum concentration for analysis of the stable carbon isotope ratio is near 10 μg/L.

The mass spectrometer does not measure the ratio of the stable carbon isotopes to each other. Rather, it measures the deviation of the ratio in the sample from the ratio of a standard used to calibrate the instrument. The substance used as the international standard for stable carbon isotopes (Vienna Standard Pee Dee Belemnite) has a ratio of ^{13}C to ^{12}C of 0.0112372. The conventional notation for the ratio of ^{13}C to ^{12}C in a sample (δ^{13}C) reports the ratio in terms of its deviation from the ratio in the standard.

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{\mathrm{standard}}}{(^{13}C/^{12}C)_{\mathrm{standard}}}\right] \times 1000 \qquad \text{(Eq. 11.3)}$$

The units for δ^{13}C are parts per thousand, often represented as $^{o}/_{oo}$, or per mil, or per mill. Figure 11.14 compares the shift (the fractionation) of the ratio of stable carbon isotopes in TCE, *cis*-DCE, VC and ethene during sequential biological reductive dechlorination of TCE in a laboratory culture. Panel A presents the progress of reductive dechlorination in the culture. Panel B presents the corresponding values for δ^{13}C in TCE, *cis*-DCE, VC and ethene. As the TCE and *cis*-DCE are transformed, the δ^{13}C of the remaining TCE and *cis*-DCE becomes progressively less negative compared to the standard (richer in ^{13}C). In the jargon of isotope geochemistry, the residual TCE and *cis*-DCE becomes heavier. The first VC produced by dechlorination of *cis*-DCE is very light. At the time that all the *cis*-DCE and TCE are exhausted, the VC has a $\delta^{13}C$ equivalent to the original parent TCE. As VC further degrades, it becomes progressively heavier. Ethene follows the same pattern. The first ethene produced from VC is very light. When the VC is essentially completely degraded, the ethene has the same $\delta^{13}C$ of the original parent TCE.

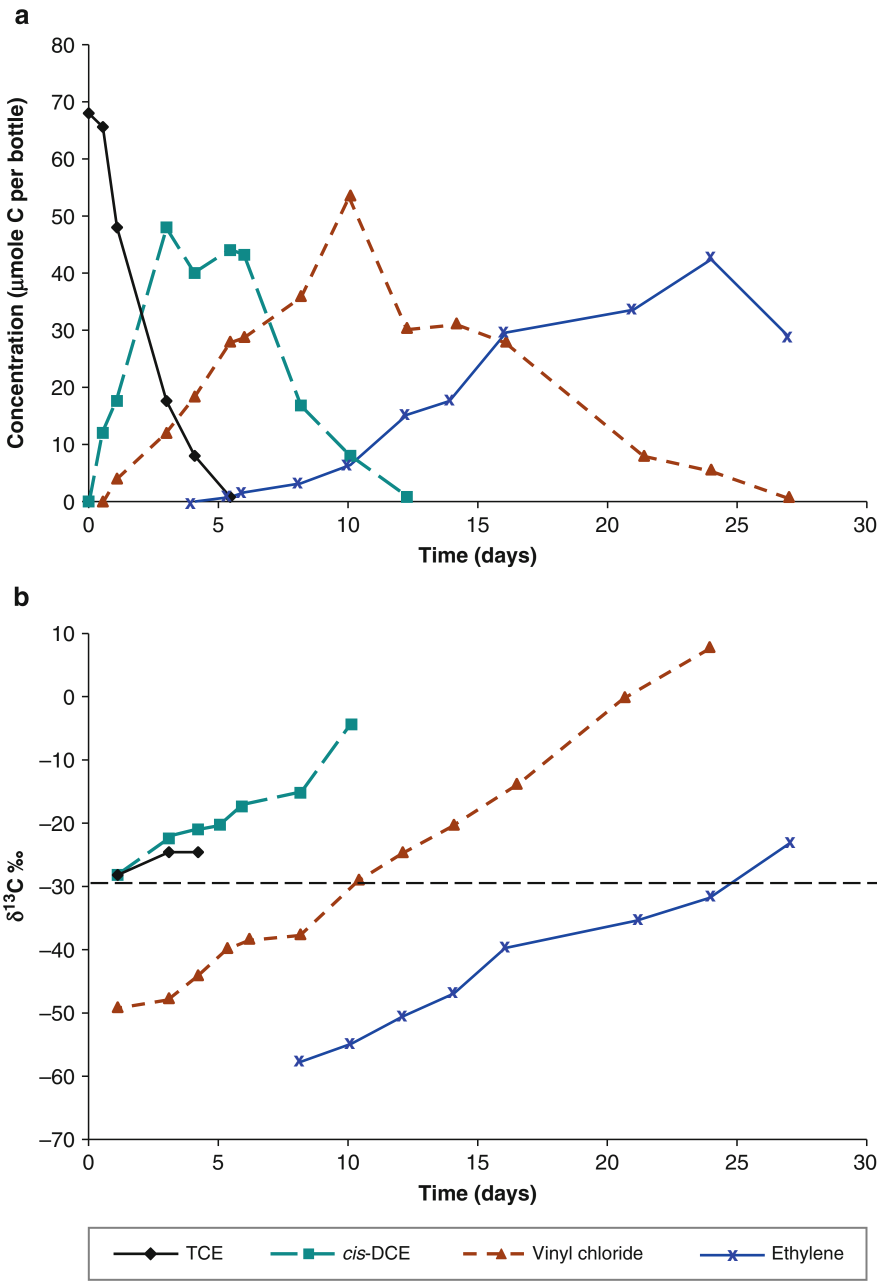

Figure 11.14. Fractionation of carbon isotopes during sequential reductive dechlorination of TCE to *cis*-DCE, then vinyl chloride and ethene (redrawn from Figure 1 of Bloom et al., 2000).

The simplified version of the Rayleigh equation, originally developed by Mariotti et al. (1981), is commonly used in the literature to relate the extent of biodegradation of organic compounds to the δ^{13}C of the material remaining after biodegradation.

$$\delta^{13}C_{\text{compound in groundwater}} = \delta^{13}C_{\text{original compound}} + \varepsilon \ln F \qquad \text{(Eq. 11.4)}$$

In the equation, ε is the isotopic enrichment factor and is an expression of the extent of isotopic fractionation during biodegradation, and *F* or *C/Co* is the fraction of the chlorinated compound remaining after biodegradation. The extent of biodegradation is simply one minus the fraction remaining. The value of ε is usually calculated as the slope of a linear regression of δ^{13}C on the natural logarithm of *F*. As a result:

$$F = \mathrm{C/Co} = e^{((\delta^{13}C_{field} - \delta^{13}C_{\text{original compound}})/\varepsilon)} \qquad \text{(Eq. 11.5)}$$

As a practical matter, δ^{13}C$_{\text{original compound}}$ is usually not known with certainty. There are two common approaches to estimate δ^{13}C$_{\text{original compound}}$. In the first approach, the lightest value of δ^{13}C measured in groundwater at a spill site is taken as the estimate of δ^{13}C$_{\text{original compound}}$. In the second approach, the heaviest value of δ^{13}C reported for the chlorinated solvent of interest as used in commerce is used as an estimate for the δ^{13}C of the material originally spilled. The first approach is subject to the criticism that there may have been more than one spill at a site, and the comparison is actually being made between the unaltered δ^{13}C of two different spills instead of δ^{13}C in the source area of a spill and δ^{13}C in material downgradient that has been fractionated by biodegradation.

However, it is unlikely that the solvent at any particular spill site will have a δ^{13}C that is the heaviest ever produced in commerce. The second approach gives away a certain amount of sensitivity to recognize biodegradation at a particular spill site, and generally the second approach will underestimate the extent of biodegradation. However, the second approach provides a robust conservative underestimate of the extent of biodegradation, and is recommended for the initial evaluation of data on fractionation of stable isotopes. Data available from the literature on the δ^{13}C of selected chlorinated solvents in commerce are presented in Table 11.3. The variation is significant. This variation probably represents differences in the methods used to manufacture the solvents (van Warmerdam et al., 1995).

Table 11.3. Range of Stable Isotopes in Samples of Commercial Chlorinated Solvents

Compound	Source	δ^{13}C (‰/PDB)	δ^{37}Cl (‰/SMOC)	Reference
PCE	Manufacturer A	−27.12±0.03	0.11±0.08	Jendrzejewski et al., 2001
	Manufacturer B	−35.27±0.12	1.20±0.20	Jendrzejewski et al., 2001
	Manufacturer C	−24.06±0.08	1.03±0.10	Jendrzejewski et al., 2001
	Dow	−23.19±0.10	0.18±0.44	van Warmerdam et al., 1995
	ICI	−37.20±0.03	0.11±0.10	van Warmerdam et al., 1995
	PPG	−33.84±0.03	−2.54±0.33	van Warmerdam et al., 1995
	Vulcan	−24.1±0.04	−0.57±0.23	van Warmerdam et al., 1995
	Range	**−23.19 to −37.20**	**1.20 to −2.54**	

(*continued*)

Table 11.3. (continued)

Compound	Source	$\delta^{13}C$ (‰/PDB)	$\delta^{37}Cl$ (‰/SMOC)	Reference
TCE	Manufacturer A	−31.53±0.01	0.91±0.13	Jendrzejewski et al., 2001
	Manufacturer B	−27.90±0.08	2.04±0.12	Jendrzejewski et al., 2001
	Manufacturer C	−29.93±0.18	3.53±0.32	Jendrzejewski et al., 2001
	Aldrich	−33.49±0.08	3.82±0.14	Jendrzejewski et al., 2001
	Dow	−31.90±0.05	4.08±0.34	van Warmerdam et al., 1995
	ICI	−31.32±0.03	2.49±0.26	van Warmerdam et al., 1995
	PPG	−27.80±0.01	−2.54±0.34	van Warmerdam et al., 1995
	Range	**−27.80 to −33.49**	**4.08 to −2.54**	
1,1,1-TCA	Manufacturer A	−31.64±0.09	−2.69±0.18	Jendrzejewski et al., 2001
	Dow	−29.42±0.06	0.87±0.29	van Warmerdam et al., 1995
	ICI	−26.64±0.09	2.03±0.29	van Warmerdam et al., 1995
	PPG	−25.80±0.46	−2.90±0.68	van Warmerdam et al., 1995
	Vulcan	−28.42±0.07	−0.530±60	van Warmerdam et al., 1995
	Range	**−25.80 to −31.64**	**2.03 to −2.90**	

Note: PDB - Pee Dee Belemnite (Vienna Standard), SMOC - Standard Mean Ocean Chloride (Standard)

As is the case with $\delta^{13}C_{\text{original compound}}$, there is considerable variation in reported estimates of the isotopic fractionation factor (ε) for carbon during biological reductive dechlorination (Table 11.4). The reported fractionation factors for PCE are relatively modest, in the range of −2 to −5.5‰. Fractionation factors for TCE range from −2.5 to −13.8‰, fractionation factors for *cis*-DCE range from −14.1 to −20.4‰, and fractionation factors for VC range from −21.5 to −31.1‰. The fractionation factor becomes more negative as the chlorine content of the organic compound decreases. This is to be expected, because the contrast between ^{13}C and ^{12}C becomes more important as the molecular weight becomes smaller. A more negative value of ε will produce a larger change in $\delta^{13}C$ for a given extent of biodegradation (C/Co). If the most negative value of ε that is available in the literature is used to estimate F or C/Co, the estimate will be a conservative lower boundary on the extent of biodegradation.

Stable isotope analysis has been used to recognize biodegradation at field scale. Sherwood Lollar et al. (2001) showed fractionation of TCE under natural conditions in a plume at Dover AFB, Delaware. The shift in $\delta^{13}C$ was 18‰, corresponding to at least 40% biodegradation of TCE. Song et al. (2002) studied anaerobic biodegradation of TCE in a basalt aquifer at the Test Area North site at the Idaho National Engineering and Environmental Laboratory. Lactate was injected to stimulate anaerobic biodegradation. Changes in the concentration of TCE, *cis*-DCE, *trans*-DCE, VC and ethene, and the $\delta^{13}C$ of these compounds were monitored in wells down-gradient. The original $\delta^{13}C$ of TCE in the aquifer was near −26.3‰. The $\delta^{13}C$ of *cis*-DCE was as high as −8.2‰, and the concentration of VC was as high as −0.4‰, indicating substantial biodegradation of *cis*-DCE and VC. Chartrand et al. (2005) studied the fractionation of *cis*-DCE and VC in groundwater in a fractured bedrock site that had been biostimulated and bioaugmented with a culture to remediate TCE that was present in the aquifer as a DNAPL. Based on the fractionation of carbon, they estimated that from 21.3% to 40.7% of the *cis*-DCE had been biologically degraded and from 15.2% to 36.7% of the VC had been degraded. Morrill et al. (2005) studied a site at Kelly AFB, in Texas, where anaerobic biodegradation was used to treat a plume of *cis*-DCE. They used fractionation of stable carbon in the *cis*-DCE to estimate rate constants for biodegradation of *cis*-DCE. Their estimates were within a factor of two to four of estimates independently derived from changes in concentration of *cis*-DCE.

Table 11.4. Range of Isotopic Enrichment Factors for Carbon Isotopes During Reductive Dechlorination of Organic Solvents and their Degradation Products (excerpted in part from Table 3 of Slater et al., 2001; Table 2 of Meckenstock et al., 2004; and Table 1 of Hunkeler et al., 2005)

Chlorinated Hydrocarbon	$^{13}C/^{12}C$	Reference
PCE	ε = −5.2	Slater et al., 2001
	ε = −2 ε = −2.7 ε = −5.5	Hunkeler et al., 1999
TCE	ε = −6.6 ε = −2.5	Bloom et al., 2000
	ε = −7.1	Sherwood Lollar et al., 1999
	ε = −13.8	Slater et al., 2001
cis-DCE	ε = −14.1 ε = −16.1	Bloom et al., 2000
	ε = −19.9	Hunkeler et al., 2002
	ε = −20.4	Slater et al., 2001
trans-DCE	ε = −30.3	Hunkeler et al., 2002
1,1-DCE	ε = −7.3	Hunkeler et al., 2002
VC	ε = −21.5 ε = −26.6	Bloom et al., 2000
	ε = −22.4	Slater et al., 2001
	ε = −31.1	Hunkeler et al., 2002
1,2-Dichloroethane	ε = −32.1	Hunkeler et al., 2002
1,1,2-Trichloroethane	ε = −2.0	Hunkeler et al., 2002

To date, there has not been an extensive application of stable isotope analysis for routine evaluation of MNA of chlorinated solvents. However, the approach has potential to resolve one of the common problems in evaluating natural attenuation. At many sites, PCE and TCE obviously have been biologically degraded to *cis*-DCE; however, there is little evidence of VC or ethene. The conventional interpretation is that these sites are "stalled" at *cis*-DCE, even though monitoring data and calibrations of transport and fate models suggest that the *cis*-DCE is being removed from the groundwater. In wells where the parent compounds are largely depleted, a comparison of the original value of $\delta^{13}C$ of the parent compound that was spilled to the $\delta^{13}C$ of *cis*-DCE in groundwater can provide evidence that *cis*-DCE is in fact being degraded.

Figure 11.15 presents the expected course of carbon isotope fractionation in TCE and *cis*-DCE as TCE is degraded to *cis*-DCE with a fractionation factor of −8.5‰. As the TCE is degraded, δ^{13}C in TCE becomes less negative. At any point during the reaction, the *cis*-DCE produced from the TCE at that instant has a δ^{13}C that is 8.5‰ more negative than the δ^{13}C of TCE. Only when the TCE is entirely consumed does the δ^{13}C in the accumulated pool of *cis*-DCE approach the original value for δ^{13}C in the original TCE. If the δ^{13}C of *cis*-DCE were less negative than the TCE from which it was produced, that would be evidence that the *cis*-DCE had been further fractionated, presumably, by degradation to VC or other products.

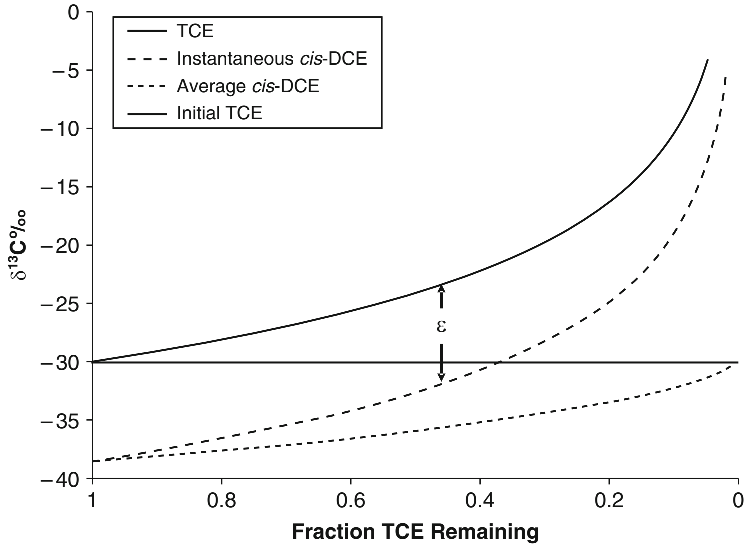

Figure 11.15. Evolution of δ^{13}C in reactant (TCE) and degradation product (*cis*-DCE) predicted by the simplified Rayleigh equation [Eq. 11.4] (redrawn from Figure 7.1 in Hunkeler et al., 2008).

The same relationship should apply to all the compounds in the chain of degradation reactions. Compare the data for concentrations of VC and ethene and the δ^{13}C of ethene in the laboratory experiment presented in Figure 11.14. After 24 days of incubation, the concentrations of TCE and *cis*-DCE were exhausted, the concentration of VC was almost exhausted, and the concentration of ethene reached its maximum. At 24 days of incubation, the δ^{13}C of ethene was slightly below the original δ^{13}C of TCE that was added to culture. After 27 days of incubation, the VC was entirely exhausted, the concentration of ethene started to decline, and the δ^{13}C of ethene was slightly above the original δ^{13}C of TCE that was added to culture. After 24 days, almost all of the original TCE had been converted to ethene, and approximately 60% of the original TCE carbon remained as ethene. The δ^{13}C in the ethene reflected the original δ^{13}C of the TCE. As ethene was further degraded by day 27, the residual ethene was further fractionated.

The behavior of VC and *cis*-DCE followed the same pattern. After 10 days of incubation, concentrations of TCE were exhausted, the concentration of *cis*-DCE was almost exhausted, and the concentration of VC reached its maximum. As was the case for ethene after 24 days of incubation, the δ^{13}C of VC after 10 days was close to the original δ^{13}C of the TCE. As degradation of VC continued, the δ^{13}C of VC became 30‰ less negative than the δ^{13}C of the original TCE. The behavior of TCE and *cis*-DCE are less obvious, but they also followed the pattern. After 5.5 days of incubation, the TCE was consumed, and approximately 65% of the original TCE carbon remained as *cis*-DCE, and approximately 41% of the original TCE carbon was further transformed to VC. After 5.5 days of incubation, the $\delta^{13}C$ of *cis*-DCE was 10‰ less negative than the $\delta^{13}C$ of the original TCE (part b of Figure 11.14), reflecting the further degradation of the *cis*-DCE.

Figure 11.16 presents the results of a thought experiment, where *cis*-DCE is fractionated during anaerobic biodegradation following the relationship in Equation 11.5. Following Equation 11.5, more negative values of the enrichment factor ε predict a larger fraction remaining and less degradation for any given difference between the $\delta^{13}C$ of *cis*-DCE in the field and the $\delta^{13}C$ of the parent compound. The thought experiment will assume a conservative value of ε of −20.4‰ (compare Table 11.4). The solid line in Figure 11.16 is calculated assuming an initial value for $\delta^{13}C$ for *cis*-DCE of −29.5‰. This is the same value of $\delta^{13}C$ as the original TCE used in the experiment presented in Figure 11.14. The dotted lines in Figure 11.16 relate the expected extent of fraction of *cis*-DCE to the range of values of $\delta^{13}C$ that would be expected in TCE in commerce (compare Table 11.3).

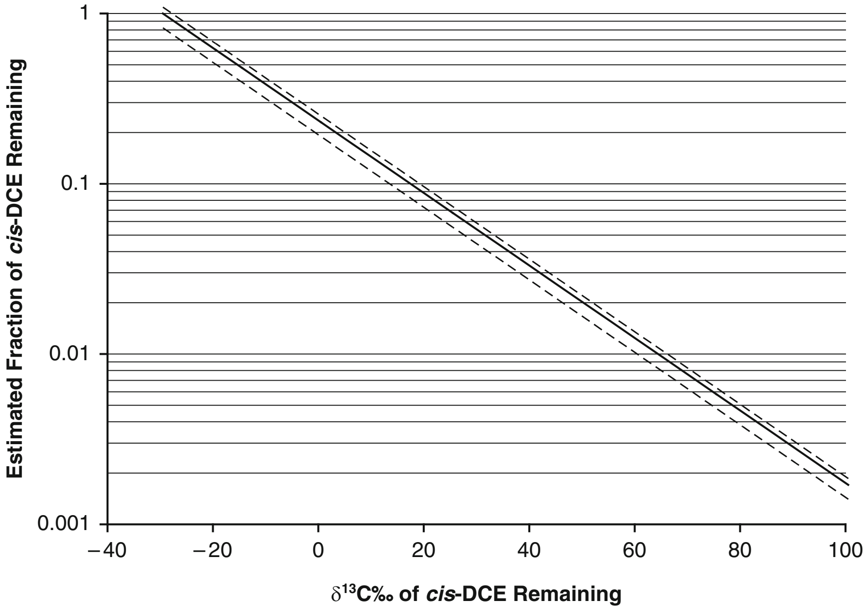

Figure 11.16. Thought experiment on the expected relationship between $\delta^{13}C$ in *cis*-DCE in groundwater and the fraction of *cis*-DCE remaining after anaerobic biodegradation. Assumes that the parent TCE has been entirely dechlorinated, the isotopic fraction factor for dechlorination of *cis*-DCE was −20.4‰, and the *cis*-DCE was formed from TCE with a $\delta^{13}C$ of −29.5‰ (solid line). The dotted lines represent the relationship based on the range of reported values for $\delta^{13}C$ in TCE in commerce.

If 90% of the *cis*-DCE is degraded, the expected $\delta^{13}C$ of *cis*-DCE is in the range of +20‰, which is easily distinguished from the $\delta^{13}C$ of the original TCE.

11.7 APPLICATION OF MNA IN THE FUTURE

As specified in USEPA (1999), MNA as applied to Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) enforcement actions is considered by USEPA to be a remedy like any other remedy. As a consequence, MNA is expected to reach a cleanup goal in a reasonable amount of time. “Reasonable” is defined by a comparison to the time that would be required for alternative active remedies (such as pump and treat) to reach the cleanup goals at the site. In the author's experience, despite the clear language in USEPA (1999), many Records of Decision for CERCLA enforcement actions do not identify a time by which MNA is expected to reach the cleanup goals. As a consequence, there is no objective basis that can be used to evaluate the performance of MNA in the five-year reviews that are required for CERCLA enforcement actions. In particular, there is no objective basis to determine whether the performance of MNA over the five-year interval covered by the review is adequate, or whether alternative remedies should be considered. Because of these difficulties in conducting a five-year review for MNA as a remedy, it is likely that the Record of Decision at many CERCLA sites will be modified to include a definition of a reasonable timeframe.

In the author's experience, many of the evaluations of MNA of chlorinated solvents that were conducted in the past did not quantitatively link the processes responsible for attenuation of chlorinated solvents to the performance of the technology. Many evaluations used the procedures outlined in the USEPA Protocol to demonstrate that the geochemical properties of the contaminated groundwater were favorable for the activity of bacteria that might carry out the complete anaerobic biodegradation of PCE or TCE to harmless products such as ethene. However, they failed to document the presence of bacteria that are capable of degrading the contaminants, or document that the density of the active bacteria was adequate to achieve the rate of attenuation necessary for biodegradation to be a remedy, or that the bacteria were actually degrading the contaminants in the groundwater. New technology based on the PCR analysis can identify bacteria that are known to completely degrade the contaminants and can determine their density in groundwater. New applications of compound-specific isotope analysis (CSIA) can document that biodegradation (or transformation by reactive minerals) has destroyed chlorinated solvents in groundwater.

In the author's experience of providing technical assistance at MNA sites, the financial burden of long term monitoring has led several responsible parties to consider options that will reduce the time required to reach the cleanup goals. These options often include additional efforts to contain or remediate the source of contamination to groundwater. A useful comparison of options requires a robust mathematical model of the behavior of the contaminants in groundwater. A robust model is particularly critical if MNA is to be used as the final polishing step in a sequence of remedial technologies.

In the past, the behavior of the contaminants was described by a model that was calibrated by adjusting a few fitting parameters to make projections that matched the existing distribution of the contaminant at the site. The selection of particular values for many of the fitting parameters was an arbitrary choice made by the person calibrating the model. These models are particularly sensitive to the rate of degradation of contaminants in water. Because there was no opportunity to extract independent estimates of the rate of biodegradation, there was no way to validate the particular rates of degradation used to calibrate the model, and the credibility of the model projections suffered.

Estimates of the density of *Dehalococcoides* DNA can be used to extract a site-specific estimate for the rate of biodegradation. Similarly, CSIA can be used to estimate the extent of biodegradation along a flow path. This information can be coupled with an estimate of the rate of groundwater flow to estimate the rate of biodegradation at field scale. These independent estimates can be used to provide a more robust calibration of the comprehensive transport and fate models. The robust transport and fate models can in turn be used to compare the expected benefits of various options for source control. The robust transport and fate models also can be used to determine the extent of source control that is necessary before it is appropriate to rely on natural attenuation processes to reach the clean goals.

In summary, MNA is moving from an era of simply recognizing in a qualitative manner the processes that were occurring at field scale, to a new era that develops a quantitative understanding of the processes, and uses that quantitative understanding to optimize engineering designs for remediation.

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CHAPTER 12

BIOSTIMULATION FOR ANAEROBIC BIOREMEDIATION OF CHLORINATED SOLVENTS

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12.1 INTRODUCTION

Chlorinated solvents often were released to the subsurface environment in wastewater or in the form of dense nonaqueous phase liquids (DNAPLs). As a result of their physical and chemical properties, chlorinated solvents are difficult to remediate once they have migrated into groundwater. However, enhanced *in situ* anaerobic bioremediation can be an effective method of degrading chlorinated solvents dissolved in groundwater, including chloroethenes, chloroethanes, and chloromethanes (collectively referred to as chlorinated aliphatic hydrocarbons, or CAHs). Advantages of enhanced *in situ* anaerobic bioremediation include the potential for complete detoxification of chlorinated solvents with little impact on infrastructure and relatively low cost compared to more active and aggressive engineered remedial systems.

Biostimulation involves stimulating anaerobic degradation of chlorinated solvents by delivering a fermentable organic substrate (to produce hydrogen) or a direct electron donor (such as hydrogen or acetate) into the subsurface for the purpose of stimulating microbial growth and development (Figure 12.1). The direct addition of electron donor creates an anaerobic treatment zone conducive to biodegradation of chlorinated solvents dissolved in groundwater. While some aquifers may already be anaerobic, sufficient sources of electron donor may not be present for optimal biodegradation of chlorinated solvents.

As detailed in Chapter 3, molecular hydrogen is used as a primary electron donor in the reductive dechlorination of chlorinated solvents. In some cases, microorganisms may need to be added (i.e., bioaugmentation) if the natural microbial population is incapable of effectively performing the required transformations. Bioaugmentation also may be used to reduce the time to achieve effective biodegradation of chlorinated solvents relative to the time required for native microbial populations to acclimate and grow under the anaerobic conditions induced by substrate addition. Bioaugmentation is described in detail in Chapter 13.

The practice of biostimulation has developed rapidly over the last decade, leading to a body of information that allows accurate and reliable comparisons with other remediation technologies, and a better ability to predict relative cost and performance. Results and observations from field applications by the Department of Defense (DoD) have greatly contributed to this body of information on biostimulation (e.g., AFCEE, 2007, 2008; ITRC, 2008a, 2008b).

A variety of organic substrates have been applied to stimulate the anaerobic reductive dechlorination of chlorinated solvents to innocuous end products (e.g., ethene). Other anaerobic degradation processes also may be stimulated by substrate addition, such as biogeochemical transformations or anaerobic oxidation of less chlorinated compounds. In light of recent advances, it is expected that research will increase not only the range of sites (e.g., DNAPL source areas; ITRC, 2008b) and contaminants amenable to this approach (e.g., energetic compounds and oxidized metals), but also will improve the tools available to implement and

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monitor biostimulation performance. Therefore, with progress over time biostimulation will hold even greater promise as a method to remediate chlorinated solvents in groundwater.

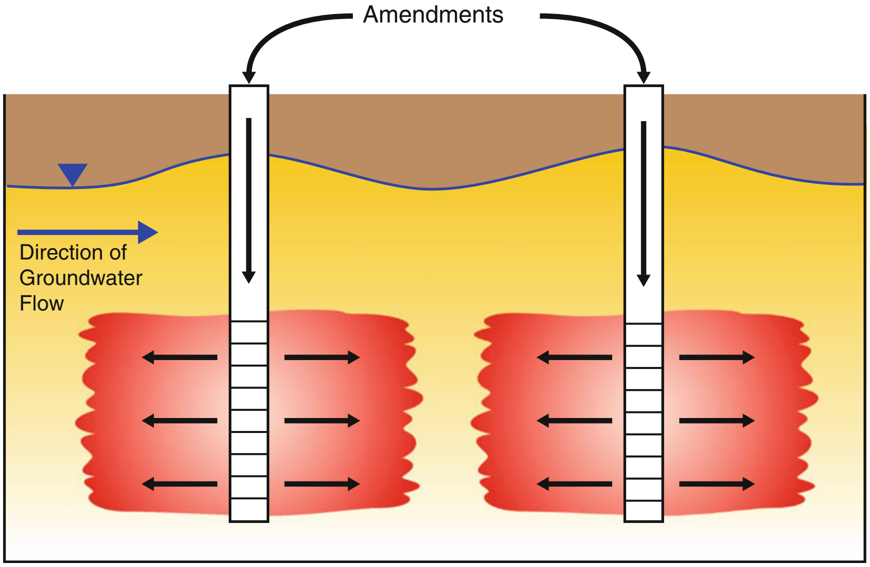

Figure 12.1. Schematic of direct subsurface injection: one example of substrate delivery for biostimulation for enhanced bioremediation of chlorinated solvents.

Although biostimulation has been applied at hundreds of sites to date (AFCEE et al., 2004), it has not been fully accepted within the environmental community, primarily due to a lack of consistency in achieving remedial objectives. It is clear that biostimulation can enhance the degradation of chlorinated solvents at most sites. However, there are likely many sites where conditions may limit or even preclude the use of biostimulation as part of the overall site remediation strategy. A user must carefully screen site conditions (Section 12.2.4) and identify "red flags" where biostimulation may not be usefully applied or that may require special design considerations or modifications (e.g., bioaugmentation or stimulation of abiotic degradation processes). Users should also be clear regarding remedial objectives that are realistic and measurable.

12.1.1 Remedial Objectives

In general, the remedial objective of biostimulation is to restore contaminated groundwater to the pre-existing level of beneficial use. In the case of drinking water aquifers, the objective is usually to meet federal or state established maximum contaminant levels (MCLs) for the contaminants of concern across the entire site. However, in some cases a downgradient point of compliance may be established. The cleanup criteria also may be less stringent than the MCL values if the impacted groundwater does not constitute a potable water supply. Other potential exposure pathways, such as surface water discharge or volatilization to soil vapor, also may dictate cleanup criteria and remedy design. Project- or site-specific remedial objectives may vary accordingly.

Defensible data have been collected and published for many sites demonstrating that biostimulation can enhance anaerobic biodegradation. There are also several sites where practitioners claim to have achieved site closure applying the process (e.g., see Appendix E of AFCEE et al., 2004). However, there are also many sites where complete clean up or site closure has not been achieved. The same is often true for other *in situ* technologies such as chemical oxidation or thermal treatment. Therefore, there continues to be a need to better understand the appropriate site conditions and design criteria necessary to apply biostimulation with a high probability of success. Those considering biostimulation for chlorinated solvents must carefully evaluate the feasibility of the technology and the potential to meet realistic remedial objectives.

12.1.2 Regulatory Acceptance

Regulatory acceptance of biostimulation has evolved and increased over the last decade. Biostimulation has been implemented at sites regulated under various federal programs, including the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Resource Conservation and Recovery Act (RCRA). The technology has been applied in at least 32 states (Parsons, 2002a), under the jurisdiction of regulatory agencies such as the United States Environmental Protection Agency (USEPA), the California Regional Water Quality Control Board, and the Florida Department of Environmental Protection.

As an example, the Navy has installed over 3,660 meters (m) (12,000 linear feet [ft]) of permeable mulch biowalls since 1999 for the remediation of perchlorate in groundwater at the former Naval Weapons Industrial Reserve Plant (NWIRP) McGregor, Texas. The biowall system covers several large perchlorate plumes that are up to several thousand feet in length, and several plumes are commingled with chlorinated solvents, primarily trichloroethene (TCE). Based in part on a designation of the biowall system as Operating Properly and Successfully (OPS), the Navy was able to transfer the entire 39 square kilometer (9,700 acre) property to the City of McGregor in November 2006 for redevelopment (CH2M Hill, 2006).

While the use of enhanced bioremediation has been approved by the USEPA (e.g., USEPA, 2000, 2002) and by the majority of the states, there remain instances when acceptance of the technology is hindered by a lack of familiarity and technical understanding of the process. A lack of consistency in achieving remedial objectives may in some cases remain an impediment to the widespread acceptance of biostimulation as a proven technology. The research and technology validation efforts by the DoD (AFCEE et al., 2004; AFCEE, 2007, 2008), the USEPA (USEPA, 2000) and the Interstate Technology and Regulatory Council (ITRC, 1998, 2002, 2008a, 2008b) provide the technical outreach required to inform and educate the regulatory community and the public about this useful technology.

Many states regulate the injection of materials into the subsurface, and may require an underground injection control (UIC) permit as mandated by the Safe Drinking Water Act. Substrates introduced into the subsurface should not include any known hazardous materials. USEPA approval of acceptable materials for *in situ* bioremediation is discussed in a December 27, 2002, memorandum “Applicability of RCRA Section 3020 to In-Situ Treatment of Ground Water” (USEPA, 2002). UIC permits generally require information regarding the chemical nature of the substrate solution and should address potential concerns with water quality resulting from the injection process. UIC permits for injection of food-grade or common commercial substrates are generally waived or implemented with minimal paperwork (for example, permitting by rule).

Reinjection of contaminated groundwater amended with a substrate also has been approved by the USEPA (2002) for RCRA sites. Use of this USEPA document and reference to historical applications is generally sufficient to gain approval for reinjection of contaminated groundwater for recirculation systems, or to use native groundwater for substrate preparation (i.e., dilution or make-up water).

12.1.3 Advantages and Limitations of Biostimulation

Advantages of biostimulation include the potential for complete detoxification of dissolved CAH mass *in situ* with little impact on site infrastructure, and with lower capital, operation and maintenance (O&M) costs relative to other more highly engineered remedial technologies. There are also limitations to biostimulation, for example the potential accumulation of intermediate dechlorination products and an extended timeframe for remediation. When selecting biostimulation relative to other technologies, the practitioner should evaluate both the advantages and limitations of this approach.

12.1.3.1 Advantages of Enhanced *In Situ* Anaerobic Bioremediation Using Biostimulation

Remediation of CAHs in the subsurface is difficult and sometimes technically infeasible due to aquifer heterogeneity and the density and hydrophobic nature of chlorinated solvent DNAPLs. Highly engineered remedial techniques such as pump-and-treat are costly due to inherent mass transfer limitations, capital expenditures, the need for treatment of secondary waste streams, energy consumption, and long-term O&M requirements. Conversely, enhanced *in situ* bioremediation using biostimulation may offer the following advantages:

- ***Lower Capital and Maintenance Costs.*** Capital costs are generally lower than other technologies, because the substrate often can be added through conventional wells or by using direct-push technology. Soluble substrates or the soluble/fermentation products of slow-release substrates potentially can migrate into and disperse within heterogeneous lithologies via advection and diffusion. Systems used to mix and inject substrates are readily designed and installed by environmental engineers, and O&M is generally routine. Slow release substrates may provide a source of organic carbon for several years, lowering long-term operational costs. Organic substrates often cost less than other reactive materials used to remediate chlorinated solvents, such as zero-valent iron (ZVI).
- ***Detoxification of Chlorinated Solvents In Situ.*** Biostimulation has the potential to completely degrade or mineralize chlorinated solvents to innocuous end products. Detoxification of contaminants *in situ* is highly beneficial because contaminant mass is not transferred to another phase, there is no secondary waste stream to treat, potential risks related to exposure during remediation are limited, and there is minimal impact on site infrastructure. The biologically mediated reactions involved can generally be accomplished by microorganisms that are already resident in the subsurface. In addition, there are multiple anaerobic degradation pathways for chlorinated solvents, not all of which are biologically mediated (Section 12.2.2).
- ***Interphase Mass Transfer.*** The biostimulation process may increase the rate of desorption or dissolution of chlorinated solvents sorbed to the aquifer matrix or in the form of DNAPL. Chlorinated solvent mass is thus transferred to the aqueous phase under conditions optimal for anaerobic degradation to occur. This has sparked interest in enhanced bioremediation as a more efficient and expeditious method for remediating chlorinated solvent source areas where remediation has been dissolution limited (e.g., by groundwater extraction).
- ***Application to Common Cocontaminants.*** In addition to chlorinated solvents, biostimulation is applicable to a variety of other cocontaminants (e.g., perchlorate and explosives) as described in Section 12.2.1. Biostimulation has the potential to treat any

contaminant that can be made less toxic or less mobile (e.g., precipitation of metals) through reduction reactions.

- ***Treatment Train Options.*** Biostimulation can be used in tandem with existing or alternative remediation systems to optimize performance (e.g., source removal via excavation or vapor extraction). Alternatively, anaerobic bioremediation systems may be coupled with downgradient aerobic reaction zones (e.g., an air sparging trench) to degrade dechlorination products that are amenable to degradation by oxidation processes such as vinyl chloride (VC) or chloroethane (CA). Biostimulation often is applied as a polishing step following more active remediation measures.

12.1.3.2 Potential Limitations of Biostimulation

Biostimulation involves the addition of an organic substrate that causes profound changes to the subsurface environment. The degree of success may be subject to site-specific hydrogeological, geochemical, and biological conditions. Some of these challenges also apply to other *in situ* remedial techniques, and therefore are not necessarily unique to biostimulation. Issues that should be considered prior to biostimulation include:

- ***Site-Specific Infrastructure and Use.*** Site infrastructure such as buildings, roadways, taxiways and utilities may interfere with installation and operation of biostimulation systems. When applying biostimulation under such infrastructure, the potential for accumulation of volatile or flammable byproducts (e.g., VC or methane) and noxious gases (e.g., hydrogen sulfide) within the vadose zone or within site-associated structures should be evaluated.
- ***Site-Specific Limitations.*** Site-specific limitations may include low permeability or a high degree of heterogeneity that limits the ability to effectively distribute the substrate throughout the impacted aquifer. It also may be impractical to maintain highly reducing conditions in high flow settings, due to the magnitude of groundwater and native electron acceptor flux. There are also depth limitations, which are related to drilling and implementation difficulties and costs, and not necessarily limitations of bioremediation processes. Other site-specific limitations may include inhibitory geochemical conditions (e.g., low pH that inhibits microbial activity) or lack of appropriate microbial communities or species.
- ***Timeframe for Remediation.*** Anaerobic bioremediation of chlorinated solvents is not an instantaneous process. The time required to develop the appropriate environmental conditions and to grow a microbial population capable of complete degradation may be on the order of several months to years at most sites. Therefore, the technology may require prolonged process monitoring and system maintenance. In some cases bioaugmentation may be effective in reducing the period required for microbial activity.
- ***Remediation of DNAPL Sources.*** Biostimulation can be a viable remedial approach for treating DNAPL source zones and limiting mass discharge in the dissolved phase (see ITRC, 2008a). However, it may be difficult to remediate source zones with large DNAPL pools or DNAPL located in low permeability materials. Displacement or mobilization of DNAPL sources during injection of organic substrates also may be of concern.
- ***Incomplete Degradation Pathways.*** Microbial populations capable of anaerobic dechlorination of highly chlorinated compounds are thought to be more or less ubiquitous in the subsurface environment. For example, the dechlorination of tetrachloroethene (PCE) and TCE to *cis*-1,2-dichloroethene (*cis*-DCE) is readily achieved at most sites, because many bacterial strains are capable of halorespiration of PCE to TCE

to DCE (e.g., Mohn and Tiedje, 1992; Holliger et al., 1993; Gerritse et al., 1996; Löffler et al., 2000; Scholz-Muramatsu et al., 1995; Krumholz, 1997; see Chapter 3). However, the dechlorination of *cis*-DCE and VC to ethene is often problematic due to energetic and kinetic constraints (see Section 12.2.2). Therefore, the ability of dechlorinators to compete with other native microbial populations or to complete the degradation of *cis*-DCE and VC is often an issue at some sites.

- ***Secondary Degradation of Water Quality.*** Degradation of secondary groundwater quality may occur during biostimulation. Degradation reactions or excessive changes in groundwater pH and oxidation-reduction potential (ORP) conditions may lead to solubilization of metals (e.g., iron, manganese, and potentially arsenic), formation of undesirable fermentation products (e.g., aldehydes and ketones), and other potential impacts to secondary water quality (e.g., total dissolved solids or biochemical oxygen demand). Many of these changes are not easily reversed, and in the case of a slow-release source of organic carbon it may take many years for the effects of the substrate addition to diminish.
- ***Generation of Volatile Byproducts and Noxious Gases.*** Stimulating biodegradation also may enhance generation of volatile byproducts and noxious gases (e.g., VC, methane, or hydrogen sulfide) that may degrade groundwater quality and/or accumulate in the vadose zone, or migrate into buildings.
- ***Biofouling or Bioclogging.*** The production of biomass or biogenic gases can reduce the permeability of portions of the aquifer, which may lead to redirection of groundwater flow and contaminant bypass. Biofouling is also an issue for injection wells used for multiple injections or for recirculation. In general, controlling the rate and frequency of substrate application can be used to control or limit the impact of biofouling or bioclogging (GeoSyntec, 2005).

While these concerns and potential limitations should be considered when evaluating biostimulation, many of them can be mitigated or compensated for by understanding the biogeochemical and hydrogeologic conditions of the aquifer system and by using an appropriate design.

12.2 TECHNOLOGY DESCRIPTION

Biostimulation can be an effective method for treating a variety of chlorinated compounds dissolved in groundwater. Enhanced anaerobic bioremediation is not applicable to a site unless the following conditions are met:

- The contaminant is anaerobically degradable;
- Strongly reducing conditions and other favorable environmental conditions (e.g., pH and temperature) either exist currently or can be generated;
- A microbial community capable of complete dechlorination is present, or can be introduced through bioaugmentation; and
- A fermentable carbon source can be distributed effectively throughout the target treatment zone.

Site-specific conditions supporting natural degradation processes (biotic and/or abiotic) may not be optimal (e.g., organic carbon limited). The addition of an organic substrate to an aquifer has the potential to further stimulate microbial growth and development, creating an anaerobic environment in which rates of anaerobic degradation of chlorinated solvents may be enhanced (see Section 12.2.3 for further discussion of the effects of groundwater geochemistry and redox state).

12.2.1 Applicable Contaminants (Chlorinated Solvents)

The most common chlorinated solvents released to the environment include PCE, TCE, trichloroethane (TCA), and carbon tetrachloride (CT). These chlorinated solvents are problematic because of their health hazards and recalcitrance to natural degradation processes. Because these compounds exist in an oxidized state, they are generally not susceptible to aerobic oxidation processes (with the possible exception of aerobic cometabolism). However, oxidized compounds are susceptible to reduction under anaerobic conditions by either biotic (biological) or abiotic (physical/chemical) processes. Biostimulation is intended to exploit these anaerobic degradation processes.

In addition to chlorinated solvents, a number of compounds are subject to anaerobic degradation processes. While not addressed in this chapter, constituents that potentially can be treated with biostimulation include: oxidizers, such as perchlorate and chlorate (Solutions IES, 2006; Stroo and Ward, 2009); explosive and ordnance compounds, such as Royal Demolition eXplosive (RDX) or trinitrotoluene (TNT) (GSI, 2008); dissolved metals, such as arsenic(V) or hexavalent chromium; and oxidized ions, such as nitrate and sulfate. The processes by which these contaminants are degraded under anaerobic conditions also vary, and intermediate products of the reduction of compounds such as RDX and TNT may not always be non-toxic or benign.

There is also potential for biostimulation to be applied to chlorobenzenes (Adrian et al., 2000; Holliger et al., 1992; Holscher et al., 2003), chlorinated pesticides such as chlordane (Fennell et al., 2003), polychlorinated biphenyls (PCBs) (Brown et al., 1987; Zwiernik et al., 1998), pentachlorophenol (MacEwen et al., 2001; Brown et al., 2003), and fluorohydrocarbons (Freon) (Krone and Thauer, 1992; Semprini et al., 1991). Many of the biostimulation techniques used to create anaerobic reactive zones for chlorinated solvents are also applicable to the design and implementation of enhanced bioremediation systems for these constituents.

12.2.2 Anaerobic Degradation Pathways for Chlorinated Solvents

There are several potential reactions that may degrade chlorinated solvents in the subsurface, under both aerobic and anaerobic conditions (Chapter 3 and Chapter 4). Not all CAHs are amenable to degradation by each of these processes. However, anaerobic degradation processes may potentially degrade all of the common chloroethenes, chloroethanes and chloromethanes. Through addition of organic substrates to the subsurface, biostimulation converts naturally aerobic or mildly anoxic aquifer zones to anaerobic and microbiologically diverse reactive zones, making them conducive to anaerobic degradation of chlorinated solvents.

Biodegradation of an organic substrate depletes the aquifer of dissolved oxygen (DO) and other terminal electron acceptors (e.g., nitrate or sulfate), and lowers the oxidation-reduction potential (ORP) of groundwater, thereby stimulating conditions conducive to anaerobic degradation processes. After DO is consumed, anaerobic microorganisms typically use native electron acceptors (as available) in the following order of preference: nitrate, manganese and ferric iron hydroxides or oxyhydroxides, sulfate and finally carbon dioxide (methanogenesis).

Figure 12.2 illustrates a chlorinated solvent plume at an idealized site where a slow-release substrate has been injected into a source area. An anaerobic treatment zone is created, with the development of progressively more anaerobic zones closer to the source of organic carbon as native electron acceptors are depleted. Anaerobic dechlorination has been demonstrated under nitrate-, iron-, and sulfate-reducing conditions, but the most rapid biodegradation rates, affecting the widest range of chlorinated solvents, occur under methanogenic conditions (Bouwer, 1994).

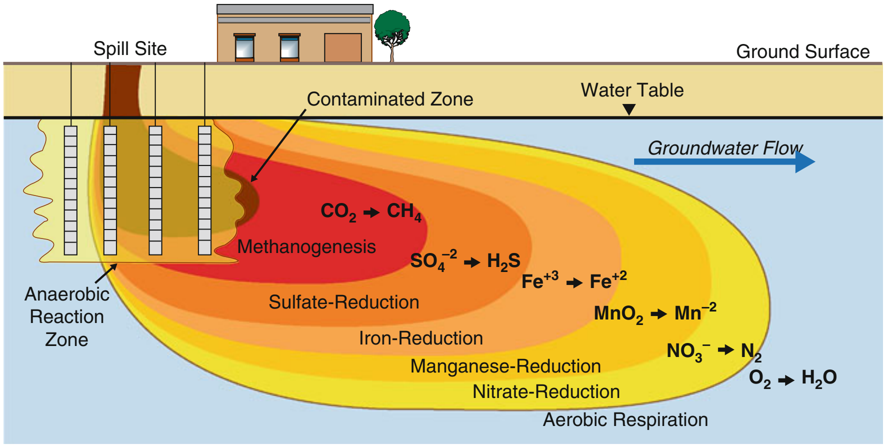

Figure 12.2. Reducing zones established downgradient of a substrate injection site (from AFCEE et al., 2004).

Anaerobic reductive dechlorination is the degradation process most often targeted when biostimulation is used to treat chlorinated solvents. There are three general reactions that can cause dechlorination of chlorinated solvents under anaerobic conditions. These are:

- ***Metabolic anaerobic reductive dechlorination*** is a biologically-mediated reaction where microorganisms gain energy as one or more chlorine atoms on a CAH molecule are replaced with hydrogen atoms in an anaerobic environment. In this reaction the CAH compound serves as the electron acceptor and molecular hydrogen typically serves as the electron donor. Hydrogen used in this reaction is supplied by fermentation of organic substrates. In general, metabolic anaerobic reductive dechlorination occurs by sequential removal of chlorine atoms. For example, the chlorinated ethenes are transformed sequentially from PCE to TCE to DCE isomers (*cis*-DCE or *trans*-DCE) to VC to ethene as illustrated in Pathway 1 in Figure 12.3. This reaction also may be referred to as halorespiration or dehalorespiration, or for strictly chlorinated compounds may be referred to as chlororespiration or dechlororespiration (USEPA, 2000; Chapter 3).
- ***Cometabolic anaerobic reductive dechlorination*** is a reaction in which a chlorinated compound is reduced by a non-specific enzyme or co-factor produced during microbial metabolism of another compound (i.e., the primary substrate) in an anaerobic environment (Chapter 3). Cometabolism of the chlorinated compound does not yield any energy or growth benefit for the microbe mediating the reaction (USEPA, 2000). For the cometabolic process to be sustained, sufficient primary substrate is required to support growth of the microorganisms that produce the non-specific enzyme or co-factor. Cometabolic reductive dechlorination is thought to be less significant relative to halorespiration due to slower rates of reaction.
- ***Abiotic reductive dechlorination*** is a chemical degradation reaction in which a CAH compound is reduced by contact with a reactive mineral (Chapter 4). For example, abiotic transformation of CT, TCA, PCE, TCE, and *cis*-DCE by metal sulfides has been investigated using pyrite (Weerasooriya and Dharmasena, 2001; Kriegman-King and Reinhard, 1994; Lee and Batchelor, 2002), troilite (Sivavec and Horney, 1997), mackinawite (Butler and Hayes, 1999, 2000), and magnetite (Ferrey et al., 2004; Lee and Batchelor, 2002). Pathway 2 in Figure 12.3 illustrates the abiotic reduction of chlorinated ethenes by reaction with iron monosulfide (FeS). This reaction typically occurs by reductive

dihaloelimination (removal of two chlorine atoms), similar to the reaction of chlorinated ethenes with zero-valent iron (e.g., Arnold and Roberts, 2000). The overall degradation pathway is referred to as ***biogeochemical transformation*** (AFCEE et al., 2008) because the reactive mineral may be formed due to both biological and chemical processes.

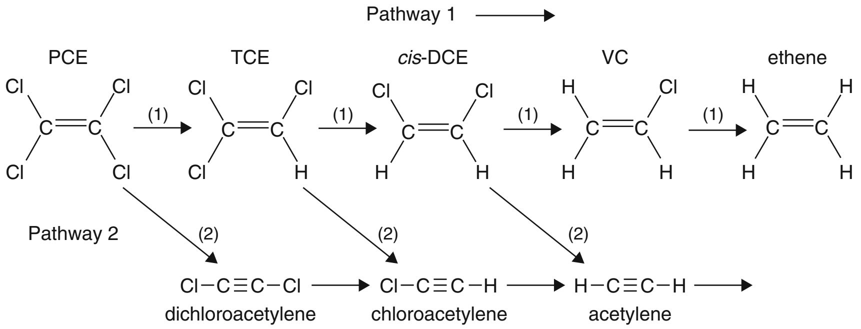

Figure 12.3. Pathways for (1) biotic transformation of chlorinated ethenes and (2) abiotic transformation by iron monosulfide (AFCEE, 2008; modified from Butler and Hayes, 2001).

These pathways are described in greater detail in Chapters 3 and 4. In practice, it may be difficult to distinguish among these three different reactions at the field scale, and all three reactions may be occurring to some degree.

A fourth anaerobic degradation process for CAHs is ***anaerobic oxidation***, a biologically-mediated reaction in which less chlorinated CAHs, such as *cis*-DCE and VC, are directly oxidized to carbon dioxide, water and chloride. This reaction has been reported to occur under iron- and manganese-reducing conditions (Bradley and Chappelle, 1996, 1998; Bradley et al., 1998a, 1998b). The significance of anaerobic oxidation relative to reductive dechlorination processes is not well understood, but warrants consideration in light of the potential accumulation of *cis*-DCE and VC during biostimulation.

Anaerobic reductive dechlorination affects each of the chlorinated compounds differently. Of the chloroethenes, PCE and TCE are the most susceptible to anaerobic dechlorination because they are the most oxidized. Conversely, VC may degrade at lower reaction rates because it is the least oxidized of these compounds, and often it is degraded by a slower cometabolic process. Therefore, the potential exists for VC to accumulate in a treatment system when the rate at which it is generated is greater than the rate at which it is degraded. This is a common concern because VC is considered more toxic than the other chloroethenes. However, there are other degradation pathways for VC, and the formation and persistence of large VC plumes (i.e., larger than the footprint of the initial chlorinated solvent plume) has not been observed in practice (AFCEE et al., 2004).

Current literature suggests that halorespiration of CAHs is carried out by relatively few metabolic classifications of bacteria. In particular, cultures containing *Desulfitobacterium*, *Dehalobacter restrictus*, *Desulfuromonas*, *Dehalospirillum multivorans* and *Dehalococcoides* are known to be capable of dechlorinating PCE and TCE to *cis*-DCE (Scholz-Muramatsu et al., 1995; Gerritse et al., 1996; Krumholz, 1997; Maymo-Gatell et al., 1997; Holliger et al., 1993; Löffler et al., 2000). In practice, microorganisms capable of degrading PCE and TCE to *cis*-DCE should be considered ubiquitous in the subsurface environment. However, complete dechlorination of PCE to ethene by a single species only has been demonstrated in the laboratory for some strains of *Dehalococcoides ethenogenes*. *D. ethenogenes* strains appear to be common, but not ubiquitous, in the environment (Hendrickson et al., 2002; He et al., 2003). Therefore, microorganisms that facilitate dechlorination of DCE and VC to ethene may not be as prevalent at those capable of dechlorination PCE and TCE to *cis*-DCE.

The primary causes of incomplete dechlorination of *cis*-DCE and VC include (1) insufficient redox conditions, due to a limited supply of electron donors or an excess of electron acceptors such as manganese and iron, and (2) the absence or low activity of microorganisms capable of dechlorinating *cis*-DCE and VC. Other potential causes may include interspecies competition for molecular hydrogen (e.g., the use of hydrogen for methane production, limiting its availability for dechlorination) or high concentrations of inhibitory substances such as sulfide or PCE (in the case of VC). Careful monitoring of substrate distribution, geochemistry and redox conditions, and use of molecular biological tools (MBTs) to determine microbial sufficiency can help determine an appropriate course of action when *cis*-DCE and/or VC accumulate to unacceptable levels. Another alternative may be to stimulate degradation processes that typically do not produce *cis*-DCE or VC, such as biogeochemical transformation.

12.2.3 Controlling Groundwater Redox Conditions

A successful application of biostimulation depends on the ability to stimulate the native microbial community and to modify and control (as needed) aquifer biogeochemistry. The subsurface environment is highly diverse in terms of sediment or bedrock materials, groundwater geochemistry and groundwater hydraulics. For example, permeability typically ranges over several orders of magnitude forming a heterogeneous environment with zones of preferential flow. This may result in non-uniform distribution of an injected substrate and non-uniform geochemical conditions.

The objective of biostimulation is to uniformly achieve strongly anaerobic conditions in the sulfate to methanogenic range throughout the targeted area. ***The ability to create uniform reaction zones of optimal ORP for biodegradation of chlorinated solvents to occur is perhaps the biggest challenge for successful implementation of biostimulation.*** In practice, there is a range of substrate concentrations across the reaction zone due to injection methods and site heterogeneity. For example, concentrations will be highest at the point of injection and lower away from the injection point as concentrations are reduced due to mixing, dilution and depletion due to biological and chemical reactions. A similar reduction in concentrations of dissolved organic carbon will occur downgradient of a permeable mulch biowall.

Figure 12.2 illustrates the progression of geochemical conditions from aerobic to strongly anaerobic based on the relative availability of organic carbon. Wiedemeier et al. (1996) proposed a classification system (Type 1, 2 and 3) for chlorinated solvent plumes based on the amount and origin of fermentation substrates that produce the molecular hydrogen that drives anaerobic reductive dechlorination. As shown on Figure 12.4, this classification depends on the relative amount of organic substrate available (regardless of origin) and the ORP conditions that predominate within the aquifer system. The relative amount of organic substrate is emphasized because biostimulation modifies this parameter to achieve ORP conditions that are optimal for anaerobic dechlorination to occur (AFCEE et al., 2004).

Type 1 environments are highly reducing groundwater systems, due to high levels of fermentable organic carbon. These conditions may be present at sites contaminated with fuel hydrocarbons, landfill leachate or other sources of anthropogenic carbon. With few exceptions (e.g., wetlands), most natural aquifers do not contain sufficient natural organic matter to generate the highly reducing conditions in which sulfate reduction and methanogenesis predominate. Importantly, a Type 1 environment may result in the rapid and extensive reductive dechlorination of chlorinated solvents and is the condition targeted by biostimulation.

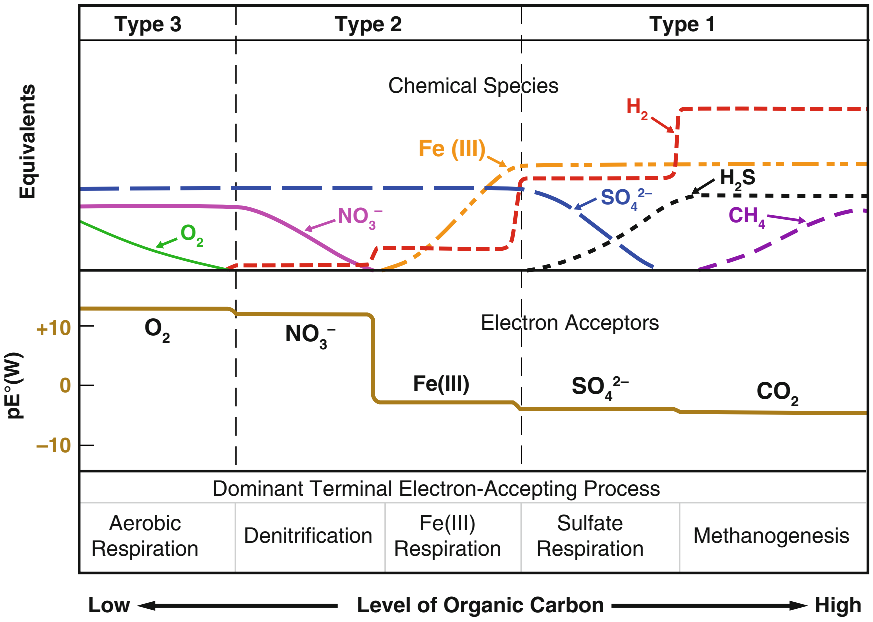

Figure 12.4. Geochemical characteristics of groundwater relative to the amount of bioavailable organic carbon (from Wiedemeier et al., 1999, modified from Bouwer and McCarty, 1984).

Type 2 environments are moderately reducing and occur in hydrogeologic settings that have relatively moderate levels of fermentable organic carbon. Type 2 environments generally result in slower dechlorination of the highly chlorinated CAHs and incomplete reductive dechlorination of less chlorinated CAHs (e.g., *cis*-DCE) compared to a Type 1 environment. However, a Type 2 environment may be readily modified by biostimulation to a Type 1 environment, resulting in faster and more complete dechlorination.

A Type 3 environment is a well-oxygenated groundwater system with little or no organic matter. Concentrations of DO typically are greater than 1.0 milligram per liter (mg/L). In such an environment, anaerobic reductive dechlorination will not occur, and highly chlorinated CAHs such as PCE, TCA and CT will not degrade by biological processes. The Type 3 environment may be a challenge for biostimulation, primarily due to a lack of an anaerobic microbial population and the necessity to overcome the natural electron acceptor supply. DO concentrations greater than 1.0 mg/L are generally toxic to anaerobic dechlorinating species, and it is logical to assume that these bacteria may be present in low numbers, confined to anaerobic microsites or low-permeability materials, and often surviving in a dormant state until conditions become more favorable. However, given the degree of microbial heterogeneity within most aquifers, and the presence of such anaerobic microsites, complete reductive dechlorination often can be induced within a reasonable time at Type 3 sites.

The scenario targeted by biostimulation involves a reaction zone in which all chlorinated compounds are dechlorinated under strongly reducing (Type 1) conditions. However, a chlorinated solvent plume can exhibit all three types of behavior in different portions of the plume. For example, Wiedemeier et al. (1996) describe a plume at Plattsburgh Air Force Base (AFB), New York, USA that exhibits Type 1 behavior in the source area and Type 3 behavior downgradient from the source. This fortuitous scenario involves dechlorination of PCE, TCE and DCE, with accumulation of VC near the source or treatment area (Type 1 behavior) and oxidation of VC (Type 3 behavior) either aerobically or via iron reduction further downgradient.

Under these conditions, VC is oxidized to carbon dioxide and does not accumulate, so the following sequence of reactions will occur:

PCE → TCE → DCE → VC → Carbon Dioxide

Note that ethene is not produced during this reaction, and that VC is typically removed from the system much faster than it is via anaerobic dechlorination.

Biostimulation systems may be designed to take advantage of mixed reaction zones. A strategy using sequential anaerobic/aerobic degradation may be employed where more highly chlorinated compounds (e.g., PCE and TCE) are dechlorinated in an anaerobic reaction zone, and less chlorinated compounds (e.g., DCE and VC) are degraded by oxidation processes in a downgradient (natural or engineered) aerobic redox recovery zone.

These three different types of plume behavior can be used to delineate zones of differing anaerobic biodegradation potential within a chlorinated solvent plume. A range of geochemical conditions will likely be present due to variations in substrate concentration and aquifer heterogeneity, but the objective of biostimulation is to uniformly achieve Type 1 conditions.

12.2.4 Site Screening for Biostimulation

The two primary factors that lead to successful biostimulation applications are (1) a thorough understanding of the site geology, groundwater geochemistry and groundwater hydraulics and (2) the ability to deliver an appropriate amount of substrate throughout the treatment zone to obtain optimal conditions for anaerobic degradation processes to occur. Therefore, site screening is a critical step in determining the potential for successful application of biostimulation.

There are many considerations when selecting and designing a biostimulation application. Table 12.1 lists a number of site characteristics that are suitable for biostimulation applications, or that may raise a "red flag" as to whether the site is suitable. The list is not inclusive, and each site will be unique and present its own challenges.

The addition of an organic substrate to the subsurface to stimulate and enhance the anaerobic dechlorination process *in situ* has been explored at many sites. Biostimulation has been applied under a broad range of site conditions, including:

- ***Hydrogeologic Settings.*** Biostimulation has been applied in hydrogeologic settings ranging from low permeability silts and clays (Zahiraleslamzadeh and Bensch, 2001; Parsons, 2002c) to high permeability alluvial sand and gravel deposits (Frizzell et al., 2004) to fractured bedrocks (Sorenson, 2003). Enhanced bioremediation has been applied at depths up to 400 ft (120 m) below ground surface (bgs) (Sorenson, 2003), and at sites with groundwater velocities ranging from less than 10 to 100 ft per year (ft/yr) (3 to 30 m/yr) (Henry et al., 2007) to several feet or meters per day (Schankweiler and Lorenz, 2002). However, there are limits to applying the technology in settings with the extremes of very high and very low rates of groundwater flow. It may be impractical to maintain reducing conditions in high flow settings due to the magnitude of groundwater and native electron acceptor flux. On the other hand, it may be difficult to inject substrates into tight formations, and the distribution of injected substrates may be limited in lowflow environments.
- ***Contaminant Levels and Distribution.*** The technology typically has been applied to groundwater plumes with concentrations of chlorinated solvents ranging from 0.01 to 100 mg/L. Sites with indications of residual or sorbed DNAPL (i.e., dissolved CAH concentrations in excess of 100 mg/L) also have been successfully treated

(e.g., Sorenson, 2003; Henry et al., 2007). However, it may not be realistic to expect rapid remediation of source areas with DNAPL pools (ITRC, 2008b).

- ***Geochemical Conditions.*** During anaerobic dechlorination, CAHs function as electron acceptors in competition with naturally occurring (inorganic) electron acceptors. For example, rapid groundwater flow coupled with high DO or nitrate concentrations may create an electron donor demand that cannot be overcome by substrate additions, given practical limitations. High concentrations of sulfate may result in utilization of substrate for sulfate reduction at the expense of dechlorination reactions, although high sulfate sites may be suitable for stimulating biogeochemical transformation of chlorinated solvents through the production of reduced iron sulfides.

Table 12.1. Suitability of Site Characteristics for Enhanced Anaerobic Biostimulation (after AFCEE et al., 2004)

Site Characteristic	Suitable for Enhanced Bioremediation	Suitability Uncertain	Suitability Unclear - Possible Red Flag - Requires Further Evaluation
DNAPL Presence	Residual DNAPL or sorbed sources	Poorly defined sources may require additional characterization	May not be appropriate for treatment of pools or inaccessible DNAPL
Plume Size	Small, a few acres or less	Medium to large, a few acres plus. May require concurrent technology.	Large plumes of many acres. May require concurrent technology.
On or Near Site Infrastructure	The risk of vapor intrusion from contaminants or biogenic gases is deemed acceptable	Target treatment zone in close proximity to sensitive infrastructure	Target treatment zone in an area where known vapor intrusion issues exist
Evidence of Anaerobic Reductive Dechlorination	Partial or slow reductive dechlorination	Limited evidence of anaerobic reductive dechlorination	No evidence of any degradation
Depth	<50 ft to groundwater (<15 m)	>50 ft to groundwater (>15 m)	>100 ft (>30 m) to groundwater or saturated thickness >50 ft (>15 m)
Hydraulic Conductivity	>1 ft/day (>3 x 10^{-4} cm/sec)	0.01 to 1 ft/day (3 x 10^{-6} to 3 x 10^{-4} cm/sec)	<0.01 ft/day (<3 x 10^{-6} cm/sec)
Groundwater Velocity	30 ft/yr to 5 ft/day (9 m/yr to 1.5 m/day)	10–30 ft/yr (3–9 m/yr) or 5–10 ft/day (1.5–3 m/day)	<10 ft/yr (<3 m/yr) or > 10 ft/day (>3 m/day)
pH	6.0 – 8.0	5.0 to 6.0 or 8.0 to 9.0	<5.0 or >9.0
Sulfate Concentration	<500 mg/L	500 to 5,000 mg/L (with caution)	>5,000 mg/L or presence of mineral gypsum

Note: ft/day = feet per day; ft/yr = feet per year; m/day = meters per day; m/yr = meters per year; cm/sec = centimeters per second; mg/L = milligrams per liter

In many cases, adverse site conditions can be mitigated with proper system design. For example, recirculation systems may be used to impose a hydraulic gradient and enhance groundwater flow at sites with very low natural hydraulic gradients. However, at some sites this strategy may require pumping significant quantities of groundwater, making the technology more expensive than pump and treat.

Development of remedial objectives, a conceptual site model (CSM) and preliminary site screening are the first steps in evaluating the potential for applying biostimulation (see Section 3.2 of AFCEE et al., 2004). Developing a CSM involves characterizing the nature of the release, the resulting contaminant plume and the site hydrogeology. In addition, an exposure pathway analysis is required to determine the risks posed by the contaminant release and to select and design an appropriate remedy. The physical and chemical characteristics of chlorinated solvents, whether in a DNAPL or aqueous phase, affect their fate and transport, and are also taken into account when developing the CSM. The CSM is important when evaluating the suitability of biostimulation for treating chlorinated solvent plumes, because such an evaluation relies on accurately addressing the decision criteria provided below.

Biostimulation may be appropriate at sites where the following is achieved:

- Site-specific data indicate that the contaminants present (including any toxic degradation products) can be readily degraded by native microbial populations under anaerobic conditions.
- Subsurface conditions (e.g., aquifer permeability) are conducive to adequate emplacement and distribution of a substrate, and creation of an *in situ* reactive zone conducive to anaerobic degradation of the targeted contaminants.
- A cost/benefit analysis indicates that the technology is cost-effective relative to other remedial measures (such as monitored natural attenuation [MNA], air sparging, groundwater extraction, ZVI permeable reactive barriers or chemical oxidation).

Conditions that may preclude the use of biostimulation include:

- Sites with impacted receptors, or with short travel times or distances to discharge or exposure points.
- Sites with inaccessible DNAPL sources.
- Hydrogeologic conditions that make it difficult to deliver amendments cost-effectively, such as low permeability or a high degree of aquifer heterogeneity. In some cases technologies such as hydraulic fracturing or excavation to install biowalls may be used to mitigate difficult hydrogeologic conditions.
- Geochemical conditions (e.g., unusually low or high pH) that inhibit the growth and development of dechlorinating bacteria. For source areas, the toxicity of the contaminants to subsurface microbes may be an additional consideration.
- The presence of cocontaminants that are less susceptible to anaerobic degradation processes (e.g., 1,4-dioxane), or the presence of naturally occurring metals that may be mobilized (reduced to a more soluble form) under anaerobic conditions (e.g., arsenic).

Additional site characterization, laboratory microcosm studies or small-scale field tests may be warranted before a field-scale system can be designed and an accurate cost estimate calculated. If a determination is made to proceed with biostimulation, site-specific factors will continue to influence the design of the remedial system and the interpretation of performance results.

12.2.5 Treatability Studies

In many cases the suitability of a site for biostimulation may be in question after a review of site-specific data. A lack of adequate site characterization may require further site investigation. Therefore, treatability studies prior to full-scale design may be warranted. The cost of treatability testing may be recovered by using the results to optimize the full-scale design. Treatability studies that can be used to evaluate sites for biostimulation include laboratory microcosm studies or small-scale field tests, combined with analytical methods to characterize anaerobic degradation processes and to evaluate microbial populations and activity. Common and emerging treatability study techniques and methods are summarized in Table 12.2. These methods are intended to reduce the uncertainty associated with implementing biostimulation.

Table 12.2. Summary of Biostimulation Microbial Screening Techniques and Methods (after AFCEE et al., 2004)

Description	Information Provided	Usefulness	Limitations
Evaluation of Existing CAH and Biogeochemical Data			
Evaluation of site data for the presence of dechlorination products and appropriate geochemical conditions.	Evidence that reductive dechlorination occurs with native microbial populations, or that reductive dechlorination is limited due to insufficient substrate.	Useful for site selection to determine whether complete reductive dechlorination can be enhanced, or whether additional site evaluation is required.	Type 2 or Type 3 sites may not have appropriate conditions for observing reductive dechlorination.
Microcosm Testing			
Microcosm tests using site-specific aquifer solids and groundwater. Can be used to test multiple substrate types or bioaugmentation cultures.	Definitive information on the extent of anaerobic reductive dechlorination that may be achieved. Evidence of predominant fermentation pathways of the substrate selected.	Provides a positive indication that complete dechlorination can be achieved. Useful to evaluate fermentation pathways and efficiency of multiple substrates. May be used to verify the effectiveness of bioaugmentation cultures.	Moderate cost and time. Must be coupled with an engineering assessment or pilot test to evaluate substrate distribution and to define engineering design parameters.
Column Studies			
Constructed using site aquifer solids and groundwater, or backfill materials for biowalls.	In addition to data provided in microcosm study, may also provide information on hydraulic and sorption properties of the material.	Particularly useful for evaluating the effects of substrate addition on permeability, or for evaluation of alternative materials for permeable mulch biowalls and bioreactors.	Moderate cost and time.
Single Well Push-Pull Tests			
Injection and periodic extraction of a well-characterized groundwater slug in a single well.	Extent and rate of *in situ* anaerobic degradation processes.	Low cost field test that provides *in situ* degradation rates and field data regarding effectiveness of substrate injection (e.g., injection pressures and flow rates, theoretical radius of influence).	May not observe degradation if groundwater conditions are not sufficiently reducing or insufficient time is allowed for microbial succession and acclimation.

(*continued*)

Table 12.2. (continued)

Description	Information Provided	Usefulness	Limitations
Field Pilot Tests			
Field-scale pilot tests to determine microbial sufficiency.	Extent and rate of *in situ* reductive dechlorination.	Can determine lag times and field degradation rates; used to refine system design parameters.	Time and cost.
Isotope Chemistry			
Shifts in relative isotope fractions in CAHs over time.	Carbon isotope fractions for chlorinated parent and dechlorination products.	Changes in carbon isotope fractions between chlorinated parent and dechlorination products may provide field evidence for microbial or abiotic degradation.	Most useful when sampling over multiple time periods.
Phospholipid Fatty Acid (PLFA)			
Profile of the phospholipid content of cell membranes.	Information on biomass concentration, community structure, diversity, and physiological status.	Provides general information on the activity and shifts in the microbial community due to substrate addition.	Does not provide positive identification of dechlorinating species. Excludes methanogens.
Molecular Biological Tools (MBT)			
Detection of genetic sequences unique to targeted microbial genus and species.	Provides positive identification of a limited number of dechlorinating species.	Positive identification of *Dehalococcoides*-related species and reductase enzymes, identify strains capable of complete anaerobic dechlorination of chlorinated ethenes.	Potential for false negative and positive responses, prone to sampling bias.

In many cases, favorable contaminant and geochemical data may suffice for site selection purposes. However, sites exhibiting marginal or difficult biogeochemical conditions may benefit from the use of a variety of microbial screening methods. The microbial screening methods most commonly used include laboratory analysis of site samples for the presence of *Dehalococcoides* species and laboratory microcosm studies. Compound-specific isotope analysis (CSIA) also can provide valuable insights into biodegradation activity at a site, particularly when results from traditional analyses are confounded by issues such as dilution, partitioning into edible oil or sorption/desorption from aquifer solids.

Microcosms constructed with site aquifer solids and groundwater can be used to assess the presence of dechlorinating microorganisms and to determine whether complete anaerobic dechlorination can be achieved. Microcosm tests may be a more practical method than field tests to compare the extent and rate of dechlorination achieved using different substrates, for example. Microcosms also can be amended with bioaugmentation cultures to evaluate increased biodegradation potential.

Small-scale field pilot tests may be conducted at a reasonable cost at many sites, and offer the opportunity to determine important engineering design parameters as well as to assess the feasibility of biostimulation. For example, field pilot tests can be used to evaluate substrate distribution, determine the effective radius of influence (ROI), measure acclimation periods under field conditions and estimate the degradation rates achievable during full-scale treatment. Pilot test configurations for biostimulation may range from single well push-pull tests to multiple well injection tests. In some cases, a pilot test may be configured to achieve an interim remedial objective such as source or "hot spot" reduction. Descriptions and methods to conduct the most common pilot test types (single well push-pull tests and multiple well injection tests) can be found in AFCEE (2007).

One important consideration in using these methods is the amount of time required for the onset of complete dechlorination in both field- and laboratory-scale testing. Pilot tests performed in the field can take a year or more to demonstrate complete dechlorination to innocuous end products. Microcosm studies typically attempt to shorten this lag period by incubating the microcosms at higher temperatures with agitation, at the expense of using conditions similar to those in the field. As a result, the microcosm results may not always be directly applicable to actual field conditions.

12.3 APPLICATION OF BIOSTIMULATION

Once biostimulation is selected as a remedy for a specific site, design criteria for implementation include selection of a substrate and a system configuration. ***It must be feasible to effectively distribute an organic substrate throughout the treatment zone and to induce strongly reducing conditions in the subsurface.*** The following sections describe some common substrate alternatives and system configurations used for biostimulation.

12.3.1 Substrate Options

There are many organic substrates that can be naturally degraded and fermented in the subsurface, resulting in the generation of molecular hydrogen. Selection of a substrate is often based on contractor experience or familiarity, or as a result of commercial marketing. ***The practitioner of biostimulation should consider the full range of substrates and configurations described in this chapter, as all of these substrates have been shown to stimulate anaerobic reductive dechlorination of CAHs.*** Examples of easily fermentable organic substrates include alcohols, low-molecular-weight fatty acids (e.g., lactic acid), carbohydrates (e.g., sugars), vegetable oils and plant debris (e.g., mulch and compost).

Table 12.3 summarizes the attributes of several substrate types. These substrates are commonly classified as soluble substrates, slowly soluble viscous or low viscosity fluids, and solid substrates. Substrates used for biostimulation include soluble substrates such as sodium lactate, molasses, ethanol, methanol, benzoate, butyrate, high-fructose corn syrup and cheese whey; viscous or low-viscosity (slow-release) substrates such as hydrogen release compounds (HRC® or HRC-X™) and emulsified vegetable oil (EVO); solid substrates such as bark mulch, compost and chitin; and gaseous substrates such as hydrogen gas (AFCEE et al., 2004). In addition, experience and research are leading to new materials or combinations of materials that combine desirable features of different substrate types (e.g., long-lasting substrates that disperse well in the subsurface as microemulsions, or coinjections of soluble and more viscous materials).

Recent protocols for soluble carbohydrates (Suthersan et al., 2002), for vegetable (edible) oils (AFCEE, 2007), and for permeable mulch biowalls and bioreactors (AFCEE, 2008) provide specific guidance for using these substrate types. In addition, most vendors of bioremediation products provide technical assistance to customers who purchase their products.

Table 12.3. Substrates Used for Enhanced *In Situ* Anaerobic Bioremediation (AFCEE et al., 2004)

Substrate	Typical Delivery Techniques	Form of Application
Soluble Substrates		
Lactate, Propionate, and Butyrate	Injection wells or recirculation systems	Acids or salts diluted in water
Methanol and Ethanol	Injection wells or recirculation systems	Diluted in water
Sodium Benzoate	Injection wells or recirculation systems	Dissolved in water
Molasses, High Fructose Corn Syrup	Injection wells	Dissolved in water
Whey (soluble or slurry)	Direct injection or injection wells	Dissolved in water or slurry
Slowly Soluble Viscous or Low Viscosity Fluids		
Hydrogen Release Compounds®	Direct injection	Straight injection of product
Emulsified Vegetable Oil	Direct injection or injection wells	Low oil content (<10%) oil-in-water microemulsions
Vegetable Oils	Direct injection or injection wells	Straight oil injection with water push, or high oil:water content (>10% oil) emulsions
Solid Substrates		
Mulch and Compost	Trenching or excavation	Trenches, excavations, *in situ* bioreactors, or surface amendments
Chitin (solid)	Trenching or injection of a chitin slurry	Solid or slurry
Gaseous Substrates		
Hydrogen	Biosparging wells	Gas injection

The substrates listed in Table 12.3 differ in the complexity of their composition, the rate at which the material is degraded or fermented by biological activity in the subsurface, and in cost. The physical nature of the substrate dictates the frequency of addition, the addition technique, and potential system configurations.

Many substrates are available as low-cost food-grade products such as molasses, vegetable oils and whey. Less complex substrates such as lactate, butyrate and ethanol may be used to target more specific fermentation reactions. Low-molecular-weight metabolic acids (e.g., propionic and acetic) produced from the biodegradation of these substrates are further fermented to produce molecular hydrogen. Therefore, these substrates are similar in that molecular hydrogen is generated from fermentation processes and is used as a primary electron donor to stimulate anaerobic reductive dechlorination.

The selection of an appropriate substrate should take into account expected performance in developing appropriate anaerobic reactive zones, the rate at which the substrate is used (efficiency of use), substrate availability and cost to implement (life-cycle cost, including cost of O&M). The physical and chemical characteristics of the substrate (e.g., phase and solubility) may make certain substrates more suitable than others in particular applications. However, a common goal is to minimize overall project cost by optimizing the number of required injection points or wells, the number of injection events and the amount of substrate needed.

Combinations of various substrates are becoming more common. For example, an easily distributed and rapidly degraded soluble substrate such as lactate may be combined with a slow-release substrate such as EVO (Ferris et al., 2006). HRC® is also available from the manufacturer in both a fast acting primer and a longer lasting HRC-X™ product. These combinations may be used to rapidly initiate anaerobic conditions while sustaining the reaction zone. The following paragraphs summarize each of the general substrate types and also describe some common substrate amendments/nutrients and bioaugmentation cultures.

Advantages of ***soluble substrates*** include the ability to readily distribute the substrate in the subsurface relative to viscous or solid substrates and the ability to modify the rate at which the substrate is applied over time to more accurately achieve the desired biogeochemical conditions. For these reasons soluble substrates are well suited for recirculation systems and for bioaugmentation applications. The primary disadvantage of this approach is the requirement for multiple injections (higher O&M and cost) and the potential for biofouling of injections wells (GeoSyntec, 2005).

Advantages of ***slow-release substrates*** include the need for less frequent injections; in fact, a single injection often may be sufficient. Because of the reduced operating requirements, use of these substrates is often less costly than using soluble substrates. The primary disadvantage is that it is difficult and costly to modify the biogeochemical conditions of the reaction zone after the initial injection, hence, there is less room for error in designing these applications relative to soluble substrate applications using multiple injections.

Solid substrates such as mulch and compost in permeable biowalls provide a low-cost alternative to other reactive barrier systems such as ZVI walls. Biowalls are effective for shallow groundwater plumes in low to moderate permeability or highly heterogeneous formations, where the trench physically cuts through the formation and uniform contact with contaminated groundwater is achieved (AFCEE, 2008). Finely ground solid substrates such as chitin may be directly injected as slurries, but the distribution in the subsurface is generally poor; hence, solid substrates are generally directly emplaced in biowall trenches or bioreactor excavations. Therefore the primary limitation of using solid substrates is the depth that can be trenched or excavated in a practical and cost-effective manner, usually limited to approximately 30 to 35 ft (9 to 10 m), rather than the depth of contamination. Other site-specific limitations may be related to difficult geology (e.g., bedrock, large cobbles or flowing sands).

12.3.2 Secondary Biostimulation Amendments

Besides electron donor sources, other amendments may be used during biostimulation. These secondary amendments may include inorganic nutrients to promote microbial growth and development, pH buffering compounds or materials, and inorganic amendments to stimulate biogeochemical transformation processes.

Under natural conditions, the aquifer may contain suitable amounts of trace nutrients for microbial growth; however, the nutritional demand imposed by rapid microbial growth in response to addition of an organic substrate may exceed the capacity of the aquifer system (Chamberlain, 2003). Substrate amendments may be used to provide additional nutrients for microbial growth, and generally include nitrogen, phosphorous, potassium and yeast extracts.

Fermentation of complex substrates to metabolic acids during anaerobic dechlorination may decrease pH significantly in poorly buffered, low-alkalinity aquifer systems. Lowering the pH to below 5.0, or certainly to below 4.0 can inhibit the growth and activity of sulfate-reducers, methanogens, and most dechlorinating microbes (Maillacheruvu and Parkin, 1996). Therefore, pH buffer amendments may be required in groundwater systems with insufficient natural buffering capacity.

In addition to evaluating the pH and alkalinity of the native groundwater, commonly available soil tests such as soil acidity or cation exchange capacity may be used to determine the suitability of soil conditions to maintain neutral pH during biostimulation. Buffering may be implemented using compounds such as sodium bicarbonate ($NaHCO_3$), quicklime (CaO), dolomitic quicklime (CaO/MgO), sodium hydroxide (NaOH) and magnesium hydroxide ($Mg(OH)_2$). It is more cost effective to add these materials during the initial injection or installation, rather than re-mobilizing to the site for an additional injection of buffering agent. For example, commercial emulsified oil products are now available in buffering formulations or with buffering mixtures that can be added when diluting and mixing the concentrated product. As another example, crushed limestone may be added as a weighting material to biowall backfill mixtures (AFCEE, 2008).

Inorganic amendments used to stimulate biogeochemical transformation (abiotic) processes include various forms of sulfate and iron, which are reduced to form reactive metal sulfides. Sulfate and iron are found naturally in aquifer systems, but quantities and concentrations are highly variable. Sulfate in groundwater at concentrations above 500 to 1,000 mg/L may be sufficient to produce the quantities of reduced metal sulfides needed for effective treatment. If additional sulfate is required, it may be dissolved in makeup water for injection of fluid substrates, or added to biowalls or bioreactors in the form of crushed gypsum or gypsum pellets commonly used as agricultural amendments.

Adding ferric iron (Fe(III)) serves two purposes. First, it is reduced to ferrous iron (Fe(II)) which precipitates with sulfide to form FeS, and the FeS can function as an abiotic reductant and directly dechlorinate solvent compounds. Second, the formation of iron sulfide minerals reduces the concentration of dissolved hydrogen sulfide, which can be highly toxic to reductive dechlorinating bacteria (Maillacheruvu and Parkin, 1996). A source for ferric iron may be found in the native formation or within sand used for backfill in biowalls. For soluble substrates, iron may be added in the form of soluble ferrous iron chloride or ferrous iron sulfate. The easiest and most cost effective way to increase the amount of iron in a biowall application is to choose a sand backfill material that is naturally high in iron. Attempts have been made to increase the mass of ferric iron in biowall materials by blending iron ore with the backfill material, but the effectiveness of adding iron ore is yet to be determined (AFCEE, 2008).

Methods for determining how much iron or sulfate should be added to stimulate biogeochemical transformation of CAHs have been not been proven, although attempts to quantify the process have been made, both at Dover AFB, Delaware, USA (Kennedy et al., 2006; Parsons, 2007a) and at Ellsworth AFB, South Dakota, USA (Parsons, 2006b). The stoichiometry and mass calculations that may be used to evaluate the potential for FeS to form, and simplistic calculations to evaluate whether a sulfate or iron amendment should be added, are described in Appendix D of AFCEE (2008). These calculations should be used with caution, as research into biogeochemical transformation of chlorinated solvents and demonstrations to stimulate these processes are still in development (AFCEE et al., 2008).

12.3.3 Bioaugmentation

In many cases, biostimulation alone is sufficient to achieve complete anaerobic reductive dechlorination of chlorinated solvents. However, bioaugmentation is a potential option for enhanced *in situ* anaerobic bioremediation, either from initiation or as a contingency measure should a biostimulation application stall at intermediate dechlorination products or fail to produce significant biodegradation. Bioaugmentation should be considered when native dechlorinating species capable of complete dechlorination of chlorinated solvents are not present, are poorly distributed, are present at low population densities, or cannot be stimulated to a high level of activity.

A pragmatic approach many practitioners follow is to do a cost/benefit analysis considering the cost of bioaugmentation, its potential benefits and the risk of not using bioaugmentation. Some practitioners have elected to use bioaugmentation as a preventative measure, to minimize the risk of *cis*-DCE or VC accumulation, or to shorten the acclimation time before complete dechlorination is achieved. Bioaugmenting as a preventative measure allows practitioners to add the cultures at the same time as electron donor addition (assuming anaerobic conditions exist), avoiding costs for a separate mobilization.

More commonly, the decision to bioaugment is made after pilot- or full-scale field applications have been performed, and the results have not met the remedial objectives (e.g., accumulation of *cis*-DCE). In such cases, the decision to bioaugment a given site is based on the observed extent and rate of dechlorination, as well as the duration of the acclimation period. Geochemical constraints (e.g., acidic pH) and insufficient substrate loading should be ruled out as causes for incomplete dechlorination before bioaugmentation is considered, because the same conditions may affect the performance of bioaugmentation cultures. Information on the science and engineering of bioaugmentation can be found in Chapter 13 and in Stroo et al., 2010.

12.3.4 Substrate Demand and Substrate Loading Rates

Many different substrate types are used for biostimulation, and the methods used to determine how much substrate to apply vary accordingly. Insufficient substrate loading rates (i.e., the volume, concentration and frequency of substrate injection) or non-uniform delivery and mixing may result in areas of the aquifer that are not sufficiently reducing for complete dechlorination to occur, thereby increasing the potential for accumulation of regulated intermediate dechlorination products (e.g., *cis*-DCE, VC or CA). The minimum or threshold concentrations of substrates that are required to sustain anaerobic degradation processes at a site may vary widely based on site-specific conditions.

The presence of excessive substrate may result in uncontrolled fermentation reactions (e.g., lowering of pH and formation of undesirable fermentation products), degradation of secondary water quality (e.g., mobilization of metals) and poor utilization of electron donor sources. The buffering capacity of the aquifer should be evaluated and controlled to prevent an adverse drop in pH that may inhibit dechlorinating microorganisms. The ability of aquifer systems to recover to pre-injection ORP conditions and the long-term impacts on groundwater quality after biostimulation are not always well documented (AFCEE et al., 2004). Furthermore, the physical presence of some substrate types (e.g., neat vegetable oil) and the often exponential growth of biomass (i.e., biofouling) may adversely impact the hydraulic conductivity of the aquifer and groundwater flow. This could result in lower permeability, contaminant bypass, unexpected deviation in plume migration or non-uniform delivery of subsequent substrate injections.

Given these effects, biostimulation applications may fail to achieve performance expectations or develop unanticipated long-term compliance problems. The costs associated with poor performance (e.g., a need for longer term operation) or with compliance issues such as degradation of secondary water quality (typically requiring additional monitoring or system modifications) may greatly increase the life-cycle costs of full-scale biostimulation applications. Therefore, determining an appropriate substrate loading rate and ensuring effective distribution of the substrate applied are critical design and operational objectives.

Protocols developed by the Environmental Security Technology Certification Program (ESTCP) and the Air Force Center for Engineering and the Environment (AFCEE) for soluble substrates (Suthersan et al., 2002), edible oils (AFCEE, 2007) and permeable mulch biowalls and bioreactors (AFCEE, 2008) provide some guidance on determining an appropriate substrate loading rate. Vendors of commercial substrates often provide spreadsheets to determine the amount of product to purchase based on site-specific conditions and/or the stoichiometry of the degradation reactions relevant to the properties of the substrate being applied. Often a design or "safety" factor is applied to account for non-specific substrate demand that is not practical to calculate. However, site-specific stoichiometric calculations are still useful for evaluating the site hydrogeological, geochemical and contaminant conditions, and for a first approximation of the substrate loading rate.

Substrate demand for biostimulation of chlorinated solvents can be described in terms of (1) the CAH electron acceptor supply, (2) the native electron acceptor supply and (3) non-specific demand. There is a stoichiometric relationship for the electron donor (hydrogen) required to satisfy the CAH and native electron acceptor requirements (e.g., Appendix C of AFCEE et al., 2004). Thus, the amount of hydrogen required (stoichiometric demand) to reduce CAHs and native electron acceptors can be calculated given the reaction sequences are known. Table 12.4 lists a few examples of some common half reactions that utilize hydrogen as an electron donor for reduction of native electron acceptors and CAHs. For example, on a mass basis, 1.0 gram (g) of molecular hydrogen is sufficient to dechlorinate 20.6 g of PCE to ethene, assuming 100% utilization of molecular hydrogen by the dechlorinating microorganisms.

Table 12.4. Examples of Half Reactions Using Hydrogen as the Electron Donor (from AFCEE et al., 2004)

Electron Acceptor	Electron-Acceptor (Reduction) Half Reaction
Oxygen	$2H_2 + O_2 \Rightarrow 2H_2O$ aerobic respiration
Ferric Iron	$e^- + 3H^+ + FeOOH \Rightarrow Fe^{2+} + 2H_2O$ "ferric oxyhydroxide" dissolution/reduction
Sulfate	$4H_2 + H^+ + SO_4^{2-} \Rightarrow HS^- + 4H_2O$ sulfate reduction
Carbon Dioxide	$4H_2 + CO_{2(g)} \Rightarrow CH_{4(g)} + 2H_2O$ methanogenesis
PCE	$H_2 + C_2Cl_4 \Rightarrow C_2HCl_3 + HCl$ PCE reductive dechlorination
TCE	$H_2 + C_2HCl_3 \Rightarrow C_2H_2Cl_2 + HCl$ TCE reductive dechlorination
DCE	$H_2 + C_2H_2Cl_2 \Rightarrow C_2H_3Cl + HCl$ *cis*-DCE reductive dechlorination
VC	$H_2 + C_2H_3Cl \Rightarrow C_2H_4 + HCl$ VC reductive dechlorination

The flux of groundwater and the solid aquifer matrix include native electron acceptors (e.g., dissolved oxygen or iron hydroxide minerals) that may be used preferentially over CAHs. The substrate loading rate must account for the electron donor required to reduce these more energetically favorable electron acceptors, which must be reduced before complete anaerobic reductive dechlorination of CAHs can occur. Thus, a direct stoichiometric relationship does not exist between hydrogen and CAH degradation in the subsurface or laboratory environment. However, even though the efficiency of utilization of hydrogen for anaerobic dechlorination is often estimated to be relatively low, the stoichiometric relationships for the direct anaerobic dechlorination of CAHs are relatively favorable. Table 12.5 lists a few examples of fermentation reactions where the substrate (electron donor) is fermented to produce hydrogen.

Table 12.5. Examples of Fermentation Half Reactions Using Organic Substrates as an Electron Donor to Yield Hydrogen (from AFCEE et al., 2004)

Electron Donor	Electron-Donor (Oxidation) Reaction
Ethanol	$C_2H_6O + H_2O \Rightarrow C_2H_3O_2^- + H^+ + 2H_2$ ethanol fermentation to acetate
Methanol	$CH_4O + 2H_2O \Rightarrow CO_2^- + H_2O + 3H_2$ methanol fermentation
Acetate	$C_2H_3O_2^- + 4H_2O \Rightarrow 2CO_2^- + 2H_2O + 4H_2$ acetate fermentation
Butyrate	$C_4H_7O_2^- + 2H_2O \Rightarrow 2C_2H_3O_2^- + H^+ + 2H_2$ butyrate fermentation to acetate
Propionate	$C_3H_5O_2^- + 3H_2O \Rightarrow C_2H_3O_2^- + CO_2^- + H_2O + 3H_2$ propionate fermentation to acetate
Lactate	$C_3H_5O_3^- + 2H_2O + \Rightarrow C_2H_3O_2^- + CO_2^- + H_2O + 2H_2$ lactate fermentation to acetate

Note: Fermentation reactions from Fennel and Gossett, 1998; He et al., 2002

Given the reactions by which native and CAH electron acceptors are reduced and organic substrates are oxidized or fermented, the theoretical quantity of organic substrate that is required to provide sufficient electron or hydrogen equivalents for complete electron acceptor consumption can be calculated. Therefore, substrate loading rates may be estimated, in terms of these equivalents, based on known stoichiometric reactions for both the electron acceptor mass present in the treatment zone and the electron donor reactions associated with the substrate(s) applied.

These computations require that the substrate composition and the exact stoichiometry of each anticipated degradation reaction be known. In practice, these calculations only serve as a theoretical guideline for the required substrate loading because of (1) the potential for multiple degradation pathways for some reactants, (2) the variations in natural or CAH electron acceptor flux into the treatment zone and (3) the use of electron equivalents for other processes.

Table 12.6 provides an example of calculating hydrogen demand (AFCEE et al., 2004). In this example, the total treatment zone volume is 200,000 cubic feet (ft^3) (5,660 cubic meters [m^3]). Given a total porosity of 30%, one pore volume is equivalent to approximately 448,900 gallons (gal) (1,699,220 L). The application of Darcy's Law (calculation not shown) yields a groundwater seepage velocity of 0.25 ft/day (0.076 m/day), or 91.3 ft/yr (27.8 m/yr). Based on an effective porosity of 20% (the volume of interconnected porosity through which groundwater will flow), the groundwater flux through the treatment zone is equivalent to approximately 546,200 gal per year (2,067,530 L per year).

The mass of hydrogen required to theoretically reduce the mass of each native electron acceptor species and each CAH species is calculated in Steps 3 and 4 in Table 12.6. For example, the hydrogen demand for aqueous native electron acceptor mass in the initial pore volume of the treatment zone is 16.2 pounds (lb) (7.35 kilograms [kg]) of molecular hydrogen (Step 3A in Table 12.6).

Table 12.6. Example Substrate Calculations in Hydrogen Equivalents (after AFCEE et al., 2004) (Note: green shaded boxes are user input)

1. Treatment Zone Physical Dimensions

	Values	Range	Units
Length (perpendicular to predominant groundwater flow direction)	200	1–10,000	ft
Width (parallel to predominant groundwater flow)	50	1–1,000	ft
Saturated thickness	20	1–100	ft
Treatment zone cross sectional area	4,000	–	ft^2
Treatment zone volume	200,000	–	ft^3
Treatment zone total pore volume (total volume × total porosity)	448,920	–	gal
Treatment zone effective groundwater volume (total volume × total porosity)	299,280	–	gal
Design period of performance	1	0.5 to 5	yr

2. Treatment Zone Hydrogeologic Properties

	Values	Range	Units
Total porosity	0.3	0.05–50	
Effective porosity	0.2	0.05–50	
Average aquifer hydraulic conductivity	10	0.01–1,000	ft/day
Average hydraulic gradient	0.005	0.1–0.0001	ft/ft
Average groundwater seepage velocity through the treatment zone	0.25	–	ft/day
Average groundwater seepage velocity through the treatment zone	91.3	–	ft/yr
Average groundwater flux through the treatment zone	546,186	–	gal/yr
Soil bulk density	1.7	1.4–2.0	g/cm^3
Soil fraction organic carbon (f_{oc})	0.005	0.0001–0.1	

3. Initial Treatment Cell Electron-Acceptor Demand (one total pore volume)

a. Aqueous-Phase Native Electron Acceptors

	Concentration (mg/L)	Mass (lb)	Stoichiometric Demand (wt/wt H_2)	Hydrogen Demand (lb)	Electron Equivalents per Mole
Oxygen	4.0	14.98	7.9	1.90	4
Nitrate	1.0	3.75	10.2	0.37	5
Sulfate	20	74.92	10.6	7.09	8
Carbon dioxide[1]	10	37.46	5.5	6.86	8
Soluble Native Electron Acceptor Demand (lb)				**16.2**	

(*continued*)

Table 12.6. (continued)

b. Solid-Phase Native Electron Acceptors

	Concentration (mg/L)	Mass (lb)	Stoichiometric Demand (wt/wt H_2)	Hydrogen Demand (lb)	Electron Equivalents per Mole
Manganese (IV)[2]	10	37.46	27.5	1.36	1
Iron (III)[3]	20	74.92	55.9	1.34	1
Solid-Phase Native Electron Acceptor Demand (lb)				**2.70**	

c. Soluble Contaminant Electron Acceptors

	Concentration (mg/L)	Mass (lb)	Stoichio-metric Demand (wt/wt H_2)	Hydrogen Demand (lb)	Electron Equivalents per Mole
Tetrachloroethene	2.00	7.49	20.6	0.36	8
Trichloroethene	1.00	3.75	21.7	0.17	6
cis-1,2-Dichloroethene	0.50	1.87	24.0	0.08	4
Vinyl chloride	0.10	0.37	31.0	0.01	2
Carbon tetrachloride	0.00	0.00	25.4	0.00	8
Chloroform	0.00	0.00	12.3	0.00	6
1,1,1-Trichloroethane	0.00	0.00	22.0	0.00	6
1,1-Dichloroethane	0.00	0.00	25.0	0.00	4
1,1-Dichloroethene	0.00	0.00	24.0	0.00	4
Total Soluble Contaminant Electron Acceptor Demand (lb)				**0.63**	

d. Sorbed Contaminant Electron Acceptors

	K_{oc} (mL/g)	Soil Concentration[4] (mg/kg)	Mass (lb)	Stoichio-metric Demand (wt/wt H_2)	Hydrogen Demand (lb)	Electron Equi-valents per Mole
Tetrachloroethene	263	2.63	55.83	20.6	2.71	8
Trichloroethene	107	0.54	11.36	21.7	0.52	6
cis-1,2-Dichloroethene	45	0.11	2.39	24.0	0.10	4
Vinyl chloride	3.0	0.00	0.03	31.0	0.00	2
Carbon tetrachloride	224	0.00	0.00	25.4	0.00	8
Chloroform	63	0.00	0.00	12.3	0.00	6
1,1,1-Trichloroethane	105	0.00	0.00	22.0	0.00	6
1,1-Dichloroethane	30	0.00	0.00	25.0	0.00	4
1,1-Dichloroethene	65	0.00	0.00	24.0	0.00	4
Total Sorbed Contaminant Electron Acceptor Demand (lb)					**3.33**	

(*continued*)

Table 12.6. (continued)

4. Treatment Cell Electron Acceptor Flux (per year)

a. Soluble Native Electron Acceptors

	Concentration (mg/L)	Mass (lb)	Stoichiometric Demand (wt/wt H_2)	Hydrogen Demand (lb)	Electron Equivalents per Mole
Oxygen	4.0	18.23	7.9	2.31	4
Nitrate	1.0	4.56	10.2	0.45	5
Sulfate	20	91.15	10.6	8.63	8
Carbon dioxide[1]	10	45.58	5.5	8.35	8
Total Native Electron Acceptor Demand Flux (lb/yr)				**19.7**	

b. Soluble Contaminant Electron Acceptors

	Concentration (mg/L)	Mass (lb)	Stoichio-metric Demand (wt/wt H_2)	Hydrogen Demand (lb)	Electron Equivalents per Mole
Tetrachloroethene	2.000	9.12	20.6	0.44	8
Trichloroethene	1.000	4.56	21.7	0.21	6
cis-1,2-Dichloroethene	0.500	2.28	24.0	0.09	4
Vinyl chloride	0.100	0.46	31.0	0.01	2
Carbon tetrachloride	0.000	0.00	25.4	0.00	8
Chloroform	0.000	0.00	12.3	0.00	6
1,1,1-Trichloroethane	0.000	0.00	22.0	0.00	6
1,1-Dichloroethane	0.000	0.00	25.0	0.00	4
1,1-Dichloroethene	0.000	0.00	24.0	0.00	4
Total Soluble Contaminant Electron Acceptor Demand Flux (lb/yr)				**0.76**	
Total Hydrogen Demand (lb/yr)				**43.4**	

5. Design Factors and Total Hydrogen Demand

Microbial Efficiency Uncertainty Factor	2x-5x
Methane and Solid-Phase Electron Acceptor Uncertainty	2x-5x
Remedial Design Safety Factor (e.g., substrate leaving reaction zone)	1x-2x

Total Hydrogen Demand (lb of H_2) with a 2X Design Factor:	**87**
Total Hydrogen Demand (lb of H_2) with a 5X Design Factor:	**217**
Total Hydrogen Demand (lb of H_2) with a 10X Design Factor:	**434**

[1] Estimated as the amount of methane produced.
[2] Estimated as the amount of Mn(II) produced.
[3] Estimated as the amount of Fe(II) produced.
[4] Soil concentration = K_{oc} x f_{oc} x Cgw.

The total hydrogen demand required for the selected 1-year design life is calculated by summing the hydrogen demands for initial aqueous and solid-phase native electron acceptors, initial aqueous and sorbed phase CAH electron acceptors, and the soluble native and CAH electron acceptor mass flux over time. Based on these calculations, the total electron donor demand (in pounds of hydrogen equivalents) for the example site is summarized in Table 12.7.

Table 12.7. Total Electron Donor Demand (in Pounds of Hydrogen Equivalents) for the Example Site

Example Electron Donor Demand Factor[1]	Donor Needed	
	lbs	kg
Initial aqueous native e^- acceptors in treatment zone	16.2	7.35
Solid-phase native e^- acceptors in treatment zone	2.70	1.22
Initial soluble CAHs in treatment zone	0.63	0.29
Sorbed CAHs in treatment zone	3.33	1.51
Soluble native e^- acceptor flux (per year)	19.7	8.94
Soluble CAH flux (per year)	0.76	0.34
Total Hydrogen Demand for First Year	**43.4**	**19.7**

[1] Summary of results from example site conditions provided in Table 12.6.

From these calculations it is evident that the initial and incoming native electron acceptor mass comprises the majority of the demand for hydrogen, which is probably a common situation. Further inspection of Table 12.6 shows that sulfate reduction and methanogenesis dominate for this example. Therefore, the majority of hydrogen is used simply to create and sustain the highly reducing conditions of sulfate reduction and methanogenesis.

The design (or safety) factor typically used by practitioners (to account for microbial efficiency and uncertainty in electron acceptor demand) is commonly between 2 and 10 times the calculated total hydrogen demand of the system. For this example, a design factor of 5 times yields a total hydrogen demand of 217 lb (98 kg) of molecular hydrogen for the first year of treatment.

A large percentage of substrate and fermentation byproducts also may be used by opportunistic microbes for a myriad of life processes, including cell growth. Numerous transformations of the solid mineral matrix may also occur. Finally, it is not possible to achieve a high efficiency for either substrate/contaminant contact or substrate utilization for any given site. The result of these factors is a non-specific substrate demand that is not practical to calculate, and thus a substantial design factor is typically applied when determining substrate loading rates.

Substrate loading rates are usually reported as mass of substrate per unit volume of groundwater treated. Table 12.8 lists the range of substrate concentrations typically used in field applications, and the injection frequency and life-span that can be anticipated with their use. Substrates that are rapidly depleted require more frequent injection to sustain sufficiently reducing conditions. Soluble substrates such as ethanol are considered to be readily bioavailable and are therefore depleted relatively quickly (within days to a couple of weeks). For slow-release substrates (e.g., EVO), the loading rate is multiplied by the design life of the system (typically 1 to 5 years) and all of the substrate is injected at once (unless the required loading rate exceeds the oil retention capacity of the target treatment zone).

Table 12.8. Typical Substrate Loading Rate, Injection Frequency, and Lifespan of Common Organic Substrates (AFCEE et al., 2004)

Substrate	Injected Form and Concentration	Targeted Concentration of Dissolved Organic Carbon in the Treatment Zone	Typical Injection Frequency	Typical Lifespan	Cost (per pound in U.S. dollars)*
Sodium Lactate, Potassium Lactate, Lactic Acid	Diluted to 3 to 30% by weight	50 to 300 mg/L	Continuous to bi-monthly	7 to 60 days	1.00 – 1.50
Propionate, Butyrate	Diluted to 3 to 30% by weight	50 to 300 mg/L	Continuous to bi-monthly	7 to 60 days	2.00 – 3.00
Methanol, Ethanol	Diluted to 3 to 30% by weight	50 to 300 mg/L	Continuous to weekly	1 to 7 days	0.10 – 0.30
Sodium Benzoate	Diluted to 3 to 30% by weight	50 to 300 mg/L	Continuous to weekly	1 to 7 days	0.40 – 0.80
Molasses, High Fructose Corn Syrup	Diluted to 1 to 10% by weight	50 to 500 mg/L	Daily to quarterly	7 to 90 days	0.25 – 0.40
Whey (fresh/powdered)	Powdered form can be dissolved; fresh whey injected as a slurry.	50 to 500 mg/L	Monthly to annually	1 to 12 months	0.05 (fresh) 1.00 –1.50 (powdered)
Hydrogen Release Compounds (HRC® and HRC-X™)	Pure product injected at 4 to 12 lbs per vertical foot of injection.	100 to 500 mg/L	Annually to biennially for HRC® (one-time injection may suffice). One-time injection for HRC-X™ .	9 to 24 months for HRC®; 3 to 5 years for HRC- X™	5.00 – 7.00
Vegetable Oil (food-grade soybean oil), Commercial Emulsions, LactOil™	Oil-in-water emulsions diluted to 2 to 10% oil by volume; or neat oil injection (source areas only).	100 to 500 mg/L	One-time emplacement. May require a second injection for dilute emulsions.	2 to 5 years	0.50 – 0.75 (neat oil) 1.50 – 2.50 (emulsion products)
Mulch and Compost	Mixed with sand at 40 to 60% by volume.	100 to 500 mg/L of dissolved organic carbon in the biowall or bioreactor	One-time emplacement	3 to 7 years	0.00 – 0.30
Chitin	Powdered form injected as a slurry or bulk chitin in a trench.	100 to 500 mg/L	One-time emplacement	1 to 2 years	2.00 – 4.00
Hydrogen Gas	Pure hydrogen gas or less volatile mixtures with nitrogen.	Not Applicable	Continuous to weekly (pulsed gas sparging)	1 to 7 days	0.05 – 0.11 (per standard cubic foot)

*Price per pound is for the bulk product as provided by the vendor. The amount of bioavailable organic substrate in the product may vary.

Alternately, the loading rate for soluble substrates often is based on achieving an empirical concentration of organic carbon in groundwater that passes through the treatment area. The volume and strength of the substrate are estimated to achieve a particular target level of soluble organic carbon in the aquifer after mixing and dilution. For example, Suthersan et al. (2002) suggest that loading rates for soluble substrates of between 0.001 and 0.01 lb of organic carbon per gal of groundwater flux per day are sufficient to create and maintain a reducing reactive zone. Soluble organic substrate will be degraded and depleted as it flows with groundwater, causing a concentration gradient between the point of injection and the downgradient treatment zone. Therefore, higher concentrations of organic carbon are required at the point of injection to maintain sufficient substrate concentrations throughout the treatment zone.

In summary, the practitioner of biostimulation must choose what is practical over what may be a conceptually optimum injection regime. Analytical data (e.g., DO, ORP, pH, and total organic carbon [TOC]) from injection and monitoring wells within the treatment zone are used to confirm that an appropriate reactive zone has been established. Field pilot testing is often the most practical way to optimize substrate loading rates.

12.3.5 System Configurations

Biostimulation may be used in several system configurations with many associated remedial action objectives. These include (1) source zone treatment (may include DNAPL) where uniform or extensive substrate/contaminant contact is possible, (2) plume containment using a permeable biobarrier or (3) plume-wide treatment for small plumes of less than a few acres. More than one system configuration can be combined to address site-wide objectives.

As an example of a combined approach, a source area may be targeted for remediation using a grid configuration, combined with a linear biobarrier configuration (Figure 12.5) upgradient from a point of compliance or property boundary. The appropriate application of biostimulation will be site-specific and based on a strategy that takes into account final remedial objectives and feasibility of the application.

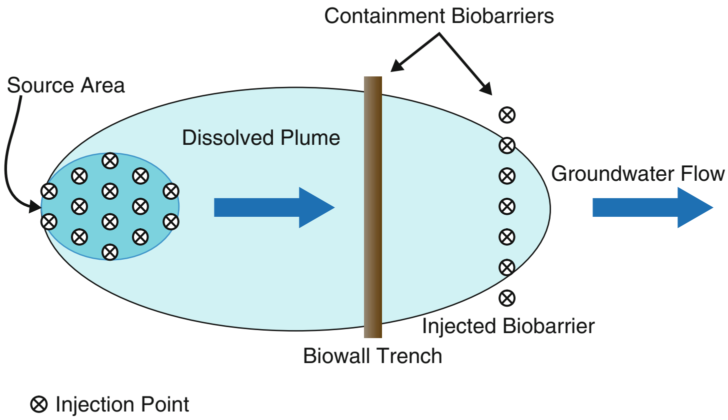

Figure 12.5. Schematic of source area and biobarrier configurations (from AFCEE et al., 2004).

12.3.5.1 Source Zone Treatment

All site closure strategies ultimately have to address contaminant sources. ***Without source treatment and accompanying reduction of mass discharge from the source area,***

biostimulation strategies that treat only dissolved contaminants may require operation for a very long period of time. With some special considerations, remediation of DNAPL sources using biostimulation holds promise (e.g., Adamson et al., 2003; Da Silva et al., 2006; ITRC, 2008b).

Reduction in mass discharge is achieved by stimulating biodegradation in the dissolved phase, which reduces the contaminant mass that can migrate downgradient with groundwater flow. Source mass removal is achieved by accelerating DNAPL dissolution or desorption and then stimulating biodegradation of the dissolved contaminants. Not all DNAPL source zones may be economically or feasibly remediated (e.g., ITRC, 2008b; USEPA, 2003). Anaerobic reductive dechlorination is a process that takes place in the aqueous phase and does not directly attack DNAPL mass. Therefore, enhanced bioremediation may be limited in its ability to rapidly treat DNAPL source zone areas with large pools of DNAPL.

Another strategy for source area treatment is the injection of a low solubility hydrophobic material such as vegetable oil directly into the source zone. The vegetable oil enables short-term sequestration of chlorinated solvent mass due to partitioning of chlorinated solvents into the oil, and a further reduction in mass discharge in groundwater due to a lowering of hydraulic conductivity. Long-term contaminant destruction is achieved by stimulating anaerobic reductive dechlorination. Ultimately the oil degrades and the sequestered contaminant mass is released from the oil back into an environment that is optimal for anaerobic dechlorination to occur. This strategy was employed by the Air Force at the Hangar K site at Cape Canaveral Air Force Station (CCAFS), Florida, USA (Parsons, 2002b; Henry et al., 2007) and at the Landfill 05 site at Hickam AFB, Hawaii, USA (Parsons, 2006a), in both cases by direct injection of edible oil into the DNAPL source area.

12.3.5.2 Plume Containment using Biologically Enhanced Barrier Systems

For large plumes having poorly defined, widely distributed or inaccessible source areas, biostimulation systems may be configured as permeable reactive barriers (biobarriers) to intercept and treat a contaminant plume (Figure 12.5). For example, biobarriers may be employed at a property boundary or upgradient from a point of regulatory compliance to prevent plume migration to potential receptors.

Biobarriers rely on the migration of contaminated groundwater through a permeable reactive zone. Therefore, key design parameters of biobarriers include (1) a continuous reaction zone, oriented perpendicular to groundwater flow, that is of sufficient cross-sectional area to intercept the entire contaminant plume, (2) sufficient residence time within the reaction zone for the complete and/or desired level of dechlorination of contaminants in groundwater and (3) maintaining permeability to avoid groundwater flow around the barrier system.

Passive or semi-passive biobarriers created using soluble substrates typically consist of a series of substrate injection wells established along a line perpendicular to groundwater flow. Continuous or frequent injection (weekly to monthly) is required to maintain the reaction zone. Biobarriers constructed by injecting long-lasting viscous fluid substrates (e.g., HRC®, EVO or Lactoil®) require fewer repeated applications, and therefore may be less expensive to deploy in terms of capital and O&M costs. Biowall trenches using mulch and compost are another biobarrier alternative, and provide for uniform contact of substrate with chlorinated solvents as the continuity of the trench eliminates potential problems associated with aquifer heterogeneity.

12.3.5.3 Plume-Wide Restoration

Biostimulation systems may be configured to treat dissolved chlorinated solvents across an entire contaminant plume. Plume-wide delivery systems typically will be configured as a large injection grid, or a recirculation well field may be employed to increase the effective area of substrate distribution with fewer wells.

Creating an anaerobic reaction zone across broad areas of a plume is an aggressive approach that may reduce the overall timeframe for remediation. If recirculating systems are used, inherent higher initial capital and operating costs may be offset by shorter remedial timeframes with lower monitoring and total long-term operating costs. However, plume-wide applications where substrate is delivered to the entire plume may be cost prohibitive for very large plumes or cost inefficient for low-level contaminant plumes. In these cases, a series of biobarriers that truncate the plume into smaller segments may be effective for attenuation of the overall plume.

12.3.6 Substrate Mixing and Delivery Systems

12.3.6.1 Delivery Options

Several system configurations and delivery strategies can be used to distribute organic substrates in the subsurface. Injection of liquid substrates directly through direct-push or permanent injection wells, groundwater recirculation systems, infiltration galleries and trenches all may be used to deliver substrate to the impacted aquifer. Table 12.9 summarizes these delivery options according to substrate type and system configuration.

Direct Injection. The most simple and common method to deliver organic substrates to the subsurface is by direct injection using either temporary direct-push points or injection wells. Direct-push methods are commonly used for shallow groundwater applications in unconsolidated formations at depths less than approximately 50 ft (15 m) . This technique is constrained by the subsurface characteristics (i.e., gravel and cobbles inhibit use of direct-push technology) or degree of cementation.

Table 12.9. Biostimulation Delivery Options (after AFCEE et al., 2004)

Substrate Type (examples)	System Configuration		
	Source	Barrier	Plume-Wide
Soluble (lactate, molasses)	Periodic injection into source. Recirculation across source.	Periodic injections into linear injection well configurations oriented perpendicular to groundwater flow (substrate drift).	Periodic injections in grid arrays or multiple linear rows of wells. Large-scale recirculation (extraction and reinjection).
Slow-Release (HRC®, emulsified vegetable oil)	Infrequent injection into source (may be one time).	Infrequent injection into linear rows of injection points oriented perpendicular to groundwater flow.	Infrequent injection in grid arrays (may be one time).
Solid Substrates (mulch, chitin)	One-time or very infrequent addition (e.g., placement in source area excavation).	One-time or very infrequent addition to linear trenches oriented perpendicular to groundwater flow.	May not be practical for large plumes. Potential for combination of source and multiple biobarrier configurations.
Gaseous Hydrogen	Biosparge injection into source (pulsed injection).	Biosparge injection in linear rows perpendicular to groundwater flow (continuous to semi-continuous).	May not be practical for large plumes.

While direct-push well points may be suitable for both soluble and slow-release substrates, care must be taken to seal and grout the well points in place to withstand the designed injection pressure and to prevent bypass of the substrate to the vadose zone or ground surface. Direct injection of fluid substrates can be made through direct-push (e.g., Geoprobe®) probes. This technique does not leave well points in place, and is only practical for long-lasting substrates such as HRC® or vegetable oil emulsions.

Permanent injection wells are used with soluble substrates where continuous or multiple injections of substrate are required, or where recirculation will be used to improve distribution. Permanent injection wells also are necessary where depth or subsurface lithology make use of direct-push technology impractical. Existing monitoring or extraction wells from previous investigation or remediation activities may be used when screened in appropriate horizons and located within appropriate portions of the plume. Horizontal wells also can be employed for shallow or thin contaminant plumes, or for plumes beneath buildings or other structures. Because most substrates are injected under pressure, these wells must be properly sealed and grouted to prevent bypass of the substrate to the ground surface or vadose zone.

Usually it is not feasible to inject substrates into zones having a hydraulic conductivity less than approximately 0.01 ft/day ($3x10^{-6}$ cm/sec). Alternate injection techniques such as hydraulic fracturing may be used in some cases. However, fracturing may lead to non-uniform distribution of substrate, and the timeframe for remediation may be very long as remediation of the vast majority of the aquifer volume will be diffusion-limited. However, hydraulic fracturing may be useful in some cases. For example, fracturing was used to inject chitin as a substrate for biostimulation at the Distler Brickyard Site in Louisville, Kentucky (Martin et al., 2002; Sorenson et al., 2002). The chitin was injected into the low-permeability silt and clay sediments in a water slurry that included sand and guar gum. The sand was included to prop the fractures open and maintain their increased permeability after injection. Preliminary results of a pilot test indicated that dechlorination of *cis*-DCE was stimulated, and elevated ethene concentrations suggested that dechlorination was proceeding to completion.

Biofouling is often a concern when using permanent injection wells for multiple injections of a soluble substrate or for recirculation. Biofouling may occur as a result of biomass growth or accumulations of biologically-produced materials, and several methods are available to prevent or mitigate biofouling (GeoSyntec, 2005). Chemical precipitation of iron also may occur during extraction and recirculation due to oxidation of soluble ferrous iron to an insoluble ferric iron precipitate. Precipitation of iron can be controlled by using a closed recirculation system and preventing exposure to ambient air (oxygen).

Injection Well Location and Spacing. Injection well configuration includes injection well layout, injection intervals and spacing. Injection wells typically are located in rows oriented perpendicular to the direction of groundwater flow. Multiple rows of wells may be installed in a grid configuration or to construct multi-line biobarriers. The depth and thickness of the targeted treatment zone will impact the drilling technique used and the vertical spacing of well screen interval(s). For thick treatment zones (i.e., greater than 5 to 6 m [15 to 20 ft]), multiple screened intervals are necessary for uniform distribution.

Horizontal well spacing is controlled by the distance that injected substrates can be distributed laterally in the vicinity of each injection well. An effective ROI should be calculated based on the volume and type of substrate used and the site stratigraphy, taking into account the mixing and dispersion of the substrate that will occur with advective transport or through a recirculation system. Well spacing perpendicular to groundwater flow may range from 1.5 m (5 ft) on center for passive systems in low permeability silts and clays, to perhaps 6 m (20 ft) or more in permeable formations.

In some cases, it may be desirable to treat broad areas of a plume or to apply a plume-wide treatment. When it is not practical to cover the plume in a grid configuration, several rows of injection wells may be used to truncate the plume into smaller segments. Spacing of the rows (distance between rows along the path of groundwater flow) should be based on the distance that substrates can migrate at concentrations sufficient to maintain the reaction zone. Suthersan et al. (2002) recommend a 100-day travel time distance as an optimal spacing of injection wells parallel to the direction of groundwater flow for plume-wide treatment. However, they also suggest that this distance could be increased to trade-off capital and initial operating costs for a longer treatment duration.

Recirculation Systems. Recirculation systems may be employed to improve the distribution of soluble substrates throughout the treatment zone (Figure 12.6). Recirculation may be continuous or pulsed, with the substrate added to the groundwater as it is reinjected into the treatment zone. Recirculation may be particularly useful for difficult hydrogeological conditions. For example, recirculation may be used to effectively mix substrate and contaminated groundwater at sites with very low hydraulic gradients and low rates of groundwater flow. Well spacing using recirculation systems may extend up to 15 m (50 ft) or more, reducing the number of injection wells required relative to passive systems.

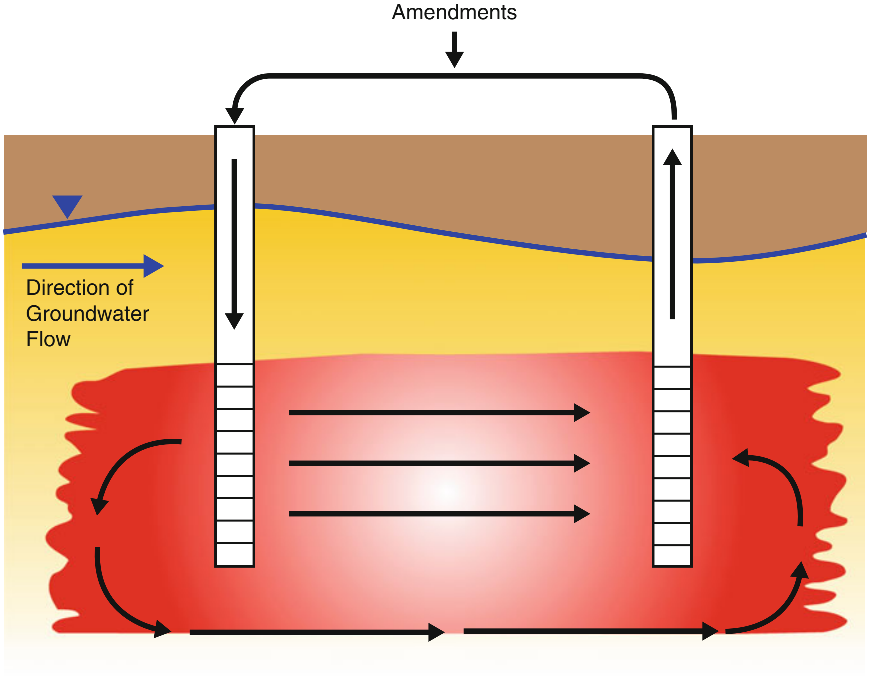

Figure 12.6. Schematic of a horizontal recirculation system: one example of substrate delivery for enhanced *in situ* anaerobic bioremediation.

The most common recirculation systems are well systems consisting of a closed network of extraction and injection wells. A discussion of a number of recirculation configurations can be found in Section 2 of the *In Situ* Bioremediation guidance prepared by ITRC (1998). Recirculation increases the retention time of contaminated groundwater in the treatment zone. The rate at which groundwater passes through the system depends on the rate of recirculation and the natural flux of groundwater through the recirculation system. Therefore, design of recirculation systems must consider hydraulic conductivity, aquifer heterogeneity and hydraulic gradient.

Soluble substrate amendments (e.g., lactate or ethanol) are typically applied in recirculation systems. These substrates are more readily controlled and distributed throughout the treatment zone relative to slow-release substrates (e.g., HRC® or emulsified vegetable oil) in passive systems. Groundwater modeling and tracer testing is therefore highly recommended when designing large-scale recirculation systems. Recirculation approaches may be the only effective method to achieve more uniform distribution of substrates and amendments at sites with difficult hydrogeological conditions (e.g., lack of a natural hydraulic gradient). Aquifer mixing and amendment addition systems, including recirculation, will be addressed in a later volume in the SERDP/ESTCP Environmental Remediation Technology Series (Kitanidis and McCarty, 2010).

Biowall or Bioreactor Excavations. Another effective delivery system is the use of a biowall trench or bioreactor excavation (AFCEE, 2008). For biowalls (Figure 12.7), the treatment method relies on the natural flow of groundwater through the biowall to promote contact with slowly soluble or slowly degraded organic matter. This configuration is particularly suitable for low permeability or highly heterogeneous formations, as the formation is physically removed and the biowall trench effectively exposes the contaminant plume to the solid substrate fill material. Other variations of using mulch and compost substrates in flow-through configurations include surface amendment infiltration plots (Haas et al., 2000), burial of mulch in excavations and recirculation of contaminated groundwater through mulch bioreactors (Parsons, 2003).

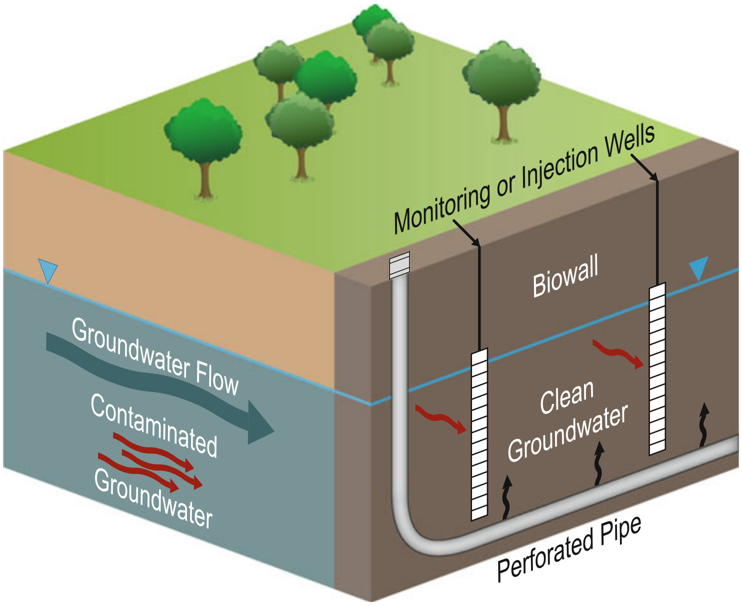

Figure 12.7 Schematic of a permeable mulch biowall (from AFCEE, 2008).

Injection of Hydrogen Gas. Hydrogen gas has been injected into the subsurface on an experimental basis, and this technique may be useful as an alternative delivery method. Because microorganisms use hydrogen as a primary electron donor during reductive dechlorination of chlorinated solvents, addition of hydrogen is the most direct approach to stimulating this process. While hydrogen may stimulate activity of dechlorinating species, their metabolism also depends on the availability of a carbon source for cell growth and reproduction. Therefore, the use of gaseous hydrogen may be better suited for aquifers with relatively high quantities of organic carbon (i.e., Type 1 and Type 2 sites).

Although hydrogen is highly combustible, it is an inexpensive substrate that can be delivered safely with the proper engineering controls. The Air Force has conducted pilot-scale treatability tests involving direct addition of hydrogen to groundwater (Newell et al., 2001, 2003; Aziz et al., 2003a; Appendix E.8 of AFCEE et al., 2004). Hydrogen typically is injected using low-volume, pulsed sparging into injection points, to allow the hydrogen to disperse throughout the reaction zone (Aziz et al., 2003b).

Besides direct addition of hydrogen to groundwater, other methods to deploy hydrogen via hydrogen-releasing compounds, hydrogen-generating electrodes and permeable membranes have been developed (Newell et al., 2003; Novak et al., 2002). Injection of gaseous substrates into the vadose zone also has been tested (ESTCP Project No. ER-0511) for *in situ* bioremediation of perchlorate (Evans and Trute, 2006). This technology, termed anaerobic bioventing or gaseous electron donor injection, also may be useful for treating CAHs and other contaminants.

12.3.6.2 Treatment Zone Volume and Radius of Influence

Biostimulation relies on uniform delivery of substrate throughout the intended treatment zone. ***Effective mixing of substrate within the chlorinated solvent plume is one of the most difficult challenges for biostimulation.*** As the size of the plume increases, the ability to treat the entire plume volume becomes increasingly difficult and costly. Many plumes at DoD sites are several thousand feet long and tens of feet thick, so that even in barrier configurations that are several hundred feet long, the volume of the treatment zone can be enormous. For example, a reactive zone 600 ft (180 m) long by 30 ft (9 m) wide, with an aquifer thickness of 40 ft (12 m) and a porosity of 40%, contains approximately 2.15 million gal (8.14 million L) of pore water.

Injecting large volumes of substrate may cause significant displacement of the contaminant plume. A common approach to limit displacement is to inject a low volume/high concentration substrate mixture (injection volumes less than 10% of the treatment area pore volume) and to rely on advection and dispersion for mixing. This approach requires relatively high rates of advection and dispersion. But caution should be used when relying on advection and dispersion to uniformly distribute a fluid substrate. These processes generally have their greatest impact immediately downgradient of the point of injection, and the majority of the flow often occurs through a small fraction of the subsurface volume. Injection well spacing will be an important design consideration when evaluating injection volumes and ROI. Recirculation may be required for sites with slow groundwater velocities, in order to effectively mix the substrate with the contaminated groundwater. Site-specific conditions such as more permeable zones or preferential flow paths should be considered when evaluating the potential for uniform substrate distribution and when designing and monitoring the biostimulation system.

12.3.6.3 Soluble Substrate Systems

Substrates applied as a dissolved or “aqueous” phase have a greater potential for uniform distribution throughout the aquifer matrix than substrates applied as a viscous fluid or solid phase. Soluble substrates travel with the advective groundwater flow, and are typically applied in a continuous or periodic (pulsed) mode to maintain a specified reactive treatment zone. As a result, it may be possible to increase the ROI and reduce the number of injection points by dispersing a larger volume of substrate from a single injection point. Therefore, soluble substrates may be better suited for treating sites where the drilling costs are high, such as those with very deep or thick contaminated aquifers. A case study of applying sodium lactate in a biostimulation application to a DNAPL source in a deep fractured-bedrock aquifer is included below.

Because they are rapidly degraded and readily mixed with groundwater, soluble substrates may not be suitable for high-flow aquifers where a high degree of mixing and replenishment of native electron acceptors occurs. These conditions may make it difficult to maintain sufficiently reducing conditions. In addition to the need for frequent injection of soluble substrates, other operational costs need to be recognized. For example, it can take a long time to optimize the dosing strategy (by adjusting concentrations and frequencies). Also, frequent high concentration injections can lead to pH changes that require addition of buffering compounds.

Sodium lactate and molasses are the most common soluble substrates, although other soluble substrates are used including ethanol, methanol, butyrate and sodium benzoate. Lactate is used as a relatively simple substrate (compared to molasses) and is available in the form of lactate salts (sodium or potassium lactate), with lactic acid being the dissociated free form in water. Lactate salts are typically mixed at a concentration of 3 to 30% in water, although mixtures as high as 60% have been used (Sorenson, 2003; Appendix E.10 of AFCEE et al., 2004).

Molasses is comprised primarily of sugars (sucrose), but may contain other minor constituents such as sulfur, sulfate and metals that may be of potential concern. Higher grades of molasses or high fructose corn syrup (HFCS) can be used in situations where the addition of additional sulfur or other impurities to an aquifer is undesirable. Molasses is typically injected in a water solution of 10% molasses or less (Suthersan et al., 2002), although higher concentrations may be injected in an effort to enhance desorption of CAHs from the aquifer matrix (Payne et al., 2006).

Soluble substrates typically are applied in a continuous or periodic (pulsed) mode to maintain a specified reaction zone. This strategy requires active (either automatic or manual) injection systems that are labor and equipment intensive relative to passive, slow-release substrate systems. However, the cost of system operation may be offset by the flexibility to modify and optimize the substrate mixture and delivery rates over time, the ability to distribute the substrate more rapidly and uniformly throughout the treatment zone, and the potential to shorten the treatment time.

Remediation designers must choose between injecting a low volume of a high-concentration solution or injecting a high volume of a low-concentration solution. That choice largely depends on how well the injected solutes will disperse and migrate in groundwater, and thereby reach the desired concentrations throughout the mixing zone. In general, low-concentration mixtures are more suitable for automated or recirculation systems, and high concentration mixtures are used for more infrequent batch injection. Other factors to be considered include dilution and density effects, as well as the relative cost of different injection scenarios.

Dilution is an issue when injecting large volumes of soluble substrate mixtures with the objective of achieving widespread distribution of the substrate. While some mixing with contaminated groundwater will occur due to advection and dispersion, large volumes of the contaminated groundwater may be displaced. When feasible, a relatively high substrate concentration and low injection volume is desirable to reduce the amount of displacement and dilution of contaminated groundwater. Recirculation systems avoid this issue, and these systems may be more effective for treating very large aquifer volumes.

Density effects may be noticeable when using high concentration mixtures of soluble substrates, such as sodium lactate products that have a specific gravity over 1.3. A downward migration of a sodium lactate mixture was observed during early injections of a high concentration substrate mixture at the Test Area North Site in Idaho (Sorenson, 2003). Therefore, potential density effects should be considered when using high concentration substrate mixtures, particularly when injecting over large saturated thicknesses (over 6 m [20 ft]) in homogeneous formations where vertical flow may occur.

A uniform substrate mixture can be prepared using a variety of methods (Suthersan et al., 2002). In general, mixing systems use power-operated submersible pumps and/or powered mixers. A series of pumps and mixing tanks are used to meter and mix the appropriate amount of substrate with potable water or extracted groundwater. Power-operated mixers can be used to agitate the solution while the mixing tanks are filled. A programmable logic controller can monitor and adjust the mixing rates automatically. The substrate mixture can be injected directly to a centralized delivery system using a general purpose centrifugal pump, or stored in a batch tank.

Case Study: Test Area North, Idaho National Engineering and Environmental Laboratory, Idaho (Sorenson, 2003; Appendix E.1 in AFCEE et al., 2004)

The Test Area North Site in Idaho is an example of biostimulation using sodium lactate to treat a DNAPL source in a deep fractured-bedrock aquifer. The chlorinated solvent plume was a result of disposal of waste material into a deep injection well. Dissolved concentrations of TCE prior to biostimulation were up to 100 mg/L, with sludge bailed from the former disposal well containing as much as 3% TCE by weight. In the area of the TCE plume, the saturated thickness was from 200 to 400 ft (60 to 120 m) bgs, and groundwater flow was approximately 0.5 ft/day (0.15 m/day). During the initial treatment period from 1999 to 2002, injection occurred into the single former disposal well at the site.

Injection of lactate stimulated complete anaerobic reductive dechlorination of TCE throughout a treatment cell approximately 500 ft (150 m) long at depths greater than 200 ft (60 m) in the plume source area (Figure 12.8). Sulfate reduction and methanogenesis were observed in the treatment zone, indicating that strongly reducing conditions had been achieved. MCLs have been met for TCE (5.0 micrograms per liter [μg/L]) and *cis*-DCE (70 μg/L) at the base of the transmissive zone (i.e., at 400 ft [120 m]) within the immediate injection area. Concentrations of VC remain above the MCL of 2.0 μg/L, but typically do not exceed 15 μg/L.

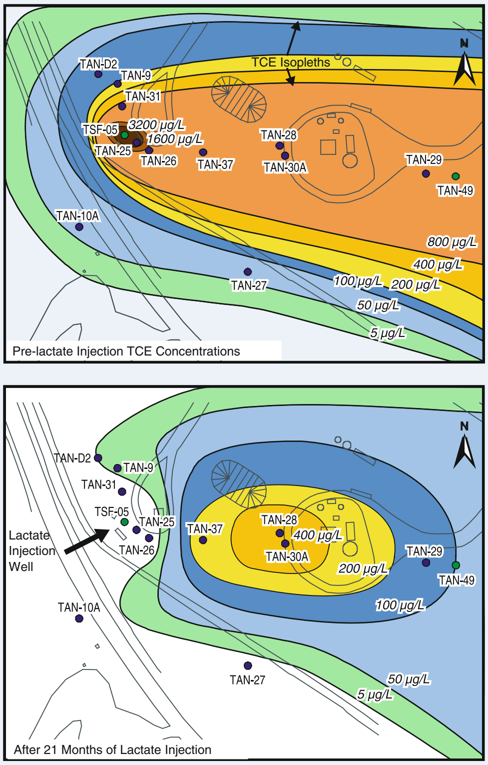

Figure 12.8. Degradation of TCE after 21 months of lactate injection as compared to 18 months of pump-and-treat (Martin and Sorenson, 2004).

The success of this project is indicated by a Record of Decision (ROD) amendment signed in 2001 that allowed the biostimulation system to replace pump-and-treat for source area cleanup. Data indicate that biostimulation has resulted in restoration of the lower half of the aquifer, where all contaminants are currently below USEPA MCL values. Attempts have been made to distribute electron donor throughout the entire treatment cell by using two injection wells and smaller lactate volumes per well to achieve the desired distribution.

This study demonstrates that soluble substrates such as sodium lactate can, in some cases, be distributed effectively over relatively large volumes of an aquifer using a relatively small number (only 1 in this case) of injection wells. Pilot test results from this site also indicate that the initial injection of high concentrations of substrate resulted in the rapid formation of strongly anaerobic conditions which are necessary for biologically mediated anaerobic reductive dechlorination. After strongly anaerobic conditions were induced, they were sustained via injection of lower concentrations of substrate. Furthermore, an injection strategy that employs large-volume injections (low substrate concentration) at a lower frequency appears to be more effective and efficient than one that involves relatively small-volume (high substrate concentration) injections at higher frequencies (Martin et al., 2001).

In summary, soluble substrates are applicable to most site conditions except perhaps aquifers with very high groundwater velocities. They are particularly well-suited for very deep aquifers, where the number of injection wells that can be practically and cost-effectively installed is more limited. The primary disadvantage to soluble substrates is the requirement for repetitive injection due to their rapid degradation. Permanent injection systems also may interfere with facility operations in some cases. Adjusting substrate loading rates and mixing ratios during the initial phase of injection often is necessary to achieve target TOC levels, avoid adverse impacts to pH and maximize the ROI. This need for optimization increases the costs of O&M during startup, and therefore the life-cycle cost of O&M for soluble substrate systems is high relative to other substrate options.

12.3.6.4 Slow-Release Substrate Systems

The most common slow-release substrates used for biostimulation include HRC® and emulsified vegetable oil. Once these substrates are injected into the subsurface, they are intended to remain in place, creating mobile plumes of soluble substrate that are dispersed by advection, dispersion and diffusion. The primary benefit of these substrates is that they require infrequent injection (perhaps only once), often with no O&M requirements other than performance monitoring. Ideally, stable reactive zones are created by sustaining elevated dissolved organic carbon concentrations at levels sufficient to stimulate anaerobic reductive dechlorination over long periods of time. The plumes of dissolved substrate generated from HRC® and vegetable oils are readily biodegraded, and the reaction zone generally does not extend more than a few tens of feet from the point of injection.

While the injection configurations used for these two substrates are similar, their physical and chemical properties vary greatly. Injection of the viscous HRC® products and neat vegetable oil require specific types of pumps and pressurized injection systems. However, the cost of the specialized equipment is minimal (can often be rented or purchased for less than a few thousand dollars). Vegetable oils are more frequently applied as dilute oil-in-water emulsions, which substantially reduces viscosity and ease of injection.

Hydrogen Release Compound (HRC®). HRC® is a bioremediation product supplied by Regenesis, Inc. According to the manufacturer's product literature, various forms of this product are available, but all contain proprietary mixtures of polylactate esters, glycerol and other materials. These products are designed to provide a slow release of lactic acid and dissolved organic carbon to stimulate *in situ* fermentation, producing hydrogen for biodegradation of chlorinated solvents. The slow release nature of these products is facilitated by the nature of the polymeric materials as well as the viscosity of the preparation.

HRC® is best suited for relatively shallow groundwater plumes where direct-push technology can be used to effectively cover large areas of a plume or to create long biobarriers. HRC® and HRC-X™ are highly viscous and are injected using specialized equipment and pumps available from the manufacturer. HRC-X™, and in some cases HRC®, must be heated to reduce viscosity prior to being injected. Depending on the depth of injection and ambient air and groundwater temperatures, it also may be necessary to heat the injection push rods by injecting or circulating steam or hot water through them.

The HRC® products are typically injected at rates of 4 to 10 lb/ft of the aquifer depth to be treated (Norris, 2004). HRC® has a density of approximately 11 lb/gal, and the physical distribution of the substrate in a radial direction is only a few inches from the actual point of injection. The rate at which dissolved lactic acid and glycerol released from the product migrate from the point of injection depends on the advective groundwater flow velocity, and will be dominated by the rate of diffusion in low-permeability aquifers. Typical injection point spacing varies from 5-ft (1.5-m) centers for low-permeability lithologies to 7.5- to 15-ft (2.3- to 4.6-m) centers for more permeable lithologies (Case et al., 2001).

The rate of application (lb/ft) of HRC® or HRC-X™ can be calculated using a spreadsheet-style program provided by the manufacturer, taking into account site-specific conditions including hydrogeology, contaminant levels and competing electron acceptors. The program also takes into account the size of the treatment area and number of injection points so that the rate of application falls within practical limits.

The typical lifespan for the standard HRC® product ranges from 9 to 24 months, and depends to some extent on the rate of groundwater flow and alternate electron acceptor flux. It is not unusual for additional injections of HRC® to be required, particularly in biobarrier configurations that typically have a design life of several years. The use of the HRC-X™ product is gaining in frequency because the vendor claims a lifespan of 3 to 5 yr, sufficient to remediate most sites with only a single application.

Regenesis also produces the HRC-Advanced® product that contains a complex molecule composed of long-chain fatty acids (oil), glycerol and glycerol tripolylactate. This product is reported by Regenesis to differ from vegetable oil emulsions in that micelles are formed which are mobile in groundwater and may continue to disperse in the aquifer after injection.

Vegetable (Edible) Oils. Various names have been used in the literature to describe the use of vegetable (edible) oil for biostimulation, including the vegetable oil (VegOil) process, emulsified vegetable oil (EVO) and Emulsified Oil Substrate (EOS®, a registered trademark of EOS Remediation). Vegetable oil emulsions have been developed in an effort to improve the distribution of substrate in the subsurface while still providing a long-lasting source of organic carbon. The use of oil emulsions is the result of lessons learned in early vegetable oil field trials in which high injection backpressures, limited ROI and reductions in hydraulic conductivity were observed using neat vegetable oil or coarse emulsions prepared in the field (AFCEE, 2007).

Microemulsions are transparent, isotropic solutions of oil, water and surfactant (and frequently co-surfactants) which are thermodynamically stable (Flanagan et al., 2005). Microemulsions form upon simple mixing of the components, and do not require the high shear conditions generally used in the formation of commercial oil-in-water emulsions used for biostimulation applications. While not adhering to a scientific definition of a microemulsion, the manner in which the term "microemulsion" is applied to biostimulation refers to an oil-in-water emulsion with an average or mean oil droplet size that is significantly less than the average or mean pore throat size of the aquifer formation into which it is being injected

(AFCEE, 2007). This allows the emulsion to be injected through the aquifer pore throats with minimal entrapment of the oil droplets.

There are numerous emulsifiers (surfactants) used in the food industry for vegetable oils, but the most common emulsifiers used for enhanced bioremediation applications include food-grade lecithin, polysorbates, mono and diglycerides, glycerol mono-oleate, amino acids, or some combination of these. It is also common to mix a rapidly degradable soluble substrate such as lactate into the emulsion to establish reducing conditions more rapidly.

Emulsions consisting of 1 to 10% vegetable oil in water by volume are relatively low-viscosity mixtures (e.g., non-dairy creamers like Coffee Mate®) compared to neat vegetable oil or HRC®. Oil droplets are immobilized by sorption to the aquifer matrix or by entrapment in very fine pore spaces. Coarse grained aquifers (low sorption potential) with high flow rates may require more frequent injections (e.g., annually) to sustain the reaction zone. Refined soybean oil is the most common oil used, and substrate loading typically is controlled by modifying the oil saturation in the emulsion (typically 1 to 5%). Oil saturations higher than 10 to 15 % may cause a large reduction in hydraulic conductivity (AFCEE, 2007).

Oil-in-water emulsions may be injected under pressure through direct-push probes or through temporary or permanent well points. In applications using sealed injection wells or points, it is common to overdevelop the well and use the development water as the makeup water for the emulsion or for a water push to increase the ROI of the substrate. Thus, a large volume of substrate can be reinjected to obtain an ROI (typically 10 to 15 ft [3 to 4.6 m]) limited only by the quantity of emulsion injected. This practice reduces the potential for displacement and dilution of contaminated groundwater. It also minimizes any disruption of native geochemical conditions in the aquifer resulting from introduction of a foreign water source (e.g., chlorinated potable water).

Care should be taken when injecting vegetable oil emulsions. Injection pressures greater that the overburden pressure (approximately 1 pound per square inch gauge [psig] per vertical ft) may cause hydraulic fracturing of the aquifer formation. This may lead to preferential flow of the substrate mixture along open fractures, resulting in non-uniform distribution. Unless hydraulic fracturing is intentional, injection pressures should be carefully monitored to prevent fracturing the formation. In low permeability formations (silts and clays), hydraulic fracturing may be used to inject the substrate. In this case, uniform distribution of the soluble component of the substrate mixture (e.g., metabolic acids) will be a slow diffusion-limited process.

A critical design parameter is the mean droplet size of the emulsion relative to the mean pore-throat size of the formation. Vegetable oils injected as emulsions can be widely distributed in most aquifers, given that the emulsion droplet size is small relative to the formation pore space. Emulsions can be mixed using static in-line mixers, high-speed shear mixers, or dairy homogenizers. Diaphragm pumps (which are capable of handling back pressure), flow meters, and mixing tanks are used to mix the emulsion to the desired composition. Field preparation using in-line mixers is capable of obtaining average droplet sizes of 5 to 20 micrometers (μm), while high-speed shear mixers are capable of obtaining droplet sizes of 2 to 15 μm. However, to get effective distribution in fine-grained sands and silts, uniform droplet sizes less than 1 μm are needed. Dairy homogenizers are capable of achieving mean droplet sizes in this range, but are not practical for field preparation. Several pre-mixed oil-in-water emulsions are available commercially (e.g., EOS® from EOS Remediation Products, Inc.; Newmans Zone® from Remediation and Natural Attenuation Services, Inc.; SRS™ from Terra Systems, Inc.; Lactoil from JRW Bioremediation Services, Inc.) that meet this requirement and that are stable over periods of several months.

Typical life spans for oil-in-water emulsions are on the order of 1 to 4 years. Life span depends on the emulsion saturation and the rate at which the oil is degraded and, to a lesser extent, on the rate of groundwater flow and alternate electron acceptor flux.

The use of pure vegetable oil is only considered appropriate for source areas, while edible oil emulsions may be used for both types of treatment. The use of pure oil has two unique impacts. First, a large proportion of chlorinated solvent mass may be sequestered into the oil due to partitioning. This mass is slowly released back into a reactive zone which becomes optimal for degradation to occur as the oil degrades. Second, neat oil acts to reduce permeability, which slows groundwater flow and mass discharge out of the source zone. A case study of injecting neat vegetable oil into a source area is included below.

Case Study: Neat Oil Injection at Hangar K, Cape Canaveral Air Force Station, Florida

The biostimulation application at the Hangar K Site at CCAFS, Florida is an example of injecting neat vegetable oil into shallow groundwater at depths of 20 to 33 ft (6 to 10 m) to treat chloroethenes in a suspected DNAPL source area (Parsons, 2002b, 2007b; Henry et al., 2007). Baseline concentrations of TCE were measured as high as 300 mg/L. The shallow soils at the site are sandy with high hydraulic conductivity (100 to 500 ft/day [30 to 150 m/day]). However, the groundwater hydraulic gradient was low (less than 0.0005), resulting in groundwater flow rates of less than a few tens of ft/yr.

The application used 33 injection points installed at a depth of 22 to 32 ft (7 to 10 m) bgs using direct-push technology; the points were installed in a grid configuration having an area of approximately 3,000 square feet (280 square meters). Approximately 55 gal of pure soybean oil was injected into each well point followed by 150 to 200 gal of native groundwater to immobilize the oil at residual saturations and to increase the substrate ROI.

Process monitoring over a period of 69 months indicated that the substrate was effectively distributed with initial concentrations of TOC as high as 3,200 mg/L in the injection points. Concentrations of TOC after 69 months declined to less than 20 mg/L at all monitoring locations, indicating that the effective lifespan of the substrate at this site was on the order of 4 to 5 years.

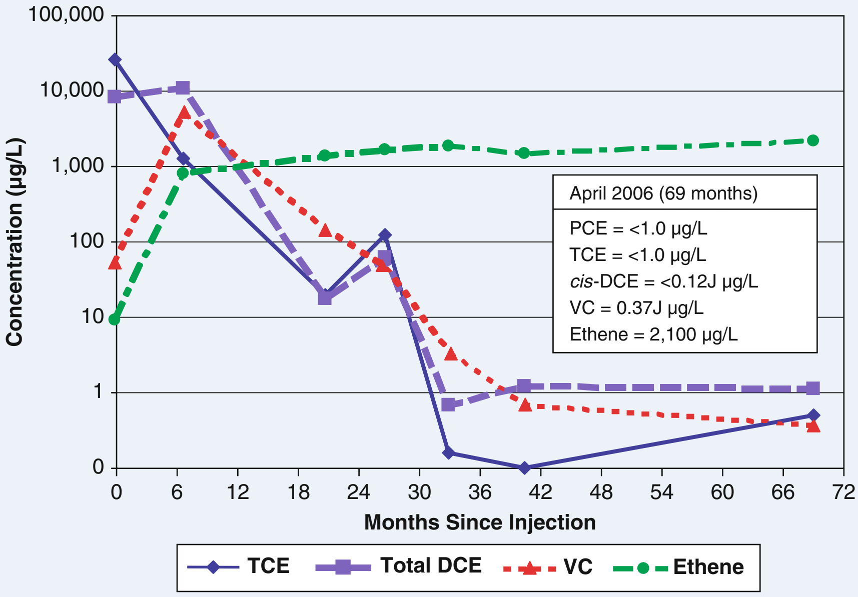

Figure 12.9. Concentrations in a monitoring well within the target treatment zone following injection of neat vegetable oil. Data from Well HGRK-MP04 at Hangar K, Cape Canaveral Air Force Station, Florida, USA (J-flag indicates estimated concentration) (from Parsons, 2007b).

Within approximately 18 months of injection, complete dechlorination of TCE to ethene was observed. Within approximately 30 months of injection, concentrations of PCE and TCE were reduced to below USEPA drinking water MCLs (5.0 μg/L for both compounds) at all locations within the treatment zone. Concentrations of *cis*-DCE and VC initially accumulated, but concentrations of *cis*-DCE declined to less than its MCL (70 μg/L) at all locations by 40 months after injection. Concentrations of VC also continue to decline, and are below the USEPA MCL (2.0 μg/L) at five locations. Reductions in concentrations of chloroethenes at well HRGK-MP04 (located within the treatment zone) are shown on Figure 12.9. It is notable that TCE concentrations have been reduced by over four orders of magnitude at this site.

One limitation to using neat edible vegetable oil is the difficulty of effectively distributing the oil throughout the aquifer matrix. Studies of oil retention with pure oil (Coulibaly and Borden, 2004) suggest that the residual saturation may be 30 to 50% or more. The volume required to distribute the oil uniformly throughout the aquifer matrix is only practical for very small source areas. However, demonstrations have shown that it is not necessary to have completely uniform distribution of the oil because soluble metabolic acids from degradation of the oil are distributed by the processes of advection, dispersion and diffusion (AFCEE, 2007).

In addition, such large residual saturations are not required for effective sequestration of PCE or TCE. For example, the partitioning coefficient for TCE listed in Table 4.3 of AFCEE (2007) is 338, or 338 times the mass of TCE will partition into oil relative to groundwater. If even 10% of the aquifer pore volume were filled with oil there would be sufficient oil to partition the majority of TCE in groundwater (i.e., 34 times the mass of TCE in groundwater) into the oil.

Therefore, applying pure edible oil at low saturations (less than 10% of the formation porosity) still may be effective, particularly at sites where a low groundwater flow rate allows for significant diffusion of chlorinated solvents toward zones filled with oil, and for highly soluble metabolic acids from biodegradation of the oil to diffuse out into the formation to stimulate reductive dechlorination. This approach was used successfully at the Hangar K site (see case study). At this site, the volume of oil injected accounted for less than 5% of the aquifer pore volume in the target treatment zone.

The site conditions encountered at the Hangar K site are optimal for this approach; not all source zones will be suitable. As the degree of aquifer heterogeneity or rate of groundwater flow increases, a lack of uniform distribution of pure vegetable oil or mixing between chlorinated solvents and the oil will likely limit the ability to effectively treat the entire source zone. Therefore, the use of pure vegetable oil should be applied only where the site is adequately characterized, the oil can be effectively injected into the treatment zone, and mixing of soluble fermentation products of the oil and chlorinated solvents can be achieved.

12.3.6.5 Permeable Mulch Biowalls

Biowalls using solid substrates (e.g., mulch and compost) are typically constructed in a trench or excavation in a permeable biobarrier configuration. Mulch generally is obtained from shredding and chipping of tree and shrub trimmings and is primarily composed of cellulose, hemi-cellulose and lignin. Often "green" plant material or compost is incorporated to provide nitrogen for microbial growth and a supply of more readily degradable organic carbon. Degradation of the substrate by microbial processes in the subsurface provides a number of breakdown products, including metabolic and humic acids, which act as secondary fermentable substrates. At many sites, mulch and compost substrates can sustain reaction zones for 3 to 7 years or more (AFCEE, 2008). Often the mulch is sprayed with vegetable oil (e.g., Heino et al., 2007;

Appendix F.1 of AFCEE, 2008) to enhance the organic carbon content, and piping can be installed to recharge the biowall using fluid substrates (e.g., vegetable oil emulsions).

Trenches may be installed using either hydraulic excavators (backhoes with extended booms) or continuous one-pass trenchers designed for installing subsurface utilities. Trench depths are limited by the type of equipment used, the stability of the formation, and the ability of the equipment to excavate the formation. In general, the greater the saturated thickness, and the sandier and less consolidated the sediments, the less depth can be achieved without the use of shoring. Trenching also may not be practical in hard, consolidated bedrock.

Continuous, one-pass trenching machines used to lay utility lines or for installing dewatering trenches are a rapid and effective way to install a biowall trench (Figure 12.10) Biowalls are limited by the depth to which the substrate can be placed and therefore are suitable only for relatively shallow groundwater plumes. Current trenching technologies are limited to depths of approximately 30 to 35 ft in optimal lithologic conditions, although deeper applications are possible by benching down prior to deploying the trenching equipment.

Figure 12.10. Continuous trenching for biowall installation, Ellsworth AFB, South Dakota, USA (from AFCEE, 2008).

It is important that the trench be extended or "keyed" into a lower permeability horizon at the lower limit of groundwater contamination. In cases where a lower confining horizon is not present, a biowall may still be used if it extends below the maximum depth of contamination that requires treatment. In addition, where only a small portion of a chlorinated solvent plume extends below the depth of trenching, it may be possible to install a limited number of injection wells and use a slow-release substrate such as emulsified vegetable oil to fill the gap in the reaction zone.

Selection of solid substrates requires careful consideration of the material composition. The degradation characteristics of mulch and compost products may vary significantly, and bench scale tests (e.g., batch or column studies) may be useful for screening the biowall material (Ahmad et al., 2007a; GSI, 2008; Shen and Wilson, 2007). Typically, mulch and compost are mixed with coarse-grained sand or pea gravel at a ratio of 40 to 60% by volume (AFCEE, 2008;

Ahmad et al., 2007b). The percentage of sand or pea gravel added should be sufficient to ensure the permeability of the biowall material is higher than that of the surrounding formation. Sand and gravel help maintain a high permeability for groundwater migration or infiltration through the mixture, as well as help stabilize the material and prevent compaction.

Biowall trenches can be modified to include wells or perforated pipe for addition of fluid substrates to the system, if necessary. Alternately, wider trenches or multiple parallel trenches may be necessary to increase groundwater residence time within the treatment zone to effectively treat plumes with high groundwater flux or high CAH concentrations. A case study of a permeable mulch biowall at Altus AFB, Oklahoma is provided below. Additional case studies can be found in AFCEE (2008).

Case Study: Permeable Mulch Biowall at OU-1, Altus AFB, Oklahoma

A mulch and compost biowall was installed at Landfill 3 in Operable Unit 1 (OU-1) at Altus AFB, Oklahoma, in June 2002 as a technology demonstration test (Haas et al., 2003; Henry et al., 2003; Parsons, 2007c). The objective of the Altus AFB application was to intercept and contain a shallow TCE/DCE groundwater plume to a depth of 24 ft (7.3 m) bgs to prevent surface water discharge and off-base migration, as well as to evaluate the technology for application at other Air Force sites. The biowall measures 455 ft (139 m) long, 24 ft (7.3 m) deep and 1.5 ft (0.5 m) wide, and is composed of approximately 50% shredded bark mulch, 10% cotton burr compost, and 40% sand by volume. The trench was installed using a continuous chain-driven trencher.

Subsurface sediments at the site consist of low permeability silt and clay that exhibit secondary porosity in the form of fractures and gypsum dissolution features. Groundwater flow rates average approximately 65 to 75 ft/yr (20 to 23 m/yr), although flow within the secondary porosity may be much higher. Concentrations of TCE immediately upgradient of the biowall have been measured as high as 8,000 μg/L. Groundwater also has sulfate concentrations of 1,600 to 2,200 mg/L.

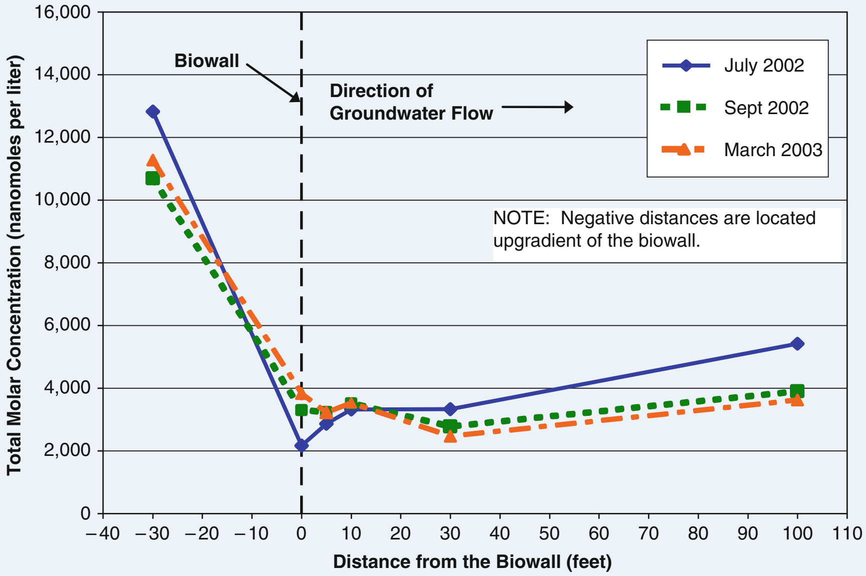

Figure 12.11. Total molar concentrations with distance along the groundwater flow path through a mulch biowall at Altus AFB, Oklahoma, USA.

The Altus AFB permeable mulch biowall was successful in stimulating the anaerobic degradation of TCE in groundwater. Within nine months, concentrations of TCE had been reduced to below 5.0 μg/L (the MCL) within the biowall. Figure 12.11 illustrates the reduction in total molar concentrations along a flow path through the biowall. Concentrations of *cis*-DCE within the biowall have decreased or remained stable, with little production of VC. The overall reduction in concentrations of total CAHs within the biowall is 86%. A reduction in total molar concentrations without accumulation of *cis*-DCE or VC suggests that the primary degradation process is biogeochemical transformation (Section 12.2.2), likely due to the formation of iron monosulfides in the high sulfate, high iron biowall environment (Kennedy et al., 2003). Concentrations of *cis*-DCE have increased downgradient of the biowall in the most contaminated portion of the plume, presumably due to biotic reduction of TCE, and persist at concentrations in excess of 1,000 μg/L.

Results of the OU-1 biowall demonstration were used to design a full-scale biowall system over 5,200 ft (1,590 m) long at another large chlorinated solvent plume at Altus AFB. Because of the potential for biogeochemical transformation of chlorinated solvents at Altus AFB, additional research is being conducted in a joint study between AFCEE, ESTCP and the USEPA to document the conditions under which biogeochemical transformation occurs (Whiting et al., 2008).

12.3.7 Health and Safety Considerations

Constructing and operating biostimulation systems poses health and safety hazards common to both construction and hazardous waste activities. All applications should include a site-specific health and safety plan, including contact information for local emergency agencies and directions to local emergency care. Health and safety considerations should address traffic in the work areas, utility clearances, spill containment measures, and procedures for working with drilling equipment and high-pressure injection systems.

Site security is necessary to prevent exposure of unauthorized, unprotected individuals to the work area. Site security should be enforced to ensure that only authorized personnel are allowed in the work area. Site personnel should have the required level of personal protective equipment (PPE) and be trained under the requirements of 29 Code of Federal Regulations (CFR) 1910.120. Trenches or excavations pose special safety issues regarding heavy construction equipment and open excavations. The work area should be clearly marked through the use of signs, barrier rope, tape, or fencing. Site personnel and sampling technicians should maintain a safe distance of at least 20 ft (6 m) from the excavation and construction equipment when in operation.

Biostimulation may enhance generation of gaseous byproducts (e.g., methane and hydrogen sulfide) that may degrade groundwater quality or accumulate in the vadose zone. In particular, caution must be exercised when operating near structures where these gases could accumulate. Monitoring of potentially explosive methane gas should be considered for public safety as well as the safety of the field staff. Analysis of select CAHs in soil gas is also warranted in locations proximate to structures or buildings where an inhalation risk may exist. Passive diffusion of these gases to the atmosphere is often sufficient to mitigate any safety concerns. If necessary, contingency plans (e.g., soil vapor extraction) should be developed for locations sensitive to noxious gases or vapor hazards.

12.3.8 Biostimulation Design Summary

There are a number of system and engineering design options for applying biostimulation. Selecting a practical technical approach and system configuration should be based on meeting site-specific remedial objectives. Once remedial goals (e.g., remediation, risk management) and a suitable technical approach (e.g., source reduction or biobarrier containment) are established, the practitioner faces a multitude of substrate and delivery options.

With few exceptions, all of the substrate types described in this chapter can be used in some form of source area or biobarrier configuration. Furthermore, all of the substrate types have been demonstrated to stimulate complete anaerobic dechlorination of PCE and TCE to ethene given delivery of sufficient levels of substrate to the treatment zone, appropriate geochemical conditions and suitable microbial populations.

Decisions regarding the substrate type and delivery system to use may be reached by a combination of life-cycle cost analysis and proven effectiveness. Given a number of reasonable approaches, it is appropriate to evaluate the life-cycle costs of alternative system designs using the various substrate types. In addition to life-cycle costs, the technical merit and effectiveness of the approach also must be evaluated. Comparing case studies of the effectiveness of different approaches for sites similar to that under consideration is one way to evaluate the proposed technical approach.

However, in many cases small scale pilot testing may be the only practical way to determine the effectiveness of a proposed biostimulation approach for a particular site. The cost to modify or change system design or operation after full-scale biostimulation is implemented may prove to be many times the cost of pilot testing. By understanding the principles and practices of biostimulation and critically evaluating proposed technical approaches, biostimulation can be a very effective remedial option for many sites contaminated with chlorinated solvents.

12.4 EVALUATING BIOSTIMULATION PERFORMANCE

Biostimulation is intended to enhance rates of contaminant degradation by processes that occur naturally. The following results are indicative of a successful biostimulation application for chlorinated solvents:

- Rates of degradation are greater (enhanced) than under natural conditions.
- The degradation pathway is complete, without the accumulation of regulated intermediate dechlorination products.
- Any adverse secondary impacts to groundwater are not sustained.

The degree to which these results help site managers achieve site-specific remedial objectives can be used to evaluate system performance. This section describes typical remedial objectives and the methods and tools that may be used to evaluate a biostimulation application.

12.4.1 Remedial Objectives

Remedial objectives and performance metrics are driven by regulatory compliance requirements. To design a successful biostimulation application, the regulatory framework should be reviewed, the regulatory community consulted, and compliance standards and remedial endpoints clearly identified. The ability of biostimulation to achieve drinking water MCLs in some settings has been demonstrated, but cannot be assumed to be possible at all sites. The use of less stringent, risk-based remedial goals may be more appropriate and achievable than default drinking water standards.

Typical remedial action objectives (RAOs) that biostimulation may be used to address include:

- Reduce chlorinated solvent concentrations to below regulatory criteria.
- Destroy chlorinated solvent mass in source zones where effective substrate/contaminant contact is possible.
- Reduce contaminant mass discharge or plume toxicity across some containment boundary.
- Enhance natural attenuation rates to reduce monitoring timeframes.

Performance objectives based on dissolved chlorinated solvent concentrations alone should be used with caution. A significant amount (usually the majority) of the total chlorinated solvent mass in an aquifer system may be present as DNAPL or sorbed to the aquifer matrix. Due to the effects of dissolution and desorption of this contaminant mass, aqueous-phase concentrations alone may not accurately reflect the amount of mass being destroyed if there is continued mass transfer from DNAPL or sorbed mass to the aqueous phase. Changes in the relative molar concentration of chlorinated solvent parent compounds and their dechlorination products, or results from forensic analyses such as CSIA, may be used to demonstrate that degradation of chlorinated solvents is occurring.

12.4.2 Measuring Performance

The primary measure of performance of a biostimulation system is typically a reduction in chlorinated solvent concentrations in groundwater to a specified remedial standard, including any regulated intermediate dechlorination products. Groundwater geochemical data collected during system monitoring also may be evaluated to demonstrate whether aquifer redox and geochemical conditions have been modified as planned, and to detect changes in environmental conditions that may optimize or reduce the efficacy of the biostimulation system. Interpretation of contaminant and geochemical data as it applies to bioremediation of chlorinated solvents is described in further detail in USEPA (1998), Wiedemeier et al. (1999), AFCEE (2000) and AFCEE et al. (2004).

Monitoring programs typically include groundwater monitoring wells located along transects parallel to the predominate direction of groundwater flow through the treatment zone. Groundwater quality is analyzed over time for both chlorinated solvent concentrations and geochemical indicator parameters. Additional monitoring wells (e.g., cross-gradient) may be useful to determine actual direction, or changes in direction, of groundwater flow during remediation. Seasonal changes or changes in groundwater flow induced by the remediation system may significantly impact the interpretation of monitoring data and system performance.

Monitoring parameters that indicate anaerobic degradation of chlorinated solvents and achievement of remedial and performance objectives include:

- Concentrations of parent compounds (e.g., PCE, TCE, 1,1,1-TCA or CT) and their dechlorination products (e.g., *cis*-DCE, VC, CA or chloromethane) are reduced to regulatory standards or the RAOs for the site.
- DO concentrations are less than 0.5 mg/L and ORP values are less than 0.0 millivolts (mV, measured relative to a standard hydrogen electrode), indicating an anaerobic environment has been achieved. Production of ferrous iron, a reduction in sulfate, and production of methane further indicate that groundwater conditions are sufficiently reducing for anaerobic reductive dechlorination to occur.
- Dissolved hydrogen concentrations are greater than 1 nanomole per liter (nmol/L), indicating that sufficient primary electron donor is present to sustain anaerobic reductive dechlorination of chlorinated solvents. Note that sampling for dissolved hydrogen requires special protocols and may be difficult to conduct.
- Ethene and/or ethane are being produced. Even low concentrations of ethene or ethane may indicate biotic reductive dechlorination is proceeding to completion, although these data are not always reliable since ethene and ethane also may be degraded or volatilized.

Common soil and groundwater analyses used to evaluate biostimulation applications are listed in Table 12.10. A more detailed listing and description of these analyses can be found in AFCEE et al., (2004), AFCEE (2007) and AFCEE (2008).

Table 12.10. Biostimulation Analytical Protocols for Soil and Groundwater (after AFCEE, 2008)

Parameter	Rationale
Soil and/or Biowall Backfill Materials	
Volatile Organic Compounds (VOCs)	Delineate source areas. Screen soil for disposal.
Fraction Organic Carbon	Used to calculate sorption of contaminants to the soil matrix.
Total Iron and Manganese	Evaluate competing electron acceptor mass and potential for formation of metal sulfides under anaerobic conditions.
Acid Volatile Sulfide	Measures the amount of sulfide present in the form of reactive metal sulfides, predominately as iron monosulfide (FeS).
Chromium Extractable Sulfide	Measures the total amount of sulfide. Measured after acid volatile sulfide extraction, it is a measure of how much elemental sulfur and metal disulfides (Fe_2S) are in the aquifer matrix.
Bioavailable Iron and Manganese	Measures the amount of ferric iron (III) and manganese (IV) in the solid phase that is bioavailable as a competing electron acceptor.
Strong Acid Solution Fe (II) and Fe (III)	Measures the total amount of ferric and ferrous iron in the solid phase. A relative measure of the amount of reduced iron in the aquifer matrix.
Nitrogen, Phosphorous, and Potassium	Determine presence of essential nutrients for microbial growth.
Groundwater	
Dissolved Oxygen (DO)	Determine whether aerobic or anaerobic conditions exist. Concentrations less than about 0.5 mg/L generally indicate an anaerobic pathway.
Oxidation-reduction potential (ORP)	The ORP of groundwater reflects the relative oxidizing or reducing nature of the groundwater system.
pH	Aerobic and anaerobic processes are pH-sensitive
Temperature and Conductivity	Primarily used as well development parameters. The rates of biological and chemical reactions are temperature dependent.
Ferrous Iron	Used as an indication of iron reduction by microbial processes.
Manganese	Used as an indication of manganese reduction by microbial processes.
Sulfide	Byproduct of sulfate reduction.
Alkalinity	Indicator of biodegradation and buffering capacity of the aquifer.
Carbon Dioxide	Byproduct of both aerobic and anaerobic biodegradation processes.
Nitrate	Substrate for microbial respiration in the absence of oxygen
Nitrite	A byproduct of denitrification of nitrate.
Sulfate	Indication of sulfate reduction by microbial biodegradation.

(*continued*)

Table 12.10. (continued)

Parameter	Rationale
Chloride	General water quality parameter. By-product of reductive dechlorination.
VOCs (chlorinated solvents)	Contaminant of concern, byproducts of anaerobic dechlorination.
Total Organic Carbon (TOC)	Indication of organic substrate available for biological metabolism.
Volatile Fatty Acids (VFAs)	Biodegradation breakdown products and fermentation substrates. Indicator of substrate distribution.
Phospholipid Fatty Acids (PLFAs)	Indicator of bioactivity, measure of biomass, and characterization of the microbial community.
Methane, ethane, and ethene	The presence of methane indicates fermentation via methanogenesis. The presence of ethane and ethene are indicative of reductive dechlorination.
Dissolved Metals	Measure potential for mobilization of metals under anaerobic conditions.
Sodium Bromide/Sodium Iodide	Groundwater tracers.

Chlorinated solvent concentrations are the primary line of evidence used to demonstrate that anaerobic dechlorination is occurring, with geochemical data providing a secondary line of evidence that optimal anaerobic conditions have been achieved. A certain percentage of conflicting data may be observed. For this discussion, conflicting data are defined to be individual or multiple results that do not correlate with expected or observed trends or subsurface geochemical conditions. Conflicting data can arise from systematic errors in sampling or analysis. For example, a high DO reading (e.g., 3.0 to 10 mg/L) in the same well that contains mg/L concentrations of methane typically represents a systematic error, since the production and persistence of methane is inconsistent with the presence of oxygen. ***Therefore, an evaluation of site data should use a multiple converging lines of evidence approach for system performance evaluation and decisionmaking.*** The presence of conflicting data should initiate a quality assurance exercise to detect and minimize any systematic errors. But major system modifications should not be initiated due to the presence of conflicting data if multiple lines of evidence support acceptable system performance.

12.4.2.1 Change in Contaminant Concentrations

The first step in evaluating a biostimulation application is documenting a reduction in chlorinated solvent concentrations over time. Changes in post-treatment concentrations relative to initial conditions is a primary line of evidence that can be used to show that the process is working to degrade contaminant mass. There are several ways to present data showing changes in contaminant concentrations and plume configuration over time or distance after substrate addition. One method consists of preparing isopleth maps of contaminant concentrations over time. The use of vertical cross-section contour plots oriented along the path of groundwater flow also is recommended, to understand the vertical distribution of substrate and contaminant mass.

Caution is advised in evaluating early data after initiation of biostimulation; changes in concentration at a single monitoring point may be influenced by displacement or dilution caused by injection, or by sorption of chlorinated solvents to substrates such as vegetable oil or bark mulch. Data over several months or a year after injection will be more representative of the degree to which anaerobic degradation of chlorinated solvents has been stimulated.

For example, Figure 12.9 illustrates a clear trend in decreasing concentrations of TCE for the biostimulation application at Hangar K, CCAFS, Florida. It is notable that concentrations of DCE and VC initially increased due to sequential dechlorination, but by 18 months a decreasing trend for TCE, DCE and VC was evident. As was noted at Hangar K, an acclimation period of 6 to 24 months or more is not unusual for a biostimulation application to achieve optimum performance.

12.4.2.2 Change in Molar Concentrations and Molar Fractions

Contaminant concentration or mass reduction also may be demonstrated by changes in the molar concentrations of parent and dechlorination products over time, or with distance along a groundwater flow path through the reaction zone. Evaluating changes in the molar (i.e., molecular) concentrations and molar ratios of parent compounds to dechlorination products can be useful in determining the efficacy of biostimulation. Biodegradation of parent compounds will result in a change in the molar concentrations and ratios of the compounds involved in the reaction.

Figure 12.12 illustrates changes in molar concentrations over time at a monitoring well for an application of biostimulation using emulsified vegetable oil at Site SS-015, Travis AFB, California, USA. It is clear from this plot that sequential anaerobic dechlorination occurred with a temporal accumulation of the intermediate dechlorination products *cis*-DCE and VC at periods of approximately 5 and 16 months after substrate addition, respectively. ***The practitioner should exercise care in interpreting early sampling results that indicate a temporal accumulation of intermediate dechlorination products, because this trend may be due to kinetic disparity where the intermediate dechlorination product is being generated faster than it is degraded, and not to an absence of appropriate dechlorinating microorganisms.*** Once the more highly chlorinated compounds are depleted (e.g., TCE), then concentrations of the less chlorinated compounds (*cis*-DCE and VC) should decline with time.

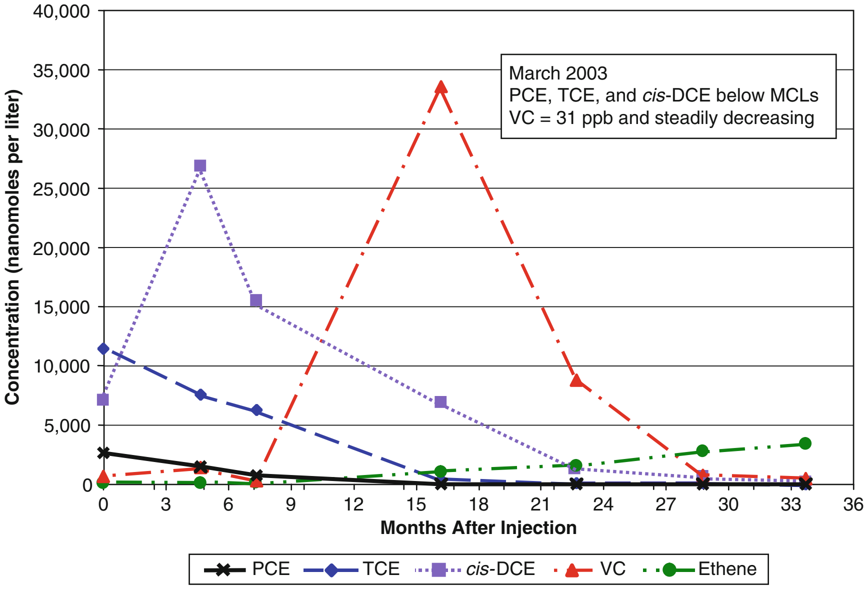

Figure 12.12. Changes in molar concentration over time following injection of emulsified vegetable oil. Data from Well MW4, Site SS015, Travis AFB, California, USA (from AFCEE et al., 2004).

A plot of the changes in molar fraction or ratio over time is another method used to determine if biodegradation has been stimulated. In particular, this method is often employed when there is a constant or continuing source of contaminant mass entering a treatment system. ***In this case, the total molar concentration may remain elevated or even increase due to a continuing mass influx, but an increase in the molar ratio of dechlorination products will demonstrate that sequential anaerobic reductive dechlorination is occurring.***

Figure 12.13 is a plot of total molar concentration and molar fractions of individual chlorinated ethenes for the same monitoring location shown in Figure 12.12. In this case, the total molar concentration was variable, and actually increased over the first 16 to 18 months of treatment. For this site the increase in total molar concentration is interpreted as enhanced dissolution or desorption of a residual source. However, changes in molar fractions clearly indicate that sequential anaerobic reductive dechlorination was occurring. Once PCE and TCE were depleted, the total molar concentration decreased as *cis*-DCE and VC were transformed to innocuous end products (e.g., ethene).

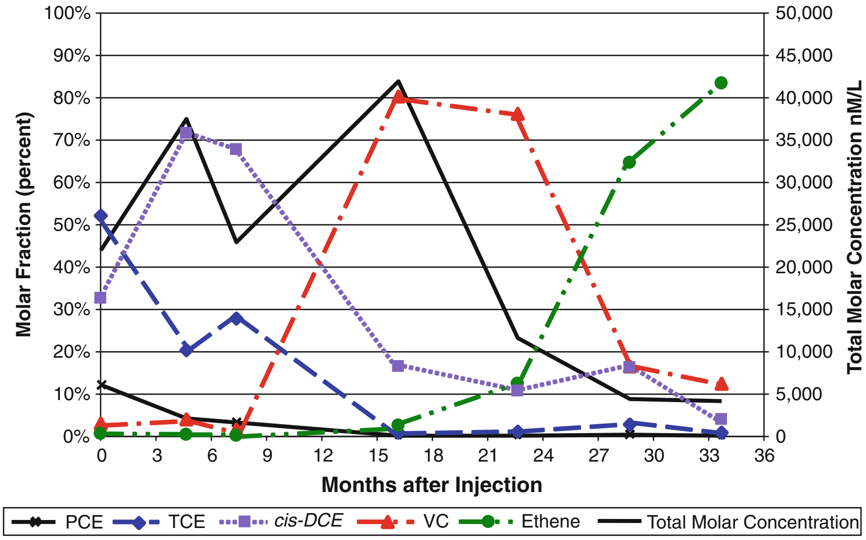

Figure 12.13. Changes in molar fraction and total molar concentration over time (Well MW4, Site SS015, Travis AFB, California, USA) (from AFCEE et al., 2004).

Concentration data also may be plotted over distance along a flow path through the treatment zone. Figure 12.11 presented a plot of the molar concentration of total chlorinated ethenes (PCE, TCE, DCE, plus VC) with distance downgradient along the groundwater flow path for several sampling events for a permeable mulch biowall at Altus AFB, Oklahoma. Note that ethene and ethane were purposely left out of the calculation because they do not represent contaminant mass (they are innocuous byproducts). The decreasing contaminant concentrations within the biowall shown on Figure 12.11 provides reasonable evidence that contaminant mass is being converted to innocuous end products.

12.4.2.3 Reductions in Plume Toxicity

Sequential reductive dechlorination can produce toxic intermediate dechlorination products that may persist in groundwater for extended periods. A common concern is that these intermediate dechlorination products, specifically VC, may pose an equal or greater risk to human health and the environment than the parent compounds. However, the potential for production of VC often overshadows the overall reduction of toxicity that may be achieved. The remediation selection processes specified by the USEPA requires that each candidate technology or approach be evaluated against nine criteria including long-term effectiveness and the reduction of contaminant toxicity, mobility and volume over time (USEPA, 1988). Accordingly, toxicity reduction is an important metric for evaluating site remedies.

The relative toxicity of site groundwater may be estimated by calculating the number of "toxicity equivalents" in the most contaminated wells at a site (Downey et al., 2006). For the purpose of this evaluation, a toxicity equivalent is defined as the individual CAH compound concentration divided by its assigned MCL. The total toxicity is defined as the sum of the individual compound toxicity equivalents. For example, a well location that contains 500 μg/L TCE, 140 μg/L *cis*-DCE, and 50 μg/L VC would contain:

$$500/5 + 140/70 + 50/2 = 100 + 2 + 25 = 127 \text{ toxicity equivalents}$$

For this calculation, the MCL is assumed to be proportional to the relative toxicity of each CAH, the MCL being the most common measure of relative toxicity of CAHs in groundwater. A relatively toxic compound (e.g., VC with a MCL of 2.0 μg/L) will yield a higher toxicity equivalent than a less toxic compound (e.g., *cis*-DCE with a MCL of 70 μg/L). This approach allows the reduction in the overall toxicity of the site to be quantified over time as the mix of CAHs changes.

Table 12.11 provides an example of baseline CAH concentrations and concentrations two years after installation of a biowall and a bioreactor demonstration at OU-1, Landfill 3, Altus AFB, Oklahoma (Appendix F.2 and F.3 in AFCEE, 2008). For the biowall application, the upgradient (baseline event) concentrations of CAHs were compared to the CAH concentrations within the biowall (two year event). For the bioreactor site, baseline or pre-treatment groundwater concentrations were compared to average post-installation concentrations from two source area wells exhibiting the highest concentrations of CAHs. Data collected two years after installation were selected to allow time for biological processes to acclimate to anaerobic conditions.

Table 12.11. Reductions in Groundwater Toxicity after Two Years of Biostimulation Treatment at OU-1, Altus AFB, Oklahoma, USA (from AFCEE, 2008)

Contaminant	MCL[1] (μg/L)	Concentration (μg/L)	Toxicity Equivalent (unitless)	Concentration (μg/L)	Toxicity Equivalent (unitless)	Percent Change (%)
		Baseline Sampling Round		Two-Year Sampling Event		
OU-1 Biowall, Altus AFB, Oklahoma (Upgradient versus Wells in Biowall)						
TCE	5.0	5,198	1,040	9.0	1.8	
cis-DCE	70	1,137	16	417	6.0	
VC	2.0	4.0	2.0	100	50	
Total			**1,058**		**58**	**–95%**
Landfill 3 Bioreactor, Altus AFB, Oklahoma (Source Wells SW5 and SW6)						
TCE	5.0	12,423	2,485	3.0	0.6	
cis-DCE	70	1,491	21	11	0.2	
VC	2.0	6.0	3.0	370	185	
Total			**2,509**		**186**	**–93%**

[1] MCL = USEPA Maximum Contaminant Level.

Even though concentrations of VC increased by over an order of magnitude, the biowall and bioreactor have achieved high levels of toxicity reduction ranging from 93 to 95%. Although VC was produced at these sites, the footprint of the VC plume has been confined to within the initial chlorinated solvent plume, with no migration of VC beyond the footprint of the TCE plume at any time. This observation suggests that VC is subject to other degradation processes downgradient of the biowall and bioreactor, and has limited mobility in groundwater at this site.

In summary, the overall reduction in toxicity achieved during biostimulation is often overshadowed by the appearance of VC and the regulatory focus on this compound. Even when DCE and VC are present, large reductions in toxicity can be achieved without expansion of the contaminant plume. The reduction of contaminant toxicity is another useful criterion for evaluating the performance of biostimulation applications.

12.4.2.4 Mass Flux

One other measure that has been proposed for evaluating remediation performance is the mass flux of contaminant, or more properly, the contaminant mass discharge. Although there are few examples to date of mass flux measurements applied to biostimulation performance monitoring, mass flux is being used more frequently to characterize and monitor groundwater contaminant plumes (Buscheck et al., 2003). The use of this tool is increasing because of recent improvements in measuring mass flux, and a growing recognition that mass flux data can provide a more complete measure of the risk posed by the contaminants than concentrations alone (Einarson and Mackay, 2001).

In many cases, mass flux measurements can better characterize a contaminated site than typical monitoring networks (Feenstra et al., 1996). Typical monitoring plans focus primarily on defining plume boundaries and concentration trends, but chemical concentrations and groundwater velocity can vary by orders of magnitude across a plume, and some sources that could be significant contributors to flux may be missed during source identification efforts. Flux measurements are designed to account for the variability in contaminant concentrations and groundwater velocity across the plume in developing an estimate of the contaminant mass discharge, and therefore can provide a more thorough characterization than conventional approaches.

In addition, the mass flux values at different times and places within a plume reflect the combined impact of all of the physical, chemical and biological processes acting on the contaminants. Understanding the mass flux is therefore essential to developing an accurate CSM, and mass flux data can help managers make better remediation decisions (Nichols and Roth, 2004; Basu et al., 2006). For example, prior ITRC documents have concluded that mass flux data can result in more credible remediation decisions than relying only on concentration data (ITRC, 2004; ITRC, 2008a).

However, regulations typically do not consider mass flux, but only the contaminant concentrations in groundwater. This focus is understandable—the concentration in groundwater is used in regulations to assess the risk to a given receptor exposed to the groundwater, given assumed ingestion rates for example. So site managers tend to focus primarily on the concentration trends over time and space, relying on data from specific monitoring wells to determine the need for remediation or to assess performance and compliance.

Though useful, mass flux estimates can be relatively difficult and costly to obtain, generally requiring transects of monitoring wells and increased amounts of data to evaluate. Further, accurately and cost-effectively measuring mass flux is technically challenging, and entails additional uncertainty beyond that associated with measuring contaminant concentrations alone. But the use of mass flux is increasing, and will increase even more as the technology improves. For example, the development and testing of improved methods to measure and estimate mass flux was identified as one of the most pressing research needs for management of chlorinated solvent sites (SERDP, 2006).

12.4.2.5 Molecular Diagnostic Tools

Recent research has led to development of two general techniques that may be useful to help characterize and monitor biostimulation sites. These two techniques are MBTs and CSIA. MBTs are techniques that can detect genes or genetic sequences characteristic of *Dehalococcoides* species or other microorganisms of interest. MBTs can be useful in determining whether complete dechlorination of chlorinated ethenes is likely to occur (Stroo et al., 2006). MBTs are most likely to produce useful results after the growth of anaerobic microorganisms has been stimulated. These MBTs also may have application to other contaminants, since *Dehalococcoides* organisms have been implicated in the dihaloelimination of 1,2-dichloroethane and 1,2-dichloropropane (Maymo-Gatell et al., 1999; Ritalahti and Löffler, 2004), the partial dehalogenation of certain chlorinated benzenes (Adrian et al., 2000), polychlorinated biphenyls (Fagervold et al., 2005; Bedard et al., 2006; Yan et al., 2006), and polychlorinated dibenzodioxins (Bunge et al., 2003; Fennell et al., 2004).

Several MBTs are commercially available for *Dehalococcoides* organisms. A USEPA method for assessing *Dehalococcoides* organisms is not currently available but efforts to standardize the techniques are being funded by the Strategic Environmental Research and Development Program (SERDP) (www.serdp.org). A recent publication (SERDP, 2005) summarized the current state of research for MBTs and provides a general overview of the various tools and their respective advantages and disadvantages.

The most widely used MBT technique involves screening for the *Dehalococcoides* 16S rRNA gene. Early field demonstrations of this semi-quantitative, genus-specific test are reported in Fennell et al. (2001), Hendrickson et al. (2002) and Major et al. (2002). Current versions of this test offer much more precise quantification (Lendvay et al., 2003) which may assist with the estimation of dechlorination rates (Lu et al., 2006).

While these 16S rRNA gene-based tests are highly effective in most cases, there is potential for both false negatives and false positives. False negatives arise because *Dehalococcoides* organisms may not be detectable in all areas of a site (e.g., Fennell et al., 2001). Thus, field sampling techniques and the degree of aquifer heterogeneity should be carefully evaluated when making a determination that *Dehalococcoides* species are completely absent. False positives may arise because different *Dehalococcoides* populations have different substrate ranges, thus *Dehalococcoides* organisms may be detected at a site but cannot dechlorinate the contaminants of concern. Also, gene-based tests count both live and dead microorganisms, so concentrations measured may not accurately reflect the viable *Dehalococcoides* population.

Recently, new MBTs have been developed to address the false positive problem. Quantitative screening for genes associated with VC reduction to ethene (vcrA and bvcA genes) indicates whether the *Dehalococcoides* population detected has the potential for complete dechlorination of chlorinated ethenes (Sung et al., 2006). Also, MBTs that quantify expression of the 16S and/or dehalogenase genes are becoming commercially available to detect only actively dechlorinating *Dehalococcoides* organisms (e.g., Microbial Insights (www.microbe.com) and SiREM Laboratories (www.siremlab.com)).

Other MBTs can be used to examine the total microbial community in the aquifer and/or test for multiple dechlorinating bacterial populations at once. These techniques are primarily based on 16S rRNA gene analysis and include terminal restriction fragment length polymorphism (T-RFLP), 16S rRNA gene cloning and denaturing gradient gel electrophoresis (DGGE) (Löffler et al., 2000; Richardson et al., 2002; Duhamel et al., 2002). However, the detection of specific populations such as *Dehalococcoides* may be subject to false negatives if the population of interest is not predominant in the overall community. In subsurface environments amended with electron donor, high concentrations of iron-reducing, sulfate-reducing and fermentative populations may mask the detection of the relatively low concentrations of dechlorinating organisms. Thus, these techniques are most productively used on laboratory cultures with relatively low microbial diversity as opposed to field samples.

CSIA is another innovative technique that can be used to determine whether a compound has undergone a chemical or biological transformation rather than a physical process such as dilution or sorption. The USEPA has recently published guidance on using CSIA to assess biodegradation and sources of organic contaminants in groundwater (USEPA, 2008). CSIA also may help elucidate biodegradation pathways, which can provide valuable data at sites where multiple chlorinated solvents are degrading to VC or other compounds of concern (e.g., Hunkeler et al., 2002, 2005). CSIA data can be used in conjunction with chemical concentration data or may provide an additional line of evidence supporting results from MBTs and microcosm studies. North American providers of CSIA services for aquifer samples include several leading universities (e.g., Oklahoma State University, University of Toronto, University of Waterloo), national government laboratories (e.g., Argonne and Livermore) and commercial laboratories (e.g., Microseeps, Inc.).

12.4.3 System Modifications and Contingencies

Various system modifications can be made during pilot-scale operation or full-scale design to deal with undesirable site conditions or developments (Table 12.12). Soluble substrate systems that use frequent injections have the most flexibility in modifying injection scenarios. When using infrequent applications of slow-release substrates, potential problems such as the need to add a buffering agent should be evaluated prior to substrate addition, and the buffer added during substrate injection as a precautionary measure when in doubt.

Table 12.12. Potential System Modifications for Special Site Conditions (modified from Suthersan et al., 2002 after AFCEE et al., 2004)

Condition	Modification
Low pH or low buffering capacity	• Use of buffering agent • Use of water push for soluble substrates • Use of slower-release substrates
Low permeability/Low groundwater velocity	• Closely spaced direct push injections • Less frequent injections
High permeability/High groundwater velocity	• Higher donor loading rates • More frequent injections
Buildings above reactive zone	• Vapor monitoring systems • Vapor control systems (e.g., soil vapor extraction [SVE])
Incomplete dechlorination	• Allow for longer acclimation periods • Lower the redox environment • Bioaugmentation • Modifications to stimulate biogeochemical transformation processes

Inadequate or excessive distribution of substrate due to aquifer permeability and/or groundwater flow rates can be adjusted by increasing or decreasing the substrate dose, and/or by modifying injection frequency or well spacing. These modifications are more easily accomplished for soluble substrates. Substrate application rates also may be increased in the event of inhibitory electron acceptor demand.

Contingencies should be provided when applying the technology near potential vapor migration pathways or accumulation areas such as utility corridors and basements. If soil gas monitoring indicates a vapor hazard (e.g., VC or methane), application of remedial measures such as soil vapor extraction may be warranted.

Incomplete or delayed dechlorination is a common limitation of biostimulation. Biostimulation of biogeochemical transformation processes using sulfate and iron amendments is being advanced as one method to limit production of intermediate dechlorination products (AFCEE et al., 2008). However, bioaugmentation with cultures capable of carrying sequential dechlorination to completion is the most common method to address accumulation of DCE and VC.

Prior to considering bioaugmentation, the system should be carefully evaluated to ensure that the proper geochemical conditions have been achieved and that a sufficient lag phase has been allowed for ecological succession and development of appropriate microbial consortia. In some situations it may be acceptable to generate VC or CA if there is an aerobic zone downgradient of the treatment area where natural attenuation is sufficient to meet the site remediation goals. In other cases, bioaugmentation with commercially available cultures or microorganisms from another site can be implemented once it has been determined that indigenous bacterial communities are not suitable for anaerobic reductive dechlorination. The marginal added cost of bioaugmentation also may be justified based on slow rates of degradation or long lag times to meet time-sensitive performance objectives.

12.5 SUMMARY

Enhanced *in situ* anaerobic bioremediation using biostimulation is a promising technology for remediation of chlorinated solvents in groundwater, and has been applied at hundreds of sites to date. Implementing biostimulation begins with adequate characterization of a site, development of a CSM and definition of the remedial objectives. Preliminary screening and evaluation of existing data is critical to determine if biostimulation is a suitable remedy for a specific site. Often additional data collection or pre-design testing are required prior to a final decision on whether biostimulation is the most reasonable choice of remedy compared to alternative technologies.

12.5.1 Practicing Biostimulation of Chlorinated Solvents

The practice of biostimulation to treat chlorinated solvents has advanced to the point that it is being applied not only for dissolved phase chlorinated solvent plumes, but also for treating DNAPL source areas. Biostimulation may be applied in source areas using grids of injection wells, or by using recirculating systems or bioreactors. The technology also may be applied in a permeable biobarrier configuration to intercept and treat downgradient portions of a dissolved chlorinated solvent plume.

There are multiple organic substrates being used for biostimulation. These substrates (Table 12.3) differ in the complexity of their composition, the rate at which the material is degraded or fermented by biological activity in the subsurface, and in cost. The selection of an appropriate substrate should take into account expected performance in developing appropriate anaerobic reactive zones, the rate at which the substrate is used (efficiency of use), substrate availability and cost to implement (life-cycle cost, including cost of O&M). A common goal is to minimize overall project cost by optimizing the number of required injection points or wells, the number of injection events and the amount of substrate needed.

The primary measure of performance for a biostimulation application is a reduction in chlorinated solvent concentrations in groundwater to a specified remedial standard, including toxic intermediate dechlorination products. Groundwater geochemical data collected during system monitoring also may be evaluated to demonstrate whether aquifer ORP and geochemical conditions have been modified as planned, and to detect changes in environmental conditions that may optimize or reduce the efficacy of the biostimulation system. Therefore, multiple lines of evidence should be used to evaluate biostimulation applications. Tools have been developed to assist in evaluating biostimulation applications and to optimize system performance. Examples include MBTs and CSIA, and the practitioner is encouraged to become familiar with these and other developing tools to increase the number of sites where the technology is successfully applied.

12.5.2 Biostimulation Protocols, Reference Documents, and On-line Resources

There are many substrate alternatives and system configurations that can be employed to stimulate anaerobic reductive dechlorination. Numerous protocols and guidance documents have been produced regarding biostimulation for remediation of chlorinated solvents. The following is a partial list of guidance documents and web sites relevant to the practice of biostimulation:

- *Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents*. Prepared by Parsons Infrastructure & Technology Group, Inc. for AFCEE, NFESC and ESTCP. August 2004. Available at: http://www.afcee.af.mil/resources/technologytransfer/programsandinitiatives/enhancedinsituanaerobicbioremediation/resources/index.asp.
- *Protocol for In Situ Bioremediation of Chlorinated Solvents Using Edible Oil.* Prepared for AFCEE by Solutions IES, Inc., Terra Systems, Inc. and Parsons Infrastructure & Technology Group, Inc. October 2007. Available at: http://www.afcee.af.mil/resources/technologytransfer/programsandinitiatives/enhancedinsituanaerobicbioremediation/resources/index.asp.
- *Technical Protocol for Enhanced Anaerobic Bioremediation Using Permeable Mulch Biowalls and Bioreactors.* Prepared for AFCEE by Parsons Infrastructure & Technology Group, Inc. May 2008. Available at: http://www.afcee.af.mil/resources/technologytransfer/programsandinitiatives/enhancedinsituanaerobicbioremediation/resources/index.asp.
- *Final Technical Protocol for Using Soluble Carbohydrates to Enhance Reductive Dechlorination of Chlorinated Aliphatic Hydrocarbons*. Prepared by ARCADIS, Inc. for ESTCP and AFCEE. December 2002. Available at: http://www.estcp.org/viewfile.cfm?Doc=CU%2D9920%2DPR%2D01%2Epdf.
- *Engineered Approaches to In Situ Bioremediation of Chlorinated Solvents: Fundamentals and Field Applications.* USEPA Office of Solid Waste and Emergency Response. EPA 542-R-00-008. July 2000. Available at: http://clu-in.org/download/remed/engappinsitbio.pdf.

- *Technical and Regulatory Requirements for Enhanced In Situ Bioremediation of Chlorinated Solvents in Groundwater.* Interstate Technology and Regulatory Council (ITRC). December 1998. Available at: http://www.itrcweb.org/Documents/ISB-6.pdf.
- *A Systematic Approach to In Situ Bioremediation in Groundwater, Including Decision Trees on In Situ Bioremediation for Nitrates, Carbon Tetrachloride, and Perchlorate.* ITRC Technical Regulatory Guidelines. August 2002. Available at: http://www.itrcweb.org/Documents/ISB-8.pdf.
- *Enhanced Attenuation: Chlorinated Organics.* Prepared by the ITRC Enhanced Attenuation: Chlorinated Organics Team. April 2008. Available at: http://www.itrcweb.org/Documents/EACO-1.pdf.
- *In Situ Bioremediation of Chlorinated Ethene: DNAPL Source Zones.* Prepared by the ITRC Bioremediation of DNAPLs Team. June 2008. Available at: http://www.itrcweb.org/Documents/bioDNPL_Docs/BioDNAPL3.pdf.
- *Bioremediation and Natural Attenuation: Process Fundamentals and Mathematical Models.* Alvarez PJJ, Illman W. 2005. John Wiley & Sons, New York, NY. 609 p. ISBN No. 0-471-65043-9.
- *Natural and Enhanced Remediation Systems.* Suthersan SS. 2001. Lewis Publishers, Boca Raton, FL. 440 p. ISBN 1-56670-282-8.
- *In Situ Remediation Engineering.* Suthersan SS, Payne F. 2004. CRC Press, Boca Raton, FL. 520 p. ISBN 1-56670-653-X.

12.5.3 The Future of Biostimulation

Biostimulation will continue to be at the forefront of technologies used for treating chlorinated solvents in groundwater for the foreseeable future. Biostimulation also is being demonstrated by the ESTCP, the Air Force, the Navy and the Army for perchlorate and energetics (Stroo and Ward, 2009), and it is anticipated that the technology will continue to be developed for other contaminants in groundwater subject to anaerobic degradation or transformation processes (e.g., heavy metals).

Research and development for biostimulation approaches is continuing. One promising research area is the potential to improve performance and efficiency by using alternate degradation processes such as biogeochemical transformations of chlorinated solvents (AFCEE et al., 2008). The process has been documented at the laboratory and field scale, and efforts are under way by AFCEE to engineer the process by modifying the biostimulation approach.

In addition, advanced diagnostic tools continue to be developed. Such tools can be used to evaluate biogeochemical or microbial insufficiencies during a biostimulation application. The use of molecular screening techniques holds promise for evaluating the presence of appropriate microbial species and communities. These diagnostic tools can be used to modify a biostimulation approach to achieve optimal performance, and the consistency with which remedial objectives are achieved using biostimulation should continue to improve.

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CHAPTER 13

BIOAUGMENTATION FOR ANAEROBIC BIOREMEDIATION OF CHLORINATED SOLVENTS

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13.1 INTRODUCTION

Bioaugmentation involves the introduction of microorganisms into soil or groundwater to improve biological activity. Though used for other purposes, such as improving agricultural yields or efficiency, the use of bioaugmentation to promote the degradation of contaminants in the subsurface has increased significantly in recent years (Gentry et al., 2004). Bioaugmentation has been viewed with skepticism in the past, but there has been increasing evidence in recent years that it can accelerate the bioremediation of some contaminants under some site conditions. Bioaugmentation has become particularly useful for treating groundwater contaminated with chlorinated solvents.

Two general bioaugmentation approaches have been used for chlorinated solvents. The first is based on the process of aerobic cometabolism, in which organisms grow on one compound yet fortuitously degrade another. Bacterial cultures capable of cometabolism of trichloroethene (TCE) when grown on another compound (such as propane or toluene) have been tested under field conditions (Hopkins et al., 1993; Hopkins and McCarty, 1995; Duba et al., 1996; Steffan et al., 1999), and bioaugmentation to enhance the aerobic cometabolism of chlorinated solvents has been used commercially to some extent (e.g., http://www.cl-solutions.com). This section will focus primarily on the second process, reductive dechlorination. Bioaugmentation to improve anaerobic reductive dechlorination has been extensively studied, and has been used successfully in several field demonstration and hundreds of commercial remediation projects to improve the rate and extent of reductive dechlorination (Lendvay et al., 2003; Major et al., 2002; ESTCP, 2005).

The conventional wisdom long has been that if the correct environmental conditions were created, the desired degradation reaction would invariably occur. That view has been largely correct for most groundwater contamination problems. However, the last decade has seen the development and commercialization of several new microbial inoculants for the remediation of chlorinated solvents in groundwater, and controlled field demonstrations have shown that these cultures can improve bioremediation performance at many sites (ESTCP, 2005). So what is different in this case?

First, the niche is relatively unique. Suitable organisms might not be present at some sites. Many organisms can degrade petroleum hydrocarbons, for example, and acclimation times are generally short. In contrast, *in situ* biodegradation of chlorinated solvents exhibits extremely long lag times in some cases. Organisms that degrade chlorinated solvents grow slowly compared to petroleum hydrocarbon degraders. Hence, even when the right "type" of solvent degraders are present, their concentrations often are too low to produce rates of biodegradation required for cost effective remediation. However, organisms introduced

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through bioaugumentation have shown an ability to become established following the development of sufficiently reducing conditions (Ellis et al., 2000; Ritalahti et al., 2005). Second, most of the new inoculants have been developed based on credible peer reviewed research that is available in the public domain. Independent research by multiple organizations has provided a comprehensive understanding of the significant biodegradation pathways and the roles of the specific microorganisms that mediate these pathways (ESTCP, 2005).

In addition, independent field verification of the performance of bioaugmentation is available for several sites and microbial cultures (ESTCP, 2005). These experiences have greatly increased confidence in the general approach and in the reliability of bioaugmentation as a credible technology. Finally, improved testing methodologies are now available to determine whether the bacteria known to be responsible for specific chlorinated solvent biodegradation reactions are present at a site (e.g., Löffler et al., 2000; Müller et al., 2004). This information can enhance the ability to predict, to some extent, whether bioaugmentation may be required at a given site, or whether it may be beneficial (e.g., by reducing cost or the duration of suboptimal performance).

Bioaugmentation is still an innovative approach to bioremediation, but progress has been rapid. New cultures and approaches will undoubtedly be developed. A review at this time will not be the final word, but it can provide a useful summary of the basis for bioaugmentation for *in situ* bioremediation of chlorinated aliphatic hydrocarbons (CAHs) in groundwater, and the options for implementing this technology.

The goals of this chapter are to (1) summarize the current status of this rapidly evolving innovative technology, (2) identify the key scientific issues confronting further implementation, (3) evaluate the lessons learned from current practical applications, and (4) provide some guidance for site managers in determining when bioaugmentation is needed to enhance the rate and/or completeness of bioremediation of chlorinated solvent contamination of groundwater.

13.2 SCIENTIFIC BASIS

Early attempts at bioaugmentation focused primarily on treating petroleum hydrocarbons and were viewed with considerable skepticism by regulators and scientific reviewers (ESTCP, 2005). One useful outcome of these early efforts was the development of criteria for evaluating bioaugmentation proposals. For example, the criteria developed by the Ontario Ministry of the Environment (Major and Cox, 1992) are summarized in Table 13.1

The need for bioaugmentation to treat CAHs is based on the fact that organisms capable of complete dechlorination are not ubiquitous and are often present in low numbers. Further, their growth rates are slow, and “stalling” of dechlorination at dichloroethene (DCE) or vinyl chloride (VC) has been observed at many sites. The ability of bioaugmentation to overcome stalling, or at least reduce the time required to achieve complete dechlorination, has been demonstrated in several carefully controlled and well monitored field studies (see Section 13.7).

This section describes the fundamental science that serves as the technical basis for bioaugmentation for chlorinated solvent remediation. This discussion will provide a basis for later sections on the practical implementation of bioaugmentation, including information on the commercial cultures available, and guidance on the selection and implementation of bioaugmentation.

13.2.1 Dehalorespiration and *Dehalococcoides*

Anaerobic reductive dechlorination of chloroethenes (e.g., perchloroethene [PCE], TCE, DCE, VC) when linked to energy yielding respiratory metabolism (as opposed to cometabolism) is commonly referred to as dehalorespiration, or more specifically chlororespiration. Dehalorespiration also encompasses the reductive metabolism of other chlorinated and brominated compounds. Dehalorespiration also can refer to reactions other than reductive dehalogenation, including dihaloelimination (Smidt and de Vos, 2004), which is particularly relevant to the reduction of chlorinated ethanes, including 1,1,2-trichloroethane (1,1,2-TCA) and 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA) (Lorah and Voytek, 2004).

Table 13.1. Criteria for Acceptance of Bioaugmentation. Developed by Ontario Ministry of the Environment (Major and Cox, 1992).

Criterion	Description
Need	Proof that bioaugmentation for a specific contaminant is necessary. Specifically, confirmation that the required degradation activity is absent from the indigenous microbial population. In some cases, bioaugmentation may not be *essential*, but it may be useful to hasten the onset of complete degradation or ensure that it can occur.
Viability	Proof that inoculants contain live, healthy bacteria with the ability to completely degrade the target contaminants, and successfully compete with indigenous bacteria.
Distribution	Proof that inoculants can be distributed in the soil and groundwater given the effect of adsorption, nutrient competition, filtration and predation.
Verification	Confirmation from replicated field trials with proper controls and monitoring that any observed contaminant degradation results from the bioaugmented microbial populations.
Quality Assurance/ Quality Control	Implementation of efficacy and quality controls to ensure a consistent composition of the microbial inoculant between production batches.
Safety	Verification that inoculants are free of plant and animal pathogens (particularly those inoculants composed of (a) consortia of microorganisms).
Cost-Effectiveness	Low cost, requiring only small amounts of added biomass, and not requiring extreme manipulations of environmental conditions to allow introduced organisms to be effective.
Credibility	Prevention of specious claims by vendors.

A decade of microbiological research on dehalorespiration and reductive dechlorination in general has laid a firm basis for the use of cultures containing select mixtures of *Dehalococcoides* species and other beneficial, syntrophically related microorganisms (e.g., hydrogen producing fermentative bacteria) to improve enhanced reductive dechlorination (ERD) systems (Major et al., 2003). Key findings from this research are summarized below.

Many microorganisms have been isolated in pure culture that can reductively dechlorinate PCE and TCE as terminal electron acceptors during oxidation of hydrogen (H_2) as electron donor, and obtain energy from the process for cell growth. Not all dechlorinators can dechlorinate PCE or TCE beyond *cis*-DCE to ethene. All of the cultures that are capable of dechlorination beyond *cis*-DCE contain organisms in the genus *Dehalococcoides* (Maymó-Gatell et al., 1997; Adamson and Parkin, 2000; Ellis et al., 2000; Fennell et al., 2001; Duhamel et al., 2002; Richardson et al., 2002; Cupples et al., 2003; He et al., 2003a).

Several gene sequences from *Dehalococcoides* 16S ribosomal ribonucleic acid (rRNA) (i.e., RNA from the 16S subunit of the ribosome, or 16S rRNA) have been analyzed to date. Although many are similar, they are not identical. These sequences fall into three clusters, designated by Hendrickson et al. (2002) as the Cornell (containing *Dehalococcoides ethenogenes* 195), Victoria and Pinellas sub groups. Hendrickson et al. (2002) also showed that although the presence of *Dehalococcoides* does not necessarily indicate that complete chloroethene reduction to ethene will occur, the converse does appear to be true (if *Dehalococcoides* is absent, then dechlorination past *cis*-DCE and VC to ethene does not occur). Similarly, Lu et al. (2006) found that the presence of detectable *Dehalococcoides* deoxyribonucleic acid (DNA) in groundwater was associated with complete dechlorination, but little attenuation was measured at sites without detectable *Dehalococcoides*.

Not all strains of *Dehalococcoides* have the same degradation capabilities. For example, strain 195 obtains energy from only the first three dechlorination steps (PCE to TCE, TCE to DCE, DCE to VC) but can only transform VC to ethene through cometabolism (Maymó-Gatell et al., 1999, 2001). On the other hand, some mixed cultures containing strains of *Dehalococcoides* rapidly dechlorinate PCE or TCE to ethene with little accumulation of intermediates. Some of these cultures demonstrate sustained dechlorination of VC to ethene when supplied with only VC as electron acceptor (Duhamel et al., 2002; He et al., 2003a), and some strains can obtain energy from VC dechlorination (Cupples et al., 2003; Löffler et al., 2003). The *Dehalococcoides* 16S rRNA gene sequences from these VC dechlorinating cultures fall into either the Pinellas or Victoria sub groups.

The implications of this research are that *Dehalococcoides* occupies a unique environmental niche. Field surveys have also shown that *Dehaloccocoides* are often present at low numbers in the subsurface or even absent from some locations (Hendrickson et al., 2002). In addition, the numbers of *Dehalococcoides* cells sometimes increase slowly in response to biostimulation, resulting in significant lag times before complete dechlorination is observed. Therefore, there has been great interest in bioaugmenting with strains capable of superior performance to reduce lag times and/or to ensure that complete dechlorination will occur. Controlled and carefully monitored microcosm and field tests have since demonstrated that added *Dehalococcoides* strains can survive and compete with other dechlorinating bacteria and can produce more rapid and complete dechlorination (e.g., Lendvay et al., 2003; Major et al., 2002).

Research has also shown that the common practice of identifying *Dehalococcoides* at a field site by the 16S rRNA gene sequence may suggest the potential for dechlorinating activity, but it is insufficient evidence by itself (He et al., 2003a; Duhamel et al., 2004). Strains virtually indistinguishable on the basis of 16S rRNA genes have demonstrably different chlorinated ethene degradation capabilities. Therefore, although more comprehensive diagnostic molecular biological tools (MBTs) may become available to make practical distinction among strains, complementary evidence (e.g., microcosms, appropriate field data) is currently required to conclusively assess dechlorinating capabilities at a site (ESTCP, 2005; Stroo et al., 2006).

Recently developed MBTs have greatly increased our ability to determine if bioaugmentation is needed. Specifically, gene probes that can detect and quantify the presence of three key reductive dehalogenase genes provide considerable insight into the biological potential for natural or enhanced attenuation (Müller et al., 2004; Holmes et al., 2006). The DNA sequences that the probes recognize are designated *tce*A, *vcr*A and *bvc*A. The *tce*A gene codes for the enzyme that can degrade TCE to *cis*-DCE, and *vcr*A and *bvc*A are both genes coding for vinyl chloride reductase enzymes. Vinyl chloride reductases catalyze the last steps of dechlorination, the degradation of VC to ethene. The *vcr* and *bvc* genes are two apparently common VC reductases, but there are others (Holmes et al., 2006). So molecular biological analysis cannot provide conclusive evidence that bioaugmentation is needed at a site, at least not yet. However, the presence of one or both of these VC reductases can be powerful evidence that bioaugmentation is not essential, and it can provide a direct measure of the desired biological activities of native or introduced microorganisms.

13.2.2 Survival and Distribution of Bioaugmentation Cultures in the Subsurface

The ability of an exogenous organism to survive and migrate through the subsurface long has been an area of interest in microbial ecology; in many cases, added organisms do not fare well. Survival of organisms added to soil or groundwater is rare. There are numerous reasons for the often observed failure of added organisms to survive (e.g., Massol-Deya et al., 1997), including predation, parasitism, inability to compete for nutrients or substrates, or environmental conditions to which they are not acclimated or adapted (e.g., Goldstein et al., 1985).

However, in some cases, the added organism may have an inherent advantage for long-term survival, particularly if the subsurface environment is also modified in such a way that added bacteria will have a selective advantage. For example, Criddle and coworkers were able to demonstrate successful bioaugmentation for enhancing carbon tetrachloride (CT) degradation by *Pseudomona*s sp. strain KC by adjusting the pH and oxidation-reduction potential (ORP) of a contaminated aquifer to favor the strain (Criddle et al., 1990; Dybas et al., 1998).

The *Dehalococcoides* have proven capable of surviving and colonizing the subsurface at many CAH contaminated sites, particularly after electron donors have been added to change the ORP conditions and provide hydrogen through anaerobic fermentation. For example, Major et al. (2002) demonstrated that the number of *Dehalococcoides* cells increased at least tenfold as a result of growth after bioaugmentation.

What factors account for this impressive ability of *Dehalococcoides* to survive and grow when its numbers in the subsurface are usually extremely low? One factor may be that the *Dehalococcoides* are efficient users of hydrogen. Their affinity for H_2 is higher and their threshold for H_2 scavenging is lower than those of competing organisms such as methanogens, (Smatlak et al., 1996) and they are capable of outcompeting other organisms for hydrogen (Fennell et al., 1997; Duhamel et al., 2004). Furthermore, the *Dehalococcoides* tolerate concentrations of chloroethenes high enough to inhibit methanogenesis (Duhamel et al., 2004). The apparently unique ability of the *Dehalococcoides* to utilize DCE and VC as electron acceptors offers these organisms an otherwise unoccupied metabolic niche. The combination of these advantages allows these organisms to compete with other subsurface organisms at chlorinated solvent sites and to colonize the subsurface upon bioaugmentation.

Bioaugmentation can be effective without significant bacterial transport if the remedial design calls for creating a relatively static biobarrier through which contaminated groundwater flows (Dybas et al., 1998). This approach is particularly applicable at sites where the source of the contamination cannot be directly treated and when it may take a considerable period of time before all of the contaminated groundwater passes through and is treated in the biobarrrier.

At many sites, it is desirable to treat the entire contaminant plume over a short period of time. In these cases, it is essential that an effective concentration of microorganisms be transported throughout the area of subsurface contamination. Efficient transport and dispersion of bacteria in the subsurface can significantly reduce the cost of bioaugmentation by reducing the number of injection points, as well as the time it takes to impact and remediate the entire volume of contaminated groundwater. In order to design remediation systems that depend on bacterial transport, it is necessary to understand the particular biological, physical and geochemical conditions that affect transport.

Microbial transport in the subsurface depends on a number of characteristics of the cells themselves and the environment into which they are introduced (Table 13.2). The factors that can affect bacterial transport include physicochemical factors such as grain size, flow velocity, solute chemistry and mineral surface charges, as well as biological factors such as cell size, motility and chemotaxis, growth and cell surface properties such as charge, hydrophobicity and

Table 13.2. Factors Impacting Microbial Transport and Growth

Impact on Microbial Growth and Survival	Impact on Microbial Transport	References
pH		
Must remain within tolerance range for specific microorganisms	Ionization of mineral grains and coatings can enhance transport at high pH.	Scholl and Harvey, 1992
Ionic Strength		
Minimal within typical range of ionic strength for groundwater	Increased ionic strength reduces electrostatic repulsion and can inhibit transport by increasing adhesion.	Scholl et al., 1990
Grain-size Distribution		
Soil particles provide sites for biofilm growth	Enhanced migration in coarse soil. Surface charge effects of clay fraction may retard particle migration. Size exclusion may enhance transport.	Harvey et al., 1989; Mayotte et al., 1996
Soil Mineralogy		
Some minerals can provide limiting nutrients (e.g., iron, phosphorus)	Metal oxyhydroxide coatings may retard transport due to charge interactions.	Rogers, 2002; Scholl et al., 1990
Nutrient Availability		
Bioavailable dissolved organic substrates may be utilized metabolically for cell growth and division	Nutrient addition increases aqueous-phase bacteria and enhances transport by promoting growth.	Murphy et al., 1997
Groundwater Velocity		
Minimal	Increasing groundwater velocity can increase cell detachment rates; higher velocity also can decrease attachment of non-motile cells.	Camesano and Logan, 1998; McCaulou et al., 1995; Marlow et al., 1991
Bacterial Cell Surface		
Multiple effects depending on the cell surface characteristic, the geochemistry and mineralogy of the subsurface	Key features include surface charge, surface polymers and proteins, hydrophobicity and the presence of flagella or pili. These affect adhesion and therefore transport.	Sharma et al., 1995; Camesano and Logan, 2000; DeFlaun et al., 1990; Ginn et al., 2002
Bacterial Motility		
Motile bacteria can move to favorable environments, enhancing growth and survival	Motile bacteria exhibit chemotaxis and have the ability to enhance their transport.	Barton and Ford, 1997; Jenneman et al., 1985; Reynolds et al., 1989
Inoculum Cell Density		
Higher cell densities provide more opportunity for added microorganisms to colonize favorable environmental niches	Higher inoculum densities may reduce transport if cell-to-cell interactions are more favorable than cell surface. Otherwise, higher cell densities may enhance transport by blocking attachment sites.	Camesano and Logan, 1998; Ginn et al., 2002; Warren et al., 1992

extracellular polymeric substances (Fontes et al., 1991; Warren et al., 1992; Weiss et al., 1995; Harvey, 1997; Ginn et al., 2002; Marlow et al., 1991).

In general, the relative homogeneity associated with most laboratory column studies underpredicts the extent of transport in the field (Scheibe et al., 2001; Mailloux et al., 2003). In part, this is due to the effects of field-scale heterogeneities and preferential flow paths that can allow rapid transport through more permeable areas (e.g., Harvey et al., 1993). Nevertheless, controlled field tests have shown that the majority of introduced bacteria do not travel very far from the injection point (Harvey, 1997; DeFlaun et al., 1997). This is most likely due to adhesion to mineral surfaces, which can be exacerbated by cell-to-cell adhesion. Attempts have been made to develop non-adhesive bacteria to improve the transport after addition (DeFlaun et al., 1997). However, growth and continued migration over time are at least as important as the initial transport in the success of bioaugmentation with *Dehalococcoides* (Major et al., 2002).

13.2.3 Emerging Applications

Subsurface bioaugmentation applications are currently overwhelmingly focused on the dehalorespiration of chlorinated ethenes by *Dehalococcoides* organisms, although in the future, bioaugmentation will undoubtedly be applied to compounds other than the chloroethenes. For example, there appears to be significant potential for using *Dehalococcoides*-type organisms for *in situ* biodegradation of chlorinated benzenes, ethanes and propanes, as well as polychlorinated biphenyls, dioxins, and brominated ethenes, ethanes and ethers (Fagervold et al., 2005; Fennell et al., 2004).

In particular, the dechlorination of some chloroethanes represents a promising target for bioaugmentation with *Dehalococcoides*. 1,2-dichloroethane (1,2-DCA) is by far the most common chloroethane contaminant of groundwater and is often recalcitrant in the environment. Given that biodegradation of 1,2-DCA is possible by aerobic and anaerobic means (Vogel and McCarty, 1985) and that high concentrations of 1,2-DCA are present in groundwater in some chemical refining and manufacturing centers, development or use of existing bioaugmentation cultures for remediation of this contaminant at field sites is likely. Other promising applications include 1,1,1-TCA, which is also recalcitrant but can be degraded anaerobically (Sun et al., 2002) and possibly 1,1,2,2-TeCA (e.g., Chen et al., 1996).

13.3 THE PRACTICE OF BIOAUGMENTATION

Bioaugmentation for improving the reductive dechlorination of chlorinated solvents in the subsurface is rapidly becoming a commercially successful practice despite several scientific uncertainties. The following sections summarize what is known about the state of the practice, including the cultures currently used for bioaugmentation to enhance reductive dechlorination, as well as the quality assurance/quality control (QA/QC) procedures and safety issues, such as ensuring the absence of potential pathogens. This section also includes a brief review of the options for implementing bioaugmentation and a discussion of the environmental factors that can affect its success.

13.3.1 Cultures Available

Several enriched microbial cultures have been described in the peer reviewed literature and developed for commercial use to bioremediate chloroethenes. The aerobic bioaugmentation cultures are summarized in Table 13.3; the anaerobic bioaugmentation cultures are summarized in Table 13.4. The anaerobic cultures include KB-1® (developed at the University of Toronto

Table 13.3. Bioaugmentation Cultures Developed for Aerobic Bioremediation of Chlorinated Solvents

Developer	Culture Source	Target Contaminants	Commercial Vendors	Primary Degradation Pathway	Growth Conditions	Pathogenicity	Key References
CDM and Colorado State University	Not specified	TCE	No vendor	Cometabolic oxidation	Aerobic basal salts medium (7.2 g/L sucrose, yeast extract) at pH=6.0, maintained at 30°C	USEPA has determined that *B. cepacia* has the potential to cause severe infection in sensitive populations (cystic fibrosis patients)	Bourquin et al., 1997
Envirogen	Adhesion deficient strain developed by Envirogen	TCE	No vendor	Cometabolic oxidation	Aerobic basal salts medium (1.6% sucrose) at pH=7.0, maintained on alternating batches of sucrose or phenol	USEPA has determined that *B. cepacia* has the potential to cause severe infection in sensitive populations (cystic fibrosis patients)	Steffan et al., 1999
Lawrence Livermore National Laboratory	Pure culture obtained from a national culture inventory	TCE	No vendor	Cometabolic oxidation	Higgin's salts minimal medium lacking added copper	Non-pathogenic	Duba et al., 1996
Michigan State University	Not reported	CT	No vendor	CT degradation to carbon dioxide (CO_2), formate, and an unidentified nonvolatile product without producing chloroform	Grown in filter-sterilized groundwater (20°C, pH=8.2, 10 mg/L phosphate, 1.6 g/L acetate) at pH 8.0–8.2	Not known (high density of "contaminant" organisms present in the culture)	Dybas et al., 1998, 2002

Note: ^{o}C - degree Celsius; g - gram; L - liter; mg - milligram; N/A - not applicable; USEPA - U.S. Environmental Protection Agency

Table 13.4. Bioaugmentation Cultures Used for Anaerobic Treatment of Chlorinated Solvents in Groundwater (from ESTCP, 2005)

Developer	Culture Source	Target Contaminant	Commercial Vendors	Primary Degradation Pathway	Key Microbial Species	Growth Conditions	Pathogenicity	Key References
KB-1 Culture								
E. Edwards (University of Toronto) and Geosyntec Consultants	TCE-contaminated aquifer, Ontario, Canada	Chloroethenes	SiREM	Reductive dechlorination (dehalorespiration)	*Dehalococcoides, Acetobacterium, Geobacter* sp., *Methanospirillum, Methanosaeta*	Anaerobic defined mineral media with TCE and methanol at 23°C and pH 7.0	Negative test results	Duhamel et al., 2002; Major et al., 2002
Pinellas Culture								
Remediation Technologies Development Forum (RTDF)	TCE-contaminated aquifer, Pinellas, FL	Chloroethenes	Terra Systems	Reductive dechlorination (dehalorespiration)	*Dehalococcoides ethenogenes* and others by terminal restriction fragment length polymorphism (T-RFLP)	Chloride free minimal media containing yeast extract, lactate and TCE at 24°C and pH 7.0	Not reported	Ellis et al., 2000
Bachman Road Culture (BC2, Bio-Dechlor)								
F. Löffler (Georgia Institute of Technology)	PCE-contaminated aquifer, Oscoda, MI	Chloroethenes	Regenesis, Bioaug-LLC	Reductive dechlorination (dehalorespiration)	*Dehalococcoides* sp., *Desulfuromonas michiganensis* strain BRS1, *Desulforomonas chloroethenica*	Anoxic bicarbonate-buffered mineral salts medium with lactate as electron donor and PCE as acceptor	Not reported	Löffler et al., 2003; He et al., 2003a, 2003b; Lendvay et al., 2003
SDC-9 Culture								
Shaw Group, Inc.	Volatile organic compound (VOC)-contaminated site	Chloroethenes	Shaw Group, Inc.	Reductive dechlorination (dehalorespiration)	*Dehalococcoides* sp.	Not known	Not reported	Personal communication, R. Steffan, Shaw Group, Inc., 2008
Multiple Mixed Cultures								
Bioremediation Consulting Inc. (BCI)	VOC-contaminated sites	Chloroethenes Chloroethanes	Bioremediation Consulting Inc.	Reductive dechlorination (dehalorespiration)	*Dehalococcoides* sp.	Not known	Negative test results	Personal communication, M. Findlay, BCI, 2005

and commercialized by SiREM), the Bachman Road culture (the source for both Regenesis's BioDechlor INOCULUM® and the BC2 inoculum marketed by BioAug LLC), and the Pinellas culture (developed by General Electric and licensed to Terra Systems). In addition, there are a number of other cultures currently being used commercially, including SDC-9, developed by Shaw Environmental, Inc., and several unnamed cultures marketed by Bioremediation Consulting Inc. (BCI).

Note that all of the commercial inocula are mixed cultures. Although pure cultures have been isolated and have proven useful for research, *Dehalococcoides* spp. do not grow as well in pure culture as in mixed cultures. For one thing, the *Dehalococcoides* require H_2 as electron donor and acetate as carbon source. Molecular H_2 is not a very practical donor to deliver to the subsurface because it is sparingly soluble and explosive. Therefore, donor is commonly delivered in a more complex form (methanol, ethanol, lactate, butyrate, carbohydrate, etc.), requiring the presence of a fermentative population to convert to H_2 and acetate. Additionally, *Dehalococcoides* strains presumably receive benefit from growth factors such as B_{12} produced by other members of the microbial community. Although many of the organisms present in augmentation cultures have been identified, the roles of the various organisms present need to be better understood (Duhamel et al., 2002).

The various *Dehalococcoides* strains in these cultures do not all have the same metabolic capabilities (Table 13.5). Some strains are capable of metabolizing each of the chloroethenes, while some strains can perform only a few dechlorination steps and others dechlorinate additional chloroethenes through cometabolism.

The enrichment and culture conditions for the bioaugmentation cultures also vary. In particular, several different soluble electron donors have been used, including methanol, ethanol, lactate, benzoate and butyrate. Some enrichment cultures are maintained on hydrogen, but soluble electron donors are more easily fed to cultures and provide both energy and a carbon source for growth.

Table 13.5. Abilities of *Dehalococcoides* Strains to Dechlorinate Selected Chlorinated Aliphatic Hydrocarbon Compounds

Strain	PCE	TCE	*cis*-DCE	VC	1,2-DCA	Reference
195	Yes	Yes	Yes	Cometabolic	Yes	Maymó-Gatell et al., 1997
VS	—	Yes	Yes	Yes	—	Cupples et al., 2003
CBDB-1	Yes	Yes	—	—	—	Bunge et al., 2003
FL2	Cometabolic	Yes	Yes	Cometabolic	—	Löffler et al., 2003
BAV1	Cometabolic	Cometabolic	Yes	Yes	Yes	He et al., 2003a
KB-1[1]	Yes	Yes	Yes	Yes	Yes	Duhamel et al., 2004
GT	—	Yes	Yes	Yes	—	Sung et al., 2006

— No activity observed
[1] Contains two *Dehalococcoides* strains with different capabilities

13.3.2 QA/QC Issues

Quality control is important for a bioaugmentation inoculum, particularly the mixed cultures used for chlorinated solvent biodegradation, for at least two reasons. First, there is some potential for adverse impacts to groundwater quality during bioaugmentation resulting from the inadvertent inclusion or introduction of pathogenic or opportunistic microorganisms. Equally important is the potential for adverse impacts to the dechlorinating activity of the bioaugmentation inoculum (e.g., as a result of contamination of, or changes to, the mixed culture used for inoculation). Implementing QA/QC protocols to prevent these impacts will encourage the effective application of bioaugmentation and, in the longer term, increase the acceptance of bioaugmentation as a credible remediation technology.

Dehalococcoides spp. and the other organisms commonly associated with bioaugmentation cultures (e.g., methanogens, acetogens) are generally non-pathogenic. There is always a concern that other unknown or unidentified organisms exist in enrichment cultures, and the potential presence of human or animal pathogens cannot be completely ruled out (Govan et al., 2000). Further, there is always some concern over the potential for pathogenicity in the consortium as it is applied because of changes that may occur as it is grown up for application.

Safe and effective application of bioaugmentation on a commercial/field scale requires vigilance beyond simply ensuring effective dechlorination. Large-scale culture production procedures and methodologies should maintain consistent microbial density, performance and composition, minimize the absence of pathogenic or opportunistic microorganisms, utilize delivery vessels and protocols that preclude exposure to oxygen and provide at least some understanding of culture performance under a wide range of site conditions.

All of the major subsurface bioaugmentation vendors listed in Table 13.4 have QA/QC procedures in place, yet the procedures differ and there are no standards for ensuring culture quality or the absence of pathogens (ESTCP, 2005). There is clearly a need for accepted QA/QC protocols for the production and shipment of bioaugmentation cultures to field sites for application. At a minimum, such protocols should ensure the following:

- The degradative activity and composition of each batch of the culture is comparable to that of the original culture for which reliable field performance and characterization data are available.
- The degradative microorganisms in the culture are not displaced or reduced in number by pathogenic or other opportunistic microorganisms (including phages) during production, shipment or introduction to the subject site.
- The density of the culture is reasonably uniform between successive production batches.
- The viability and dehalogenation activities of the culture at the time of injection are at the highest possible levels.

13.3.3 Implementation Options

Most applications of subsurface bioaugmentation have used a relatively aggressive approach of hydrologic recirculation to distribute cultures as thoroughly as possible throughout the target treatment zones. Bioaugmentation cultures are added to the subsurface in an aqueous solution through temporary or permanent injection wells and recirculated through the treatment zones by extraction from other wells and subsequent reinjection. Recirculation may be continued for several days or weeks to encourage thorough distribution. This approach is a fairly expensive one, but the advantages include relatively wide spacing of injection points and the best possible initial distribution of the added cultures (Major et al., 2005).

There also has been interest in a more passive bioaugmentation approach, in which the organisms are injected into the subsurface and allowed to spread through advection, dispersion, colonization and growth over time into areas further from the injection points. This approach has the advantages of low cost and limited on-site labor needs, but the current incomplete understanding of microbial transport makes it difficult to predict transport and dispersal in such passive systems (ESTCP, 2005).

The timing of culture addition also should be considered. Bioaugmentation is generally done soon after electron donor addition, once sufficient reducing conditions have been established in the subsurface. In some cases, augmentation has not been done until after several months of biostimulation have been attempted, and results have shown that dechlorination has apparently stalled at *cis*-DCE or VC. Although it would seem more difficult to augment a site after a community has become established following months of biostimulation, vendors report that it has been done successfully at several sites (ESTCP, 2005).

13.3.4 Factors Affecting Bioaugmentation Success

Several factors can affect the establishment and performance of bioaugmentation cultures introduced into groundwater environments. These include exposure to oxygen, competition for electron donor by organisms utilizing other electron acceptors, type and concentration of electron donor used, temperature and pH, concentrations of the target chlorinated solvents and the presence of other chlorinated solvents. These factors are briefly discussed in the following sections.

13.3.4.1 Oxygen Tolerance

Dehalococcoides spp. are strictly anaerobic microorganisms (Maymó-Gatell et al., 1997) and even minimal oxygen exposure can be toxic (He et al*.,* 2003a; Seepersad, 2001). Care must be taken during culture transport and injection to prevent or limit exposure to oxygen.

13.3.4.2 Geochemical Conditions

Geochemical conditions other than oxygen levels can impact bioaugmentation performance. The appropriate ORP status is essential for effective bioaugmentation. In general, reductive dechlorination is favored under ORP conditions that promote sulfate reduction or methanogenesis (Eh values lower than approximately -200 millivolts [mV]), suggesting that oxygen, nitrate and manganese/iron oxides should be reduced prior to bioaugmentation (AFCEE, 2004). Apparent sulfate inhibition has been observed in several cases, but the issue has been a confusing one. For example, Heimann et al. (2005) observed no sulfate inhibition when electron donor was present in excess, although 240 mg/L of sulfate inhibited dechlorination when electron donor concentrations were limiting. Recent work may have cleared up the confusion by showing that sulfide (naturally present or formed during sulfate reduction) is actually responsible for the toxic effects. This sulfide toxicity can be alleviated by precipitating the sulfide into unavailable mineral forms, for example, by natural or added iron (Hoelen and Reinhard, 2004; Jeong and Hayes, 2003).

Other environmental factors to consider include iron availability, pH and temperature. Iron effects are not well understood, but ferric iron levels may inhibit dechlorination at some sites (Koenigsberg et al., 2002). As with most microbial processes, groundwater pH can affect dehalorespiration. KB-1®, for example, exhibits no dechlorination below pH 5 and above pH 10, and the optimal pH is between 6.0 and 8.3. Although groundwater temperatures in northern climates will undoubtedly slow dechlorination rates, complete dechlorination has been demonstrated in microcosms at temperatures as low as 10°C. Maximum dechlorination rates occur between 20°C and 30°C.

13.3.4.3 Volatile Organic Compound Concentration

The common belief that bioremediation processes are ineffective in high concentration dense nonaqueous phase liquid (DNAPL) source areas has historically restricted the application of the technology to plume containment or treatment (Pankow and Cherry, 1996). However, recent data demonstrate that dechlorinating microorganisms are active over a wide range of chloroethene concentrations. Duhamel et al. (2002) reported that KB-1® promoted dechlorination of PCE, TCE, *cis*-DCE and VC at initial concentrations of 132, 197, 77 and 87 mg/L, respectively. Other researchers have also measured dechlorination in the presence of VOC concentrations typical of groundwater in contact with DNAPL (Adamson et al., 2003; Isalou et al., 1998; Maymó-Gatell et al., 1997; Yang and McCarty, 2000; Carr et al., 2000).

13.3.4.4 Inhibition by Selected Volatile Organic Compounds

While chloroethenes are inhibitory to reductive dechlorination activity only at extremely high aqueous concentrations, several other VOCs have been shown, or are suspected, to exert inhibitory effects on some cultures at much lower concentrations. Specifically, both chloroform and 1,1,1-TCA can inhibit VC dechlorination to ethene by KB-1® (Duhamel et al., 2002). The results suggest competitive inhibition is responsible for the decreased activity, and the VOCs are not irreversibly toxic to the dechlorinators. Chloroform also inhibited *cis*-DCE dechlorination at a concentration of 190 micrograms per liter (µg/L), and PCE dechlorination at 1,000 µg/L (Maymó-Gatell et al., 2001). Inhibition of some dechlorinating cultures by a common cocontaminant such as 1,1,1-TCA suggests that bioaugmentation cultures must be selected carefully and that some cultures may be inappropriate for treating mixed-waste sites. However, TCA-degrading cultures have been found (Sun et al., 2002), and vendors report success in mixing TCA degraders with chloroethene reducing cultures to treat mixed-contaminant plumes (ESTCP, 2005).

13.4 TECHNOLOGY SELECTION ISSUES

Those considering bioaugmentation must address two related questions: whether to bioaugment and, if so, when? Bioaugmentation can be a significant cost item in absolute terms, especially at large sites, at sites requiring aggressive dispersal after the cultures are added (e.g., by hydraulic recirculation), or if conditions necessitate separate injection events solely for the purpose of bioaugmentation. However, in most cases, it represents a small fraction of the total remediation costs. There is also an economic gamble in the timing. Several months of suboptimal performance following biostimulation can cost more than bioaugmenting at the start of treatment. The issues involved are summarized in the following sections.

13.4.1 Whether to Bioaugment

The decision to bioaugment involves economic, political and technical considerations. From a technical perspective, there should be no need to bioaugment sites that have indigenous populations of competent *Dehalococcoides* strains, those mediating complete dechlorination, unless the rates of biodegradation are too slow to meet remedial objectives. According to Hendrickson et al. (2002) and Rahm et al. (2006), most sites examined do have competent indigenous dechlorinating populations. However it is common to observe temporary or even permanent stalling at *cis*-DCE, and bioaugmentation can reduce the time and uncertainty involved in bioremediation. Hence, from an economic and political perspective it appears that bioaugmentation may become a more integral part of bioremediation practice.

It is critical from the start to realize that bioaugmentation is not a “magic bullet” that alone will make bioremediation at any problematic site successful. Several geochemical factors can cause poor performance at sites with competent microbial populations. Some have therefore advocated a “diagnostic” approach to problem sites, in which microbial competence is only one of the potential limitations addressed (Koenigsberg et al., 2004).

There has been considerable debate over whether bioaugmentation is generally beneficial. Some believe that at the vast majority of sites, the desired activities will occur, and it is simply a matter of “more time and more electrons” (e.g., Suthersan et al., 2002; Koenigsberg et al., 2002). While many practitioners agree that bioaugmentation may be necessary to achieve complete dechlorination at relatively few sites, it can make economic sense at many more, because the cost of adding organisms will be less than the cost of the increased time and electron donor (Major et al., 2005; ESTCP, 2005; AFCEE, 2004).

The recent guidance on Enhanced Anaerobic Bioremediation (AFCEE, 2004) recommends that project managers explicitly evaluate the costs and benefits of bioaugmentation before starting a bioremediation project. The costs for bioaugmentation may represent a small fraction of the total costs, and bioaugmentation may in fact pay for itself if it reduces the time until complete dechlorination is achieved by only a few months (Major et al., 2005). The benefits can include reduced electron donor costs, reduced operations and monitoring time (and costs), and increased regulatory acceptance as performance is more rapidly demonstrated. Table 13.6 provides a summary of typical goals for an enhanced *in situ* bioremediation (EISB) program and the factors that can determine whether bioaugmentation will be helpful in achieving those goals.

Table 13.6. Common Goals for *In Situ* Bioremediation and Factors To Be Considered in Deciding Whether Bioaugmentation Can Be Helpful in Achieving Those Goals

Goal	Factors Affecting Decision to Bioaugment
Reduce the time to achieve complete dechlorination	• Microbial capacity is absent and EISB without bioaugmentation will not be successful • Client, regulator and public require faster results to be comfortable or accept EISB as a remedy
Reduce monitoring costs	• Long response times may create demand/desire to conduct more frequent monitoring/sampling to demonstrate that complete dechlorination will occur
Reduce risks during EISB implementation	• Build up and/or persistence of more toxic intermediates (e.g., VC) • Potential exposure to parent of toxic intermediates (e.g., vapor intrusion to nearby buildings, shallow contamination) • Need to rapidly decrease concentrations of parent and intermediate compounds
Reduce expansion of VOC plumes	• Application of EISB in source areas can enhance the flux of VOCs due to formation of more soluble, partially dechlorinated intermediates (e.g., *cis*-DCE from TCE)
Maximize donor value and the efficiency of donor use	• Need to improve efficiency of donor use by decreasing competing processes (e.g., methanogenesis) • Avoid loss of donor value (e.g., donor is being used earlier to achieve complete dechlorination)

Project managers will decide whether or not to bioaugment based on the goals identified in Table 13.6 and the cost to do so. In some cases, a simple technical justification is that EISB will not work because the requisite microorganisms are simply absent or at such low population densities and are so poorly distributed at a site that it would take too long to achieve the remedial objectives. However, there will be many cases where the case for bioaugmentation will not be so clear cut; in those instances, the additional cost of bioaugmentation must be weighed against its value and the relative costs of other components of typical EISB remedies, as indicated in Table 13.7.

Based on one vendor's analysis, AFCEE (2004) reported that the operation and maintenance (O&M) of EISB systems typically consumed 50+% of the total life cycle cost, with substrate representing 10%. This analysis indicates that the vast majority of the cost of EISB is associated with O&M, monitoring and substrates; these cost items also represent the greatest opportunities for cost savings during EISB. Bioaugmentation may represent a significant absolute cost for use at large sites, but it can potentially reduce substrate and monitoring costs substantially, and it is usually a one time event that typically represents 1–5% of the total capital cost for site remediation (Major et al., 2005).

Table 13.7. Tools Available for Evaluating the Need for Bioaugmentation

Tool	Advantages	Limitations
Direct Detection (quantitative polymerase chain reaction [qPCR]): 16S rRNA and functional genes (e.g., *vcr*A)	• Can provide direct proof of *Dehalococcoides* presence • May indicate biological potential for complete dechlorination	• May be very high spatial and temporal variability • Not all functional genes are known
Microcosm Testing	• Proof of desired functions under controlled conditions • Allows time for needed acclimation and growth	• May require 3 to 18 months • More costly than direct detection methods
Geochemical Characterization	• Direct field evidence of desired reactions and environmental conditions	• May require considerable time • Relatively high cost if bioaugmentation is eventually needed

The costs for bioaugmentation are determined largely by the number and type of wells, the well spacing and the distribution system used. If the site is sufficiently shallow and permeable, direct injection (i.e., injection through temporary holes created by Geoprobe rigs), can reduce initial costs, but the use of permanent injection and monitoring wells is common. Well spacing is a function of the hydraulic conductivity and heterogeneity of the subsurface materials, but is also affected by the time allowed for measurable responses and the distribution system used (since passive distribution systems generally require closer spacing than more active systems using recirculation).

The distribution system affects costs in several ways. Most field-scale demonstrations of bioaugmentation have used an active recirculation approach, which requires ongoing pumping and extraction, with resulting labor and equipment costs. However, the recirculation approach has been used primarily to ensure rapid and thorough distribution for the purpose of demonstrating the technology's efficacy in a short time period. Passive injection approaches have been used successfully for several commercial applications, but rigorous demonstrations of the effectiveness of passive injection have not yet been performed (ESTCP, 2005). Some of the advantages of passive systems in terms of lower O&M costs, are offset by the need for a large number of closely spaced wells to achieve adequate distribution of the donor and inoculum (though smaller amounts of the culture can be injected at each point). In some cases, the bioaugmentation culture can be added with the electron donor, using the same distribution methods, so the additional costs for bioaugmentation can be relatively low (culture costs and some additional labor and equipment time).

A key factor in deciding whether to bioaugment at sites with competent *Dehalococcoides* spp. already present is the effect of bioaugmenting on the time required for complete dechlorination. Vendor reports suggest that acclimation times of 6 to 18 months are common in the absence of bioaugmentation and that these can be shortened to perhaps a couple of months. The controlled experiment performed at the Bachman Road site showed that bioaugmentation reduced the time until complete dechlorination was observed from 12 to 6 weeks, despite a competent indigenous *Dehalococcoides* population (Lendvay et al., 2003; see Section 13.7).

Bioaugmentation also may be appropriate at sites where the indigenous *Dehalococcoides* microorganisms are present but are not uniformly distributed. Fennell et al. (2001) reported that the activity of an indigenous *Dehalococcoides* population was nonuniformly distributed in a chlorinated ethene contaminated aquifer at Cape Canaveral Air Force Station, Florida, reporting a direct correlation between the presence of *Dehalococcoides* and the ability to achieve complete dechlorination of *cis*-DCE and VC to ethene. These findings demonstrate that the detection of *Dehalococcoides* in a single location should not be used to infer the microorganisms are present throughout the aquifer. Similarly, the absence of detection from an insufficient number of sampling points should not be inferred to indicate absence of *Dehalococcoides* anywhere on site.

Finally, the regulatory environment can be an important factor in the decision making process. If bioaugmentation reduces the time and uncertainty involved in a bioremediation application, it may well reduce the monitoring and regulatory interaction costs. On the other hand, some regulators are wary of adding organisms, particularly a mixed culture in which not all of the organisms are fully characterized. In such cases, bioaugmentation can increase the design and permitting time and costs.

13.4.2 When to Bioaugment

Regardless of the site-specific extent of dechlorinating activity, bioaugmentation may be employed at several time points during the implementation of an enhanced bioremediation strategy. Currently, the most common application is the use of bioaugmentation as a contingency in the event that the indigenous microbial community does not express sufficient dechlorinating activity (e.g., dechlorination stalls at *cis*-DCE) following electron donor addition.

However, others favor a prophylactic approach, in which organisms are included at the start of electron donor addition if there is any reason to suspect that complete dechlorination may not occur (e.g., based on a combination of treatability and field evidence). Given current practices, the cost of bioaugmentation is low relative to the cost of prolonged electron donor addition, and the prophylactic approach may be preferable since it will improve the likelihood of promoting complete dechlorination and shorten the lag time prior to the onset of ethene formation. Further, it seems possible that bioaugmentation may be more effective if done early rather than allowing competing organisms to become established over several months of donor addition.

A common bioaugmentation practice at industrial sites is to bioaugment immediately following electron donor addition to minimize the establishment of competitive, nondechlorinating microorganisms that may deplete essential nutrients. As well, at field sites where groundwater is aerobic, an initial period of electron donor addition is typically used to deplete dissolved oxygen, which is toxic to *Dehalococcoides*, and develop reducing conditions prior to bioaugmentation. Alternatively, addition of oxygen scavengers or prior reduction of the injection water may allow simultaneous injection of the donor and bioaugmentation culture, reducing implementation costs.

13.5 TOOLS TO ASSESS THE NEED FOR BIOAUGMENTATION

Currently, there are three methods to assess the need for bioaugmentation: direct detection of *Dehalococcoides* using molecular analyses, microcosm testing and interpretation of field geochemical evidence (AFCEE, 2004). While these methods can be used independently, combining assessment methods will lead to a stronger conclusion. The basis, benefits and limitations of each assessment method are discussed in the following sections and are summarized in Table 13.7.

13.5.1 Direct Detection

The unique growth requirements of *Dehalococcoides* spp., and their associations with other microorganisms, preclude using conventional microbial detection techniques such as plate counts for detecting these organisms. Instead, molecular biological techniques using the polymerase chain reaction (PCR) are commonly used to detect and count *Dehalococcoides* spp. in soil or groundwater via the 16S rRNA gene. Improvements in PCR technology have been rapid, and the qPCR methods commercially available can accurately determine the number of *Dehalococcoides* 16S rRNA gene copies in environmental samples (Smits et al., 2004).

PCR methods may also provide information regarding the potential to achieve complete dechlorination at a site, by identifying the strain(s) present. As indicated previously, there are differences in the ability of specific strains of *Dehalococcoides* to dechlorinate chloroethenes; therefore, strain identification may be useful. For example, studies have shown that VC accumulation is associated with strains of both the Cornell and Pinellas sequence subgroups of *Dehalococcoides* (Hendrickson et al., 2002; Maymó-Gatell et al., 1997; He et al., 2003a). The presence of strains from these subgroups can be confirmed through DNA sequencing of PCR products.

Of potentially more value than detecting *Dehalococcoides*, or differentiating its many strains, is the ability to detect key functional genes. Two sets of genes involved in VC dechlorination (VC reductases *vcr* and *bvc*) recently have been discovered and sequenced (Seshadri et al., 2005; Müller et al., 2004; He et al., 2003b). Sequencing has allowed the development of commercially available PCR-based tests for these important functional genes. In addition, new techniques based on quantitative PCR allow the specific measurement of expression products from the functional genes, demonstrating not only the presence of reductive dehalogenase genes but also their active expression (Lee et al., 2006; Johnson et al., 2005). Combining these analyses has great promise for assessing the need for bioaugmentation despite the fact that not all of the reductive dehalogenase genes are known at this time (Ritalahti et al., 2006).

A complicating factor in the use of PCR methods is the interpretation of results below the detection limit. Negative detection of *Dehalococcoides* may result from the detection limit of the assay, although typical methods detect as few as 100 gene copies per liter. However, a particular sample might not contain sufficient *Dehalococcoides* DNA for detection, even at sites that contain this organism at other locations, due to sampling bias inherent in sampling groundwater rather than soil particles. Therefore, the absence of detectable *Dehalococcoides* DNA over several site samples is suggestive (but not conclusive) that *Dehalococcoides* is absent.

13.5.2 Microcosm Testing

Prior to the development of molecular assays, microcosms containing site soil and groundwater were the main laboratory approach for assessing the presence of dehalorespiring microorganisms. Microcosm studies are still used in conjunction with molecular screening to determine the dechlorination activity associated with detected organisms, to determine degradation rates, acclimation periods and dechlorination products, and to optimize electron donor type and dosage. Assessing the need to bioaugment a given site involves comparing the rate, extent and acclimation period (e.g., time to initiate reductive dechlorination and achieve complete dechlorination to ethene) of dechlorination between non-bioaugmented and bioaugmented microcosms. Electron donor amended microcosms that do not dechlorinate PCE or TCE past *cis*-DCE after several months of incubation suggest that bioaugmentation is required.

Helpful guidance on microcosm testing is available from many sources. In particular, guidance on testing for *in situ* bioremediation of chlorinated solvents is included in AFCEE (2004), and a limited discussion of bioaugmentation testing is included in ESTCP (2005).

13.5.3 Geochemical Characterization

There are several geochemical conditions that can be indicative of when bioaugmentation is likely to be required to enhance bioremediation of chloroethenes in groundwater. These include the following:

- **Sites with high ORP conditions:** Aerobic sites, and sites with mildly anaerobic conditions (Eh values greater than -50 millivolts [mV]) generally show little or no evidence of key anaerobic processes (nitrate and/or sulfate are present, iron and manganese are present in oxidized forms, and methane and sulfides are absent). Such conditions will not likely have provided the opportunity for strict anaerobes such as *Dehalococcoides* to become established, although they may well be present in anaerobic microsites.
- **Sites with no VC or ethene before treatment:** Some sites will show evidence of reductive dechlorination of PCE and/or TCE to *cis*-DCE, but VC and ethene may not be present at significant concentrations relative to the parent products and *cis*-DCE. Additionally, it is possible that the presence of PCE or TCE daughter products could be associated with past dechlorination activity (e.g., associated with now depleted cocontaminants that once served as electron donors). In and of itself, the presence of lesser chlorinated daughter products is not evidence of current, or even recent, reductive dechlorination activity. Of note, some production of VC and ethene can occur through other processes, such as anaerobic cometabolic reactions. Accordingly, the presence of trace amounts of VC and ethene in groundwater samples should not be used to infer that complete dechlorination by anaerobic microorganisms is necessarily occurring unless supported by additional lines of evidence (e.g., microcosm studies, molecular screening).
- **Sites that stall during treatment:** Often, production of VC or ethene is not observed within a reasonable timeframe after establishing appropriate ORP/geochemical conditions. While quantification of “reasonable” is subjective, a period of 9 to 12 months of electron donor addition should allow for an increase in an initial *Dehalococcoides* population of 10^2–10^3 cells/L groundwater (a cell concentration near or below typical detection limits) to 10^7 cells/L (a cell concentration correlated with the detection of ethene at field sites by Lu et al. (2006)) based on an assumed doubling time of 20 to 30 days. While longer electron donor periods can be pursued, the cost of long term ineffective electron donor addition is likely to far exceed the cost of an early bioaugmentation.

In addition, it should be noted that the use of compound stable isotope analysis has shown promise as a tool to confirm complete dechlorination and assess the rate and extent of dechlorination (Sherwood-Lollar et al., 2001; Song et al., 2002; Chapter 11 this volume).

13.6 UNCERTAINTIES

To date, bioaugmentation has been conducted using a variety of designs and infrastructure, including both direct injection and recirculation approaches. However, despite the increasing number of bioaugmentation applications, there is still considerable uncertainty and a lack of bioaugmentation protocols. Improved protocols (e.g., injection technique, injection rate, cell density) will likely increase the success and predictability of this technology. Key research questions include:

- **Aquifer Preconditioning:** Current bioaugmentation practices favor a period of aquifer preconditioning during which nutrients, most commonly electron donors, are added to the aquifer to establish the desired ORP conditions (through the activity of indigenous bacteria) prior to bioaugmentation (Ellis et al., 2000; Major et al., 2002). In many cases, the preconditioning phase is also used to assess the degradation potential of the indigenous bacteria and to confirm the need for bioaugmentation. However, the optimal preconditioning approach is not clear. A preconditioning period that is too short may be harmful to the added organisms, but an overly long time may result in poor survival of the added bacteria because of competition with the conditioned indigenous microflora.
- **Culture Requirements:** To date, most field applications of bioaugmentation have involved small-scale demonstrations, or small sites, where the amount of organism added has a minimal effect on treatment costs. In these cases, it may not be necessary to optimize the amount of culture added. However, at sites where large volumes of culture are required, knowing the minimum amount of culture needed for successful remediation could result in considerable cost savings (in absolute terms, even though the percentage of the total costs may still be small). The key driver in determining the amount of culture needed is often the time desired before performance can be measured; greater initial numbers and distribution are needed for rapid responses, while *in situ* growth can be relied upon to a greater extent if more time can be allowed before results are observed.
- **Delivery Methodology:** The bioaugmentation field applications that have been demonstrated to be highly effective have employed recirculation systems rather than direct injection. Several of these studies demonstrated transport, establishment and growth of dehalorespiring bacteria within the subsurface environment. Unfortunately, there is little peer reviewed information regarding the efficacy of bioaugmentation through direct injection, though this method can be far less costly.
- ***In Situ* Transport and Distribution:** Significant questions remain regarding the transport of the various microorganisms in bioaugmentation cultures in the subsurface. While several field demonstrations have shown that *Dehalococcoides* spp. are relatively mobile, little to no information is available describing the transport of other organisms contained in the bioaugmented consortia. Furthermore, little information is available regarding the spatial distribution of dechlorinating activity achieved at the test sites. This information has important ramifications with regard to design of bioaugmentation systems and, in particular, the spacing of bioaugmentation delivery points.

- **Electron Donor Addition and Survival:** A variety of electron donors and feeding strategies have been employed for bioaugmentation projects. However, there is currently little understanding regarding the impact of varying electron donor addition strategies on survival and activity of the introduced cultures. For example, some practitioners believe, based on field experience that controlled release of electron donors will favor the establishment and activity of dehalorespiring bacteria, while others believe that the "overfeeding" approaches more commonly employed in bioremediation projects will work at least as well.
- **Effects of Timing of Augmentation:** Bioaugmentation has been viewed as either a prophylactic insurance measure or a contingency if biostimulation fails. In some cases, systems may be operated for 6 to 18 months in the absence of bioaugmentation before intervening with an inoculant. However, waiting to augment until biostimulation systems have operated for several months entails a risk similar to that described earlier for aquifer preconditioning – other organisms may have become established, leading to increased competition or predation that may make the added beneficial organisms less effective.
- **Performance Monitoring Validation:** Bioaugmentation projects should continue to incorporate quantitative techniques for enumerating the introduced organisms to help improve understanding of the establishment, growth, activity and survival of introduced organisms. Furthermore, research would be beneficial to develop better microbial monitoring methods (e.g., DNA- or ribonucleic acid [RNA]-based methods, or perhaps even the monitoring of key proteins, to assess the presence and expression of key genes).

13.7 CASE STUDIES

Bioaugmentation of subsurface chlorinated solvent contamination has been demonstrated in several carefully controlled and well monitored field tests (e.g., Ellis et al., 2000; Lendvay et al., 2003; Major et al., 2002). Results from three of these tests are summarized in Table 13.8 and briefly described in this section. In addition to these, several other cases of successful bioaugmentation have been reported in recent years (e.g., Dybas et al., 1998; Fam et al., 2002; Finn et al., 2003; French et al., 2004; McMaster et al., 2002; Sharma et al., 2004; Sharma and Bourquin, 2005). Several of these case studies are described in a recent white paper on bioaugmentation (ESTCP, 2005).

13.7.1 Bachman Road, Michigan

The first case study is the controlled field test done at the Bachman Road site in Michigan. Lendvay et al. (2003) conducted a field demonstration of the relative performance of bioaugmentation and biostimulation through side-by-side, closed loop, recirculatory remediation tests. Molecular analysis indicated that indigenous *Dehalococcoides* populations existed at the site. This population was enriched (the Bachman Road Culture) and used for the bioaugmentation plot. Two test plots (4.6 × 5.5 meters [m] or 15 × 18 feet [ft]) were constructed perpendicular to groundwater flow, separated by one plot of the same size.

Each plot consisted of an extraction well, two injection wells, and a series of performance monitoring points. A bromide tracer study was performed to quantify the hydraulics of each test plot, and a design recirculation flow rate of 7 gallons per minute (gpm) was selected for each plot. Both the biostimulation and bioaugmentation plots received lactate as an electron donor. The bioaugmentation test plot was preconditioned with a lactate (0.5 to 1.0 millimolar [mM]) nutrient feed prior to bioaugmentation. On Day 29, 200 L (10^8 cell/milliliter [mL]) of the Bachman Road Culture was introduced into the bioaugmentation plot.

Table 13.8. Summaries of Case Histories

Dates	Conditions	Key Findings
Dover Air Force Base (AFB), DE		
1998–2000	• No indigenous *Dehalococcoides* detected • *cis*-DCE stall • Bioaugmented after lactate-only additions for 9 months • Sandy aquifer	• Microcosm, column and field studies all showed bioaugmentation needed for complete dechlorination • Added *Dehalococcoides* colonized site and survived at least 3 years • Lack of unaugmented side-by-side control in pilot test was a potential concern
Kelly AFB, TX		
2000–2002	• Two control and one bioaugmented recirculating test plots • No indigenous *Dehalococcoides* detected before test or during electron donor additions to control plots	• Indigenous bacteria stalled at *cis*-DCE • Complete dechlorination achieved, with ethene the dominant product within 5 months after bioaugmentation • Introduced *Dehalococcoides* grew *in situ* and colonized test plot
Bachman Road, MI		
2001–2003	• Side-by-side, closed loop recirculation test plots • Biostimulation and bioaugmentation plots • Indigenous *Dehalococcoides* present and enriched for augmentation culture	• Bioaugmentation reduced time to complete dechlorination from 4 months to 6 weeks • *Dehalococcoides* numbers

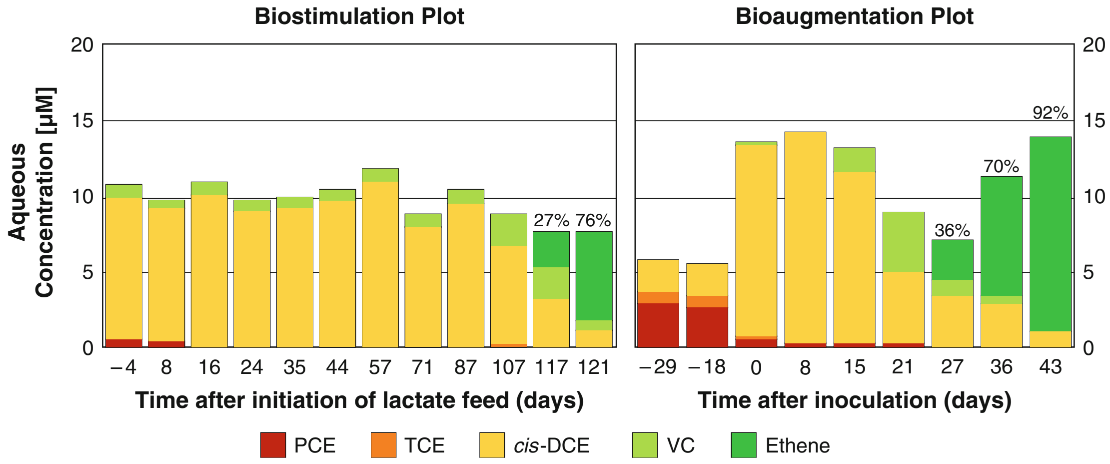

Figure 13.1. VOC concentrations (micromolar [μM]) in biostimulation and bioaugmention plots at the Bachman Road, Michigan site (from Lendvay et al., 2003). Bioaugmentation resulted in faster and more complete dechlorination. Percentages of the initial total VOC mass converted to ethene are indicated on the figure.

Relative to the biostimulation plot, bioaugmentation resulted in a significant reduction in the time it took to achieve complete dechlorination to ethene (Figure 13.1). Complete dechlorination (e.g., production of ethene or ethane) was achieved within 6 weeks after inoculation in the bioaugmentation plot, whereas after 4 months of operation, nearly 76% of the PCE was converted to ethene in the biostimulation plot. Important findings of this work include (1) dechlorination in the bioaugmentation plot was demonstratively linked to the presence of *Dehalococcoides*, (2) *Dehalococcoides* populations grew (measurable numbers increased) as system operation proceeded, (3) bioaugmentation significantly shortened lag times to the onset of dechlorination and (4) biostimulation approaches can achieve complete dechlorination to ethene at sites where certain *Dehalococcoides* populations occur naturally. Complete dechlorination also occurred in the biostimulated plot, but the lag time was about 3 months longer.

13.7.2 Dover Air Force Base, Delaware

The Remediation Technologies Development Forum (RTDF), a collaborative effort between federal and industrial partners (www.rtdf.org), evaluated accelerated anaerobic bioremediation and natural attenuation of TCE in groundwater at Dover AFB, Delaware. The RTDF constructed more than 1,000 microcosms using site soil and groundwater amended with various electron donors including volatile fatty acids (acetate, lactate), alcohols, sugars (including molasses), and complex organics (Lee et al., 1998). Although TCE was reduced to *cis*-DCE regardless of the amendment used, conversion past *cis*-DCE to VC and ethene were observed in only a small percentage of microcosms incubated during the course of these studies (up to 500 days) even when methanogenesis was occurring. This study shows that *Dehalococcoides* was sparsely distributed at this site because TCE should have been dechlorinated beyond *cis*-DCE in a greater percentage of the microcosms. Thus it can be concluded that microorganisms capable of converting *cis*-DCE to ethene were either absent, very sparsely distributed or inactive at this site.

Harkness et al. (1999) demonstrated the need for bioaugmentation using columns filled with soil from the Dover AFB site. TCE was not degraded beyond *cis*-DCE in columns that had been fed only electron donors for up to 200 days. This timeframe should have been sufficient to stimulate the growth and activity of any indigenous *Dehalococcoides* spp. Injection of a small volume of a culture containing *Dehalococcoides* (the Pinellas culture) into one of the columns stimulated complete dechlorination of *cis*-DCE to ethene within 20 days. The same effect was later observed in a second column injected with the same culture. VC production was transient in both bioaugmented columns, with rapid conversion to ethene. This finding supports the conclusion that *Dehalococcoides* microorganisms were not initially present in the aquifer material but were responsible for complete dechlorination after their addition.

This conclusion was supported by the results of a field bioaugmentation demonstration at the site (Ellis et al., 2000). The pilot treatment area was fed lactate for 269 days, during which time TCE was stoichiometrically dechlorinated to *cis*-DCE. VC and ethene were not produced during this interval. Only after the aquifer was amended with the same culture used in the column studies was *cis*-DCE completely reduced to ethene (Ellis et al., 2000) (Figure 13.2).

This result demonstrates the value of bioaugmentation when evidence clearly indicates the absence of organisms capable of complete conversion of *cis*-DCE to ethene. Follow-on analysis using molecular probes (Hendrickson et al., 2002) demonstrated that the *Dehalococcoides* spp. present in the culture used for inoculation were detected only within, and not outside of, the pilot test area (PTA), again indicating the need for, and success of, bioaugmentation. Additional sampling performed two and three years after the completion of the pilot test detected the continued presence of *Dehalococcoides ethenogenes*-like bacteria within the PTA, but again not in the upgradient background wells. These data indicate that *Dehalococcoides* spp.

can survive for long periods in the subsurface, and continue to dechlorinate as long as an anaerobic environment is maintained.

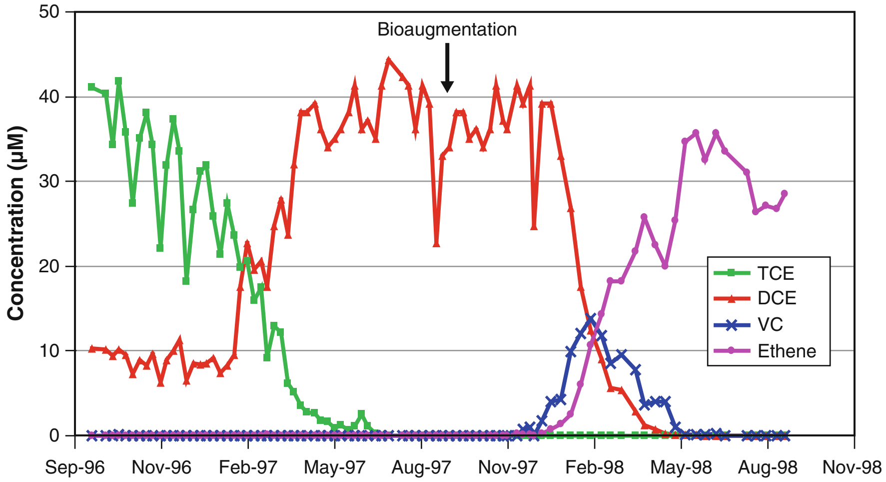

Figure 13.2. Concentrations of TCE, DCE, VC and ethene over time at MW-11D, Dover AFB, DE. Results show persistent stalling at DCE and complete dechlorination to ethene only after the aquifer was bioaugmented with *Dehalococcoides* (modified from Ellis et al., 2000).

13.7.3 Kelly Air Force Base, Texas

Major et al. (2002) conducted a SERDP-funded demonstration of bioaugmentation for treating dissolved-phase PCE, TCE and *cis*-DCE at Kelly AFB in San Antonio, Texas. Prior to the demonstration, the site groundwater contained about 1 mg/L of PCE and lower amounts of TCE and *cis*-DCE, without any detectable VC or ethene. Analysis with 16S rDNA-based PCR methods did not detect *Dehalococcoides* spp. in any groundwater or sediment samples from the PTA. Laboratory microcosm studies showed that non-bioaugmented treatments containing lactate or methanol resulted in stoichiometric conversion of TCE to *cis*-DCE, without further dechlorination of *cis*-DCE to VC or ethene. Microcosms bioaugmented with KB-1® and methanol stoichiometrically converted all of the TCE to ethene. The field test consisted of three recirculation plots: two that served as control plots and one that was bioaugmented with KB-1®.

The test plot was recirculated for 89 days to equilibrate the system and to conduct the bromide tracer test. From Day 90 to Day 175, methanol and acetate were added as electron donors to establish reduced conditions and to stimulate reductive dechlorination by the indigenous bacteria. Bioaugmentation with 13 L of KB-1® occurred on Day 176. Performance monitoring of the control and test plots showed that in the presence of methanol and acetate, the indigenous bacteria could be stimulated to dechlorinate PCE to *cis*-DCE. However, no dechlorination past *cis*-DCE was observed in the control plots for the remainder of the test. In contrast, VC was detected 52 days after bioaugmentation with KB-1® in the test plot and by Day 318 ethene was the dominant product.

Calculated half lives for degradation were on the order of minutes to hours. 16S rDNA-based PCR methods were used to monitor the migration and growth of the KB-1® culture after injection. Molecular monitoring showed that the culture had completely colonized the 9.1 m-long (29.8 ft) aquifer test plot within 115 days after the one time injection of KB-1®. The two control plots were installed and operated in the same manner as the test plot, but were never amended with KB-1®. In these control plots, dechlorination stalled at *cis*-DCE, with no VC observed during 216 days of operation. Molecular analysis confirmed that *Dehalococcoides* spp. were not present in the control plots.

The most conclusive evidence for the need for bioaugmentation at this site was obtained from molecular techniques, which showed that the "fingerprint" of the *Dehalococcoides* species in the KB-1® culture had spread throughout the bioaugmented test plot, whereas *Dehalococcoides* spp. were not detected in the control plots or outside of the bioaugmented test plot. This study also showed that there were naturally occurring *Dehalococcoides* species present at a geographically isolated area of Kelly AFB. Interestingly, these *Dehalococcoides* species were located in a waste pit that was very clayey, with little to no groundwater movement, and that had received organic waste and chlorinated solvents for decades. These *Dehalococcoides* species had a different "fingerprint" than the KB-1® bioaugmentation culture, and this different signature was not detected in the field pilot plot that was bioaugmented.

13.8 SUMMARY

Bioaugmentation has progressed into a credible and economically attractive technology. In particular, bioaugmentation can be a useful option in chlorinated solvent treatment because *Dehalococcoides* spp. are unusual bacteria. To date, they appear to be uniquely capable of the final steps of reductive dechlorination, and although they are present at many sites, they are not ubiquitous. Further, their numbers are often very low and their distribution within the subsurface is often patchy. As a result, adding mixed cultures containing *Dehalococcoides* spp. has proven essential for achieving complete dechlorination at a few sites, and more commonly, it has significantly reduced the time needed before the onset of complete dechlorination.

Although there is much still unknown, there has been rapid progress in the understanding of this technology. Proven cultures are commercially available, and their value has been demonstrated under field conditions. Cultures can be grown efficiently, transported to field sites effectively, successfully injected and, in most cases, they will survive and grow in aquifers given proper environmental conditions. The key issues appear to be determining *a priori* whether bioaugmentation will be beneficial, ensuring adequate distribution and concentration of added cultures throughout a target zone, overcoming potential inhibitory conditions and keeping costs low while ensuring adequate quality assurance.

Project managers considering the use of bioaugmentation should address the issue as early in the design stage as possible. They should complete an explicit cost benefit assessment, including a life cycle cost analysis, to determine whether bioaugmentation has the potential to improve the time, costs and regulatory acceptance of a bioremediation approach. Site-specific testing can be performed to aid in making this decision, including the use of focused microbial analyses and molecular biological tools to identify the capabilities of microorganisms at a specific site.

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CHAPTER 14

AIR SPARGING FOR THE TREATMENT OF CHLORINATED SOLVENT PLUMES

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14.1 INTRODUCTION

In its simplest form, *in situ* air sparging (IAS) is a source zone and dissolved groundwater plume remediation technology that involves injection of air into an aquifer through a collection of vertical wells screened below the water table. Modifications to this basic design may include the use of horizontal wells placed below the water table, vertical wells placed in an engineered trench, the delivery of gaseous reactants (hydrogen, propane, oxygen, etc.), the use of vapor recovery and treatment systems, pulsing of the gas injection and heating of the injection gas. The basic process components of IAS systems are shown in Figure 14.1.

IAS systems have been employed to treat contaminant source zones containing immiscible hydrocarbon liquids, both light nonaqueous phase liquids (LNAPLs; typically petroleum fuels) and dense nonaqueous phase liquids (DNAPLs; typically chlorinated solvents) at or below the capillary fringe. IAS systems also have been used to remediate dissolved contaminant plumes and create flow-through chemical migration barriers as shown in Figure 14.2. Treatment is generally accomplished through a combination of volatilization and biodegradation processes, although IAS systems can also deliver gaseous reactants to achieve abiotic contaminant destruction (e.g., ozone injection). The extent to which each mechanism contributes to removal depends on the application (i.e., source zone vs. dissolved plume treatment), chemical properties (i.e., solubility, vapor pressure and biodegradability) and the system design (i.e., density of wells and pulsed/continuous operation of the gas injection) as discussed by P. Johnson et al. (2001a).

IAS gained acceptance as a remediation technology in the late 1980s and early 1990s, in part because the basic components of an IAS system are neither complex nor significantly different from those in other remediation systems (blowers/compressors, piping, timers, and air injection wells). The technology was adopted by practitioners before a thorough understanding of the factors controlling performance was developed. As a result, the technical literature reflects a range of hypotheses, misconceptions and design approaches that have evolved with time. A review and synthesis of key points identified through research, field testing, and empirical analysis can be found in P. Johnson et al. (2001a).

In the context of dissolved chlorinated aliphatic hydrocarbon (CAH) plumes, IAS is an option for the remediation of smaller ($<$1 acre [0.4 hectare (ha)]) plumes. Its use for large dissolved plume remediation is typically impracticable as close injection well spacings are often required. For larger dissolved CAH plumes, IAS may be used for creating *in situ* permeable flow-through treatment barriers at the leading edge of the plume (or some intermediate distance along the plume). Most CAHs are relatively resistant to aerobic biodegradation, so removal by a basic IAS system is likely to occur by volatilization, unless the system is

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specifically designed to promote anaerobic or cometabolic aerobic biodegradation (through injection of hydrogen, propane, or other reactants) (ESTCP 2001; 2003a).

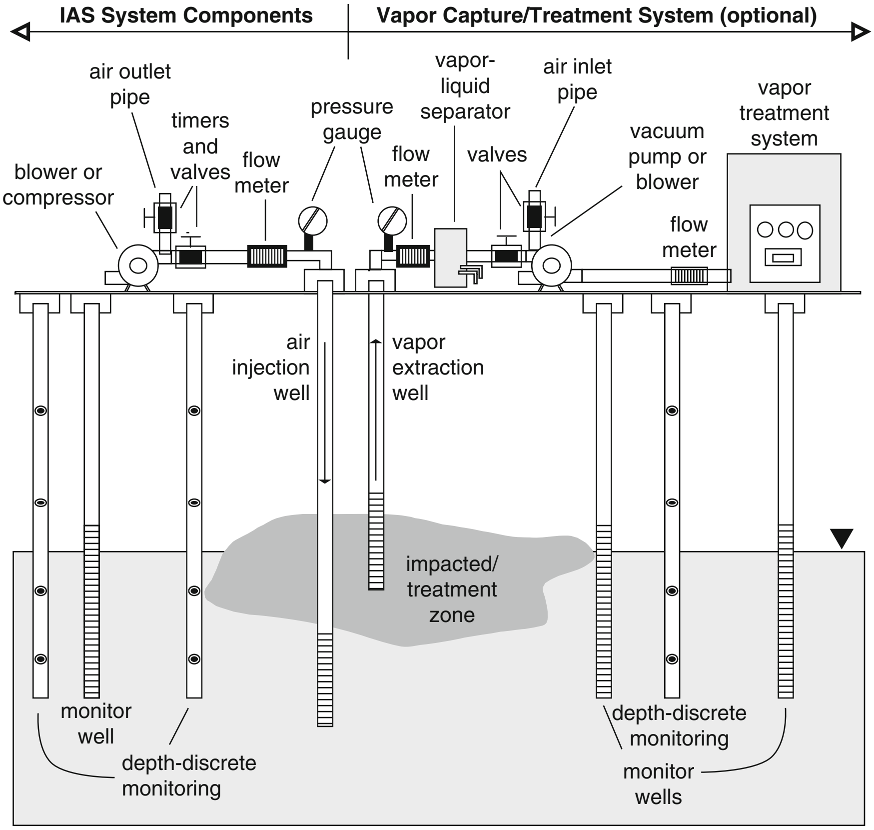


Figure 14.1. Basic IAS system components.

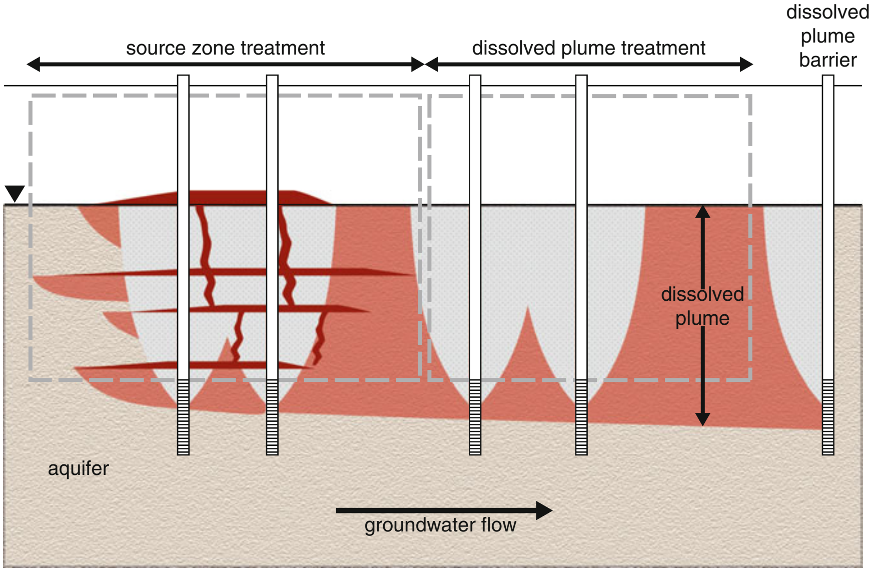


Figure 14.2. IAS applications: source zone treatment, dissolved plume treatment and dissolved plume flow-through barrier treatment system.

This chapter focuses primarily on IAS feasibility assessment, system design, monitoring and operation. It draws heavily from the paradigm proposed by P. Johnson et al. (2001b), and the supporting articles of Amerson et al. (2001), Bruce et al. (2001), P. Johnson et al. (2001a) and R. Johnson et al. (2001a, 2001b, 2001c). A compilation of this information also can be found in Leeson et al. (2002), from which Battelle (2001) was derived. The paradigm development followed field and laboratory studies sponsored by the Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP), conducted with support from the U.S. Naval Facilities Engineering Service Center (NFESC). The paradigm was also reviewed by an expert panel comprised of practitioners, program managers, and industry representatives. The basis for the paradigm is first discussed, with emphasis on those aspects that are relevant for dissolved CAH plume treatment.

14.2 IAS DESIGN PARADIGM BASIS

The following key concepts are central to the IAS paradigm presented below.

14.2.1 Primary Factors Controlling Performance

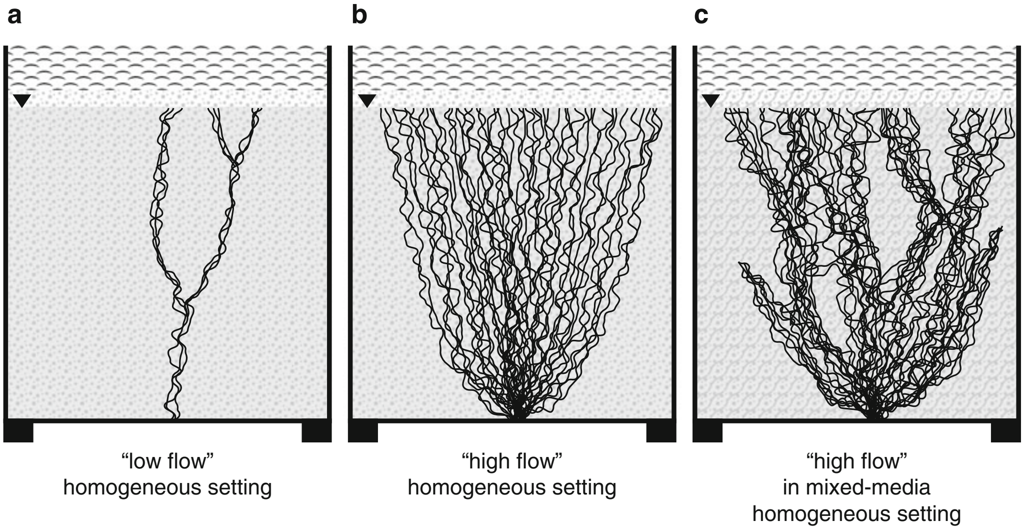
In brief, IAS performance is primarily determined by (1) the air flow and air distribution achieved in the target treatment zone, (2) the distribution (location and concentration) of contaminants relative to the air distribution, and (3) properties of the contaminants targeted for treatment (in particular the solubility, vapor pressure and biodegradability).

14.2.2 Air Flow and Air Distributions in Aquifers

Field and laboratory data have shown that:

- Air flow away from injection wells screened below the water table usually occurs through a network of discrete air flow channels. Bubbling flow only occurs in very coarse (gravelly) aquifer materials.
- Air flow surrounding vertical and horizontal gas injection wells placed in homogeneous and relatively permeable media is typically limited to within about 5 to 20 feet (ft) (1.5 to 6 meters [m]) laterally away from the injection well.
- Air distribution in less homogeneous and more layered settings is likely to be irregular in shape, with preferred directions of flow away from injection wells. The air may travel laterally for large distances (sometimes as much as 300 ft [91 m]) in some layered settings. The air may also accumulate beneath finer grained units as it travels laterally through the coarser units, and in doing so cause desaturation of those regions.
- Air distributions are sensitive to subtle changes in soil structure that are difficult to identify by conventional characterization methods.
- Lower air injection rates (e.g., <5 cubic feet per minute [ft^3/min]) generally yield less extensive and less effective air distributions.
- Increasing air flow rate (and injection pressure) generally results in an increase in the density of the air flow network; it can also cause air to break up through layers under which it might normally be stratified at lower injection flow rates and pressures.

Graphics from laboratory-scale physical model visualization studies conducted by Ji et al. (1993) effectively illustrate many of these key points. For example, Figure 14.3 parts a and b illustrate effects of flow rate changes on the air distribution in a model uniform particle-size homogeneous setting. Buoyancy forces drive air vertically up from the point of injection and there are few air channels at low air flow rates. With increased flow rate, the air distribution broadens and the air channel network becomes denser. At some point, further increases in air injection flow rate do not yield further expansions of the air flow zone, and instead cause increases in the density of air channels, an overall desaturation of water from within the established air flow zone, and a reduction in permeability to water flow through the air flow region (Rutherford and Johnson, 1996). Figure 14.3 part c shows an irregular air distribution in another homogeneous setting with a bi-modal well mixed particle distribution. The distribution is composed of complete air channels leading from the injection point to the unsaturated zone, incomplete air flow paths, and bypassed zones within the overall boundaries of the air flow distribution. The maximum width of the air distribution is approximately equal to the depth of injection in Figure 14.3 parts a and b; however, widths in analogous field settings could be less. For example, in the field study of Lundegard and LaBreque (1998), the lateral extent of the air distribution (6 to 10 ft [1.8 to 3 m]) at a relatively sandy and homogeneous site was about half the depth to the screened interval of the air injection well.



"low flow" homogeneous setting

"high flow" homogeneous setting

"high flow" in mixed-media homogeneous setting

Figure 14.3. Visualization of flow distributions in homogeneous settings (Ji et al., 1993: reprinted from Ground Water Monitoring & Remediation with permission of the National Ground Water Association. Copyright 1993.)

Figure 14.4 parts a and b correspond to low and high air flow rates, respectively, in a model stratified geology. In this case, there are layers of 0.2 millimeter (mm) diameter glass beads within 0.75 mm diameter glass beads. As can be seen, the finer-grained layers impede the vertical movement of air so that stratified air layers are formed. Note that this happens even though the difference between the mean particle diameters is only a factor of three to four. Eventually, the air finds a route to the surface, either through a discontinuity in the finergrained material, or through a build-up of pressure with time to the point where the air entry pressure of the finer-grained material is exceeded. As can be seen, increasing the air injection flow rate (and pressure) causes air to break through the finer-grained layers. Thus in more heterogeneous and layered settings, some degree of air stratification should be expected. Air stratification can be viewed as having both positive and negative implications for IAS performance. On one hand it helps to achieve a broader air distribution; however, it also limits contact between the air lying below a finer-grained lens and contaminants that may be present along the top of that lens.

There has been speculation that pulsed air injection (turning the gas injection on and off) results in air channel distributions that change with each injection cycle. Laboratory-scale visualization studies and field results suggest that the macroscopic features and overall extent of the air flow distribution are unlikely to change during pulsed injection (assuming constant pressure and flow for each cycle). The results also show that pulsed injection enhances removal from source zones and increases delivery efficiency of oxygen, suggesting that pulsing does enhance mixing of the dissolved phase and result in fluctuations of air flow path positions at the pore scale.

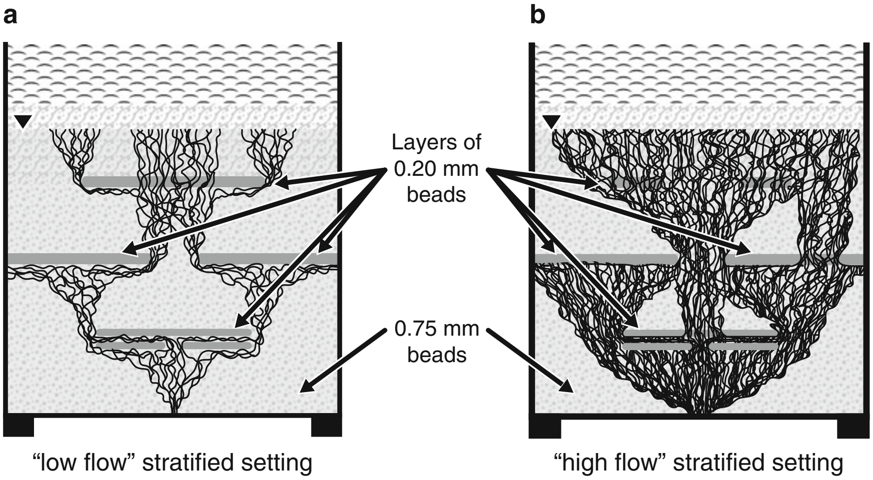


Figure 14.4. Visualization of flow distributions in stratified settings (Ji et al., 1993: reprinted from Ground Water Monitoring & Remediation with permission of the National Ground Water Association. Copyright 1993.)

14.2.3 Contaminant Removal during IAS

Removal of dissolved groundwater contaminants by IAS in the short term (hours to days) is dominated by volatilization from within air channels. The removal rates are greatest during this phase because of the direct contact between flowing air and contaminants in the air channels. Removal in the long term is dominated by removal of contaminants from the water saturated zones outside of the air channels, and is limited by liquid phase mass transfer processes. Given that the active air flow zone typically occupies a small fraction of the total pore space, removal rates measured in short term pilot tests are not likely to be representative of removal rates in the long term.

Removal of contaminants from outside of the air channels by volatilization requires movement of those chemicals to the air channels, and this is accomplished by diffusion induced by concentration gradients and by the flow of water induced by water evaporation. Removal may become limited by these dissolved-phase mass transfer processes, and if so, will be independent of the chemical properties normally associated with volatilization processes (vapor pressure and Henry's Law constant). Liquid phase diffusion coefficients are similar for many CAHs (to within a factor of two) and dissolved phase removal is proportional to the diffusion coefficient and dissolved concentration; therefore, the removal efficiency by volatilization (percentage of initial mass removed) is expected to increase in proportion to the dissolved contaminant concentration and decrease in proportion to the total contaminant concentration in source zone settings where immiscible phase contaminants are present (P. Johnson, 1998). For CAH dissolved plumes, the removal efficiency with time will be dependent on the partitioning between the dissolved and sorbed phases. In weakly sorbing settings (most of the chemical mass is in the dissolved phase and the plume is only slightly retarded relative to groundwater flow), removal efficiency by volatilization should be similar for all compounds in the dissolved plume. In more strongly sorbing settings, removal efficiency will be greater for those CAHs with lower sorption coefficients.

One should also be aware that the mechanisms responsible for removal of contaminants also have the potential to cause their redistribution in the short term, particularly in cases where clean water overlies deeper groundwater contamination.

Field data, laboratory studies, and modeling results all suggest that the effectiveness of CAH dissolved plume remediation by IAS will typically be more effective for systems achieving a higher density of air channels in the target treatment zone. The only qualification to this statement is when IAS is employed to create an *in situ* flow-through chemical migration barrier. In those cases, care must be taken to balance the desire for a dense air flow distribution with the need not to reduce permeability to groundwater flow through the treatment zone (which would cause groundwater to flow around the treatment zone) (Rutherford and Johnson, 1996). One way of accomplishing this is to utilize pulsed gas injection, with a frequency based on consideration of groundwater velocity through the treatment zone (the time between air injections is less than the groundwater flow time through the IAS treatment zone and the duration of air injection is just enough to treat the water in the treatment zone). Each pulsed injection will cause a lateral displacement of groundwater in the immediate vicinity of the flow-through chemical migration barrier, but this will be at most about 5 to 50% of the width of the barrier (equivalent to the percentage of the pore space occupied by air) and can be accommodated by extending the width of the system beyond the width of the plume to be treated.

When IAS systems are used to deliver gaseous reactants for biotic or abiotic processes (hydrogen, oxygen, propane), pulsed gas injection involving short high-intensity flows is generally more efficient and effective than continuous gas injection. Groundwater is displaced by gas when gas injection starts and groundwater flows back into the air flow zone when gas injection stops, but not all of the gas is displaced in this rewetting phase. As much as 2 to 5% of the pore space might be occupied by trapped gas, which dissolves over time into groundwater flowing past the trapped gas. This reservoir of gaseous reactant may persist for days to weeks (unless it reacts quickly with the aquifer solids).

14.2.4 Implications for Feasibility Assessment and Design

The key lessons learned summarized above have the following implications for feasibility assessment, design and operation:

- Given the importance of the air distribution and the inability to anticipate it from conventional site investigation data (except in the simplest of geologies), the actual air distribution in the target treatment zone should be characterized during the pilot testing and full implementation phases.
- The degree to which the air distribution is characterized at the pilot test scale should be balanced by the system design. For example, a high degree of uncertainty in the air distribution at the pilot-scale level can be compensated for by a high density of air injection wells at the full-scale level. Conversely, distances between injection wells at the full-scale level can be optimized (and the number of wells minimized) when the air distribution is more fully characterized at the pilot-scale level.
- At this time, long-term IAS performance (cleanup levels, cleanup times, etc.) cannot be predicted reliably from data collected during short-term pilot tests. Because of this, pilot-scale testing activities should focus on looking for indicators of infeasibility (clear indicators that IAS will not be successful), in addition to characteristics of the air distribution.

14.3 IAS DESIGN PARADIGM

This design paradigm reflects a combination of theory and empiricism, and the acceptance that, prior to full implementation, there is significant uncertainty in the degree and rate of cleanup that might be achieved at any site. The sequence of activities involved in the IAS Design Paradigm is presented in Figure 14.5. As with other technologies, there are site characterization,

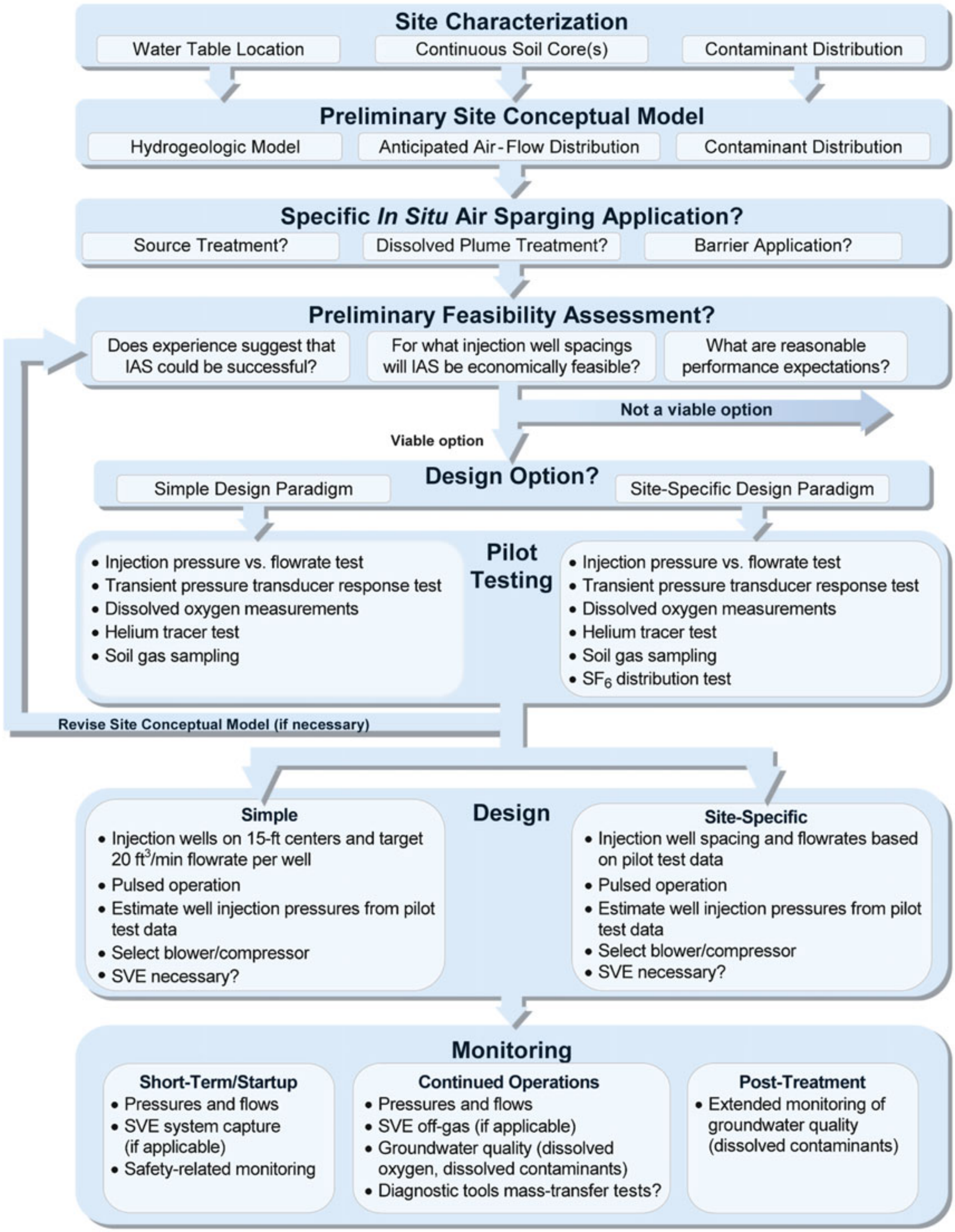


Figure 14.5. Air sparging design paradigm (P. Johnson et al., 2001b). (Note: SF_6 - sulfur hexafluoride; SVE - soil vapor extraction)

technology screening, pilot testing, design and implementation steps. However, within each of these steps there are differences from conventional design paradigms. For example, there are two parallel tracks that users may follow in the pilot testing and design stages. Also, the technology screening involves an "infeasibility assessment" rather than the more common feasibility assessment. At each step in the process the user makes choices to balance uncertainty in performance and cost against robustness in system design.

14.3.1 Site Characterization

Site characterization activities should be focused on collecting data necessary to create graphics (e.g., cross sections and plan view maps) showing the hydrogeologic setting (subsurface materials, depth to groundwater, etc.), locations of key physical features (tanks, sewers, wells, etc.), the extent of the dissolved plume, the target treatment zone and the anticipated air distribution during IAS.

For IAS applications, it is critical to adequately characterize the subsurface from an air flow perspective. At a minimum, one or more continuous cores should be collected between the water table (or upper boundary of contamination) and the top of the anticipated screened interval of any air injection wells (usually placed 2 to 10 ft [0.6 to 3 m] below the deepest contamination). Continuous cores should be logged and photographed; in some cases, determination of relevant quantitative characteristics (e.g., grain size distribution, permeability) of the aquifer materials is warranted. Direct-push and geophysical tools may prove cost effective in identifying gross features of the target treatment zone.

Prediction of air flow and air distributions from conventional site characterization data is not possible at this time; however, the gross features of air distributions can be anticipated for simple geologies (e.g., highly permeable and homogeneous settings; settings with large macro-scale heterogeneities such as clay layers in otherwise sandy materials), and therefore, knowledge gained from visual review of soil cores is often invaluable for IAS applications. For example, in homogeneous and relatively permeable settings (sands), it is likely that the air flow distribution will not extend more than 6–20 ft (1.8–6 m) from air injection wells, and will roughly resemble the distributions in Figure 14.3. In stratified settings, it is likely that air pockets will build up under the lower permeability layers, move horizontally, and travel vertically up through a small number of discrete channels in the lower permeability layer as shown in Figure 14.4. In settings other than the highly permeable and homogeneous ones, it is also unlikely that the air distribution will be symmetrical about the injection well. Users may find the work of Ji et al. (1993), Lundegard and LaBreque (1998), Amerson et al. (2001) and Bruce et al. (2001) helpful in developing their intuition for anticipated air distributions in various hydrogeologic settings.

With flow-through systems there is the possibility of mineral precipitate or biomass accumulation in the pores over time. If this happens, it can cause a reduction in effective permeability to groundwater flow. The potential for mineral precipitation can be investigated by performing chemical analyses of site groundwater to determine the mass of precipitate per unit volume of groundwater. This information, along with the knowledge of groundwater flow rate to the barrier system can be used to calculate the maximum mass accumulation per year and the potential for that to reduce pore space in the barrier region. Reductions in permeability due to biomass accumulation are less likely to happen in most systems, as the microbial population is self regulated by the rate at which target chemical flows to the barrier system.

14.3.2 Initial Screening of Technologies

As discussed above, it is important to recognize the limitations in predicting IAS performance and to consider a wide range of input derived from both experience and theory. It is suggested that practitioners focus on the following basic questions:

- Does experience suggest that IAS could be successful at this site?
- For what injection well spacings would IAS be practicable?
- What are reasonable performance expectations for this IAS system?
- What are the challenges likely to be at this site (stratification, vapor control, well construction, etc.)?

These four questions are the focus of the discussion below. To better illustrate the initial technology screening phase, a hypothetical one-acre (160 ft × 260 ft × 20 ft or approximately 50 m wide × 80 m long × 6 m thick) dissolved CAH plume is assessed in the discussion below. Results of the analysis are summarized in Tables 14.1 though 14.4.

Table 14.1. Sample IAS Technology Screening Input Summary Table for a Hypothetical One-Acre Site

Site Characteristics and Application Goals	
Treatment goal (dissolved plume treatment or barrier)?	Dissolved plume treatment
Release scenario (attach plan view map)	Historical solvent disposal
Target contaminants for treatment	PCE, TCE, DCE, TCA, DCA, VC
Aerobically biodegradable contaminants?	No (not without addition of substrate)
Depth to groundwater	7 ft (2 m) bgs
Hydrogeologic setting (describe qualitatively and attach cross section and photos of continuous core[s])	Relatively homogeneous, interbedded sands-silts
L - Approximate treatment zone length	264 ft (80 m)
W - Approximate treatment zone width	164 ft (50 m)
D - Approximate treatment zone thickness (bgs)	7–26 ft (2–8 m) bgs
C_w^o - Approximate average initial dissolved contaminant concentration(s) in target treatment zone	All concentrations in the 10–1,000 microgram per liter (μg/L) range
C_w/C_w^o - Approximate average desired concentration reduction after treatment	0.001–0.01
Initial Technology Screening	
Q1: Does experience suggest that IAS could be successful at this site? Is this setting and contaminant "typical" of IAS applications?	Yes. Successful applications reported in literature (Bass and Brown, 1995)
Q2: For what injection well spacings would IAS be practicable?	Predominantly semi-conical homogeneous setting-type air distribution of limited lateral extent is expected; there is some potential for air stratification and preferential flow direction; 160 injection wells required if placed on 15 ft (5 m) spacings prescribed in standard design approach; 800 ft^3/min (33,000 m^3/day) air flow needed (at 20 ft^3/min [860 m^3/day] per well and 25% cycling time)
Q3: What are reasonable performance expectations for this IAS system?	Screening-level calculations and past applications suggest time frames in the one- to three-year range, under ideal conditions (see Tables 14.2 and 14.3).
Q4: What are the challenges likely to be at this site (stratification, vapor control, well construction, etc.)	Number of injection wells required may be impracticable and economically unfavorable unless direct-push technology can be used for installation.

Note: bgs = below ground surface; DCA = dichloroethane; DCE = dichloroethene; PCE = perchloroethene; TCA = trichloroethane; TCE = trichloroethene; VC = vinyl chloride.

14.3.2.1 Question 1: Does Experience Suggest that IAS Could Be Successful at This Site?

When assessing applicability, it is useful to first review what is known from experience (Bass and Brown, 1995, 1997; Bruell et al., 1997; Gordon, 1998; R. Johnson et al., 1993; Klemm et al., 1997; Plummer et al., 1997; ESTCP, 2001, 2002, 2003a, 2003b; USEPA, 1992). IAS has been successfully applied for source zone treatment at gasoline release and smaller scale CAH spill sites (e.g., dry cleaners). IAS systems also have been implemented as barriers at larger-scale chlorinated solvent dissolved plume sites and for other more recalcitrant chemicals (e.g., methyl tertiary butyl ether [MTBE]). IAS systems are generally not used for plume treatment or plume barriers when dealing with readily degradable compounds as the plume extent tends to be constrained by natural attenuation, and plume dissipation occurs relatively quickly once the source zone has been successfully remediated; however, they can be used to accelerate these processes if desired.

Aquifers and target treatment zones found at depths less than about 50 ft (15 m) below ground surface (bgs) and sandy/silty soils are typical candidates for IAS applications. Deeper aquifers, fractured aquifers, highly stratified aquifers and aquifers composed of soils that become finer with depth are more challenging. In some of those settings pump-and-treat systems will prove to be more robust (less risk of failure) and also preferable from an economic perspective. IAS is not expected to be effective in most clayey settings. If the anticipated contact between the air distribution and the dissolved contaminant distribution is likely to be poor, then IAS has a low probability of success.

14.3.2.2 Question 2: For What Injection Well Spacings Would IAS Be Practicable?

If experience suggests that the IAS application could be successful, then users should determine if the cost of injection well installation is likely to be prohibitive, and if so, what injection well spacing is economically feasible. The results of this analysis are used for feasibility assessment here and later for pilot test design. The Simple Design Paradigm path shown in Figure 14.5 specifies 15-ft (5-m) injection well spacings, so users should first determine if the cost of that well spacing is cost prohibitive. The 15-ft (5-m) spacing specification stems from the discussion above of air distributions in near homogeneous and highly permeable settings. If that well spacing is cost prohibitive, then the smallest well spacing that is not cost prohibitive should be determined from an economic analysis and then effectiveness of that spacing should be tested in the field, if it is not obvious that the economically determined spacing would be ineffective. In the context of this analysis, a well spacing is cost prohibitive when the projected IAS costs greatly exceed ranges estimated for other technologies under consideration at this stage (pump-and-treat, bioremediation, etc.).

In the context of the hypothetical 1-acre (0.4-ha) dissolved plume, approximately 160 air injection wells on 15-ft (5-m) spacings would be required for entire plume treatment if following the simple design approach in Figure 14.5. This number of wells would likely be viewed as being cost prohibitive unless they could be installed with direct-push methods instead of traditional drilling and installation methods. If pilot testing identified that 30-ft well (9-m) spacings would be effective, then the number of air injection wells would be reduced by a factor of four. If IAS were to be used to create a flow-through chemical treatment barrier at the leading edge of the plume, then only about 10 air injection wells would be needed.

14.3.2.3 Question 3: What Are Reasonable Performance Expectations for this IAS System?

As discussed above, it is difficult to predict performance with confidence at this time. However, it is possible to place some bounds on reasonable performance expectations. First, empirical summaries (e.g., Bass and Brown, 1995; Bruell et al., 1997) and experience suggest that many IAS systems are operated for periods of less than three years; however, it is not clear what criteria are being used to decide termination. IAS barrier control systems may be operated for longer (or shorter) time periods, dictated not by IAS performance, but by the length of time that the migration barrier is needed.

As discussed above, theory suggests that contaminant removal during IAS occurs through a combination of volatilization and biodegradation. Most CAHs of interest are not readily biodegradable aerobically, except through cometabolism (except for vinyl chloride [VC] and possibly dichloroethene [DCE]; see Chapter 3); volatilization is likely to be the dominant mechanism at many CAH sites. Exceptions to this generalization could occur in mixed petroleum and CAH dissolved plumes, and in IAS systems specifically designed to promote CAH biodegradation (e.g., through hydrogen or propane injection) (ESTCP, 2001, 2003a).

For the case of CAH dissolved plume remediation using typical IAS air-only injection systems, the following performance bounding calculations should be considered.

Best-Case Treatment Performance: The upper performance bound estimate is derived from the analysis of a well-mixed system with equilibrium partitioning between air and groundwater phases. For this case, the dependence of concentration reduction on time is:

$$\frac{C_w(t)}{C_w^o} = \exp\left[-\frac{\left(\frac{QH_i}{V\theta_w}\right)t}{\left(1+\frac{H_i\,\theta_v}{\theta_w}+\frac{k_s\,\rho_b}{\theta_w}\right)}\right] \qquad \text{(Eq. 14.1)}$$

where $C_w(t)/C^o_w$ is the fraction of the initial dissolved concentration remaining with time t [day], Q is the air injection flow rate [m^3/day], H_i is the chemical-specific Henry's Law constant [m^3-H_2O/m^3-air], V is the total volume of the impacted groundwater zone [m^3], θ_w is the volumetric water fraction in the aquifer [m^3-H_2O/m^3-aquifer], θ_v is the volumetric air fraction in the aquifer [m^3-air/m^3-aquifer], k_s is the chemical- and aquifer-specific sorption coefficient [m^3-H_2O/kg-aquifer-solids], and ρ_b is the bulk density of aquifer solids [kg-aquifer-solids/m^3-aquifer]. For most CAHs and aquifers, the denominator in the exponential in Equation 14.1 will range from about 1–10, Henry's Law constants lie between 0.1–1.0 m^3-H_2O/m^3-air, and Q is typically about 20 ft^3/min (about 0.5 m^3/min) per well with each well being on about 25% of the time. For the hypothetical one-acre example site, an air injection rate of approximately 800 ft^3/min (33,000 m^3/day) would be required for the simple design approach; 160 air injection wells operating in pulsed mode with a net injection frequency of 6 hour (hr)/24 hr = 25%.

Using Equation 14.1 and inputs specific to the hypothetical one-acre site, minimum times needed to reduce the concentrations of typical CAHs of interest by one- to three-orders-of-magnitude were calculated and summarized in Table 14.2. It is important to keep in mind that these times were estimated for the case of ideal well-mixed conditions, which are not normally achieved in aquifer systems. Thus, they should be interpreted as being an ideal upper-bound on practically-achievable removal for a given operating time, or a lower-bound on the time required to achieve a specified reduction. As can be seen, most times are on the order of a few months to a year, with the exception of the two chemicals with the lowest Henry's Law constants (1,2-dichloroethane [1,2-DCA] and 1,1,2-trichloroethane [1,1,2-TCA]). The results will differ for other scenarios and the cleanup time estimates decrease linearly with decreases in the ratio (V/Q) (decreasing dissolved plume size and increasing air injection rate).

Table 14.2. Sample Performance Estimate Calculations Using Equation 14.1 for the Hypothetical One-Acre CAH Dissolved Plume Site

Chemical Name	Henry's Law Constant H_i (16°C) (m^3-H_2O/m^3-air)	Organic Carbon Partitioning Coefficient K_{oc} (m^3-H_2O/kg-carbon)	Sorption Coefficient (1) K_s (L-H_2O/kg-solids)	Minimum Time t [d] to Achieve Prescribed Fractional Reduction in Dissolved Concentration $C_w(t)/C^\circ_w$		
				0.1	**0.01**	**0.001**
1,1 DCE	0.79	65	0.65	3	6	9
1,2 DCE (*cis*)	0.11	35	0.35	14	28	42
1,2 DCE (*trans*)	0.27	38	0.38	6	12	18
1,1 DCA	0.16	53	0.53	13	26	39
1,2 DCA	0.026	38	0.38	63	126	189
1,1,1 TCA	0.48	135	1.35	9	18	28
1,1,2 TCA	0.023	75	0.75	117	234	351
TCE	0.28	94	0.94	12	23	35
PCE	0.47	265	2.65	17	35	52
Vinyl Chloride	0.89	19	0.19	1	3	4

Chemical properties source: http://www.epa.gov/Athens/research/regsupport/properties.html
(1) – for $f_{oc} = 0.01$ kilogram (kg)-OC/kg-solids
$Q = 800\ ft^3/min = 33{,}000\ m^3/d$
$V = 1$ acre footprint x 20 ft thickness $= 24{,}000\ m^3$
$\theta_v = 0.02\ m^3$-air/m^3-aquifer
$\theta_w = 0.33\ m^3$-H_2O/m^3-aquifer
$\rho_b = 1.7$ kg-solids/L-aquifer
All results calculated using Equation (14.1)

Treatment Performance Estimate Based on Field-Scale Mass Transfer Measurements: Loss controlled by liquid-phase diffusion, R_{diff} (kg/d), can be approximated by equations of the form:

$$R_{diff} = A\, D^{eff}\, \frac{C_W}{\delta} \qquad \text{(Eq. 14.2)}$$

where A is the surface area of channels in the treatment zone (m^2-area/m^3-volume); D^{eff} is the effective porous media diffusion coefficient (m^2/d); δ is the distance the contaminant must diffuse to reach the air channel (m); and C_w is the dissolved contaminant concentration (kg-contaminant/m^3-water). Typical saturated zone D^{eff} values are roughly 10^{-5} m^2/d, C_w is obtained from site data, A is highly uncertain and practicably immeasurable *in situ*, and δ is also not measurable and may increase with time. If we assume that the ratio (AD^{eff}/δ) is constant with time and that the aquifer is well mixed outside of the mass-transfer limited region, the following expression can be derived:

$$\frac{C_w(t)}{C_w^o} = \exp\left[-\frac{\left(\frac{D^{eff} A}{V\,\theta_w\,\delta}\right) t}{\left(1 + \frac{H_i\,\theta_v}{\theta_w} + \frac{k_s\,\rho_b}{\theta_w}\right)}\right] \qquad \text{(Eq. 14.3)}$$

Our ability to anticipate A and δ is limited; however, Amerson (1997), Amerson et al. (2001) and Bruce et al. (2001a) report on tracer gas delivery tests in which the tracer gas (SF_6; sulfur hexafluoride) concentration reached 10 to 90% of its dissolved saturation value in the aquifer over 24 hours within the active air flow zone. Using that information, one can estimate ($AD^{eff}/V\theta_w\delta$) values that are >0.1 day^{-1}. This lower bound 0.1 day^{-1} value and Equation 14.3 have been used to estimate the times needed to reduce the concentrations of typical CAHs of interest by one to three orders of magnitude (Table 14.3). The results are similar to those in Table 14.2 in that most cleanup time estimates are on the order of a year, with the exception of perchloroethene (PCE). Again, this analysis suggests that cleanups can be achieved in reasonable timeframes, if a good air flow distribution is achieved and operation of the IAS system induces some mixing (by operating it in a pulsed mode).

Table 14.3. Sample Performance Estimate Calculations Using Equation 14.3 for the Hypothetical One-Acre CAH Dissolved Plume Site

Chemical Name	Henry's Law Constant H_i (16°C) (m^3-H_2O/m^3-air)	Organic Carbon Partitioning Coefficient K_{oc} (m^3-H_2O/ kg-carbon)	Sorption Coefficient (1) K_s (L-H_2O/ kg-solids)	(D^{eff} A/ (V $\theta_w\delta$)) (est. from tracer study) [d^{-1}]	Minimum Time t [d] to Achieve Prescribed Fractional Reduction in Dissolved Concentration $C_w(t)/C°_w$		
					0.1	**0.01**	**0.001**
1,1 DCE	0.79	65	0.65	0.1	101	202	304
1,2 DCE (*cis*)	0.11	35	0.35	0.1	65	129	194
1,2 DCE (*trans*)	0.27	38	0.38	0.1	68	137	205
1,1 DCA	0.16	53	0.53	0.1	86	172	258
1,2 DCA	0.026	38	0.38	0.1	68	136	204
1,1,1 TCA	0.48	135	1.35	0.1	184	368	551
1,1,2 TCA	0.023	75	0.75	0.1	112	224	336
TCE	0.28	94	0.94	0.1	135	270	405
PCE	0.47	265	2.65	0.1	338	676	1,014
Vinyl Chloride	0.89	19	0.19	0.1	47	94	140

Chemical properties source: http://www.epa.gov/Athens/research/regsupport/properties.html
(1) – for $f_{oc} = 0.01$ kg-OC/kg-solids
$Q = 800$ ft^3/min $= 33{,}000$ m^3/d
$V = 1$ acre footprint × 20 ft thickness $= 24{,}000$ m^3
$\theta_v = 0.02$ m^3-air/m^3-aquifer
$\theta_w = 0.33$ m^3-H_2O/m^3-aquifer
$\rho_b = 1.7$ kg-solids/L-aquifer
All results calculated using Equation (14.3)

***Worst Case Estimate of Treatment Performance, Evaporation Controlled Removal*:** The worst case scenario is the one where there is limited to no liquid-phase mixing and poor contact between the air distribution and target treatment zone. In this case removal becomes controlled by the evaporation of water into the air channels. The water evaporation draws water flow and dissolved CAHs towards the air channels, where they volatilize into the air flow. For injection of dry air into an aquifer at a temperature of about 15 degrees Celsius (°C), and assuming 100% humidity leaving the aquifer, it is possible to evaporate about 0.5 liters (L)-H_2O/day per ft^3/min of air injection. In this worst case scenario, the IAS system essentially operates as a slow pump and treat system, so the time required for plume remediation is the time required to evaporate the groundwater in the dissolved plume, compensated for the partitioning of chemical to the aquifer solids. Thus the remediation time estimate becomes:

$$t = \frac{\left(\frac{\rho_w V \theta_w}{Q C_{w,v}}\right)}{\left(1 + \frac{H_i \theta_v}{\theta_w} + \frac{k_s \rho_b}{\theta_w}\right)} \qquad \text{(Eq. 14.4)}$$

Here $C_{w.v}$ [kg-water/m^3-air] represents the water vapor concentration at 100% humidity and the aquifer temperature, ρ_w represents the liquid density of water [kg/m^3-H_2O], and all other terms are as defined above in Equation 14.1. Table 14.4 presents worst case cleanup times for typical CAHs of interest in the hypothetical one-acre x 20-ft thick dissolved plume. As can be seen, hundreds of years of treatment are projected for cases of poor contact between the air distribution and the target treatment zone. This calculation further illustrates that the key to IAS implementation is designing systems that will achieve good air contact with the dissolved contaminants.

Table 14.4. Sample Worst Case Performance Estimate Using Equation 14.4 for the Hypothetical One-Acre CAH Dissolved Plume Site

Chemical Name	Henry's Law Constant H_i (16°C) (m^3-H_2O/m^3-air)	Organic Carbon Partitioning Coefficient K_{oc} (m^3-H_2O/kg-carbon)	Sorption Coefficient $^{(1)}$ K_s (L-H_2O/kg-solids)	Maximum Cleanup Time t for Evaporation-Limited Scenario [d]	Maximum Cleanup Time t for Evaporation-Limited Scenario [y]
1,1 DCE	0.79	65	0.65	8.2E+04	2.3E+02
1,2 DCE (*cis*)	0.11	35	0.35	5.3E+04	1.4E+02
1,2 DCE (*trans*)	0.27	38	0.38	5.6E+04	1.5E+02
1,1 DCA	0.16	53	0.53	7.0E+04	1.9E+02
1,2 DCA	0.026	38	0.38	5.5E+04	1.5E+02
1,1,1 TCA	0.48	135	1.35	1.5E+05	4.1E+02
1,1,2 TCA	0.023	75	0.75	9.1E+04	2.5E+02
TCE	0.28	94	0.94	1.1E+05	3.0E+02
PCE	0.47	265	2.65	2.8E+05	7.5E+02
Vinyl Chloride	0.89	19	0.19	3.8E+04	1.0E+02

Chemical properties source: http://www.epa.gov/Athens/research/regsupport/properties.html
(1) – for f_{oc} = 0.01 kg-OC/kg-solids
Q = 800 ft^3/min = 33,000 m^3/d
V = 1 acre footprint x 20 ft thickness = 24,000 m^3
θ_v= 0.02 m^3-air/m^3-aquifer
θ_w= 0.33 m^3-H_2O/m^3-aquifer
ρ_b = 1.7 kg-solids/L-aquifer
All results calculated using Equation (14.4)

***Flow-Through IAS Barrier Applications*:** The reduction in concentration achieved as groundwater flows through the treatment zone can be estimated from:

$$\frac{C_w}{C_w^o} = \exp\left[-\frac{Q_T H_i}{W q_w T_p}\right] \qquad \text{(Eq. 14.5)}$$

where Q_T [m^3-air/day] is the total air flow rate into the IAS barrier (assumed to be evenly distributed along the IAS barrier), W [m] is the width of the barrier perpendicular to the groundwater flow direction, Tp [m] is the plume thickness, and q_w [m^3-H_2O/m^2-aquifer/day] is the groundwater specific discharge.

14.3.2.4 Question 4: What are the Challenges Likely to Be at This Site (Stratification, Vapor Control, Well Construction, etc.)?

For this hypothetical one-acre site, the major challenge appears to be determining ways to minimize the cost of injection wells, either through innovative installation procedures (using direct-push methods), or through a site-specific pilot demonstration that larger injection well spacings will be sufficiently effective.

In summary, the initial feasibility screening suggests that IAS might achieve the desired treatment at the site within a reasonably short time frame; however, the standard IAS system design and costs would have to be compared with other competing technologies. With respect to the economics, there is likely to be sufficient incentive to determine injection well spacing on a site-specific basis in the pilot-testing phase (as discussed below).

14.4 PILOT TESTING

The IAS pilot test should be designed to: (1) look for indicators of infeasibility, (2) characterize the air distribution to the extent practicable and (3) identify any safety hazards to be addressed in the full-scale design. This section provides a brief overview of the pilot test activities included in this Simple Design Paradigm (Table 14.5); a more complete discussion can be found in R. Johnson et al. (2001a).

Table 14.5. Summary of Possible IAS Pilot Test Activities

Activity	Question(s) Answered	Simple Design Approach	Site-Specific Design Approach
Injection Pressure - Flow Rate Test	Is it possible to achieve desired flow rate at reasonable pressures?	X	X
Transient Pressure Transducer Response Test	What are the general characteristics of the air distribution—is it likely to be more like the semi-conical homogeneous-setting air distribution or is there a significant degree of stratification?	X	X
Dissolved Oxygen Measurements	What is the approximate lateral extent of the air distribution? Are there indications of preferred directions?	X	X
Helium Tracer Test	What is the approximation of lateral extent of the air distribution? Are there indications of preferred directions?	X	X
Soil Gas Sampling	What is the volatilization rate? Are there any obvious safety hazards?	X	X
SF_6 Distribution Test	What are the vertical and lateral extent of the air distribution in the target treatment zone? What are the mass transfer rates to and from groundwater?		X
Other Geophysical Tools	What is the vertical and lateral extent of the air distribution in the target treatment zone?		X

Prior to planning the pilot test, the user should:

- Define the target treatment zone,
- Propose a conceptual model for the air distribution in the treatment zone,

- Determine by economic analysis if 15-ft (5-m) injection well spacings are cost prohibitive, and if so, determine the minimum injection well spacing that is not cost prohibitive,
- Propose the depth, location and construction specifics of a pilot test well, and
- Determine the expected range of operating pressures for the injection well.

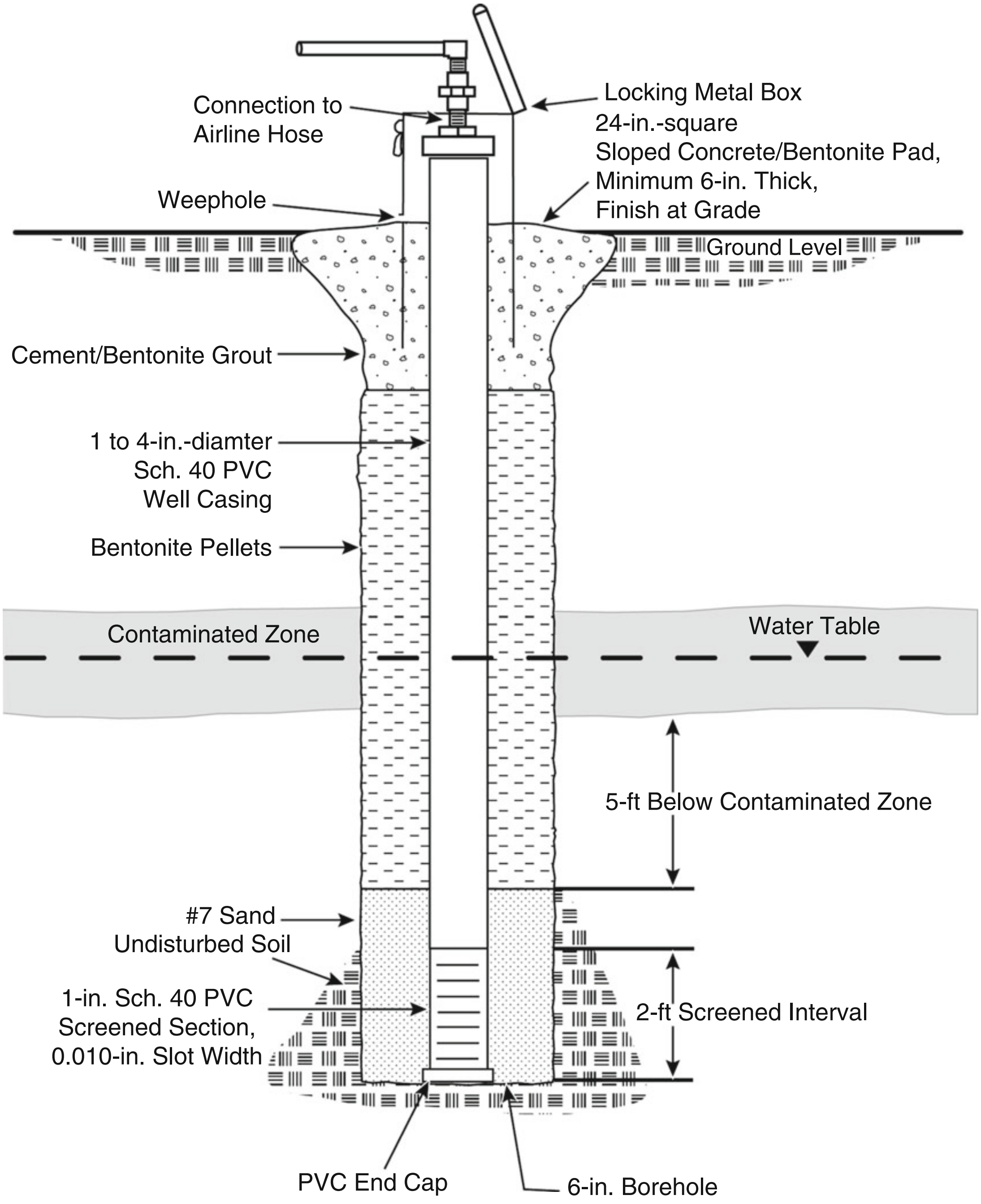
Recommended pilot test activities are summarized in Table 14.5; details of these can be found in Bruce et al. (2001) and R. Johnson et al. (2001a, 2001b, 2001c). Five of the activities are common to both the simple and site-specific design approaches, while the SF_6-distribution test (Bruce et al., 2001) is unique to the site-specific paradigm. In deciding whether or not to perform the additional SF_6-distribution test, the cost of the additional testing, the potential cost savings of larger injection well spacings, the impact of larger or smaller well spacings on remediation performance, and the benefits of better understanding the air distribution should be considered.

Users may also consider the use of geophysical tools for air distribution characterization. For example, use of neutron probes, capacitance probes and electrical resistance tomography are reported in the literature (e.g., Acomb et al., 1995; Daily et al., 1995; Lundegard and LaBreque, 1998).

The following are needed for an IAS pilot test:

- At least one air injection well, but preferably more, constructed in the same way wells might be constructed for the full-scale application. A typical air injection well is 1 to 4 inches (2.5 to 10 centimeters [cm]) in diameter with a 2 to 5 ft (0.6 to 1.5 m) long screened section placed about 5 ft (1.5 m) below the deepest extent of contamination. Multiple wells screened at different depths may be necessary for sites with the potential for significantly stratified air distributions. Figure 14.6 presents a schematic of a typical air injection well.
- An air supply compressor or blower capable of supplying 20 to 30 ft^3/min at an injection pressure falling in the range $0.43H_w$ to $0.73H_T$ pounds per square inch gauge (psig), where H_w [ft] is the depth to the top of the well screen below the groundwater table and H_T [ft] is the total depth below ground surface to the top of the well screen. $0.43H_w$ [psig] is the minimum pressure needed to displace water from the well down to the top of the well screen and $0.73H_T$ [psig] is the estimated soil fracture pressure. It is not unusual to reach pressures that are 5 to 10 psig greater than $0.43H_w$ [psig] before measurable flow into the aquifer begins.
- A pressure gauge and flow meter capable of measuring the injection pressure at the well head and air flow rate into the well.
- Three groundwater pressure monitoring wells with data-logging water pressure transducers capable of measuring the transient changes in the groundwater pressure. These wells are constructed like typical groundwater monitoring wells, with screened intervals spanning the target treatment zone thickness, and are placed at different distances away from the air injection well as shown in Figure 14.7.
- Six to twelve discrete aquifer/vadose zone monitoring locations capable of sampling groundwater in the treatment zone and soil gas immediately above the groundwater table. These are usually smaller diameter wells with <1 ft screened intervals. In shallow settings (<30 ft) they may be installed as co-located direct-push wells at different depths and in deeper settings they are usually installed as multiple completions within a single borehole at each location. These discrete sampling wells are generally distributed to be able to detect asymmetries in the air distribution about the injection well. A sample pilot test layout is shown in Figure 14.7. Additional soil gas sampling points also should be located in close proximity to locations of concern (e.g., buildings).

- A helium detector, dissolved oxygen meter, portable gas detector (suitable for the chemicals of interest) and gas and groundwater sampling equipment.
- A vapor extraction and treatment system, if needed. For the case of dissolved CAH plume treatment, vapor treatment systems may not be needed.



NOT TO SCALE

Figure 14.6. Typical air injection well construction (Battelle, 2001).

In brief, an IAS pilot test involves:

- Obtaining pre-test measurements of groundwater pressure, dissolved oxygen concentrations in groundwater, helium and contaminant concentrations in deep soil gas, and SF_6 in groundwater, if the site-specific design paradigm is being used.
- Data-logging with the groundwater pressure transducers from pre-test to post-test conditions.
- Turning on the compressor and increasing the pressure at the injection well head to the point where the desired air flow rate is initiated (estimated to be roughly 5 to 10 psig greater than $0.43H_w$ [psig]). Then controlling the pressure to maintain a constant air flow rate; usually this requires slowly decreasing the well head pressure with time until steady flow is achieved.
- Adding helium tracer to the air injection flow and frequently monitoring deep soil gas for helium and contaminants for about 30 min; this is done only after reaching stable air injection flow and pressure conditions and stable groundwater pressure transducer readings. Monitoring the deep soil gas pressure to look for increases over background levels.
- Sampling groundwater to look for increases in dissolved oxygen after several hours (to several days) of air injection.
- Adding SF_6 to the air injection line for 12 to 24 hours and sampling groundwater to look for its appearance (if the site-specific design paradigm is used).

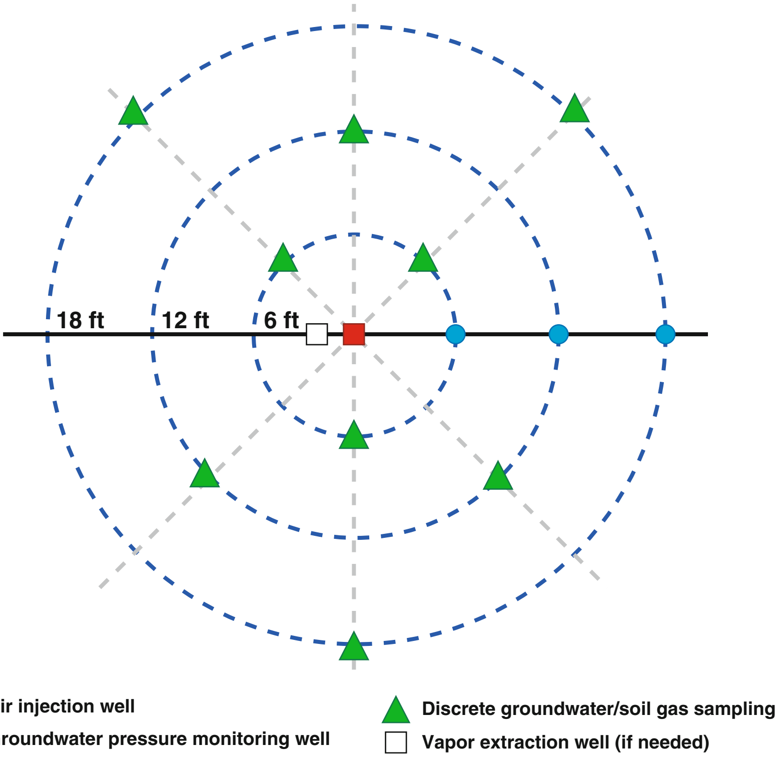


Figure 14.7. Sample IAS pilot test layout.

R. Johnson et al. (2001a; 2001b; 2001c) and Bruce et al. (2001) discuss pilot test activities and data reduction in detail and readers should review that work. In summary:

- Injection air pressure and air flow rate data help to determine compressor requirements for full-scale IAS application.

- Groundwater pressure vs. time data provide qualitative insight to the air flow distribution. As shown in Figure 14.8, pressure responses that rise and then drop down to pre-test baseline pressures are usually indicative of pressure distributions like those shown in Figure 14.3. Pressure responses that increase and then decline more slowly to a level above pre-test conditions are usually indicative of stratified air flow and growth of air pockets beneath finer-grained strata as shown in Figure 14.4.
- Rapid deep soil gas helium appearance at injection concentrations, groundwater dissolved oxygen concentration increases with time, and soil gas pressure increases provide insight to the lateral extent and symmetry/asymmetry of the air flow distribution.
- SF_6 data, if collected, provide insight to the lateral and vertical extent of the air flow distribution, its symmetry/asymmetry, and mass transfer between the air flow distribution and groundwater.
- Soil gas data can be used to determine if a soil vapor extraction system is needed for the site.

At the end of the pilot test, users should revisit and revise their answers to questions 1 through 4 discussed above in Section 14.3.2, and again assess if IAS is a feasible option for their site. If so, the next step is system design.

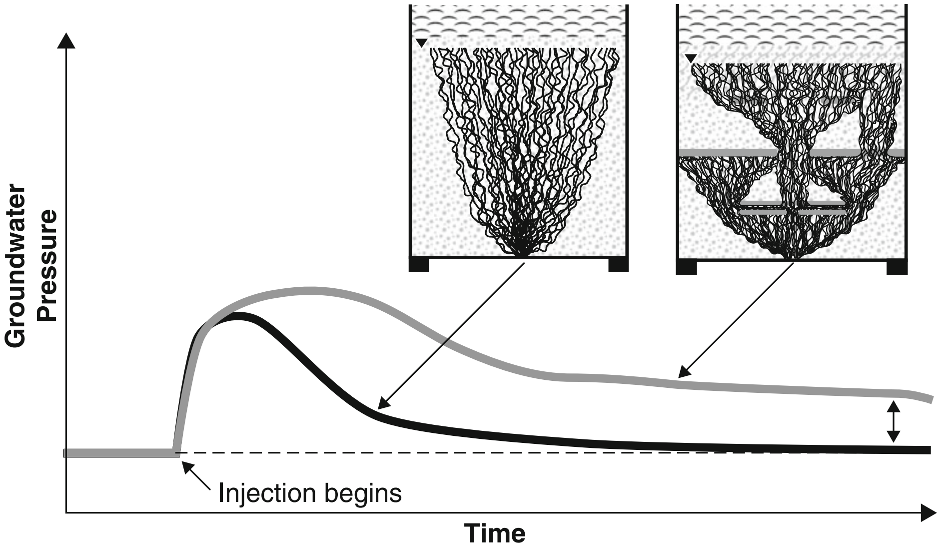


Figure 14.8. Qualitative interpretation of transient groundwater pressure data from IAS pilot test (air sparging overlays based on Ji et al., 1993: reprinted from Ground Water Monitoring & Remediation with permission of the National Ground Water Association. Copyright 1993.)

14.5 SYSTEM DESIGN

When designing an IAS system, the practitioner must first:

- Define the target treatment zone area and depth interval,
- Propose/revise a conceptual model for the air distribution in the aquifer,
- Identify injection well locations and screened intervals that ensure adequate air distribution throughout the target treatment zone based on pilot test results; if the Simple Design Paradigm is selected, 15-ft (5-m) well spacings are used; it will likely be necessary to install injection wells having a range of screened interval depths when dealing with stratified air distributions,

- Define the range of air injection operating pressures, and
- Determine if a soil vapor extraction system is necessary

If a soil vapor extraction (SVE) system is necessary, it may be convenient and cost effective to collocate the air injection and soil vapor extraction wells in the same borehole. SVE wells generally can be more widely spaced than IAS wells, so co-located SVE and IAS wells in each IAS well location will not likely be needed at most sites. For IAS barrier systems, it is very unlikely that SVE wells would be needed given that the flux of dissolved contaminants to IAS barriers is generally very low; however, local regulations specific to this issue should be checked. In considering the placement and spacing of wells, one should consider that systems with more densely spaced wells will be more robust (greater probability of success and more options for optimization).

The piping and manifolding of the wells needs to be designed so that each well has its own dedicated pressure gauge and flow meter, and that these can be easily read by a user adjusting the control valves. A common design flaw in IAS systems is the use of common pressure gauges and flow meters for multiple wells. In addition, sampling access ports should be installed at least in the main air injection and soil gas extraction manifold(s), if not in each individual line (this facilitates diagnostic tests used to optimize the system).

Pulsed operation of banks of two to five injection wells should be considered for the following reasons: (1) the difficulty of controlling a multi-well air injection system increases as the number of wells manifolded together increases, (2) the required system injection flow capacity is lower in this mode, (3) studies suggest that performance can be improved by operating in a pulsed mode and (4) pulsed operation may be necessary in IAS barrier applications to prevent groundwater bypassing due to water relative permeability reductions caused by air injection. Thus, the total air flow capacity of the system, Q_T (ft^3/min), is dictated by the number of wells in each well bank, the flow to each well and the frequency at which each well bank is operated. For systems having identical numbers of wells in each well bank (N_{wells}), equal flow rates to each injection well ($Q_{inject,i}$), and equal injection frequencies (F_i):

$$Q_T = N_{Wells} \times Q_{inject,i} \times N_S \times F_i \qquad \text{(Eq. 14.6)}$$

where N_S is the number of banks to be operated simultaneously. For example, in the case of the 160 wells required in the simple design for the hypothetical one-acre site discussed above, the total air flow rate required is calculated:

$$QT(\text{plume treatment}) = 5\,\text{wells} \times 20\,\text{ft}^3/\text{min} \times 32\,\text{banks} \times 6\,\text{hr}/24\,\text{hr} = 800\,\text{ft}^3/\text{min} \qquad \text{(Eq. 14.7)}$$

for a system using five wells per bank and a total of six hours of on-time per day for each bank. For the IAS barrier application and this dissolved plume, an average air injection rate is:

$$QT(\text{barrier}) = 5\ \text{wells} \times 20\,\text{ft}^3/\text{min} \times 2\ \text{banks} \times 6\,\text{hr}/24\,\text{hr} = 50\,\text{ft}^3/\text{min} \qquad \text{(Eq. 14.8)}$$

It is important that the blower(s) or compressor(s) be capable of providing the desired flow at the air injection pressure range determined in the pilot test, and be capable of long-term steady operation. Economics may dictate the use of multiple compressors (rather than one large one) for systems requiring flows in excess of 100 to 200 ft^3/min. As discussed above, the compressor will need to be capable of operating at pressures that are 5 to 10 psig above $0.43H_w$ where H_w [ft] is the depth to the top of the well screen below the groundwater table. In addition, practitioners will have to be wary of using pressures in excess of $0.73H_T$ psig (where H_T [ft] is the total depth below ground surface to the top of the well screen) as this may induce soil fracturing about the injection well. Compressor selection should always be discussed with a reputable manufacturer.

There is little fundamental basis for determining how to choose pulsing frequencies (defined by on and off times). SVE system off-gas data, if available, provides a direct measure of volatilization removal rates, and therefore can be used to assess how changes in pulsing conditions affect volatilization rates. If aerobic biodegradation or gaseous reactant delivery is the goal (instead of volatilization), simple calculations suggest that periods between injections (the "off" times) can be as long as several days to weeks as trapped reactant gas remains in the aquifer pores between injections, provided that the reactant does not react with the aquifer solids. Some feel that the minimum active duration of injection (the "on" times) should be consistent with transient pressure transducer response data (Figure 14.8). Air injection needs to last at least as long as the time necessary to reach the peak in transducer response, and preferably as long as the time required to reach the asymptote. It is thought that these are representative of the times for air to emerge from the aquifer into the vadose zone, and the times necessary to reach near-steady flow conditions (R. Johnson et al., 2001b).

A typical well construction schematic is presented in Figure 14.6. It should be noted that competent annular well seals are critical to successful IAS operation, and they can fail. In their absence, the injected air will flow up along the well bore and the well will be ineffective. In some settings, adding a few feet of blank casing below the screened interval may be desired as air injection wells can become clogged over time with the fines that flow back into the well with water at the beginning of each "off" cycle. This problem can be minimized to some degree by standard well development practices prior to use of the well for air injection. Also, one might consider the potential for some small fraction of their air injection wells to fail when selecting the placement and number of wells.

It should be noted that the comments above are specific to conventional well designs and some are investigating alternate designs that might offer the potential for adjustable depth air sparging from a single well (e.g., Drucker, 2001).

14.6 IAS SYSTEM MONITORING AND OPTIMIZATION

It is important to view the initial IAS system design and installation as a starting point and to anticipate the need for system optimization. Thus, monitoring IAS performance is critical to maximizing system operation.

At start-up, and any time the operating conditions are changed, the following measurements should be conducted:

- The flow to and pressure at each injection well, and
- The on/off duration (timer sequence) for flows to each well.

In addition, to address safety concerns associated with IAS system operation and to verify vapor extraction/capture system performance (if applicable), the following should be considered:

- Soil gas monitoring at nearby locations of concern (basements, sewers, etc.) if liberated contaminant vapor concentrations could be significant enough to be of concern from a health and safety standpoint,
- A helium distribution test to assess distribution and migration of liberated vapors; this is conducted by blending helium into the injection air,
- A helium recovery test to assess soil vapor extraction recovery efficiency (if appropriate), and

- Control systems to ensure shut-down of the air injection system if the SVE system ceases operation.

During continued operation, the following measurements should be made on a periodic basis (quarterly, semi-annual, etc.):

- IAS system injection flow rates (daily to weekly); if applicable, SVE system off-gas concentration and flow rate monitoring (daily to weekly),
- Groundwater quality monitoring—dissolved oxygen and contaminant concentrations (quarterly to semi-annual), and
- Groundwater level measurements in wells unaffected by air injection (seasonal) to assess the position of the groundwater table relative to the injection and extraction wells screened intervals.

IAS system optimization generally involves: (1) adding new air injection wells, (2) changing air injection flow rates and (3) changing pulsing frequencies. Again, the goal is to modify the system to achieve good air distribution throughout the target treatment zone.

During continued IAS system operation, volatilization removal rates typically decline to low (and often non-detect) levels (Johnson et al., 2001a). At that point it is difficult to assess real-time system performance via traditional measurements (e.g., groundwater monitoring, SVE off-gas sampling, etc.). In those cases, if real-time assessment is important, users should consider the tracer-based tests utilized by Amerson et al. (2001) and Bruce et al. (2001).

Post-treatment measurements should include groundwater quality monitoring at quarterly intervals for at least one year, with concurrent groundwater level measurements.

14.7 TYPICAL DESIGN AND OPERATION FLAWS WHEN EMPLOYING IAS SYSTEMS

Based on the authors' experiences, the following are typical design and operating flaws of concern:

- Under designing the air injection well network by using injection well spacings that are too large to achieve the necessary air distribution in the target treatment zone. Often this happens when the system economics are not well understood, leading practitioners to think that saving money on well installation costs will reduce overall project costs, without realizing the cost increases associated with longer system operation and reduced treatment effectiveness. Misinterpretation of pilot test data (in particular transient pressure response data) may also lead to under designed injection well networks.
- Not properly designing and instrumenting the system so that flow directed to each individual air injection well can be verified and measured. It is the authors' experience that many systems do not have this level of instrumentation. Quite frequently systems have a single flow measurement for an entire manifold of air injection wells. In those systems, one cannot determine the flow to each well, or even if there is flow to a given well in a multiple well system (unless only one well operates at a given time during normal system operation). It is the authors' experience that, in systems containing injection wells sharing a common manifold, all the air may be flowing to only a few of the manifolded wells. As discussed in P. Johnson et al. (2001a), the combination of variations in screened intervals, variations in soil properties, and the complex nature of air flow–injection pressure relationships leads to this common problem. Thus, individual flow meters, pressure gauges and valves are critical to proper IAS system operation.

- Misinterpretation of groundwater quality data. As illustrated by P. Johnson et al. (1997), groundwater quality data obtained from conventional monitoring wells can be compromised by IAS system operation. In such cases, practitioners often observe rapid increases in dissolved oxygen levels and rapid declines in dissolved contaminant concentrations. Then, after system operation, contaminant concentrations may rebound to near pre-treatment levels; in some cases, this rebound may occur over periods of 1 to 12 months. Thus, one must be cautious when interpreting monitoring well data at IAS sites. To help minimize the potential for errors, P. Johnson et al. (1997) suggest: (1) long-term (12 months) monitoring following system shut-down; (2) use of discrete (narrowly-screened) groundwater sampling installations; or (3) short-term (12 to 24 hr) continuous slow-purging of conventional monitoring wells (or discrete sampling points) with time-series sampling. With respect to the latter, it has been observed that short-term continuous purging eventually yields samples that are more representative of formation conditions than in-well conditions, and that this might replace the need for longer-term groundwater quality monitoring.
- Installing and operating a system, but failing to optimize its performance over time.

14.8 SUMMARY

This chapter has provided an overview of IAS feasibility assessment, system design, monitoring, and operation as applied to dissolved CAH plumes. For a more in-depth discussion readers are referred to the sequence of articles co-authored by Amerson et al. (2001), Bruce et al. (2001), P. Johnson (2001a, 2001b) and R. Johnson (2001a, 2001b, and 2001c), as well as the articles listed below.

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CHAPTER 15

CHEMICAL OXIDATION AND REDUCTION FOR CHLORINATED SOLVENT REMEDIATION

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15.1 INTRODUCTION

In situ chemical oxidation (ISCO) is the intentional use of chemical oxidants to destroy or degrade chemical contaminants of concern, including chlorinated solvents. The typical end products for chlorinated solvents treated with ISCO are carbon dioxide and chloride ion. *In situ* chemical reduction (ISCR) is the intentional use of chemical reductants to transform or degrade chemical contaminants, including chlorinated solvents. The end products for ISCR treatment of chlorinated solvents vary from completely dechlorinated compounds (i.e., ethene from trichloroethene [TCE]) to carbon dioxide and chloride ion.

ISCO and ISCR are mirrored technologies, both involving the transfer of electrons. In chemical oxidation, electrons are transferred from the substrate to the oxidant. The substrate loses electrons and becomes oxidized; the oxidant gains electrons and becomes reduced as illustrated in the oxidation of TCE by ozone.

$$H_2O + ClHC = CCl_2 + 3O_3 \rightarrow 2CO_2 + 3Cl^- + 3H^+ + 3O_2 \qquad \text{(Rx. 15.1)}$$

$$\text{Substrate: } ClHC = CCl_2 + 4H_2O \rightarrow 2CO_2 + 3Cl^- + 9H^+ + 6e^- \qquad \text{(Rx. 15.2)}$$

$$\text{Oxidant : } 3[O_3 + 2e^- + 2H^+ \rightarrow O_2 + H_2O] \qquad \text{(Rx. 15.3)}$$

In chemical reduction, electrons are transferred from the reductant to the substrate. The substrate gains electrons and becomes reduced; the reductant loses electrons and becomes oxidized as illustrated in the reduction of TCE by zero-valent iron.

$$ClHC = CCl_2 + Fe^0 \rightarrow HC \equiv CCl + 2Cl^- + Fe^{+2} \qquad \text{(Rx. 15.4)}$$

$$\text{Substrate : } ClHC = CCl_2 + 2e^- \rightarrow HC \equiv CCl + 2Cl^- \qquad \text{(Rx. 15.5)}$$

$$\text{Reductant : } Fe^0 \rightarrow Fe^{+2} + 2e^- \qquad \text{(Rx. 15.6)}$$

An important question in understanding the applicability of chemical oxidation and reduction to the treatment of chlorinated solvents is determining which solvents are amenable to oxidation and/or reduction. How susceptible a chlorinated solvent is to oxidation or reduction is ultimately determined by its chemical structure. In general, solvents with carbon atoms that are electron rich are more susceptible to oxidation than those that are electron deficient. Conversely, solvents with carbon atoms that are electron deficient are more susceptible to reduction than those that are electron rich.

General reactivity principles of ISCO and ISCR for chlorinated solvents are that (1) double bonds increase electron density (Pi cloud), making the solvent more susceptible to oxidation and (2) chlorine atoms (electron withdrawing) decrease electron density, making the solvent more susceptible to reduction. These principles are illustrated by looking at the effect of double

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bonds and chlorine atoms on the ionization potential (IP) for several chlorinated solvents. The IP is a measure of how readily a compound gives up an electron, and is therefore oxidized. Table 15.1 presents the IP for a series of saturated and unsaturated chlorinated solvents.

Table 15.1. Ionization Potentials of Selected Chlorinated Solvents (data obtained from Montgomery, 1996)

Saturated Compound	IP	Unsaturated Compound	IP
Chloroethane	10.98	Vinyl Chloride	10.0
1,2-Dichloroethane	11.12	*cis*-Dichloroethene	9.65
Chloropropane	10.78	Chloropropene	10.04
Dichloropropane	10.87	Dichloropropene	9.82
Chloromethane	11.28		
Dichloromethane	11.35		
Chloroform	11.37		
Carbon Tetrachloride	11.47		

The addition of chlorine generally increases the IP, the addition of a double bond decreases it. The lower the IP, the more easily the solvent is oxidized; the higher the IP, the more easily the solvent is reduced. Of note, the effect of adding a double bond on lowering the IP is much greater than the effect of adding chlorines on raising the IP. This effect of structure on the IP translates to rules-of-thumb for the *in situ* chemical oxidation and/or reduction of chlorinated solvents. Chlorinated solvents with double bonds are generally oxidizable. Chlorinated solvents with multiple chlorines are generally reducible.

Another way of understanding the oxidation and reduction of chlorinated solvents is to note that chlorine is an oxidant. The more chlorines added to a solvent the more oxidized the solvent is and the more resistant it will be to further oxidation. Consider the number of electrons generated in the theoretical oxidation half-reactions for methane and the chloromethanes:

$$CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^- \qquad \text{(Rx. 15.7)}$$

$$CH_3Cl + 2H_2O \rightarrow CO_2 + 7H^+ + Cl^- + 6e^- \qquad \text{(Rx. 15.8)}$$

$$CH_2Cl_2 + 2H_2O \rightarrow CO_2 + 6H^+ + 2Cl^- + 4e^- \qquad \text{(Rx. 15.9)}$$

$$CHCl_3 + 2H_2O \rightarrow CO_2 + 5H^+ + 3Cl^- + 2e^- \qquad \text{(Rx. 15.10)}$$

$$CCl_4 + 2H_2O \rightarrow CO_2 + 4H^+ + 4Cl^- \qquad \text{(Rx. 15.11)}$$

Methane is completely reduced and yields eight electrons when oxidized. Carbon tetrachloride is fully oxidized and can yield no more electrons; it cannot be further oxidized.

The theoretical equations for the sequential chemical reduction of the chloromethanes show the opposite effect, the more chlorines present, the more electrons can be adsorbed (reduction).

$$CCl_4 + H^+ + 2e^- \rightarrow CHCl_3 + Cl^- \text{(reduction to } CH_4 \text{ requires eight electrons)} \qquad \text{(Rx. 15.12)}$$

$$CHCl_3 + H^+ + 2e^- \rightarrow CH_2Cl_2 + Cl^- \text{(reduction to } CH_4\text{, six electrons)} \qquad \text{(Rx. 15.13)}$$

$$CH_2Cl_2 + H^+ + 2e^- \rightarrow CH_3Cl + Cl^- \text{(reduction to } CH_4\text{, four electrons)} \qquad \text{(Rx. 15.14)}$$

$$CH_3Cl + H^+ + 2e^- \rightarrow CH_4 + Cl^- \text{(reduction to } CH_4\text{, two electrons)} \qquad \text{(Rx. 15.15)}$$

Carbon tetrachloride, being fully oxidized, will “consume” eight electrons to be completely reduced to methane. Chloromethane, being lightly oxidized, can only consume 2 electrons.

ISCO and ISCR both have roots in industrial waste treatment. Their use for the *in situ* treatment of chlorinated solvents began in the 1990s. Both treatment technologies are still evolving. The following discussion will detail the current state-of-the-practice for both technologies and will also discuss some of the development trends.

15.2 *IN SITU* CHEMICAL OXIDATION (ISCO)

15.2.1 Development of ISCO

There are four classes of oxidants that are currently used for ISCO. These include hydrogen peroxide based systems, the permanganates (sodium and potassium), activated sodium persulfate and ozone. Each of these oxidant systems has had an independent and varied history and each has a different level of site utilization for chlorinated solvents treatment. Hydrogen peroxide and potassium permanganate are the two oxidants that have been used the longest and are currently the most widely used for chlorinated solvents. Ozone has had more limited application. Activated sodium persulfate is the most recently developed of the oxidant systems and is gaining wider usage.

Hydrogen peroxide was the first chemical oxidant used *in situ* to treat organic contaminants. It was used in 1985 to treat a formaldehyde spill at Monsanto’s Indian Orchard Plant in Springfield, MA (Brown et al., 1986). A 10% solution of hydrogen peroxide was injected through shallow screened wells into a dissolved formaldehyde plume. The use of hydrogen peroxide for *in situ* treatment of groundwater was based on three concurrent applications of hydrogen peroxide. The first was the use of hydrogen peroxide to treat industrial waste water contaminants such as sulfides and phenols. Most industrial hydrogen peroxide systems were loosely based on the work of H.J.H. Fenton (1894) and used iron salts at a pH of 3 to 5 to catalyze peroxide reactivity. The second hydrogen peroxide technology that provided a basis for ISCO was the use of hydrogen peroxide for *in situ* uranium mining which began in the mid 1970s (The Texas State Historical Association, 2001). This application was based on injecting hydrogen peroxide into subsurface formations to treat contaminants (Brown and Norris, 1986). The third was the use of hydrogen peroxide solutions to stimulate *in situ* biodegradation (Raymond et al., 1986; Ward et al., 1988). Hydrogen peroxide was injected to provide oxygen. This application helped to develop the infrastructure for using hydrogen peroxide on sites and for injecting peroxide solutions to treat groundwater. The synthesis of these three applications provided the genesis of hydrogen peroxide based ISCO.

Beginning in the mid to late 1990s there was rapid growth in the use of hydrogen peroxide based systems to treat groundwater contaminants. Three companies were founded in 1995 that provided commercial application of “Fenton’s Reagent,” Geo-Cleanse, Clean-Ox (successor is MECX, LLC), and ISOTEC (*In Situ* Oxidative Technologies, Inc.). Geo-Cleanse and MECX used acid and iron salts to catalyze the hydrogen peroxide; ISOTEC used a chelated iron at neutral pH. The initial applications of hydrogen peroxide were focused primarily on treating benzene, toluene, ethylbenzene, and total xylenes (BTEX) and other fuel hydrocarbons. This focus reflects the initial concern of the groundwater remediation industry on hydrocarbon sites. Treating gasoline sites fueled the growth of hydrogen peroxide for ISCO. As the remediation industry began to shift focus from hydrocarbons to chlorinated solvents, hydrogen peroxide based ISCO was already accepted as a “proven” remediation technology. As a result, hydrogen peroxide was investigated both in the laboratory and the field for treating chlorinated solvents (Leung et al., 1992; Ravikmur and Gurol, 1994; Gates and Siegrist, 1995).

The development of permanganate based ISCO parallels, to some degree, the development of hydrogen peroxide. Prior to being used for ISCO, permanganate was used for industrial waste treatment, primarily for treating sulfides and phenols. However, unlike hydrogen peroxide, permanganate does not oxidize benzene. As a result, the development of permanganate for treating chlorinated solvents did not have the benefit of having been "proven" in the hydrocarbon market. Beginning in the early 1990s, permanganate was successfully demonstrated in the laboratory as an oxidant for treating chlorinated solvents (Truax, 1993; Vella and Veronda, 1994). However, injection of permanganate solutions for treating contaminants did not occur until the late 1990s (Schnarr et al., 1998). Permanganate technology lacked the infrastructure for field application that had been developed for hydrogen peroxide. Once the technology was available for injecting permanganate solutions, use of permanganate for ISCO grew rapidly.

By the end of the 1990s ISCO was an established remedial technology. The DoD Environmental Security Technology Certification Program (ESTCP) published a report, Technology Status Review: *In Situ* Oxidation, in 1999 that documented 42 sites that had used ISCO (ESTCP, 1999). Table 15.2 summarizes the characteristics of the sites reviewed.

Hydrogen peroxide was the most prevalent oxidant used (88% of sites). Applications were essentially equally divided between chlorinated solvents (48%) and hydrocarbons (total petroleum hydrocarbons [TPH]/BTEX) (52%). Only 35% of the sites were full scale; most of the applications were pilot scale (65%). The use of ISCO was moderately successful; 45% of the sites met performance objectives.

Ozone has had a more limited application for chlorinated solvents. Ozone has two limitations that have affected its use at chlorinated solvent sites. First, it is a gas and is used as a 5 to 10% component in an air or oxygen stream. Injecting ozone into areas of high chlorinated solvent concentrations can lead to stripping and volatilization of the solvents, necessitating equipment to capture and treat the solvent vapors. Second, since ozone is a component of a gas stream, and is of limited solubility in water, it is difficult to rapidly apply significant quantities of ozone to a site. A "large" ozone generator will produce less than 25 kilograms (kg) of ozone per day. By comparison, a 5% solution of potassium permanganate contains 50 kg of permanganate per cubic meter (1,000 liter [L]) of solution, which at an injection rate of 10 L/min could be applied in less than two hours. Given these limitations, ozone has been generally limited to treating low to moderate level dissolved chlorinated volatile organic compound (CVOC) plumes.

The development of sodium persulfate for ISCO began in the late 1990s (Pugh, 1999; Hoag et al., 2000). Interest in persulfate was fueled by two factors. The first factor was the chemistry of persulfate. The second was the limitations of peroxide and permanganate. Persulfate is a peroxygen compound and therefore potentially shares some of the pathways and the "universal" reactivity of hydrogen peroxide. It is used in total organic carbon (TOC) analysis because of its ability to completely oxidize most organic compounds (when heated). Thus persulfate could potentially equal the reactivity of peroxide with the added benefit that it is much more stable than hydrogen peroxide and therefore has the potential to last longer and spread further *in situ*. One of the primary limitations to peroxide use *in situ* is its stability. Peroxide does not persist long enough in many situations to be effectively transported. Permanganate, the second most common oxidant, has two significant limitations that have also generated interest in other oxidants. First, it basically only treats chlorinated solvents that have double bonds. Second, permanganate is readily consumed by soil organics. Persulfate has the potential to oxidize a wider range of chlorinated solvents and does not appear to be highly reactive to soil organic material.

Table 15.2. Characteristics of Sites That Have Used ISCO (ESTCP, 1999)

	DoD[1]	DOE	Private	Total
Number of Sites	14	3	25	42
Contaminants				
CVOC	6	3	10	19
BTEX/TPH	5	—	16	21
Both	1	—	—	1
Unknown	1	—	—	1
Media Treated				
Soil Only	0	0	0	0
Groundwater	2	0	17	19
Both	10	3	7	20
Unknown	2	—	1	3
Oxidant				
Hydrogen Peroxide	12	1	24	37
Potassium Permanganate	1	2	1	4
Ozone	1	0	0	1
Vendor				
GeoCleanse	8	1	4	13
Clean-Ox	3	0	13	16
ISOTEC	1	0	7	8
Other	2	2	1	5
Scale				
Pilot/Demo Only	9	3	15	27
Full Only	1	0	4	5
Both	4	0	6	10
Outcome[2]				
Success	5	3	11	19
Failure	6	0	0	6
Uncertain	3	0	14	17

[1] DoD Breakdown: Navy (NFESC) = 5; Army (USACOE)/AF = 7; Army (Base Contract) = 2

[2] Outcome determinations are relative terms based on available Phase 1 information provided by facility representative (e.g., direct comments or pilot-scale tests that led to full-scale operations). These terms denote the ISCO technology's ability or lack thereof to satisfy facility-specific program performance objectives.

The focus of persulfate development has been on the use of activator systems. Even though persulfate is a strong oxidant it requires activation to enhance the rate of reaction. The initial persulfate technology used Fe(II) salts or heat to activate the persulfate (Hoag et al., 2000). Since these initial activator systems were identified, a number of other activators have been developed including chelated iron, high pH and hydrogen peroxide (Block et al., 2004). Two of the new activator systems, high pH and peroxide, have demonstrated broad reactivity with chlorinated solvents, being able to treat chloroethenes, chlorobenzenes, chloroethanes and chloromethanes (Block et al., 2004).

Application technologies have developed in parallel with the oxidizer chemistries as ISCO technology has evolved. The earliest ISCO application systems were generally variations of conventional injection wells. There has been some initial work done with deep soil mixing and hydraulic fracturing (Siegrist et al., 2001). Deep soil mixing has been used with both hydrogen peroxide and permanganate. The hydraulic fracturing was used to emplace solid permanganate or a permanganate-clay mixture. Development of direct push injection as a delivery method has been an important factor in the growth of ISCO (Frazier et al., 2004). Oxidant is injected successively in discrete intervals over the zone under treatment. This technique allows for the rapid application of oxidants. Another innovation in soil mixing technology using mixer heads and one track excavators has led to growth in the application of oxidants through soil mixing (Redox Tech, 2007). This approach has two advantages over the earlier use of deep-soil mixing, it is much less expensive and has a much smaller footprint. Its disadvantage is that its depth limit is 20 to 30 feet.

The use of ISCO for chlorinated solvents continues to develop on two fronts – improved oxidant chemistry and improved delivery. Oxidant chemistry is continually expanding the range of solvents treatable. Delivery techniques are lowering the cost of application and increasing oxidant-contaminant contact and, therefore, the effectiveness.

15.2.2 Oxidants Used for ISCO

As previously discussed, there are four oxidant systems currently used in ISCO for treating chlorinated solvents. These four are hydrogen peroxide based systems, permanganate systems, persulfate systems and ozone systems. For each of these oxidant systems there are several variations in reaction conditions. Table 15.3 summarizes the different oxidant systems, giving equivalent weights and oxidation potentials.

Table 15.3. Comparison of Oxidant Systems

Oxidant	Formula	Molecular Weight	Number of Electrons Transferred	Equivalent Weight	Oxidation Potential
Hydrogen Peroxide	H_2O_2	34	2	17	1.77
Hydrogen Peroxide, Fenton's	H_2O_2	34	1	34	2.76
Calcium Peroxide	CaO_2	72	2	36	0.9*
Magnesium Peroxide	MgO_2	56	2	28	0.9*
Sodium Percarbonate	$2Na_2CO_3–3H_2O_2$	314	6	52	0.9*
Potassium Permanganate	$KMnO_4$	158.04	3	52.7	1.7
Sodium Permanganate	$NaMnO_4$	141.9	3	47.3	1.7
Sodium Persulfate	$Na_2S_2O_8$	238	2	119	2.01
Activated Sodium Persulfate	$Na_2S_2O_8$	238	2	119	2.6
Ozone	O_3	48	2	24	2.07

*Alkaline pH

Table 15.4 summarizes key data that can be used to assess the applicability of ISCO to various chlorinated solvents. The stoichiometric ratio for oxidizing a solvent with a particular oxidant is calculated by dividing the equivalent weight of the oxidant (Table 15.3) by the equivalent weight of the solvent. The maximum contaminant level (MCL) gives an indication of how low clean-up goals may be and therefore how aggressive treatment needs to be. Generally the lower the MCL the more difficult it is to achieve. The solubility and the soil organic carbon-water partition coefficient (K_{oc}) give an indication of how the solvent will partition into groundwater and, therefore, how significant a factor soil treatment may be. The more strongly adsorbed a solvent is, the more difficult it will be to oxidize since most of the oxidant systems are aqueous. With strongly sorbed solvents, the rate limiting factor is often the rate of dissolution.

Table 15.4. Applicability of ISCO for Remediation of Chlorinated Solvents (data obtained from Montgomery, 1996; Verschueren, 2001)

	Molecular Weight	Equivalent Weight	Density (g/mL)	Solubility (mg/L)	Log Koc	MCL (mg/L)
Chloromethanes						
Chloromethane	51	8.41	Gas	7,250	1.4	
Dichloromethane	84.93	21.23	1.336	20,000	1.44	0.005
Chloroform	119.4	59.69	1.489	8,000	1.57	0.1
Carbon Tetrachloride	153.8		1.594	785	2.2	0.005
Chloroethanes						
Chloroethane	64.5	5.38	0.903	5,710	0.51	
1,1-Dichloroethane	98.96	9.9	1.176	5,500	1.48	*0.005*
1,2-Dichloroethane	98.96	9.9	1.235	8,300	1.28	0.005
1,1,1-Trichloroethane	133.4	16.68	1.339	1,500	2.41	0.2
1,1,2-Trichloroethane	133.4	16.68	1.44	4,400	1.75	0.005
1,1,2,2-Tetrachloroethane	167.85	27.97	1.595	3,230	1.66	*0.001*
Chloroethenes						
Vinyl Chloride	62.5	6.25	Gas	1,100	0.39	0.002
cis-1,2-Dichloroethene	96.94	12.12	1.28	800	1.8	0.07
trans-1,2-Dichloroethene	96.94	12.12	1.256	600	1.77	0.1
1,1-Dichloroethene	96.94	12.12	1.218	2,250	1.81	0.007
Trichloroethene	131.39	21.9	1.464	1,100	1.86	0.005
Tetrachloroethene	165.83	41.46	1.623	150	2.32	0.005
Chloropropanes						
1,2-Dichloropropane	112.99	7.06	1.156	2,800	1.71	0.005
1,3-Dichloropropylene	110.97	7.93	1.224	2,000	1.36	*0.0005*
Chlorobenzenes						
Chlorobenzene	112.56	4.02	1.106	502	2.1	0.1
1,2-Dichlorobenzene	147	5.65	1.305	100	2.25	0.6
1,3-Dichlorobenzene	147	5.65	1.2881	69	2.23	
1,4-Dichlorobenzene	147	5.65	1.247	74	2.45	0.075

Note: Unless italicized, MCL values are U.S. Environmental Protection Agency (USEPA) federal drinking water standards. Italicized MCL values are California EPA drinking water standards. Note: g/mL - grams per milliliter; mg/L - milligrams per liter.

Table 15.4 does not give a direct indication of the reactivity of the solvents listed. There are a couple of generalizations that can be used to assess reactivity. First, solvents with double bonds, ethenes and benzenes, are generally easier to oxidize. Second, the fewer the number of chlorines, the easier the solvent is to oxidize.

Following is a discussion of different oxidant systems, their variations, performance, and limitations. An important consideration with any oxidant is the competing, non-beneficial reactions. Generally there are two types of non-beneficial reactions; reaction with naturally occurring reduced materials (organics and metals), and decomposition. Naturally occurring reduced materials are referred to as "natural oxidant demand" (NOD; also known as soil oxidant demand [SOD]). The relative importance of these two types of reactions varies with each oxidant.

15.2.3 Hydrogen Peroxide

Hydrogen peroxide, H_2O_2, is a simple chemical (structurally) that has complex reactions. Hydrogen peroxide is typically sold as a 20 to 70% solution. It is generally diluted on site before application. Its basic physical and chemical properties can be found on manufacturer's websites (FMC, 2007; US Peroxide, 2007b).

Hydrogen peroxide is recognized as a strong and broadly reactive oxidant. However, it is also recognized as being readily decomposed by metals in soils. The primary limitation of the use of peroxide in ISCO is its stability.

15.2.3.1 Non-Beneficial Reactions

As discussed above, one consideration in the use of oxidants is that they can react non-beneficially. They decompose or they can react with materials other than the contaminant. Either of these types of reactions will increase the amount of oxidant required.

Both types of reactions have been studied for hydrogen peroxide based systems. The importance of peroxide stability to peroxide utilization has been summarized by Watts (2006):

"Hydrogen peroxide stability is the primary limitation to the successful field implementation of CHP [catalyzed H_2O_2 propagations] ISCO . . .. Hydrogen peroxide residuals are usually maintained for no more than a few days, and in many cases H_2O_2 decomposes to undetectable concentrations within hours."

15.2.3.2 Decomposition

A key to understanding the use and limitations of hydrogen peroxide is, therefore, to understand its decomposition. Hydrogen peroxide decomposes exothermically (adiabatically) to form oxygen and water (and heat):

$$2H_2O_2 \rightarrow 2H_2O + O_2 + \Delta \qquad \text{(Rx. 15.16)}$$

Two aspects of this decomposition are important to understand, the temperature generated and the gas volumes released. Figure 15.1 shows the temperatures that are attained by hydrogen peroxide decomposition as a function of the concentration of hydrogen peroxide (FMC, 1969).

Three regions of Figure 15.1 illustrate the relationships between H_2O_2 concentration and temperature. From 0 to 11.5% hydrogen peroxide, the temperature is below 100 degrees Celsius (100°C). The temperature increase is linear above the ambient temperature with increasing peroxide concentration. At 11.5% hydrogen peroxide, sufficient energy is released that the water present begins to boil (100°C). The temperature stays at 100°C until the next critical concentration is reached, 64.7%. At this concentration, enough thermal energy is released by decomposition to completely vaporize all of the water present. Above a concentration of 64.7%, superheated steam is formed and the temperature rises rapidly. Hydrogen peroxide based rocket motors produce superheated steam to provide propulsion.

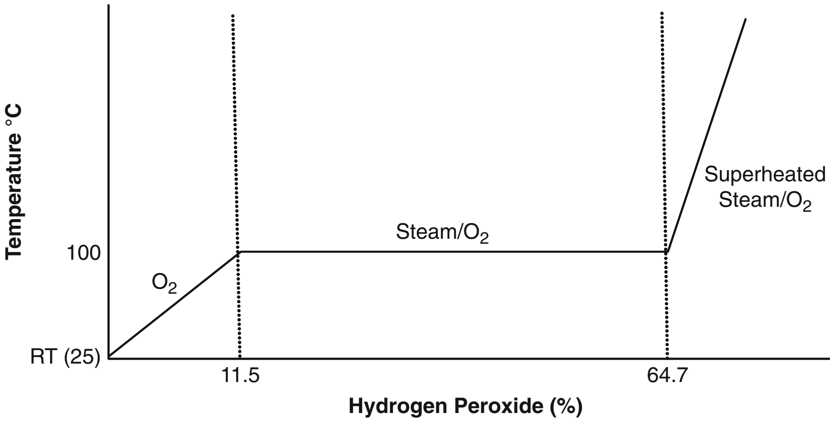


Figure 15.1. Hydrogen peroxide decomposition (adapted from FMC, 1969) (RT = room temperature)

A second aspect of peroxide decomposition is the gas volumes generated by decomposition. Figure 15.2 shows the gas volumes generated by decomposition as a function of the concentration of hydrogen peroxide (FMC, 1969). Two regions of Figure 15.2 are important. There is a break point at 11.5% peroxide where the water present begins to boil. Both regions are linear. However, the rate of volume increase is higher above 11.5% due to reaching the boiling point of water and the subsequent generation of steam.

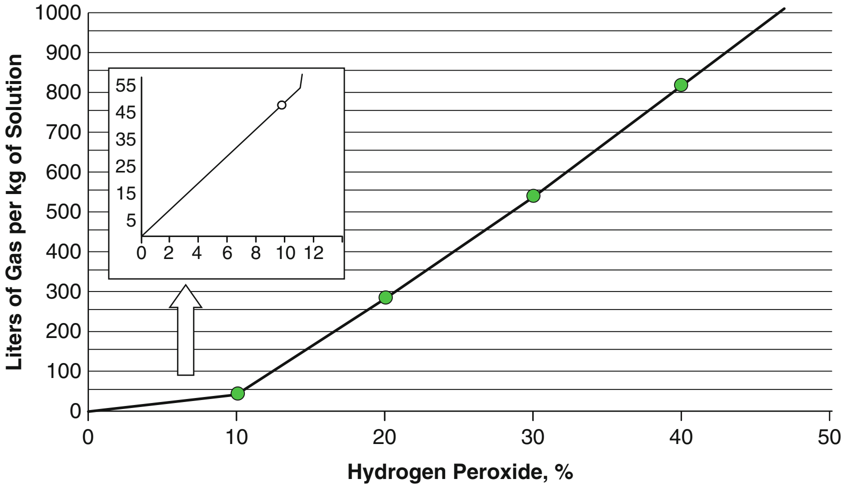


Figure 15.2. Gas volumes generated during decomposition (adapted from FMC, 1969)

A second inflection point, not pictured on Figure 15.2, occurs at 64.7% H_2O_2 where superheated steam is formed. The rate of volume increase above 64.7% is approximately four times the rate of volume increase between 11.5% and 64.7%. There is a significant volume expansion that occurs with peroxide decomposition. At 10% the gas volume generated is 45 times the injected volume; at 25%, 400 times.

Generation of large gas volumes can strip VOCs from groundwater and generate a vapor intrusion problem if the peroxide is applied near an occupied building. The volume and rate of gas generation may be too great to control with a soil vapor extraction (SVE) system.

Another important consideration in the decomposition of hydrogen peroxide is the production of oxygen. Each kilogram of hydrogen peroxide (100% basis) that decomposes generates 470 grams of oxygen. This can create a hazardous situation if there are volatile, combustible materials present. As the oxygen content increases the lower explosive limit (LEL) decreases, the upper explosive limit (UEL) increases and the auto-ignition temperature decreases. This can and has lead to the ignition of combustible vapors (Department of the Navy, 1999).

Also, hydrogen peroxide decomposition occurs in a short period of time during which there can be a number of deleterious effects. First, stripping of chlorinated VOCs from groundwater will occur. This can and has lead to the production of vapors. If the concentration of peroxide is greater than 11.5% the groundwater temperature will be 100°C. Given that the boiling points of many chlorinated solvents are below 100°C, volatilization from soil, nonaqueous-phase liquid (NAPL) or groundwater will occur. If occupied buildings are near the area of peroxide injection, vapor intrusion can be exacerbated. Thus, peroxide decomposition can create health hazards. Second, peroxide decomposition limits the longevity of peroxide in the subsurface. If there are adsorbed phase CVOCs present, their desorption is a rate limiting step. If the peroxide decomposes too rapidly, adsorbed phase material will not be treated and significant rebound can occur.

Decomposition of hydrogen peroxide is a function of two factors. The primary one is the presence of catalysts such as transition metals, particularly manganese and iron (Watts, 2006), or biological material containing catalase (Petigara et al., 2002). The second factor is surface area. Peroxide decomposition is proportional to surface area (Teel et al., 2007). As a result, peroxide is generally less stable in silts or clays than it is in sands and gravels. This effect of soil surface area (and other soil properties) on peroxide decomposition was, however, not confirmed by recent Strategic Environmental Research and Development Program (SERDP)-funded research (Watts, 2006). It may be that the effect of active catalysts is so dominant that surface area effects are statistically insignificant. However, for a given soil mineralogy, the surface area can exacerbate the decomposition. The implication for assessing peroxide stability is to first assess the mineralogy and then to assess the soil lithology. Soils that are high in iron or manganese, and have high surface area, may not be well suited to the use of hydrogen peroxide.

Precautionary implications of peroxide decomposition on the use of hydrogen peroxide for ISCO include:

- Rapid decomposition of hydrogen peroxide can create serious health and safety issues.
- Peroxide decomposition can limit the performance of ISCO.
- Peroxide decomposition is site specific and is strongly tied to the mineralogy and to a lesser extent, the lithology.
- There are sites at which the use of peroxide may be impracticable and/or unsafe.
- Peroxide decomposition should be assessed to determine the applicability of hydrogen peroxide for a given site.
- Potential stabilizers for peroxide should be evaluated for soils that have high manganese or iron.

15.2.3.3 Natural Oxidant Demand (NOD)

Decomposition is by far the dominant non-beneficial reaction for hydrogen peroxide. The other type of non-beneficial reaction, oxidation of naturally occurring reduced materials, can play a minor role. The two types of reduced materials, metals and organic matter, have different effects on peroxide utilization.

If naturally occurring reduced metals are present, they are most typically going to be either iron or manganese based, often generated by biological activity. Iron and manganese reduction are both significant anaerobic metabolic pathways. Both metals will affect peroxide utilization. However, the primary mechanism is decomposition and not oxidation. Both metals catalyze the formation of active oxygen species from hydrogen peroxide.

The effect of soil organic matter (SOM) is complex and was studied in SERDP project CU-1288 (Watts, 2006). This study of SOM concluded that it does not affect reactivity of the peroxide at acidic pH (3) and enhances reactivity at neutral pH (7), and its effect on utilization is pH dependent; at acidic pH (3) peroxide will react with SOM, but at neutral pH (7) it will not.

Thus it is clear that assessment of peroxide utilization efficiency should focus on decomposition. All other factors are minor compared to decomposition. If peroxide decomposes too quickly it will have poor utilization efficiency and could create hazardous working conditions.

15.2.3.4 Stabilization of Hydrogen Peroxide

Stabilizers have been investigated to increase the useful life of peroxide in soils and therefore its effectiveness and efficiency. The focus of stabilization research has been on deactivating metal catalysts.

Two types of stabilizers show promise, inorganic phosphates and chelating compounds. Inorganic phosphates function by forming insoluble ferric phosphates. In a recent test of H_2O_2 oxidation of TCE in 30 centimeter (cm) soil columns, treatment of the soil with KH_2PO_4 significantly improved peroxide stability and TCE oxidation (Baciocchi et al., 2004).

Chelants function by complexing with iron. The effects of three different chelants on hydrogen peroxide stability in soil amended with hematite (Fe_2O_3) is illustrated in Figure 15.3. The three stabilizers, citrate, malonate and phytate, all significantly improved peroxide stability. None of the stabilizers decreased the production of hydroxyl radicals or superoxide.

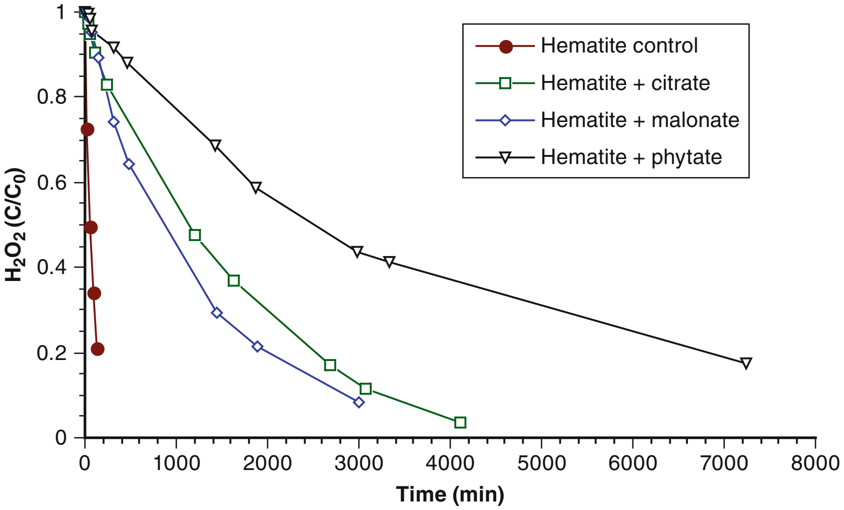


Figure 15.3. H_2O_2 decomposition by hematite at pH 7 with and without stabilizers (Watts, 2006)

There does not appear to be any difference in stabilizer activity between preconditioning the soil with the stabilizer and then adding unstabilized peroxide or pre-mixing the stabilizer and the peroxide before application.

A final consideration with respect to peroxide stability is that the hydrogen peroxide decomposition reaction is self-accelerating (autocatalytic). As the temperature increases, more peroxide decomposes, generating higher temperatures that promote more peroxide decomposition. This aspect of peroxide decomposition can be controlled to some extent by keeping the concentration of hydrogen peroxide applied to under 10%.

15.2.3.5 Reactivity

The nature and mechanisms of hydrogen peroxide based ISCO systems have been variously described as "Fenton's Chemistry," "Fenton's Reagent," "Fenton-like reactions," and "Modified Fenton's." As these names all imply, the conventional view of hydrogen peroxide based ISCO is that the primary reactive pathway is the creation of hydroxyl radicals ($HO^{\bullet}$). However, recent research has shown that the reaction of hydrogen peroxide with iron or manganese results in a rich mixture of active oxygen species:

"The suite of reactive oxygen species generated in CHP [catalyzed H_2O_2 propagations] reactions, including hydroxyl radical, superoxide, and the strong nucleophile hydroperoxide, provide a near-universal treatment matrix (Watts, 2006)."

Increasingly researchers are focusing on the reactivity of a wide variety of reactive oxygen species that are interrelated. These include:

Hydroxyl Radical - $HO^{\bullet}$
Hydroperoxide Anion - HOO^{-}
Singlet Oxygen - $^{1}O_2$
Perhydroxyl radical - $HOO^{\bullet}$
Superoxide - $^{\bullet}O_2^{-}$
Hydrogen Peroxide - H_2O_2

Some of these reactive oxygen species are oxidants, some are reductants. Given that they can co-exist, it is possible to get simultaneous oxidation and reduction reactions occurring. Considering the variety of reactive oxygen species possible, a more appropriate term for peroxide based ISCO systems should be, "catalyzed H_2O_2 propagations, CHP" (Watts, 2006).

Four reactive oxygen species are responsible for the oxidation of various chlorinated solvents (Table 15.5). Hydrogen peroxide based ISCO has the potential to treat virtually the entire range of chlorinated solvents. However, oxidation of chlorinated solvent mixtures may require varying conditions over the course of treatment.

Table 15.5. Reactivity of Various CVOCs with Reactive Oxygen Species (Watts, 2006)

Class of Contaminant	Reactive Oxygen Species Responsible for Degradation
Chlorinated Ethenes (e.g., TCE, Perchloroethene [PCE])	Hydroxyl Radical and Superoxide
Chlorinated Ethanes (e.g., Carbon Tetrachloride, Chloroform)	Superoxide
Electron-Poor Regions of Molecules (e.g., Trichloroethane [TCA])	Hydroperoxide Anion
Sorbed Contaminants	Superoxide (Desorption)

15.2.3.6 Variations in Using Hydrogen Peroxide

There are basically two methods of applying hydrogen peroxide for chlorinated solvent remediation. Most commonly, peroxide is used as a liquid; usually diluted with water and amended with acid and/or metal catalysts. It also can be added as a solid adduct which then hydrolyzes and releases hydrogen peroxide.

As previously discussed, hydrogen peroxide solutions are sold in concentrations ranging from 20 to 70%. In addition, there are three solid products offered commercially that can be used to supply hydrogen peroxide:

- Calcium peroxide ($CaO_2 + 2H_2O \rightarrow Ca(OH)_2 + H_2O_2$),
- Magnesium peroxide ($MgO_2 + 2H_2O \rightarrow Mg(OH)_2 + H_2O_2$), and
- Sodium percarbonate (sodium carbonate peroxide) ($2Na_2CO_3 \cdot 3H_2O_2 \rightarrow 4Na^+ + 2CO_3{}^{-2} + 3H_2O_2$).

These products result in a high pH (>10.0) solution of hydrogen peroxide. The likely reactive species from the hydrolysis of these materials are hydroperoxide anion and superoxide. Any hydroxyl radicals which are formed react with the hydroperoxide anion to form superoxide (Guay et al., 2000).

Systems using liquid hydrogen peroxide generally are metal (iron) catalyzed and can be divided into two categories, acidic formulations and circumneutral formulations. The acidic systems typically use inorganic iron salts and an acid (US Peroxide, 2007a).

The circumneutral systems use chelated iron and stabilized peroxide and are termed “modified Fenton’s reagent” (Isotec, 2007). Both systems are described as generating hydroxyl radicals but, in fact, likely generate a mixture of reactive oxygen species.

More recently, Watts (2006) has developed an improved peroxide system termed catalyzed H_2O_2 propagations (CHP) which employs peroxide mixed with a stabilizer. CHP relies on natural soil minerals to catalyze the hydrogen peroxide. This technology has the potential to enhance the effectiveness of hydrogen peroxide based ISCO.

Table 15.6 summarizes the different peroxide based systems.

15.2.3.7 Guidance on Using Hydrogen Peroxide Based ISCO

Hydrogen peroxide based ISCO has the potential to effectively treat chlorinated solvents. However, it is not a panacea. There are definite limitations to the use of hydrogen peroxide for remediation regardless of the type of peroxide system used. The stability of hydrogen peroxide is the primary factor limiting its use as an oxidant.

Based on research on the decomposition of hydrogen peroxide with different minerals, it appears the problem with decomposition is not that reactive species are not formed but that they are formed too rapidly and react with each other (Watts, 2006):

$$4HO^{\bullet} \rightarrow 2H_2O + O_2 \qquad \text{(Rx. 15.17)}$$

$$2O_2^{\bullet -} + 2H^+ \rightarrow H_2O_2 + O_2 \qquad \text{(Rx. 15.18)}$$

Controlling the rate of formation of the reactive species can decrease decomposition and increase reaction efficiency.

Peroxide lifetime (stability) affects the treatment of chlorinated solvents in a number of ways. First, it affects the treatment of sorbed phase solvents. In general, desorption is a slow process compared to the rate of reaction in the aqueous phase. If the rate of decomposition is significantly faster than the rate of desorption, peroxide will not persist long enough to treat the sorbed material. Second, it affects distribution. If peroxide distribution is relying in part or in whole on groundwater flow, the rate of decomposition must be less than the travel time of the solution.

Table 15.6. Comparison of Peroxide Based ISCO Systems

Components	Advantages	Disadvantages
Conventional Fenton's		
• Acid (sulfuric) • Ferrous sulfate solution • Hydrogen peroxide 5–25%	• Low cost components • Coincidental stripping • Fast reaction	• Low pH can mobilize metals • Poor peroxide stability • Reacts with soil organic material • Frequent rebound • Volatilization of VOCs • Multiple applications
Modified Fenton's		
• Hydrogen Peroxide (5–20%) • Chelated iron solution • Stabilizers (proprietary)	• No pH adjustment • Improved peroxide stability • Broad reactivity • No reaction with soil organic material	• Limited (or decreased) lifetime in some mineralogies • Cost of chelates and stabilizer • May require multiple applications to treat adsorbed phase
Stabilized Catalyzed H_2O_2 Propagations		
• Hydrogen peroxide (1–10%) • Stabilizer (citrate, malonate, phytate)	• No pH adjustment • Improved peroxide stability • Broad reactivity • No reaction with soil organic material	• Limited (or decreased) lifetime in some mineralogies • Cost of stabilizer • May require multiple applications to treat adsorbed phase
Calcium Peroxide		
• Calcium peroxide slurry	• Slow release of peroxide • Long life time • Alkaline peroxide solution	• Slow release of peroxide • Calcium peroxide is insoluble • Injection of slurry • Limited distribution of agent
Magnesium Peroxide		
• Magnesium peroxide slurry	• Slow release of peroxide • Long life time • Alkaline peroxide solution	• Slow release of peroxide • Magnesium peroxide is insoluble • Injection of slurry • Limited distribution of agent
Sodium Percarbonate		
• Sodium percarbonate solution • Chelated iron catalyst sometimes used	• Alkaline peroxide solution • Sodium percarbonate is moderately soluble • Broad reactivity	• Limited peroxide lifetime • Carbonate is a hydroxyl radical scavenger

Thus it is critical to assess the stability of hydrogen peroxide under the conditions in which it will be used. Figure 15.4 illustrates a simple method of measuring peroxide decomposition. It consists of a stoppered Erlenmeyer flask equipped with a stoppered addition funnel and connected to a 10 L Tedlar bag.

The flask is charged with 200 g of moist site soil. Hydrogen peroxide is added to the soil and the volume of gas generated is measured over time. The test is done with 100 mL of 10%

peroxide and 200 mL of 5% peroxide. Each peroxide charge will generate approximately 4.5 L of gas (primarily O_2) at room temperature. Percent decomposition is calculated as:

$$\text{Percent decomposition} = \frac{\text{Gas volume (L) measured}}{4.5} \times 100 \qquad \text{(Eq.15.1)}$$

If the half life of peroxide is less than 8 to 12 hours, the peroxide may be too unstable to be used. If the peroxide foams or fizzes on contact with the soil, the test does not need to be continued since clearly, the peroxide is grossly unstable.

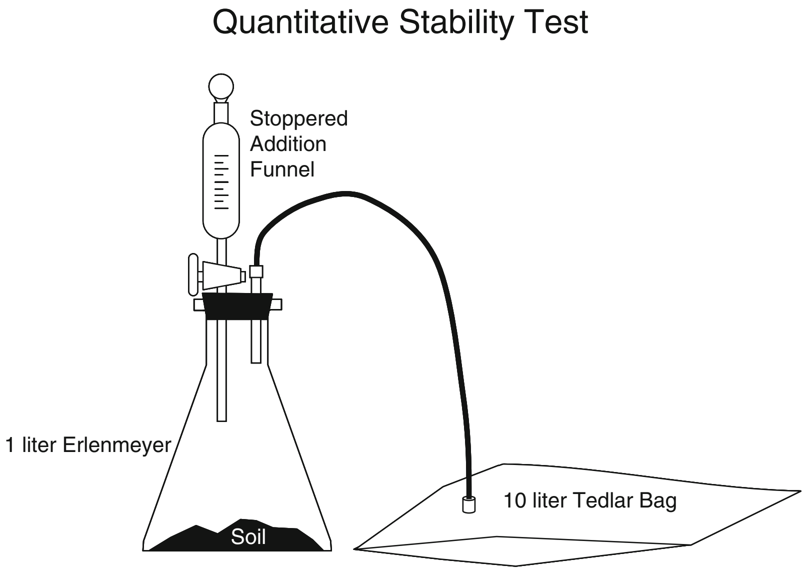


Figure 15.4. Apparatus for measuring H_2O_2 stability

The same apparatus can be used to test the stability of sodium percarbonate or calcium/ magnesium peroxide. To test stability of sodium percarbonate, 32 grams is dissolved in 200 mL of water, and then this solution is added to the soil. This charge will generate 4.5 L of gas if it completely decomposes. To test calcium or magnesium peroxide, the dry solid is pre-mixed with the soil. Water (200 mL) is then added via the addition funnel and the gas volume is measured. Either 52 g of MgO_2 or 66.8 g of CaO_2 is used for the test.

If the peroxide is sufficiently stable, the next consideration is to assess the treatment effectiveness of the peroxide systems being contemplated. Microcosms should be set up using soil and groundwater (10–20% solids). The tests should be run with zero headspace. No more than a 3% peroxide solution (or equivalent for solid peroxygens) should be utilized to minimize gas build-up and or pressurization. Appropriate controls should be run. It is recommended that several different peroxide systems be tested since each has a different reactivity and a different cost structure.

The final consideration in assessing the applicability of a peroxide-based system is the mass distribution of the chlorinated solvents. If the bulk of the contamination is in the dissolved state and there are minimal sorbed contaminants and no appreciable NAPL, a peroxide based system could be a cost effective choice. If there is significant sorbed or NAPL phase solvent, a peroxide-based system may be ineffectual or would require multiple applications.

If hydrogen peroxide is considered applicable, the issue is how to effectively distribute it. Injection/distribution systems have two basic approaches. They can be emplacement systems, where the oxidant is distributed as rapidly as possible over the area/volume that is to be treated. Or they can be circulation systems, where the oxidant is first injected and then distributed over the volume/area to be treated. The distribution process is much slower than the injection process. Distribution can be through active pumping or through relying on groundwater flow.

15.2.4 Permanganate

Permanganate has been used extensively in municipal water treatment to treat iron, manganese, tastes, odors, color and turbidity. It also has been used in industrial wastewater treatment to treat sulfides, mercaptans, cyanides and phenols. As a result, it has been recognized as a strong oxidant for treating waste material. Permanganate also has been used extensively in organic synthesis for oxidizing a number of functional groups.

Of particular interest in the treatment of chlorinated solvents is the reaction of permanganate with double bonds. Under acidic or neutral conditions this reaction cleaves the double bond, which is the basis for effectiveness of permanganate in treating chlorinated ethenes such as PCE, TCE, dichloroethene (DCE) and vinyl chloride (VC).

There are two common permanganate salts used in ISCO, sodium and potassium. There is no difference in the reactivity of the two permanganates, only in their solubility. Potassium permanganate ($KMnO_4$) is sold as a solid. It has a solubility of 6.4 g/100 mL at 20°C. Sodium permanganate is generally sold as a 40% solution. This solution is miscible with water in any proportion. The basic chemical properties of both permanganates are available on the manufacturer's web site (Figure 15.5). A recent review of permanganate use in ISCO provides comprehensive information on permanganate (Siegrist et al., 2001).

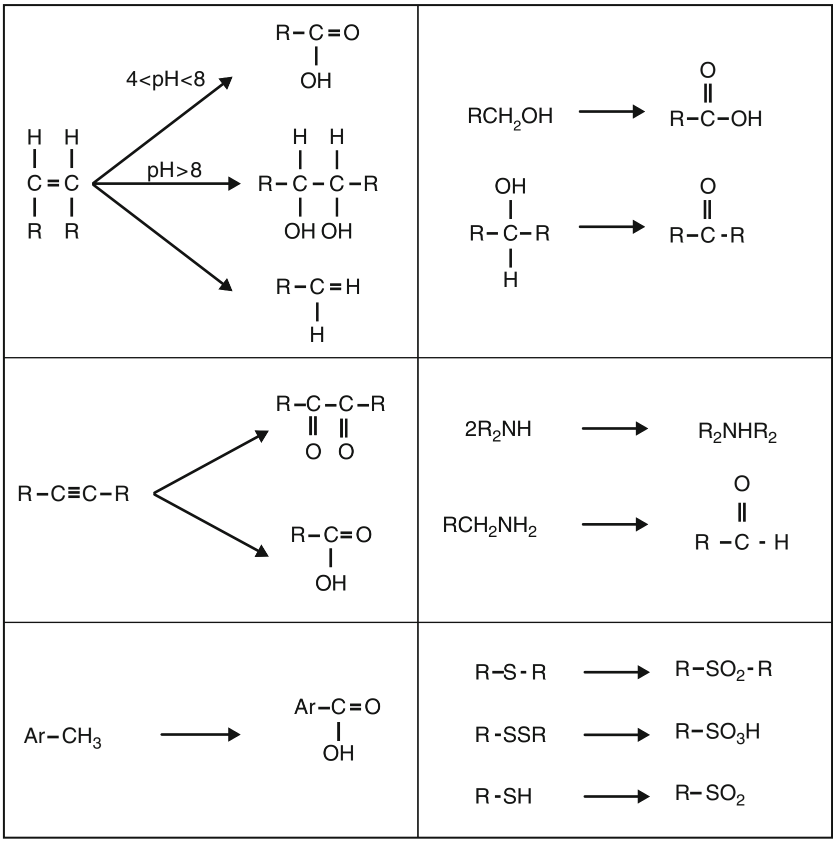


Figure 15.5. Functional group oxidation by permanganate (Carus, 2007b)

15.2.4.1 Non-Beneficial Reactions

In terms of its use in ISCO for treating chlorinated solvents, permanganate is a more limited oxidant than hydrogen peroxide or sodium persulfate. It essentially only reacts with solvents that contain double bonds, such as the chloroethenes. In treating chloroethenes, however, it has one substantive advantage over hydrogen peroxide and persulfate – it is generally stable in soil environments. However, a limitation to the use of permanganate is its reaction with naturally occurring soil organic matter or reduced soil minerals. These materials are referred to as "natural oxidant demand" (NOD).

15.2.4.2 Decomposition

Permanganate will decompose, but slowly. The decomposition reaction produces oxygen:

$$4MnO_4^- + 2H_2O \rightarrow 4MnO_2 + 3O_2 + 4OH^- \qquad \text{(Rx. 15.19)}$$

This reaction is auto-catalyzed by the production of manganese dioxide (MnO_2), the primary reaction product of permanganate oxidation reactions (Zhao et al., 1990). The reaction may be surface catalyzed.

The effect of MnO_2 solids on permanganate stability has been confirmed in the laboratory. Increasing amounts of a 200 mesh MnO_2 solid were added to 100 mL of a 0.359 molar (M) permanganate solution. The permanganate concentration was measured after 10 days (Figure 15.6).

The consumption of permanganate caused by or attributed to NOD may be exacerbated by the generation of MnO_2. If there is significant NOD present, the reduced materials react with permanganate, generating MnO_2. The produced MnO_2 then decomposes more permanganate, generating more MnO_2, and causing even more permanganate decomposition. In such situations, the use of permanganate may be entirely precluded.

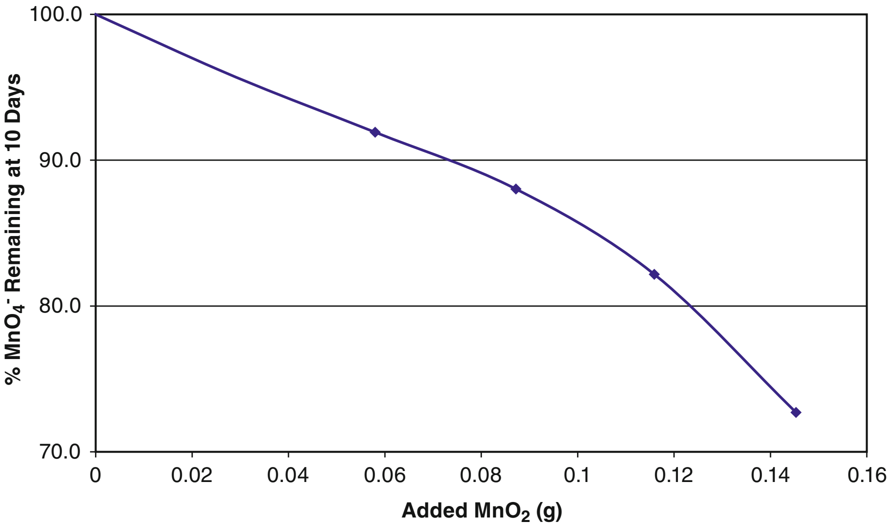


Figure 15.6. Decomposition of permanganate by MnO_2 (R.A. Brown, unpublished research, 2000)

15.2.4.3 Natural Oxidant Demand (NOD)

There are two primary components to NOD, reduced minerals and soil organic material. All oxidants will react with reduced soil minerals. The most common reduced soil minerals are iron and manganese containing minerals, including oxides and sulfides. The primary oxidation-reduction half reactions are:

$$\text{Iron}: \text{Fe}^{+2} \rightarrow \text{Fe}^{+3} + e^{-}; E_o = 0.771\ \text{v} \qquad (\text{Rx. } 15.20)$$

$$\text{Manganese}: \text{Mn}^{+2} + 2\text{H}_2\text{O} \rightarrow \text{Mn}^{+4}\text{O}_2 + 4\text{H}^{+} + 2e^{-}; E_o = 1.23\ \text{v} \qquad (\text{Rx. } 15.21)$$

All of the oxidants used for remediation have an oxidation potential that is greater than that required to oxidize reduced iron or manganese.

Biological activity can directly reduce both manganese and iron. Iron reduction and manganese reduction are major metabolic pathways for the reduction of organic compounds in aquifers. Biological activity using sulfate reduction can also form sulfides.

Permanganate is unique among the oxidants used in ISCO in that it also reacts readily and substantially with soil organic material. Neither hydrogen peroxide nor sodium persulfate appear to react to any significant extent with soil organic material (Watts, 2006; Brown and Robinson, 2004), although soil organic matter can catalyze the decomposition of peroxide (Siegrist et al., 2006). Reaction with NOD is the primary non-beneficial consumption of permanganate.

Naturally occurring soil organic material is composed of humic and fulvic acids. These are condensed, multi-ring structures that are substituted with oxygen and nitrogen atoms. An example of a humic acid is pictured in Figure 15.7 (Stevenson, 1982). Double bonds, which are abundant in humic acid structure, offer a possible explanation for the reactivity between permanganate and soil organic matter.

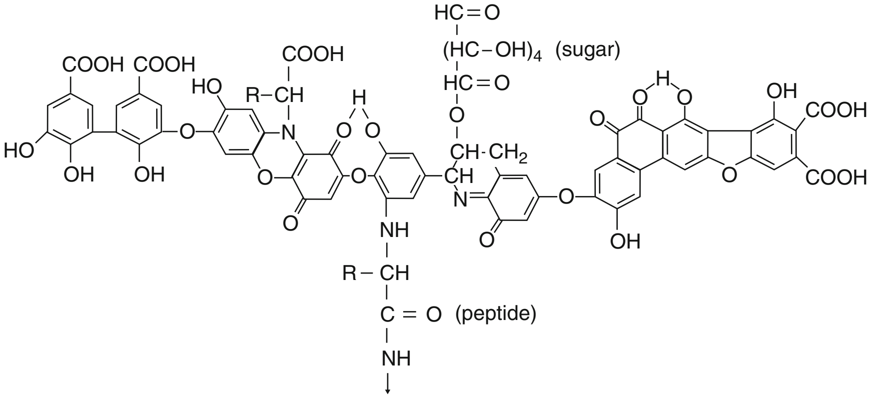


Figure 15.7. Model structure of humic acid (Stevenson, 1982)

The impact of soil constituents on NOD is, however, not straightforward because there is no apparent correlation between TOC (total organic carbon), COD (chemical oxidant demand) and the NOD (Table 15.7). NOD data in Table 15.7 were obtained by exposing soil to a graduated series of permanganate concentrations over a 7 day period. The NOD value is calculated from the lowest permanganate concentration showing persistent permanganate after 7 days.

Although there is no correlation between either the TOC or COD and the NOD, there is a weak correlation between TOC and COD. In general, the higher the TOC, the higher the COD. TOC is a measure of the total organic content of the soil, both reactive (i.e., oxidizable) and non-reactive. COD is a measure of both the reactive organics and the reduced metals. These data indicate that (1) NOD can be a significant sink for permanganate and (2) NOD must be measured.

In many cases the NOD may be the major factor in determining the effective dose of permanganate. Consider a site contaminated with TCE at a soil concentration of 100 mg/kg. TCE has an equivalent weight of 21.9 grams. Based on the equivalent weight of potassium permanganate (56 g), the stoichiometric demand for oxidation of TCE by potassium permanganate is 2.55 g/g. At 100 mg/kg TCE, the stoichiometric demand for permanganate is 448 g/m^3 of soil. If the soil had an NOD of 3g/kg, which is a low-to-moderate NOD, the amount of permanganate needed to satisfy the NOD would be 5.28 kg/m^3, approximately 12 times the stoichiometric demand.

Table 15.7. Examples of TOC, COD, and NOD in Soils (R.A. Brown, unpublished work)

TOC mg/kg	COD mg/kg	NOD g/kg	TOC mg/kg	COD mg/kg	NOD g/kg
48,100	49,800	0	1,420	3,600	0.45
32,300	6,960	1.8	1,334	252	8.1
31,000	110	7.5	943	213	3.8
29,300	11,500	20	793	3,170	0.05
28,400	47	7.5	500	200	0.04
13,789	371	21.4	500	200	0.04
5,740	27,000	20	396	1,381	16
5,377	318	1.65	350	31	0.1
4,866	5,992	3.9			
2,520	19,900	3.4	**Correlations**		
2,514	324	16.2	TOC:COD	COD:NOD	TOC:NOD
2,230	5,200	0.9	0.54	0.021	0.120

Measuring the NOD is an important part of the application design. If it is underestimated, permanganate will not be added at sufficient concentrations to effectively oxidize the contaminants present.

15.2.4.4 Reactivity

The reaction of permanganate with chlorinated solvents has been extensively studied (Siegrist et al., 2001). Recently, Waldemer and Tratnyek (2006a; b) published rate constants and half lives for the oxidation of various chlorinated solvents by permanganate (see Figures 15.8 and 15.9. for rate constants).

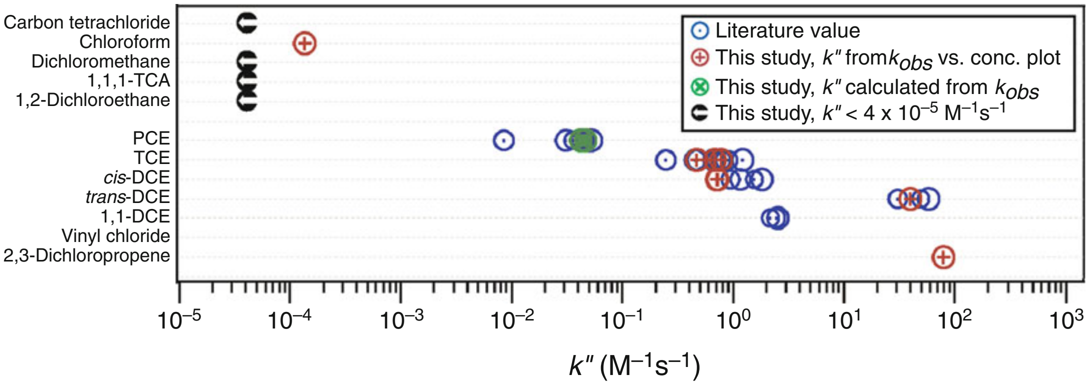


Figure 15.8. Rate constants for permanganate oxidation of chlorinated solvents (adapted from Waldemer and Tratnyek, 2006a)

As can be seen from Figure 15.8, permanganate reacts preferentially with the chlorinated ethenes. The reaction rates were used to calculate half lives for various solvents at two permanganate concentrations. Figure 15.9, excerpted from a more extensive figure, provides the half lives for the chlorinated ethenes.

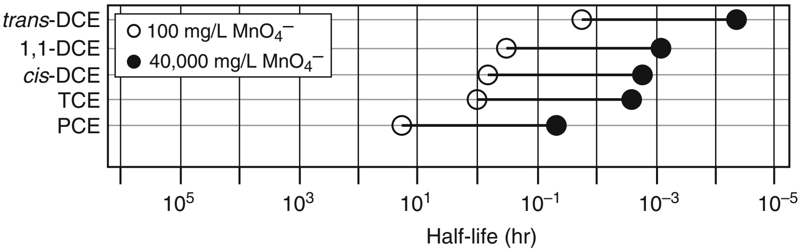


Figure 15.9. Half lives of chlorinated ethenes (adapted from Waldemer and Tratnyek, 2006b)

Two general conclusions can be drawn from Figures 15.8 and 15.9 about the reactivity of permanganate with chlorinated solvents.

- Solvents with double bonds are more reactive than those without double bonds.
- Reactivity increases as chlorination decreases. The fewer chlorines present for a given carbon structure, the more reactive the solvent.

15.2.4.5 Effect of the Formation of MnO_2 on Permanganate Reactivity

At pH values above 2.0 the primary product of the reaction of permanganate is MnO_2. MnO_2 is an insoluble precipitate. The formation and precipitation of MnO_2 can limit the effectiveness of permanganate. There are two potential deleterious effects of MnO_2 formation. First it can precipitate in pore spaces causing a decrease in permeability. Second, in the presence of high organic matter concentrations, the MnO_2 can form a "rind" around the organic material limiting further oxidation (Conrad, 2002).

However, there are several mitigating factors. First is the concentration of the contaminant being oxidized, which largely determines the mass of MnO_2 formed. Generally, at low contaminant concentrations, the formation of MnO_2 has little or no effect on the permeability. Second is the nature of MnO_2 precipitate. The physical and chemical nature of the MnO_2 formed can change over time due to incorporation of other metals (Post, 1999) and subsequent remineralization. Conrad (2002) observed that three months after formation of the MnO_2 rind, the encrusted dense nonaqueous phase liquid (DNAPL) pool had remobilized. Observations of MnO_2 precipitates in the laboratory show that they morph over time from a gelatinous material into a dense granular material (Figure 15.10). And third, the manner in which the permanganate is injected is important. Varying the injection rate and the concentration can significantly mitigate the formation of a rind.

15.2.4.6 Variations in Using Permanganate

The primary variation in the application of permanganate in ISCO is the type used—sodium and potassium. There is no difference in the reactivity of the two permanganates, only in their solubility. However, high concentrations (10–20%) of sodium permanganate are used to promote density-driven application because they are denser than water and will sink through the water table.

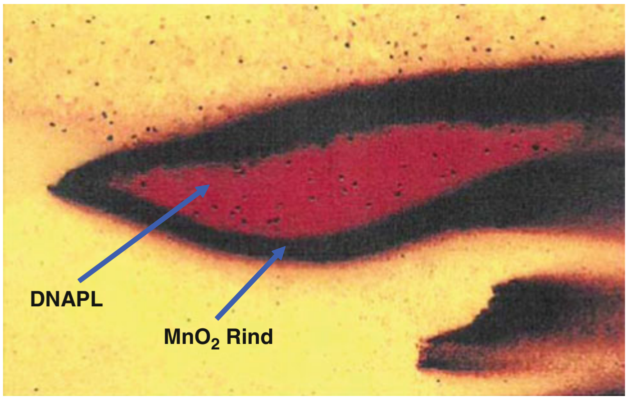


Figure 15.10. MnO_2 rind around DNAPL pool (Conrad, 2002)

Of interest to practitioners is the difference in cost of sodium and potassium permanganate. Potassium permanganate is about 1/4 to 1/5 the cost of sodium permanganate. However, there are costs associated with handling and mixing potassium permanganate which lessen the cost differential between the two for field application. In general, for small scale applications (<500 kg) sodium permanganate is easier to apply and saves labor and equipment for mixing and handling. For larger applications, permanganate suppliers often provide application support. For example, they will prepare and deliver ready-made, tank-truck solutions of potassium permanganate, or they will supply and/or lease equipment to handle and dissolve bulk potassium permanganate.

Generally there is little variation is the application conditions for permanganate. Most commonly, a permanganate solution is injected without modification of pH and without the addition of other materials or agents. This simplicity of application is one of the reasons that permanganate enjoys wide application.

However, the reactivity of permanganate is ultimately a function of pH. In a pH range of 4 to 8, the most common reaction conditions, the reaction is a three electron transfer resulting in the formation of MnO_2 as the primary reaction product:

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \qquad \text{(Rx. 15.22)}$$

At alkaline pH values the reaction is also a three electron transfer with MnO_2, still, as the primary reaction product:

$$MnO_4{}^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^- \qquad \text{(Rx. 15.23)}$$

However, at very low pH values, <2–3, the reaction is a five electron transfer, with soluble Mn^{+2} as the reaction product:

$$MnO_4{}^- + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O \qquad \text{(Rx. 15.24)}$$

Low pH application of permanganate has been studied. One potential advantage is that it does not form solid MnO_2 and thus could be used to enhance the oxidation of DNAPL (Huang, 2004).

Research on the use of additives such as surfactants and metal chelators has focused on improving the treatment of DNAPLs (Dugan, 2005).

Most permanganate applications involve injection of permanganate solutions, either batch or continuous. A variation is the use of permanganate-clay-grout aggregates to create a permanganate reactive barrier (Siegrist et al., 1999; Li and Schwartz, 2004). Potassium permanganate crystals are mixed with a grout or clay to form a slow-release aggregate. This mix can be emplaced through hydraulic fracturing or by trenching.

15.2.4.7 Guidance on Using Permanganate Based ISCO

The application of permanganate is generally viewed and approached as a simple technology. However, there are some “rules” that will increase the potential for successful permanganate applications and there is growing evidence that permanganate based ISCO should be an “engineered” process.

Basic guidance for the use of permanganate for treatment of chlorinated solvents includes:

- Make sure that the solvents are amenable to permanganate oxidation. This essentially means that they should contain double bonds.
- Determine the dosage of permanganate required. The dosage is a combination of the stoichiometric requirement, driven by the type and the mass of the chlorinated solvent present, and the NOD, determined by the presence of soil organic material and reduced metals.
- Choose an appropriate application method. The key to successful application is to contact the contaminant with the permanganate solution. The more efficient the contact the more effective the application.

15.2.4.8 Amenability to Permanganate Oxidation

For practical purposes, permanganate is only effective in treating chlorinated solvents and non-chlorinated cocontaminants that contain a double bond, such as chloroethenes—PCE, TCE, DCE (*cis*-, *trans*- and 1,1-) and vinyl chloride, chloropropenes and chlorobenzenes (except monochlorobenzene). The only significant exception is that permanganate does not easily treat benzene. The treatability of contaminants (chlorinated and non-chlorinated) not containing double bonds, if not previously investigated, should be determined with bench studies.

15.2.4.9 Determining Dosing Requirements

The dosing requirement for any oxidant is the sum of three factors: the stoichiometric demand, the reaction with reduced species in the soil matrix (commonly referred to as the Natural Oxidant Demand [NOD] or the Soil Oxidant Demand [SOD]), and the loss due to decomposition. Since permanganate is essentially stable, its dosing is, on a practical basis, the sum of the stoichimetric requirement and of the NOD.

Stochiometric Demand is the stoichiometric requirement times the mass of the contaminant. The stoichiometric requirement is easily calculated:

$$\text{Stochiometric Requirement} = \frac{\text{Equivalent Weight Oxidant}}{\text{Equivalent Weight CVOC}} \qquad \text{(Eq.15.2)}$$

Equivalent weight is the molecular weight divided by the number of electrons transferred. The equivalent weight, assuming a three electron transfer, is 52.6 g for potassium permanganate and 47.3 g for sodium permanganate. Table 15.8 provides equivalent weights of CVOCs that are amenable to permanganate oxidation.

Table 15.8. Equivalent Weight of CVOCs

	Molecular Weight	Equivalent Weight	$KMnO_4$ Stoichiometry (g/g)	$NaMnO_4$ Stoichiometry (g/g)
Chloroethenes				
Vinyl Chloride	62.5	6.25	8.42	7.57
cis-1,2-Dichloroethene	96.94	12.12	4.34	3.90
trans-1,2-Dichloroethene	96.94	12.12	4.34	3.90
1,1-Dichloroethene	96.94	12.12	4.34	3.90
Trichloroethene	131.39	21.9	2.40	2.16
Tetrachloroethene	165.83	41.46	1.27	1.14
Chlorobenzenes				
Dichlorobenzene (1,2-; 1,3-; 1,4-)	147	5.65	9.31	8.37
Chloropropenes				
Chloropropenes	76.5	4.78	11.00	9.90
Dichloropropenes	110.97	7.93	6.63	5.96

Determining the mass of contaminant is a difficult and highly inexact exercise. There are three mass components that should be considered—dissolved, adsorbed and NAPL. Generally there is more data for the dissolved phase than for adsorbed or NAPL. Also, there is inherently more variability in data for adsorbed or NAPL than for groundwater. Both adsorbed and NAPL CVOCs may be present in discrete, thin bands. Also, if there is dissolved contamination present, then generally there also will be an adsorbed fraction. The partitioning of CVOCs from groundwater to the soil is a function of the octanol-water partition coefficient (K_{oc}) and the fraction of organic content (foc) of the soil.

In assessing the stoichiometric demand of a site, groundwater data can be used to assess the importance and significance of the mass loading. There are generally three categories of sites:

1. Low-Level Dissolved Sites. If the maximum groundwater concentration of total CVOCs is <500 micrograms per liter (µg/L) and any individual CVOC is <200 µg/L, then the contamination is essentially dissolved. The mass loading is the groundwater concentration times the volume of water plus the estimated amount of CVOCs partitioned to the soil. This can be calculated:

$$C_t = (C_w(K_d P_b + n))/P_b \qquad \text{(Eq. 15.3)}$$

$$K_d = K_{oc} f_{oc} \qquad \text{(Eq. 15.4)}$$

where:
C_t = Concentration of contaminant in soil (mg/kg)
C_w = Concentration of contaminant in water (mg/L)
K_d = Partition coefficient between pore water and soil (as defined above)
P_b = Bulk soil density
n = Porosity
K_{oc} = Octanol-water partitioning coefficient (obtained for each compound from reference literature)
f_{oc} - Fraction organic content (default = 0.1%)

Typically for low-level dissolved sites the stochiometric demand will be quite small. A groundwater concentration of 500 μg/L would yield a mass loading of about 0.5 g/m^3. Most likely, as will be discussed below, the NOD will be significantly greater than the stoichiometric demand.

2. Moderate-Level Dissolved Sites. If the maximum groundwater concentration of total CVOCs is <10 mg/L but >500 μg/L and any individual CVOC is >500 μg/L but <5 mg/L, it may be assumed that there are adsorbed phase CVOCs present above that which partitions from groundwater. Soil data should be obtained in areas of high groundwater levels to estimate the mass loading in the soil. The total mass loading is equal to the mass loading in groundwater and the mass loading in the soil. The mass loading in groundwater is the concentration times volume of groundwater. The mass loading in soil is equal to the mass that partitions from groundwater (see category 1 above) and the material adsorbed directly onto soil. This is calculated by multiplying the soil concentration (mg/kg) times the soil mass. Measuring the soil concentration is a difficult task. There are several methods of obtaining soil concentrations. Most commonly, soil samples are obtained and analyzed with laboratory instruments. More recently, *in situ* techniques such as membrane interface probes (MIP) have been used. The advantage of a technique like MIP is that it can give continuous, real time data. Soil contamination levels of 100 mg/kg yield a mass loading of about 200 grams per cubic meter (g/m^3) of aquifer material. For sites with a low NOD (<0.05 g/kg or 88 g/m^3) the stoichiometric demand will be the dominant demand factor. However at a high NOD (>0.25 g/kg), the NOD is the dominant demand factor.
3. High-level Dissolved Sites. If the maximum groundwater concentration of total CVOCs is >10 mg/L and any individual CVOC is >5 mg/L then it may be assumed that there is a potential for NAPL to be present. The mass loading due to NAPL will be the dominant demand factor. A 1% TCE NAPL saturation would have a sodium permanganate demand of close to 9 kg/m^3. Obviously, if there is a potential for NAPL to be present, accurate delineation is critical. In such cases, delineation techniques such as MIP should be used.

Natural Oxidant Demand (NOD) is a measured value (generally expressed as g/kg of soil) and is a function of reduced minerals and reactive natural organic material present. As previously discussed, it is not possible to estimate NOD from soil data such as TOC or COD. NOD must be measured.

Typically, NOD is determined by exposing soil to different concentrations of permanganate and measuring the residual permanganate after a period of time ranging from 2 to 21 days. Figure 15.11 shows a generalized NOD response to permanganate loading for an extended period of time (Thomson et al., 2006). The response follows the same behavior for a range of NOD values. Important observations include:

- There is an initial fast response, wherein 40–60% of the NOD is reacted.
- The NOD continues to increase with time until a maximum value is reached.
- NOD values are a function of the permanganate concentration. Generally the higher the concentration to which the soil is exposed, the higher the NOD value.
- Column tests give different results, usually lower than batch tests.

NOD testing is critical. A difference of 1 g/kg in NOD will affect the permanganate demand by as much as 2 kg/m^3. However NOD determinations can be highly variable depending on the time of exposure and permanganate loading. Because of the importance of NOD testing, considerable effort is going into development of a standard NOD test (ASTM, 2007). The following steps are recommended for NOD testing:

- NOD testing should be done in two steps. The initial test assesses the maximum NOD value using a Permanganate COD test, which requires only 2–4 hours. If the NOD_{COD} is <0.25 g/kg, the site may be assumed to have a low NOD and further testing would not be required. If the NOD_{COD} is >0.25 g/kg, further testing using batch or column studies (preferred) would be required. Not all sites have a significant NOD.
- If batch or column studies are done, the duration and the permanganate loading should reflect the conditions that will be applied in the field. The duration of the test should be based on the desired residence time or on the travel time for the permanganate. The permanganate loading used should bracket the projected field concentration(s).
- Column tests are preferred for the second level of testing because they reflect dynamic conditions, utilize a more representative sample, and can be more easily extrapolated to field conditions. The flow rate through the column should be similar to the flow rate anticipated in the field.

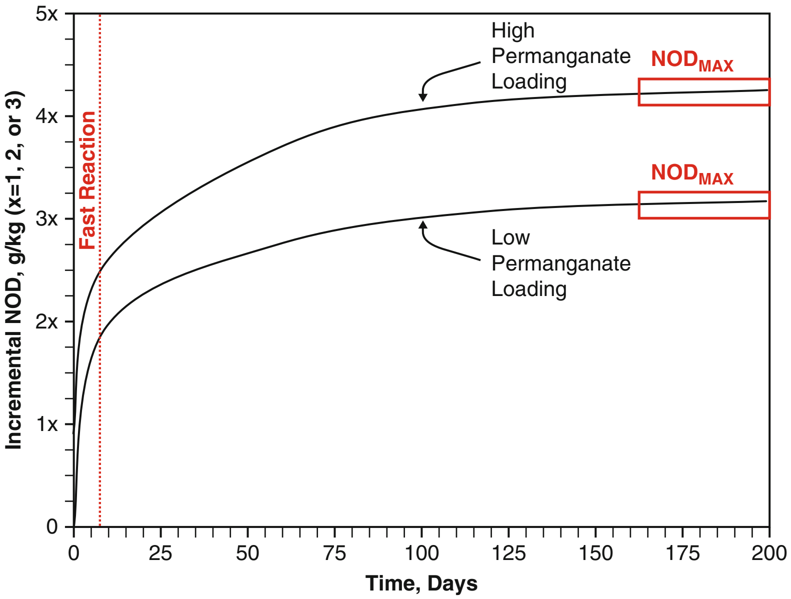


Figure 15.11. Representative NOD response for permanganate (Thomson et al., 2006).

In determining the NOD, a basic principle should be kept in mind, especially for sites where the NOD is a significant component of the overall demand. It is safer to overdose than it is to under dose. Each 1 g/kg of NOD increases the overall permanganate demand by 1–2 kg/m^3. As a result, a conservative testing methodology should be used.

15.2.4.10 Choosing an Application Method

There are two approaches for permanganate application—emplacement and circulation. Since permanganate is relatively stable, circulation technologies that are based on the migration of permanganate can be used. Conversely, since permanganate reacts rapidly with chloroethenes or other amenable CVOCs, emplacement technologies can be used to provide rapid treatment. Table 15.9 summarizes the different application methods that can be used for permanganate.

Table 15.9. Application Methods for Permanganate

Injection Force	Application Points	Best Geological Fit	Geological Limits	Maximum Radius, Response
Ambient Pressure Injection	Galleries, Drilled wells, Driven points	Permeable homogeneous	Heterogeneous, low permeability, layered, clay	Response is non-radial. Travels with GW flow.
Pressurized Injection	Drilled wells, Driven points	Homogeneous Gravels – silts	Heterogeneous, low permeability, clay, layered	Radial response 15–20 ft sands 5–10 ft silts
Pneumatic Fracturing	Drilled wells, Driven points	Moderate to low permeability, clays	Fractured rock, Expensive for sands, Shallow soils	Radial response 30–50 ft silts 20–35 ft clay
Hydraulic Fracturing	Drilled wells, Driven points	Moderate to low permeability, clays	Fractured rock, Expensive for sands, Shallow soils	Radial response 30–50 ft silts 20–35 ft clay
Physical Mixing	None	Unconsolidated, Shallow soils (<30 ft)	Hard tills, Rock	Radius is limited to mixing zone. Works in all unconsolidated soils.

The application method should be chosen to give the best distribution for a given geology and contaminant architecture (i.e., distribution of adsorbed and NAPL within geological matrix). Application methods vary by the injection force and by the types of application points.

15.2.4.11 Other Engineering Considerations

Success in ISCO is defined as having sufficient oxidant in contact with the contaminant for a long enough period of time to achieve the results desired. The engineering rigor that needs to be applied to the application of permanganate to achieve this success depends on the complexity of the site. Complexity has two components – geology and contaminant. For simple sites, those having low levels of contamination, a permeable, homogeneous geology and a low NOD, the application of permanganate has a lot of flexibility and forgiveness. Simple injection will suffice. For complex sites, those having a geology with low permeability and/or high heterogeneity, a substantial and complex mass distribution, and a substantial NOD, rigorous engineering is beneficial. Two application parameters need to be balanced, the concentration injected and the rate of injection (Siegrist et al., 2006). This research project found that in some cases a slow injection of a low concentration is most effective; in other cases rapid injection of high concentration is desirable.

15.2.5 Sodium Persulfate

Persulfate is the newest ISCO agent presently in use. While persulfates have been used in industry for a considerable length of time as a bleach, as an etchant and as a polymerization agent, their use for environmental applications only began in the late 1990s. In contrast to peroxide and permanganate, persulfates did not have widespread use for industrial waste treatment prior to their use for *in situ* treatment. As a result, there is not a significant background of information on the reactivity and application of persulfates. The environmental chemistry of persulfate is still under development.

Persulfates (specifically dipersulfates) are strong oxidants that have been widely used in many industries for initiating emulsion polymerization reactions, clarifying swimming pools, hair bleaching, micro-etching of copper printed circuit boards and TOC analysis. In the last few years there has been increasing interest in sodium persulfate as an oxidant for the destruction of a broad range of soil and groundwater contaminants. Persulfates are typically manufactured as the sodium, potassium and ammonium salts. The sodium form is the most commonly used for environmental applications.

The persulfate anion is the most powerful oxidant of the peroxygen family of compounds and one of the strongest oxidants used in remediation. The standard oxidation—reduction potential for the reaction

$$S_2O_8^{-2} + 2e^- \rightarrow 2SO_4^{-2} \qquad \text{(Rx. 15.25)}$$

is 2.1 volts (V), as compared to 1.8 V for hydrogen peroxide (H_2O_2) and 1.4 V for the peroxymonosulfate anion (HSO_5^-). This potential is higher than the redox potential for the permanganate anion (MnO_4^-) at 1.7 V, but slightly lower than that of ozone (O_3) at 2.2 V.

In addition to direct oxidation, sodium persulfate can be induced to form sulfate radicals, thereby providing free radical reaction mechanisms similar to the hydroxyl radical pathways generated by Fenton's chemistry. The generation of sulfate radicals is

$$S_2O_8^{-2} + \text{initiator} \rightarrow SO_4^{\bullet -} + (SO_4^{\bullet -} \text{ or } SO_4^{-2}) \qquad \text{(Rx. 15.26)}$$

The sulfate radical is one of the strongest aqueous oxidizing species with a redox potential estimated to be 2.6 V, similar to that of the hydroxyl radical at 2.7 V.

In addition to its oxidizing strength, persulfate-based sulfate radical oxidation has several advantages over other oxidant systems. First, it is kinetically fast. Second, the sulfate radical is more stable than the hydroxyl radical and thus able to transport greater distances in the subsurface. Third, persulfate has less affinity for natural soil organic matter than does the permanganate ion (Brown et al., 2003) and is thus more efficient in high organic content soils. These attributes combine to make persulfate a viable option for the chemical oxidation of a broad range of contaminants.

Persulfate is very soluble, at 73 g/100 mL of water at 25°C. High solubility makes it easy to apply concentrated solutions of persulfate.

Persulfate is manufactured in North America by FMC Corporation, the sole North American producer. There is considerable information available on line on the properties of persulfate (FMC, 2009a; b). FMC also has an internet resource center with information on the use of persulfate (FMC, 2009c).

15.2.5.1 Non-Beneficial Reactions

For persulfate, decomposition appears to be by far the most important non-beneficial reaction. In general, the ultimate fate of persulfate in the subsurface is decomposition. It will, as do all oxidants, react with reduced metals. But unlike permanganate, persulfate does not react appreciably with natural organic material.

15.2.5.2 Decomposition

Persulfate, as a peroxygen compound, will decompose to oxygen and sulfate ion:

$$^{-}O_3S - O - O - SO_3^{-} + 2H_2O \rightarrow 2SO_4^{-2} + 2H^{+} + O_2 \qquad \text{(Rx. 15.27)}$$

The peroxygen bond is inherently unstable. However, with persulfate as compared to peroxide, the peroxygen moiety appears to be protected by the two sulfate groups.

Persulfate behavior in soils is illustrated in Figure 15.12. Oxidant loss does not plateau as is typically observed in the permanganate NOD test. Persulfate loss continues to occur over time for all concentrations of persulfate. Decomposition of persulfate over time increases with increasing levels of added persulfate. Persulfate loss at any concentration increases with time. These observations suggest that the loss mechanism for persulfate is decomposition and not reaction with NOM.

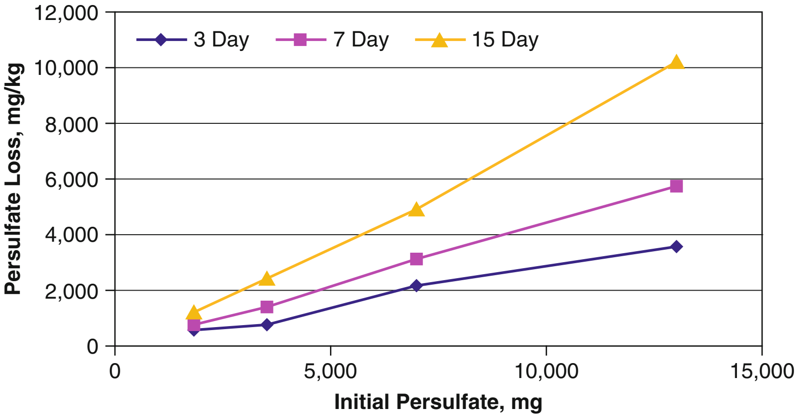


Figure 15.12. Persulfate response in soils

Persulfate decomposition is affected by the same factors as is hydrogen peroxide. In particular, persulfate decomposition is catalyzed by iron and manganese. Manganese, as is observed with hydrogen peroxide, appears to be the more active decomposition catalyst.

15.2.5.3 Natural Oxidant Demand

The only component of NOD that affects persulfate is reduced metals. Persulfate does not appear to react with natural organic material (NOM). The reaction with reduced metals appears rapid and near stoichiometric. The reaction of persulfate with NOM is very slow and undistinguishable from decomposition.

The basis for the assertion that persulfate does not react with NOM is a comparative study with permanganate wherein a soil with a high organic contact was exposed to both permanganate and persulfate (Brown et al., 2003). A synthetic soil was constructed by combining 75% by weight of sand, 15% by weight of commercial topsoil and 10% by weight of crushed limestone. First the NOD was measured in parallel for both persulfate and permanganate. For the permanganate NOD test, 25-g aliquots of the soil were exposed to a series of increasing permanganate concentrations. The persulfate NOD was determined by initially adding 1 g of persulfate to 200 g of soil in 350 mL of water, and then adding an additional 2.5 g of persulfate after one week. The residual persulfate was titrated at one (before the addition of added persulfate) and three weeks. Three different activator systems were tested with persulfate. The results for these NOD tests are given in Table 15.10. The NOD for permanganate is significantly higher than for persulfate by almost an order of magnitude.

Table 15.10. Natural Oxidant Demand with Oxidant Treatment (Brown et al., 2003)

Oxidant Treatment	Natural Oxidant Demand, g/kg soil	
	1 Week	3 Week
Permanganate	40.8	61.6
Persulfate, no catalyst	0.98	8.1
Persulfate, Fe(II)	2.2	7.9
Persulfate, Fe-EDTA	2.1	5.1

In another experiment, aliquots of the soil were exposed to the three different persulfate oxidant conditions (no catalyst, Fe(II), Fe-ethylenediaminetetraacetic acid (Fe-EDTA)) for a total of eight weeks. Over that period of time a total of 9.7 g of persulfate was added to each of the reactors. At the end of the eight weeks the soil from each reactor was recovered and used in a one-week permanganate NOD test (Table 15.11).

Table 15.11. Permanganate Natural Oxidant Demand (Brown et al., 2003)

Persulfate Reaction Conditions	1 Week Permanganate Natural Oxidant Demand, g/kg soil, After 8 Week Persulfate Exposure
Persulfate, no catalyst	41.3
Persulfate, Fe(II)	41.5
Persulfate, Fe-EDTA	41.2

There is virtually no difference between the permanganate NOD of the original synthetic soil and the permanganate NOD after eight weeks of persulfate exposure. These results suggest that persulfate does not react appreciably with NOM.

15.2.5.4 Reactivity

While the persulfate anion by itself is a strong oxidizer, its reaction rates are kinetically slow for the more recalcitrant contaminants, such as trichloroethene. However, the kinetics of persulfate oxidation can be significantly enhanced by the generation of sulfate radicals and other active species (Block et al., 2004; Brown et al., 2006; Watts, 2006).

Sulfate activation can be achieved through the application of heat, transition metal catalysts or ultraviolet (UV) radiation (House, 1962). With transition metal activation, Balazs et al. (2000) points out that the mechanism is dependent on catalyst type, organic substrate and oxidant concentration.

Ferrous iron (Fe(II)) historically has been the most common activator for transition metal catalysis (an adaptation of hydrogen peroxide activation). Generally, 100 to 250 mg/L of iron is used to activate persulfate. Additions of ferrous iron in excess, greater than 750 mg/L, can lead to the rapid decomposition of persulfate and a loss in remediation performance. If significant amounts of reduced metals are available in the subsurface, addition of metal catalysts may not be necessary to catalyze the persulfate. Divalent iron activated persulfate effectively oxidizes chlorobenzene, dichlorobenzene, DCE, TCE and PCE. However, its effectiveness against chlorinated ethanes, such as TCA, and chlorinated methanes, such as chloroform, is limited. This lack of broad reactivity has lead to the development of other activators, including heat.

Heat activated persulfate (>99°C) is the basis for many wet-chemical TOC analyzers. Hoag et al. (2000, 2002) discusses divalent metal catalysis and the application of heat in the range of 40 to 99°C to oxidize VOCs. Heat-activated persulfate has been demonstrated in aqueous systems to be applicable to a wide range of contaminants. The activation temperature required varies by compound. Table 15.12 lists the oxidation of various compounds as a function of temperature. At 45°C and above all the compounds tested were oxidized. Bruell (2001) has shown that heat-catalyzed persulfate oxidation of organics in a soil environment requires higher temperatures than in aqueous systems.

Table 15.12. Effects of Acclimation Temperature on the Oxidation of Chlorinated Solvents

CVOCs with >90% Destruction Treated with Persulfate @ 20°C	1,1-DCE 1,2-Dichlorobenzene 1,3-Dichlorobenzene 1,2,4-Trichlorobenzene
Additional CVOCs with >90% Destruction Treated with Persulfate @ 35°C	1,2-DCE PCE TCE Vinyl Chloride Carbon Tetrachloride 1,1-DCA 1,2-DCA
Additional CVOCs with >90% Destruction Treated with Persulfate @ 45°C	Methylene Chloride Chloroform 1,1,1-TCA

While heat and Fe(II) activation of persulfate are effective in bench scale oxidation studies, they both have limitations for field application. Inorganic Fe(II) tends to oxidize and precipitate out as insoluble ferric oxides, limiting the effectiveness of Fe(II) as an activator. Heat activation requires installation of a parallel heating system to heat the aquifer matrix to the desired temperature. This entails both capital expenditures as well as additional operating expense. The options for *in situ* heating include steam or hot air injection, electrical resistance (joule) heating, or radio frequency heating. Generally heating is best applied for source treatment where the target area is limited. *In situ* heating, with an external heating source, is impractical for treating large groundwater plumes. Hence, new and improved persulfate activation systems are needed that:

- Are transportable in a groundwater system,
- Increase the reactivity of persulfate with a broad range of organic contaminants, and
- Are easy to apply in a variety of subsurface conditions.

Several new persulfate activation systems have been recently developed that address these issues (Block et al., 2004, Brown et al., 2006). A few of these technologies use novel non-metal routes to activate persulfate.

15.2.5.5 Chelated Metal Catalysts

Chelated metal catalysts are complexes of transition metals bound to strong chelating agents. Previous work (Pignatello and Sun, 1992) demonstrated the benefit of chelated iron complexes to activate hydrogen peroxide for the destruction of complex pesticides. In addition to Fe(II) as discussed above, chelated trivalent iron Fe(III) was found to have excellent oxidation performance. Laboratory tests were conducted to test the efficacy of chelated iron catalysts for persulfate activation utilizing several different iron–chelant complexes. The best performing complex, Fe(III)–EDTA, is shown in Table 15.13.

Table 15.13. Performance of Persulfate and Iron Catalysts at Ambient pH: 21-Day Results, µg/L

	Control	Persulfate Alone	Persulfate Fe(II)	Persulfate Fe(III)-EDTA
Chloromethanes	35,000	34,000	29,100	32,000
Chloroethanes	50,000	52,000	37,600	38,000
Chloroethenes	32,700	9,830	0	0
Chlorobenzenes	34,800	9,300	0	360
pH	6.9	2.2	2.3	2.2

The 21-day results are shown in Table 15.13, which compares persulfate alone and persulfate with non-chelated Fe(II) and Fe(III)-EDTA. A distilled water control was also run. These data show that none of the persulfate/iron catalysts are effective with the chloroethanes or chloromethanes. All persulfate solutions resulted in a low pH. Fe(II) and Fe-EDTA complex gave comparable performance.

Of significance is that the results in Table 15.13 are at a pH of 2, where metal solubility and activity is not an issue.

Under neutral pH conditions that may be found in the field, chelating the transition metal catalyst provides protection from hydroxide addition and subsequent precipitation. Table 15.14 shows the results for different iron catalysts with persulfate at different pH values. Under acidic conditions, pH 2, Fe(II) is soluble and is an effective catalyst. With the pH controlled at 7-8, only the Fe-EDTA catalyst with persulfate showed activity; the un-chelated iron had reduced activity. The solubility and availability of the transition metal catalysts are critical factors in the activation of persulfate. Chelation is an effective means of maintaining metal activity at neutral or alkaline groundwater conditions.

Table 15.14. Performance of Iron Catalysts with Persulfate, Controlled pH (7-8), 21-Day Results, µg/L

	Control	Persulfate Ctrld pH	Fe(II) Amb pH	Fe(II) Ctrld pH	Fe-EDTA Ctrld pH
Ethenes	34,083	32,606	0	27,730	9,870
Ethanes	67,115	62,379	61,908	63,702	50,246
Methanes	51,983	48,180	42,261	45,597	44,900
Chlorobenzenes	56,089	36,990	0	31,824	7,428
pH	6.7	8.5	2	7.5	7.6

15.2.5.6 Sodium Persulfate and Hydrogen Peroxide

An activator system utilizing hydrogen peroxide and sodium persulfate has been developed that combines the reactivity of peroxide with the enhanced stability of persulfate (Sethi et al., 2009). The combination of hydrogen peroxide and persulfate may have several synergistic attributes. First, hydroxyl radicals can initiate persulfate radical formation. Similarly, sulfate radicals can stimulate formation of hydroxyl radicals. Second, hydrogen peroxide may react with a significant portion of the more reactive contaminants, allowing the sulfate radicals to destroy the more recalcitrant compounds of concern. Third, a combination of peroxide and sulfate radicals may provide a multi-radical attack mechanism, yielding either a higher efficiency in destroying contaminants, or allowing for recalcitrant compounds to be more readily degraded. Table 15.15 presents degradation rates for selected chlorinated solvents with a mixture of 4% sodium persulfate and 12.5% hydrogen peroxide. Significant reductions in concentrations were measured not only for chlorinated ethenes, but for chlorinated ethanes as well. The combined peroxide-persulfate reaction system appears to have a broad range of applicability. It not only oxidizes compounds generally amenable to persulfate oxidation, but also oxidizes compounds not readily oxidized by conventional iron activated persulfate technology.

Table 15.15. Degradation of Contaminants with 4% Sodium Persulfate and 12.5% Hydrogen Peroxide (results in mg/L) (Block et al., 2004)

Contaminant	Time 0	Day 8
1,1-DCE	4.5	0.1
TCE	2.8	non-detectable
1,1-DCA	1.1	non-detectable
1,1,1-TCA	12.0	0.6

15.2.5.7 Alkaline Persulfate

Persulfate is known to be highly reactive at low pH (<3), but it is also highly reactive at pH values greater than 10. Hence, it should be possible to "activate" persulfate at high pH values. Table 15.16 shows the degradation of chlorinated compounds with the addition of potassium hydroxide at 0.5 and 0.8 KOH:persulfate mole ratios. The pH was above 10 for both. In most cases, "acclimated" alkaline persulfate completely degraded chlorinated solvent compounds including those historically difficult-to-degrade such as chlorinated ethanes and methanes. These results indicate that alkaline persulfate has a broad reactivity and that alkaline activation of persulfate is possible with a number of different bases. However, each base may have a different optimal ratio and/or breakpoint. In applying the alkaline persulfate activator technology it is important to add sufficient base to compensate for soil acidity. There are reaction pathways for persulfate that are not currently well understood and may be further optimized. The reaction of persulfate under basic conditions is a novel technology that needs further study.

Multiple reactive species can be generated from persulfate:

$$S_2O_8^{2-} + Fe^{2+} \rightarrow \mathbf{SO_4\bullet^-} + SO_4^{2-} + Fe^{3+} \text{ Sulfate Radical} \quad \text{(Rx. 15.28)}$$

$$SO_4\bullet^- + H_2O \rightarrow \mathbf{OH\bullet} + HSO_4^- \text{ Hydroxyl Radical} \quad \text{(Rx. 15.29)}$$

$$S_2O_8^{2-} + H_2O \rightarrow HSO_4^{2-} + \mathbf{HSO_5^{2-}} \text{ Peroxymonosulfate} \quad \text{(Rx. 15.30)}$$

$$S_2O_8^{2-} + 2H_2O \rightarrow 2HSO_4^{2-} + \mathbf{H_2O_2} \text{ Hydrogen Peroxide} \quad \text{(Rx. 15.31)}$$

Since persulfate can also hydrolyze to hydrogen peroxide, it can also generate all the active species associated with hydrogen peroxide.

Table 15.16. Destruction of Recalcitrant Compounds with Alkaline Persulfate—14 Day Results (μg/L)

Contaminant	Control @ pH = 7	0.5 mol KOH : Persulfate	0.8 mol KOH : Persulfate
1,1,1-TCA	19,000	14,400	3,400
1,1,2-TCA	25,000	ND	ND
1,2-DCA	22,000	ND	ND
1,1-DCA	17,000	1,600	ND
Carbon Tetrachloride	18,000	ND	ND
Methylene Chloride	20,000	ND	ND
Vinyl Chloride	195	ND	ND

15.2.5.8 Variations in Using Persulfate

There are two other persulfate salts that are commercially available, ammonium persulfate ($(NH_4)_2S_2O_8$) and potassium persulfate ($K_2S_2O_8$). Both have the same reactivity as the sodium form and are generally not used for environmental applications.

The primary variability in using persulfate lies in the activator system. There are, as previously discussed, six types of activator systems:

- Ambient conditions—typically relying on direct oxidation or on naturally occurring transition metals, no activator is added;
- Fe(II) salts;
- Chelated Fe(II) and Fe(III) complexes, the most common being Fe(II)-EDTA;
- Heat, typically in the range of 40 to 70°C;
- Hydrogen peroxide; and
- Alkaline pH, typically above 10.0.

Persulfate also can be activated by UV light, generating sulfate radicals.

15.2.5.9 Guidance on Using Persulfate

There are two key decisions that must be made in the use of persulfate for degradation of chlorinated solvents—type of activator system and dosage.

Choosing an Activator: The choice of an activator system is a function of the contaminant(s) being treated and site conditions. Of the chlorinated solvents, the chlorobenzenes and 1,1-DCE are the most reactive with persulfate. They will react under ambient conditions. The next most reactive are the chloroethenes such as PCE, TCE, DCE (including all isomers) and vinyl chloride. These chemical species typically require the addition of a metal activator such as Fe-EDTA. The chloroethanes and chloromethanes require an aggressive activator system such as hydrogen peroxide, heat or high pH. The choice of activator will depend on site conditions. Soils with high levels of iron and/or manganese will not be compatible with hydrogen peroxide activation, since they will catalyze the decomposition of both hydrogen peroxide and persulfate. Strongly acidic soils ($pH < 4$) are typically not compatible with alkaline activation. Highly permeable soils with rapid groundwater flow are not compatible with heat activation. Alkaline activation and heat activation are probably the least sensitive to site conditions and offer the most universal applicability.

Determining the Persulfate Dose: The persulfate dose is a function of the stoichiometric demand and of the amount needed to compensate for decomposition. The stoichiometric demand is calculated using the equivalent weight of persulfate and the equivalent weight of the contaminant being oxidized. Table 15.17 gives the theoretical stoichiometric dose for a number of chlorinated solvents, assuming that persulfate is a two-electron oxidant. It should be noted that the stoichiometric requirements for persulfate are more than two times greater than those for permanganate. This is due to the fact that persulfate has a much higher equivalent weight (119 g) than does permanganate (52.6 g – K; 47.3 g – Na). The actual stochiometric requirement is the stoichimetric demand times the mass of the solvent present.

Table 15.17. Stoichiometry of Persulfate Dose

	Molecular Weight	Equivalent Weight	$Na_2S_2O_8$ Stoichimetry (g/g)
Vinyl Chloride	62.5	6.25	19.04
cis-1,2-Dichloroethene	96.94	12.12	9.81
trans-1,2-Dichloroethene	96.94	12.12	9.81
1,1-Dichloroethene	96.94	12.12	9.81
Trichloroethene	131.39	21.9	5.43
Tetrachloroethene	165.83	41.46	2.87
Chlorobenzene	112.56	4.02	29.6
Dichlorobenzene (1,2-, 1,3-, 1,4-)	147	5.65	21.08
Chloropropenes	76.5	4.78	24.89
Dichloropropenes	110.97	7.93	15.00

The second factor that determines the persulfate dose is its rate of decomposition. The decomposition of persulfate should be measured by titration using a procedure similar to the following:

- Prepare 50% (wt-wt) slurries of persulfate and soil from the site. Persulfate concentrations should be 50, 100, and 150 g/L (5, 10 and 15%).
- Take a 5 mL aliquot of the liquid, add 25 ml of 25% H_2SO_4, and stir for 2 minutes.
- Add dried (105°C for 24 hours) ferrous sulfate heptahydrate ($FeSO_4{}^\bullet 7H_2O$). Add 0.75g for the 5%; 1.4 g for the 10%; and, 2.0g for 15%. Stir for 10 minutes.
- Titrate to a persistent pink color with 0.1N $KMnO_4$.
- Calculate the concentration of persulfate by the following formula:

$$Na_2S_20_8\,g/L = \left[\frac{\left\{\frac{\text{Weight FeS}0_4\cdot 7H_20}{278.01}\right\} - \left\{\frac{\text{mL KMn}0_4}{1000}\times \text{N KMn}0_4\right\}}{\frac{\text{mL of Sample}}{1000}}\right]\times 119 \qquad \text{(Eq. 15.5)}$$

This titration procedure should be done every 2–5 days for a total of 10–20 days. The length of time between samples depends on the rate of decomposition of the persulfate.

15.2.6 Ozone

Ozone also is an oxidant that can be used to treat chlorinated solvents. Ozone is a strong oxidant in its own right. It has an electrode potential of 2.07 V.

$$O_3 + 2H^+ + 2e^- \rightarrow H_2O + O_2 \qquad \text{(Rx. 15.32)}$$

Ozone can generate a number of active species such as superoxide anion or hydroxyl radicals. These species increase the range of compounds with which ozone will react.

Ozone has been used extensively in water treatment for over 100 years, primarily for disinfection. In the last 25 years it also has been used for treatment of hazardous chemicals (Rice, 1981; Masten and Davies, 1994) in industrial waste waters. In the early 1990s, ozone was explored for treating recalcitrant organics in soils and groundwater (Brown and Nelson, 1994).

However, ozone is fundamentally different than the other three oxidants previously discussed. First, it is a gas, and second, it is inherently unstable and must be generated on site from either air or oxygen. Third, ozone is only a minor component (<12%) in the gas stream after generation. This means that there are significant quantities of non-reactive gas that are also injected with ozone, which can strip VOCs from soil and groundwater. And fourth, the mass of ozone that can be produced by a typical generator is limited. A large-scale ozone generator for environmental applications will produce 25 kg of ozone per day.

Ozone is an allotrope of oxygen. It is formed from oxygen:

$$3O_2 \rightarrow 2O_3 \qquad \text{(Rx. 15.33)}$$

The quantity and concentration of ozone that can be produced is a function of the ozone generating system, the feed gas used, and the operating conditions.

There are two methods of generating ozone – UV-light and high voltage electricity (corona discharge). UV light systems are limited in both the quantity and concentration of ozone produced. A typical UV-based ozone system produces less than 0.5 kg per day of ozone at a concentration of less than 1%. Most large scale ozone generating (>1 kg/day ozone) systems use corona discharge. Typical ozone generators used for environmental applications produce ozone in the range of 3 to 25 kg/day.

The two typical feed gases for generating ozone are air and oxygen. When air is used, the resulting ozone concentration is 3 to 5%. If oxygen is used, ozone concentrations in the 8–12% range can be generated. With most ozone generators the mass per day produced and the concentration are inversely related; the higher the concentration generated, the lower the mass produced per day. If oxygen is used as a feed, it can either be produced on site by a pressure swing adsorption (PSA) generator or it can be brought to the site in pure form as liquid oxygen or in oxygen gas tubes.

The operating conditions for the ozone generator are important. Ozone generation efficiency is higher at lower temperatures. Ozone generation also requires a low feed gas dew point ($< -62°C$). These operating requirements often necessitate an air dryer and a chiller (to cool the generator) for on-site ozone generation.

Ozone is applied with a gas injection system. A common view of ozone has been that it must dissolve in the aqueous phase in order for it to react with contaminants. However, ozone reacts through several different pathways (Figure 15.13). Ozone can dissolve in the water phase and react with dissolved constituents or with adsorbed materials in contact with the aqueous phase. It can also react in the gas phase when it contacts adsorbed or separate phase contaminants. The gas phase reactions of ozone are a significant contribution to the efficacy of ozonation (Skladany and Brown, 2006).

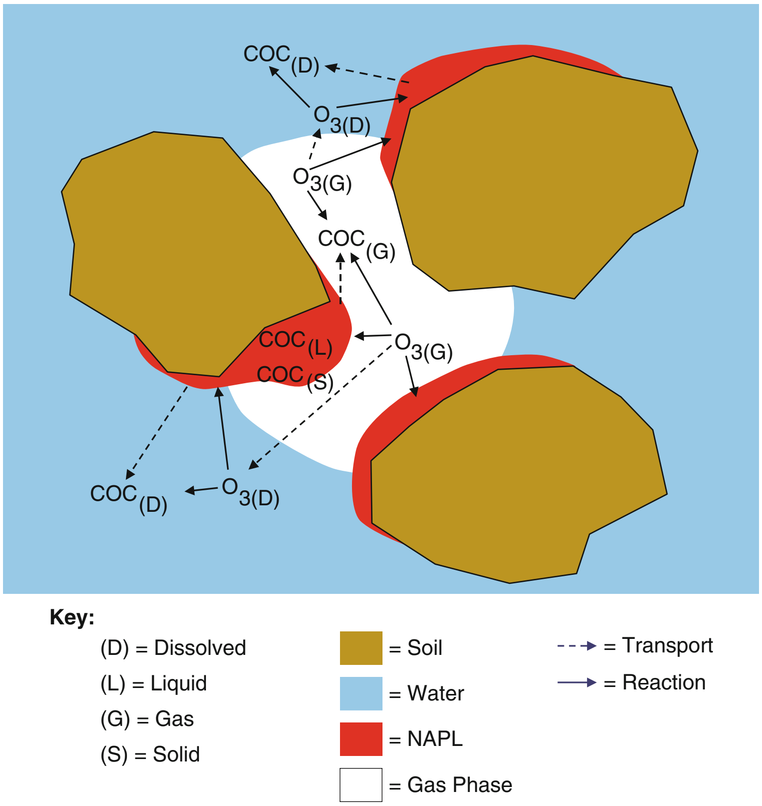


Figure 15.13. Depiction of reaction pathways for ozone (Skladany and Brown, 2006)

15.2.6.1 Non-Beneficial Reactions

Ozone is both an unstable and reactive molecule. It will decompose over time as shown in Table 15.18 and has a limited half life in both the gas and aqueous phase (Ozone Solutions Inc., 2007). The decomposition of ozone is complex. It is generally via free radical chain reactions. The rate of decomposition is faster at high pH than low as the hydroxide anion is an initiator of free radical chain reactions (Lenntech, 2007c).

Table 15.18. Typical O_3 Half Life versus Temperature (Ozone Solutions Inc., 2007)

Gaseous		Dissolved in Water (pH 7)	
Temp (°C)	Half Life *	Temp (°C)	Half Life
-35	18 days	15	30 minutes
-25	8 days	20	20 minutes
20	3 days	25	15 minutes
120	1.5 hours	30	12 minutes
250	1.5 seconds	35	8 minutes

*These values are based on thermal decomposition only. No wall effects, humidity, organic loading or other catalytic effects are considered.

The stability of ozone in water is also a function of the water quality as is seen in Figure 15.14 (Lenntech, 2007c). It appears that the stability of ozone is affected by both organic substances and minerals.

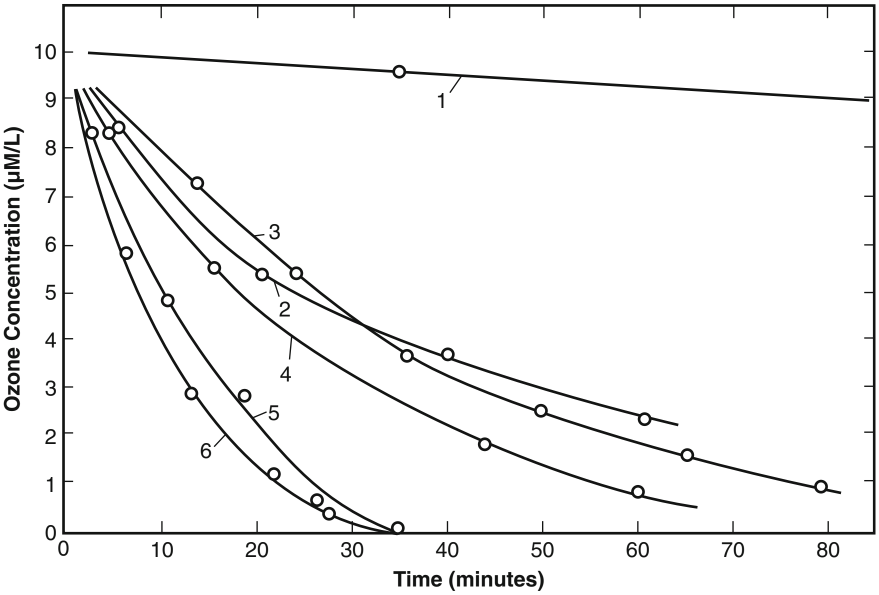
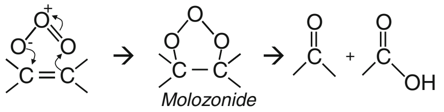


Figure 15.14. Ozone decomposition in different types of water at 20°C. 1 = double-distilled water; 2 = distilled water; 3 = tap water; 4 = groundwater of low hardness; 5 = filtered water from Lake Zurich (Switzerland); 6 = filtered water from the Bodensee (Switzerland) (Lenntech, 2007c).

The effect of soil organic matter on ozone stability is complex. Humic acid can act as both a promoter of ozone reactivity and as an inhibitor. Depending on the free radical species formed and on the substrate being oxidized (Lenntech, 2007b, Masten and Davies, 1994).

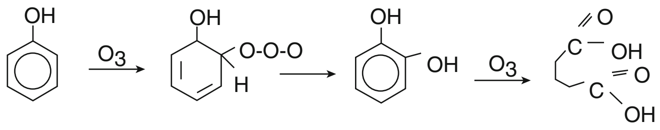
15.2.6.2 Reactivity

Ozone reacts by two different mechanisms. It can react directly with organic molecules as a 1,3-dipole, an electrophilic agent or a nucleophilic agent. In a 1,3-dipole cyclo-addition, ozone adds across a double bond generating a molozonide which then degrades into a carboxylic acid and an aldehyde or ketone.



(Rx.15.34)

As an electrophilic agent it will attack electron rich molecules such as phenols (Lenntech, 2007a):



(Rx.15.35)

Ozone also can react indirectly, generating different reactive species such as superoxide or hydroxyl radicals:

Superoxide: $O_3 + H_2O \rightarrow 2HO_2^{\bullet}$ $HO_2^{\bullet} \rightarrow O_2^{\bullet -} + H^+$

Hydroxyl Radical: $O_3 + H_2O \rightarrow 2HO^{\bullet} + O_2$

(Rx. 15.36–38)

The formation of these active species depends on soil and groundwater conditions and on the particular organic compounds being oxidized. Superoxide and hydroxyl radical are highly reactive and are known to oxidize a variety of organic compounds.

15.2.6.3 Variations in Using Ozone

The basic ozone system involves direct injection of a gas to produce ozone. The gas may be air or oxygen. Combining ozone and hydrogen peroxide is one variation of ozone treatment. This process is called the Peroxone Process. The combination provides an increased production of hydroxyl radicals:

$$2O_3 + 3H_2O_2 \rightarrow 4O_2 + 2HO\bullet + 2H_2O \qquad \text{(Rx. 15.39)}$$

While ozone will directly produce hydroxyl radicals, their production is a minor component of the ozone chemistry. The addition of hydrogen peroxide significantly increases the production of hydroxyl radicals which can accelerate treatment. Hydroxyl radicals are primarily effective for the treatment of chloroethenes and chlorobenzenes. The oxidation of the chloromethanes and chloroethanes involves the superoxide anion. As a result, peroxone chemistry will have limited effectiveness with these CVOCs.

A second variation in application of ozone systems is in the approach. Most ozone systems for water treatment involve continuous ozonation. One of the important discoveries in the use of ozone for soil treatment is that pulsed ozone is effective in treating recalcitrant organic compounds and is much more efficient than continuous ozonation. Pulses of one hour per 24 hours were effective in treating polychlorinated biphenyls (PCBs) and PAHs (Robbinson, et al., 2002). The primary benefit of pulsing is that it reduces the capital costs for ozone treatment by distributing the cost of the generator over multiple application points.

15.2.6.4 Guidance in Using Ozone

Several considerations must be taken into account with the application of ozone for chlorinated solvents. The first is ozone's reactivity with CVOCs. The second is the management of the gas stream. The third is the type of application.

Ozone is most reactive with chlorinated ethenes and benzenes. It has limited effectiveness with chlorinated methanes and ethanes. Ozone will potentially treat all phases of ethenes and benzenes – dissolved, adsorbed and NAPL.

Management of the gas stream is an important part of ozone systems. Ozone gas is toxic. The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) is 0.2 mg/m^3 (0.1 part per million by volume [ppmv]). But ozone is only about 10% of the injected gas stream. Volatile organic compounds present in groundwater or soils have the potential to be stripped and released to the atmosphere. As a result, most ozone systems are installed in conjunction with a soil vapor extraction system to collect fugitive ozone and any volatilized organic compounds. Residual ozone is generally destroyed by passing the collected gasses through a heated MnO_2 catalyst bed. Then the entrained organic compounds can be treated with conventional methods.

There are several types of application systems for ozone. Ozone can be directly injected into soil or groundwater (Figure 15.15). Each injection system is paired with a gas collection system. The injection design should insure that the gas stream contacts the area(s) of contamination. The gas injection and recovery systems are designed using conventional SVE or air sparging design methodology. The presence of ozone does not affect gas distribution.

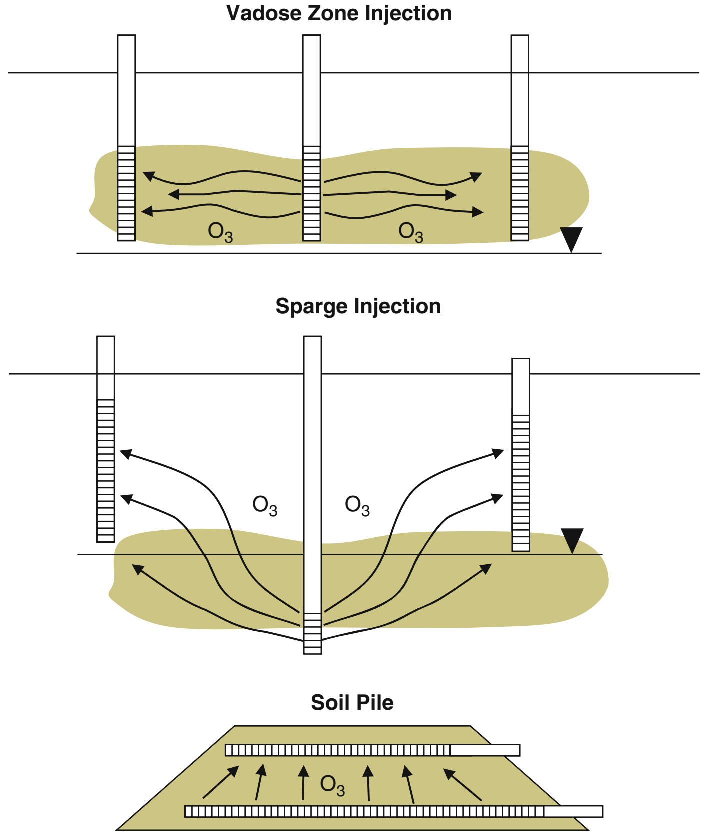


Figure 15.15. Ozone application system

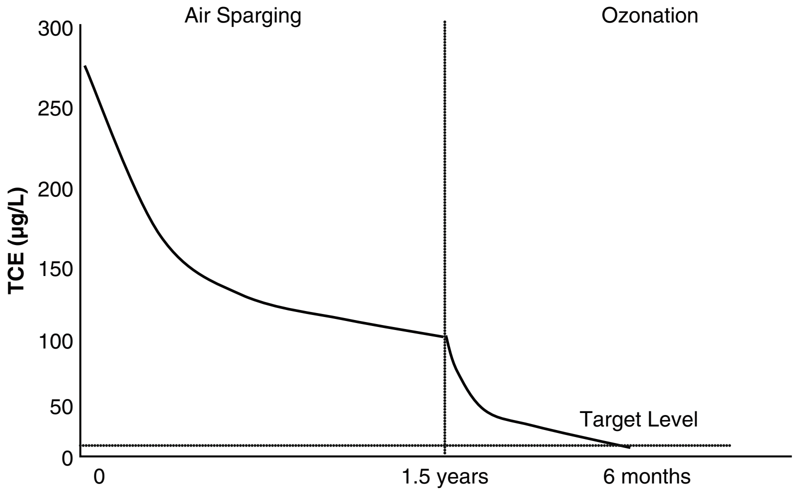


Figure 15.16. Polishing groundwater with ozone

Where there are high levels of CVOCs present, the sparging and/or SVE systems are often run initially without ozone. Once the CVOC recovery begins to reach the asymptote, ozone is added to finish the treatment and bring a site to closure. The site depicted in Figure 15.16 was an industrial dry cleaner site. After 1.5 years of air sparging, the groundwater concentrations had reached an asymptote. The sparge points were retrofitted for ozone injection. After six months of ozone injection, the closure levels were reached.

A second type of ozone application is development of an ozone sparge barrier. A series of ozone sparging points are placed perpendicular across a ground water plume. Ozone is injected into the sparge points to oxidize dissolved constituents. Often the sparge system can be run without any vapor capture.

15.2.7 Conclusion

ISCO is an important tool for the remediation of chlorinated solvent sites. It is a technology that is still in development. There are significant choices and decisions that must be made in applying ISCO.

There are four oxidants that can be used – hydrogen peroxide, permanganate, persulfate and ozone. All are effective in treating chlorinated ethenes and benzenes. Only peroxide and persulfate are potentially effective in treating chlorinated ethanes and methanes.

With all of the oxidants, there are non-beneficial reactions that can occur to severely limit their effectiveness. These are of two types – decomposition and reaction with indigenous reduced materials such as reduced metals and natural organic material. Peroxide and persulfate are mostly affected by decomposition; permanganate by reaction with soil organics. Generally the effect of these non-beneficial reactions must be measured to determine the proper oxidant dosage.

The basic requirement for success in ISCO is having sufficient oxidant in contact with the contaminant for a long enough period of time to achieve the results desired. "Sufficient oxidant" refers to the dosage. "In contact" refers to the oxidant distribution system. "A long enough period of time" refers to oxidant persistence and kinetics. And "achieving the results desired" depends on the overall design and management of the ISCO system and the remedial objectives.

ISCO is still an active field of research, especially regarding overall effectiveness and treatment of NAPLs.

15.3 *IN SITU* CHEMICAL REDUCTION

In situ chemical reduction (ISCR) is a relatively new technology for the treatment of chlorinated solvents. While elements of ISCR, such as zero-valent iron (ZVI), have been employed since the early 1990s, it only has been in the last five years that there has been a unifying theory of reductive processes that has coalesced into ISCR. ISCR is primarily the use and manipulation of reduced iron solids or minerals, both zero-valent and dual-valent (ferrous), to dechlorinate organic contaminants. From its base in ZVI permeable reactive barriers, "iron walls," ISCR is undergoing rapid development. This section provides an overview of ISCR technology and its state of application.

15.3.1 Foundations of ISCR

The development of ISCR has been based on four basic principles:

- All abiotic reductive processes involve a form of reduced metal, typically iron, that can be either zero-valent or dual-valent (Fe(II)) iron.
- Abiotic, iron-mediated reductive pathways are, in general, different and more diverse than those that typically occur with biologically mediated reduction.
- Iron-based reductive processes are strongly surface dependent.

- Iron-mediated reductive processes can be enhanced through the use of chemical and/or biological reduction.

These principles are based on and are derived from concurrent technical developments in reductive processes to treat chlorinated organic chemicals. This section provides an overview of the historical development of these principles and the technical basis of ISCR.

15.3.1.1 The Use of Reduced Metals (Iron)

Metal based reductive chemistry first focused on zero-valent metals. Zero-valent metals were first used to dechlorinate dissolved haloorganic compounds in the late 1970s (Sweeney, 1980). Sweeney was able to treat a wide range of chlorinated organics including dichlorodiphenyltrichloroethane (DDT), chlorobenzene, endrin, heptachlor, chloroform and hexachlorocyclopentadiene with copper-doped iron and aluminum. Early work focused on industrial wastewater streams. The technology, however, never gained widespread use due to the lower costs of alternative technologies such as air stripping or carbon adsorption.

Two events in the study and use of reductive processes for treating chlorinated organic compounds have fueled the growth of ISCR, a shift from wastewater treatment to groundwater treatment and a focus on iron chemistry. Beginning in the mid 1980s, research in water treatment began to focus increasingly on groundwater contaminants. Zero-valent metals such as aluminum and magnesium long have been used in the laboratory for the dechlorination of organic chemicals. Zero-valent iron has not been used as extensively in organic synthesis as has aluminum or magnesium due to its slower reaction rate. This controlled reactivity is, however, an advantage for groundwater systems.

The focus in reductive groundwater treatment has been primarily on the use of iron, particularly ZVI. Iron-based reductive chemistry was first applied in the field for groundwater treatment with the emplacement of ZVI barriers in the early 1990s (Gillham, 1993). By 1995, the USEPA cited 10 ZVI barrier demonstration projects (USEPA, 1995).

Early in the development of ZVI technology, the potential role of dual-valent iron (DVI) in reductive dechlorination reactions was considered. Ferrous iron, formed by the corrosion (reaction) of ZVI, was thought to also react with chlorinated solvents (Matheson and Tratnyek, 1994; Johnson et al., 1996).

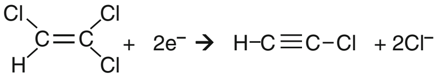
Parallel to the investigation of ferrous iron associated with ZVI, other researchers have specifically investigated the reactivity of reduced iron minerals such as pyrite and demonstrated that a suspension of pyrite was able to dechlorinate carbon tetrachloride (Kriegman-King and Reinhard, 1994) and reduce dinitrotoluene (DNT) (Jiayang et al., 1996). Recent research has shown that chemically-precipitated ferrous iron is also an active reductant for CVOCs (Brown, 2005).

Naturally occurring, ferrous-containing minerals also undergo reactions with chlorinated solvents. In 2002, a plume of *cis*-DCE was shown to be abiotically degraded by magnetite (Ferrey and Wilson, 2002). The abiotic reduction of chlorinated solvents by reduced iron minerals is thought to be a major natural attenuation pathway for chlorinated solvents (Wilson, 2003).

15.3.1.2 Reductive Pathways

In his investigation of haloorganic reduction in aqueous waste streams, Sweeney (1980) postulated that a number of probable reductive reactions were involved, including hydrogenolysis, hydrolysis, ring-opening, rearrangement and condensation, all catalyzed by the zero-valent metal. In 1987, Vogel et al. (1987) postulated a number of two-electron reductive pathways for chlorinated aliphatics including hydrogenolysis (the replacement of a chloride by hydrogen), dihalo-elimination (removal of two adjacent chlorine atoms generating a carbon-carbon bond) and, coupling (the removal of two chlorides from two different molecules generating a carbon-carbon bond combining the two molecules). Early publications presaged the diversity and complexity of metal-mediated reductive reactions.

The early understanding of *in situ* metal-based reductive processes was not, however, based on the pioneering work of Vogel and Sweeney. Originally, much of the literature assumed that ZVI reduced chlorinated solvents by sequentially replacing chlorine atoms with hydrogen, which is the same process observed with biologically mediated reductive dechlorination. This two-electron reduction is termed hydrogenolysis. With this mechanism, ZVI would convert PCE to TCE, TCE to *cis*-DCE, *cis*-DCE to VC, and VC to ethene. What has been discovered, however, is that ZVI operates by more diverse mechanisms than just the hydrogenolysis pathway. With PCE, TCE and *cis*-DCE, a key reductive pathway is postulated to be a β-elimination (dihalo-elimination), wherein two chlorines are removed via a two-electron reduction and the ethene is converted to an acetylene (Arnold and Roberts, 2000):



(Rx. 15.40)

The mechanisms of the reaction of ZVI with chlorinated solvents are quite complex and generate multiple products. Orth and Gillham (1996), in a study of the reaction of TCE with ZVI, found that ethene and ethane (in the ratio 2:1) accounted for over 80% of the original equivalent TCE mass. The typical daughter products formed biologically, such as cis-DCE and VC, accounted for only 3% of the original TCE mass. Additional byproducts were found including hydrocarbons (C_1 to C_4) such as methane, propene, propane, l-butene and butane.

Other researchers have found similar mixtures from the reaction of TCE and PCE with ZVI (Campbell et al., 1997). VC, *cis*-DCE, 1,1-dichloroethene, methane, chloroacetylene, acetylene, ethene, ethane, and $C_{3;5}$ alkenes and alkanes were observed as products.

One of the important discoveries key to the development of ISCR, is that DVI (ferrous iron) reacts with chlorinated solvents by mechanisms similar to those observed for ZVI. Chloroacetylenes were observed as products in the reaction of TCE with reduced iron-containing sediments (Szecsody et al., 2004).

The significance of this diversity of reaction pathways for the iron-based reduction of chlorinated solvents is that toxic byproducts (e.g., VC) do not accumulate with abiotic reduction as is often observed with biologically-mediated reductive dechlorination. The lack of toxic byproducts eliminates the concerns with intermediates that arise with biological reduction.

15.3.1.3 Surface Catalyzed Reactions

ZVI technology is, by its nature, a surface-based reaction. Much of the technology development for ZVI has focused on understanding the mechanisms of the reaction of chlorinated solvents with ZVI surfaces. Matheson and Tratnyek (1994) postulated three possible reductive mechanisms (Figure 15.17). These pathways include direct reduction, electron shunting through ferrous iron, and reduction by production and reaction of hydrogen.

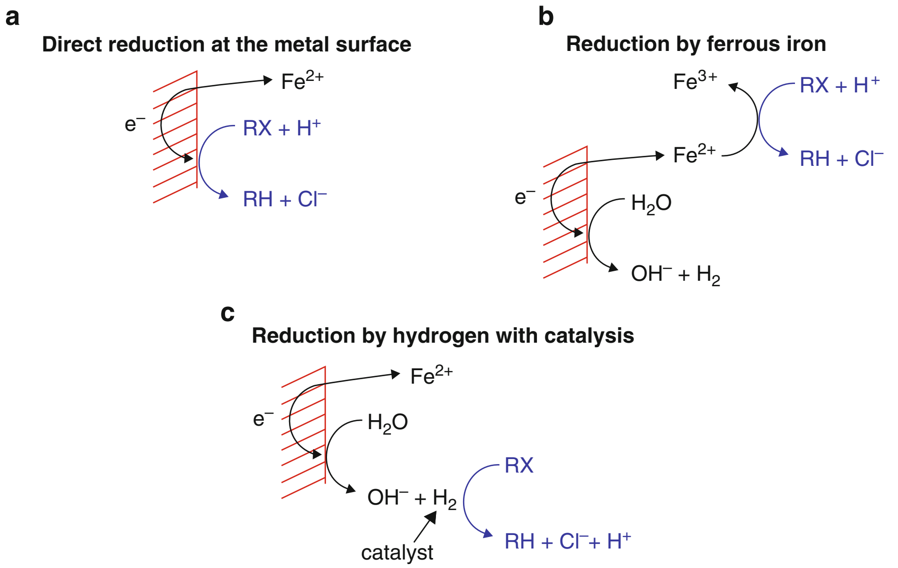


Figure 15.17. ZVI reduction mechanisms (Matheson and Tratnyek, 1994)

In reviewing the mechanisms of ZVI reduction, Richards (1998) postulated that the reduction of chloroethenes is a six-electron transfer with the ethene being bound to the metal surface by "strong chloroethene-iron pi bond..." which "prevents desorption until dechlorination is complete...".

Subsequent work on reductive reactions with ferrous iron have shown that the reactions are also surface catalyzed (Elsner, 2002). The reactivity of bound ferrous iron was found to be a function of the surface area and of the geochemical conditions.

Recent studies have suggested that soluble ferrous iron has a role in the activity of ferrous iron minerals. The reduction of *cis*-DCE with magnetite was enhanced with the addition of soluble ferrous iron (Ferrey et al., 2004). The role of the soluble ferrous iron is unknown but may be related to the regeneration of active sites (Scherer, 2005).

The significance of the role of surface reactions in ISCR is that the application of ISCR lends itself to creating effective barriers to contain, control and treat chlorinated solvent plumes.

15.3.1.4 Enhancement of Reductive Pathways

Abiotic reductive processes can be enhanced by two methods. First, the amount of reduced iron available can be enhanced to increase the rate of reduction observed. The amount of reduced iron can be increased by chemical or by biological means. Second, the reducing ability of the iron can be enhanced by coupling it with other chemical reductants or with biological reduction. As will be discussed below, both approaches are being actively developed and have been effectively utilized.

15.3.2 Ongoing Development

ISCR is a new and developing area of remediation technology. While some of the elements of ISCR are established and have been actively employed since the early 1990s, only recently has there been an appreciation for the potential of the technology and the utility of reductive, metal-based, processes. ISCR encompasses reduced ionic metals as well as zero-valent metals. However, the two most common embodiments of ISCR currently are the use of ZVI and DVI.

ISCR is also an important component of monitored natural attenuation (MNA) – abiotic attenuation. ISCR can be enhanced by and combined with biological processes. The development of ISCR into a cohesive remediation technology is based on continued development.

The ongoing development of ISCR can be divided into three categories – enhancing the reactivity of zero-valent iron, enhancing the reactivity of naturally occurring iron minerals, and the addition or synthesis of reduced iron solids. In addition, the effective distribution of reactive species is an important area of development (Lowry, 2007).

15.3.2.1 Enhancing the Reactivity of ZVI

Much of the research on zero-valent iron has focused on enhancing the transfer of electrons from the iron to the substrate. This objective has two aspects. The first is to increase the electron density of the iron. The rate of remediation is a function of electron density. Electron density is a function of the surface area of the metal. Generally the smaller the particle size, the greater the surface area and the greater the electron density. This fact has led to the development of microscale and nanoscale iron. The second aspect of enhancing electron transfer has been the use of bimetallic systems where the iron is coated with a second metal such as nickel, palladium or platinum. The secondary metal is present at low concentrations (<0.1%). The secondary metal facilitates the transfer of electrons from the iron.

An alternative approach to enhancing the reactivity of ZVI has been the biological or chemical enhancement of ZVI to lower the reduction potential. At very low reduction potentials (< -500 millivolts [mV]) many chlorinated solvents are thermodynamically unstable and will degrade (Dolfing and Meuller, 2006).

Biological enhancement is one approach to enhancing ZVI. Adventus (www.adventus.us) has developed a proprietary product (EHC^{TM}) that combines a controlled release carbon with ZVI (Figure 15.18). This combination results in a very low reduction potential. The carbon creates anaerobic conditions, which enhances the reducing ability of the ZVI, resulting in a very low potential. At this potential, chlorinated solvents are chemically unstable (Mueller, 2004; Dolfing and Meuller, 2006). TCE degrades under these conditions without the production of chlorinated daughter products (Seech, 1995).

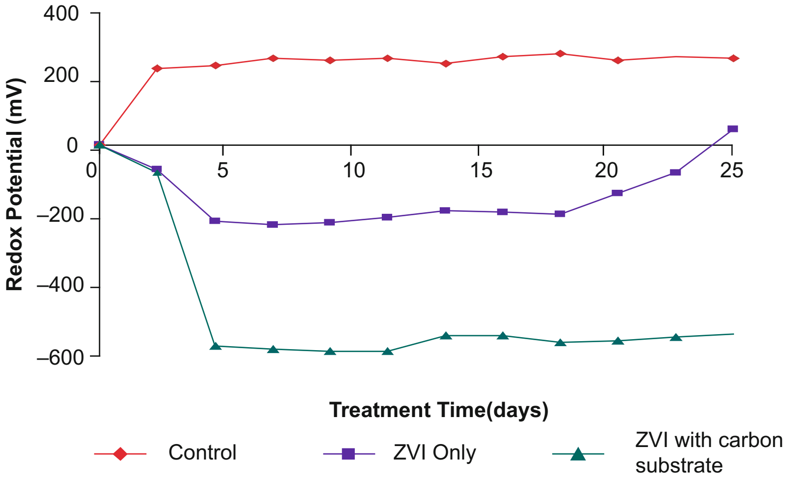


Figure 15.18. Reduction potential for combined ZVI and carbon (courtesy of Adventus, Inc.)

Another variation of biological enhancement of ZVI is the emulsified zero-valent iron (EZVI) developed by the U.S. National Aeronautics and Space Administration (NASA) (2007). This technology imbeds nanoscale ZVI in a micelle of soybean oil. The oil has a number of functions. First, it adsorbs the solvents from the water phase. Second, it stimulates reductive dechlorination. And third, it releases the solvent and its daughter products to the iron interior of the micelle.

A second enhancement of iron-based reduction is coupling iron with other reductants or reductive processes. Research by Brown (2004) showed that adding a soluble chemical reductant to ZVI also enhanced the reduction of chlorinated solvents. The rate of reduction of a variety of CVOCs by ZVI was significantly enhanced by the addition of sodium dithionite. The increase in activity was proportional to the ratio of dithionite to iron; the more dithionite added, the greater the rate increase (Figure 15.19).

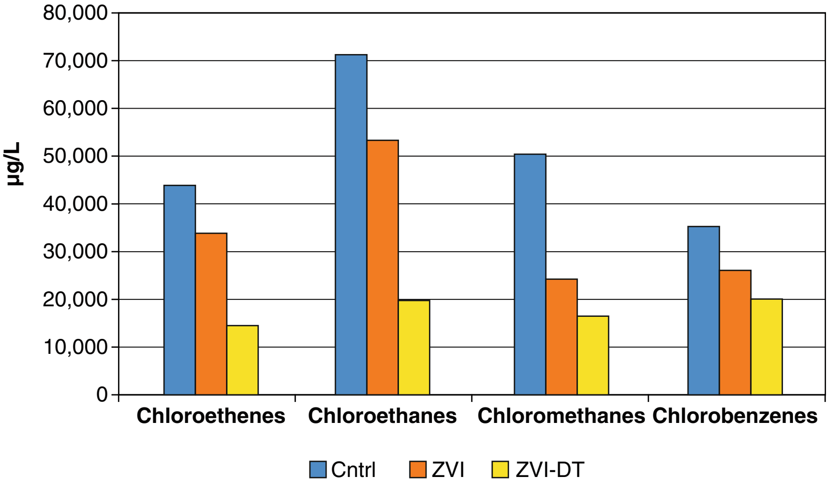


Figure 15.19. Enhancing ZVI reactivity with sodium dithionite (DT)—contaminant concentrations after four weeks (Brown, 2004)

The enhanced reduction may have been due to a lowering of the reduction potential similar to that observed with EHC® (Figure 15.20).

The significance of these findings is that enhancing the reducing conditions increases the effectiveness of ISCR. This observation means that ISCR has the potential to be an engineered system. Also, the ability to increase the efficacy of reduced iron by the addition of a soluble chemical reductant or by biologically creating anaerobic conditions suggests that ISCR may become an easier-to-apply technology than emplacing ZVI barriers, which is to date the most commonly applied ISCR technology. ZVI is an effective technology, but it is often difficult and expensive to apply.

15.3.2.2 Enhancing the Reactivity of Naturally Occurring Iron Minerals

Iron minerals can be chemically or biologically enhanced to increase the presence and reactivity of reduced species. For example, researchers at Battelle Pacific Northwest National Laboratory (PNNL) developed an *in situ* technology using sodium dithionite to reduce iron in a ferroaluminosilicate, creating a reactive reduced zone (Vermeul et al., 2000). The technology was originally developed to treat chromium VI, but was later found to reduce TCE effectively. The TCE was degraded by reductive elimination yielding acetylene and ethene. This technology demonstrated that the activity of reduced iron could be artificially stimulated or increased by the injection of a non-metallic, soluble chemical reductant.

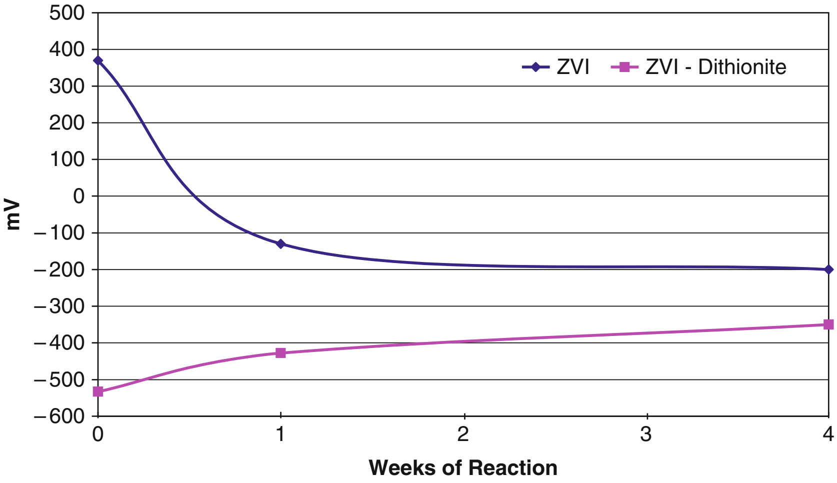


Figure 15.20. Change in ORP with time after addition of ZVI alone or with sodium dithionite

Work by Chemburkar et al., (2006) on the reduction of 1,1-DCE and 1,1-DCA demonstrated that the use of calcium polysulfide and sodium dithionite could enhance the reducing capacity of bedrock and overlying sands. The sand contained about 1% recoverable iron and the bedrock about 2 to 2.4%.

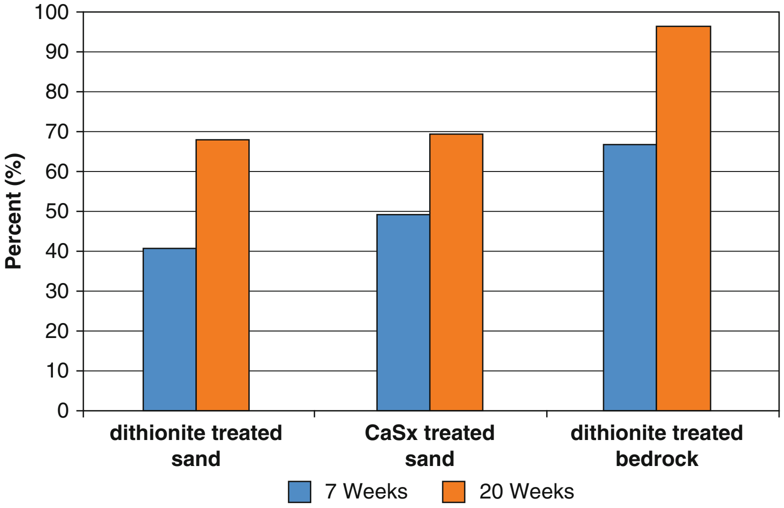


Figure 15.21. Percent loss of 1,1-DCE normalized to GW control

Biological reduction also can increase the concentrations of reduced minerals that are active dechlorinating agents. Lee et al. (2002) used sulfate-reducing conditions to produce ferrous sulfide in an iron bearing formation by injecting sulfate with an edible oil substrate. Ferrous sulfide was produced through bacterial action. TCE was rapidly degraded to ethene without significant production of cis-DCE or vinyl chloride. While acetylene was not detected, the depletion of TCE without production of *cis*-DCE or vinyl chloride was taken as proof of abiotic degradation.

15.3.2.3 Addition and/or Synthesis of Reduced Iron Minerals

In formations that are deficient in iron, it is possible to add or synthesize reduced iron minerals. This can be done by adding an iron containing mineral and subsequently reducing it, or by adding a soluble iron compound and precipitating it. This approach to ISCR is the least developed but has potential to increase the utility of ISCR for treating groundwater contaminated with chlorinated solvents.

An example of adding an iron material and subsequently reducing it is the biogeochemical reductive dechlorination (BiRD) process (Kennedy, 2006). Sulfate reducing bacteria are stimulated to produce iron sulfide minerals. The iron sulfide minerals then reduce chlorinated compounds by pathways similar to those observed for ZVI. The approach for this technology is to create a permeable reactive barrier (PRB). The barrier typically adds sulfate from mineral gypsum ($CaSO_4 \cdot 2H_2O$), organic material from mulch waste products, and iron from indigenous sediments or from added minerals such as goethite ($FeOOH$) to produce iron sulfides.

An example of the use of soluble iron is the injection of soluble ferrous iron and its subsequent precipitation by pH adjustment. Chemically precipitated ferrous iron is an active reductant for chlorinated volatile organic compounds (CVOCs) (Brown, 2005).

15.3.3 Field Applications of ISCR

Early applications of ISCR focused primarily on barriers/PRBs to intercept groundwater plumes. More recent developments and applications of ISCR have included source treatment, plume-wide treatment and abiotic MNA in addition to developments in the "traditional" plume intercept approach of PRBs.

15.3.3.1 Source Area Treatment

Two technical developments have fostered development of source area treatment with ISCR. One is the production of small-particulate zero-valent iron products. The other is the development of enhanced methods of emplacing particulate products.

There has been a push to decrease the particle size of zero-valent iron to increase the surface area and therefore the reactivity of the ZVI. A collateral benefit has been that the small particle ZVI is also easier to inject and distribute. This improvement in both the reactivity and distribution has allowed ZVI to be applied to source areas. It has also allowed the ZVI to be formulated with other materials to create enhanced products. Some of these enhanced products are Adventus' EHC® product line and NASA's EZVI formulation and Colorado State University's ZVI-clay. Adventus' EHC and NASA's EZVI are biologically enhanced ZVI. The ZVI-clay helps to disperse DNAPL as a Pickering Emulsion, making it more reactive to ZVI (Bozzini et al., 2006).

The second development that has extended the application of ISCR to source area treatment is the improvements in injection methods. These include pneumatic fracturing, hydraulic fracturing and soil mixing. Pneumatic fracturing uses high pressure gas to "liquefy" the soil matrix and disperse the iron products (Schnell, 2004). Hydraulic fracturing, adapted from oil field technology, uses high pressure water to create closely spaced fractures filled with reactive material such as zero-valent iron (Knight, 2005). Soil mixing of ZVI-clay employs mobile auger rigs or hydraulic soil mixers (Bozzini et al., 2006).

As the result of these two technical developments of small particle ZVI and enhanced delivery, ISCR is becoming a viable option for source area treatment of chlorinated solvents.

15.3.3.2 Plume-wide Treatment

In formations that contain iron minerals, it is possible to create a reducing environment that will dechlorinate chlorinated solvents. The key to this approach is to increase the amount of ferrous iron minerals present. A chemical reductant such as sodium dithionite will react with oxidized iron minerals to form a reduced iron mineralogy that is effective in dechlorination (Szecsody et al., 2004). Soluble reductants can be injected throughout the plume to enhance abiotic reduction.

15.3.3.3 Abiotic MNA

An outgrowth of the development of ISCR has been an appreciation of the importance of abiotic processes for MNA. While acknowledging that reduction of chlorinated aliphatics through a two-electron transfer could occur chemically, early MNA researchers concluded that such reactions were primarily microbially-induced since chemical reduction was thought to be too slow (Vogel et al., 1987). This assumption that chemical-based reductive processes are slow compared to biological processes has led to a predominantly biotic focus in natural attenuation. Abiotic degradative pathways are typically overlooked when evaluating natural attenuation at chlorinated solvent sites. Beginning in the mid-1990s and continuing even as late as 2003, the recommended monitoring focus in MNA for CVOCs has been the production of daughter products and ultimately ethene or ethane as “proof” of natural attenuation (Wiedemeier et al., 1998; NRC, 2003). This focus presupposes a biological pathway.

An important discovery that has been key to understanding abiotic attenuation is the discovery that ferrous iron minerals react with chlorinated solvents by mechanisms similar to those observed for ZVI (Figure 15.22). Chloroacetylenes were observed as products in the reaction of TCE with reduced iron-containing sediments (Szecsody et al., 2004). This discovery has led to the identification of markers for abiotic attenuation being the loss of the parent compounds without the sequential production of mono-dechlorinated products (Brown et al., 2006).

15.3.3.4 Developments in PRB Technology

The understanding that reduced iron minerals (DVI) can be active dechlorinating minerals opens the possibility for PRB technology to employ these minerals. There are two approaches to creating reduced iron mineral barriers. They can be chemically created by injection and precipitation of ferrous iron. Or they can be biologically created by utilizing sulfate reduction to create iron sulfides. The biological approach has been implemented using mulch barriers (Kennedy et al., 2006). Precipitated ferrous oxide/hydroxide has been found to have activity comparable to ZVI.

15.3.4 Research Needs

Even though part of its basis (e.g., ZVI) has been in place for over 20 years, ISCR is a relatively new technology. Additional research and development on ISCR is needed to:

- Identify the factors that control the reactivity of reduced iron minerals. Recent work has seen a difference in reactivity between natural, chemically produced and biologically produced iron minerals (Scherer, 2005). Soluble iron and pH may be factors in controlling reactivity.

- Understand the interaction between biological reduction and abiotic reduction. Considering the range of natural and applied conditions that have been studied, the two processes may be synergistic, antagonistic or non-interactive.
- Elucidate the interaction of soluble reductants with reduced iron minerals by (1) examining the efficacy of different reductants and (2) determining the effect of residual reductant. Some studies suggest that residual reductant is beneficial (Brown, 2005); others suggest it is detrimental (Vermeul at al., 2000).

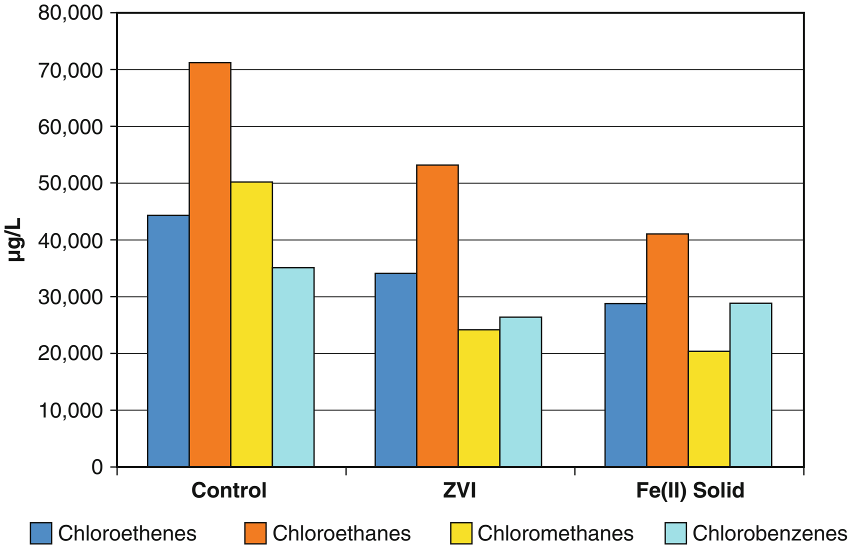


Figure 15.22. Reduction of chlorinated solvents with ferrous oxide/hydroxide

15.3.5 Conclusions

Important conclusions for practitioners regarding the reactivity and effectiveness of ISCR include:

- Reduced iron minerals (DVI) can effectively degrade chlorinated solvents including chloroethenes (PCE, TCE), chloroethanes (TCA, DCA) and chloromethanes (carbon tetrachloride).
- Reduced iron minerals generally react by the same pathways as ZVI to dechlorinate chlorinated solvents.
- A number of iron minerals such as pyrites, green rust (mixed Fe(II) and Fe(III) oxides and hydroxides) and magnetite are active reductants.
- Oxidized iron minerals can be reduced *in situ* by applying a chemical reductant or by biological reduction generating active reduction zones.

ISCR, though still in its initial phase of development, has the promise of becoming a key remediation technology. It complements some of the existing remedial systems such as BiRD (biological reductive dechlorination) and ISCO. It is been extended to a range of contamination problems from source treatment to MNA.

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CHAPTER 16

IRON BARRIER WALLS FOR CHLORINATED SOLVENT REMEDIATION

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16.1 INTRODUCTION AND BACKGROUND

Over the past decade, permeable reactive barrier (PRB) technology has progressed through the conceptual, experimental and innovative stages to its current status as accepted standard practice for groundwater remediation. As represented in the schematic of Figure 16.1, a PRB can be defined as an *in situ* treatment zone positioned such that it passively captures a contaminant plume and removes or degrades the contaminants, discharging uncontaminated water. The recent development of PRB technology has been stimulated largely by the use of granular iron "walls" for treatment of groundwater containing chlorinated organic contaminants. While this continues to be the most common application of PRBs and is the subject of this chapter, it should be noted that many other reactive materials have been proposed and tested for removal of a wide range of groundwater contaminants (ITRC, 2005).

Historically, the development of the granular iron PRB technology rests on the recognition of two advances: first, that metallic iron degrades chlorinated organic compounds, and second, that the reactions can proceed *in situ* under ambient groundwater conditions. Metals have been used as catalysts in the commercial production of chlorinated organic compounds since early in the 20th Century, and there is a further body of literature concerning the corrosion of metal containers used for storage and shipping. Because this body of literature concerns pure solvents rather than dilute aqueous solutions and the processes frequently occur at elevated temperatures and pressures, it was overlooked by the environmental community. Of greater relevance, Sweeny and Fischer (1972) showed zero-valent metals to be effective in degrading pesticides and other chlorinated organic compounds in aqueous solution. This work was also overlooked, possibly because it appeared only in the patent literature and also because it preceded, by several years, awareness of chlorinated solvents in groundwater as a major environmental problem.

In the mid-1980s, a graduate student at the University of Waterloo was studying the potential for sampling bias caused by sorption of chlorinated organic contaminants to well casings and other materials commonly used in groundwater sampling. While it was clear that contaminants were lost from solution as a consequence of diffusion into polymer materials, losses were also observed when solutions were in contact with a variety of metals, and the pattern of loss was not consistent with a diffusion process. No literature was found that was directly relevant; however, reductive dechlorination was proposed as the most likely cause (Reynolds et al., 1990). This was confirmed by subsequent tests that showed that several transition metals had the capacity to degrade a wide range of chlorinated aliphatic compounds (Gillham and O'Hannesin, 1994).

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doi: 10.1007/978-1-4419-1401-9_16,

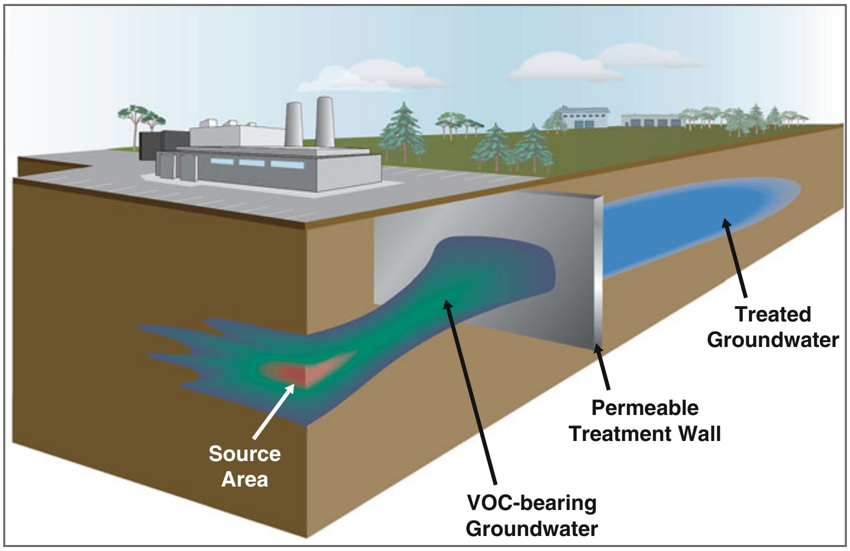

Figure 16.1. Conceptual drawing of a permeable reactive barrier (adapted from EnviroMetal Technologies Inc.)

Through similar work concerning the degradation of carbon tetrachloride (CT) by iron, Matheson and Tratnyek (1994) supported the general observations of Gillham and O'Hannesin (1994) and further suggested three possible mechanisms of degradation, with direct electron transfer at the solid surface as the most probable. Stimulated in part by these early publications, the use of metals to degrade organic contaminants developed rapidly as a major area of environmental research, with over 1,100 citations currently listed on the web site maintained by Dr. Tratnyek (http://cgr.ese.ogi.edu/ironrefs/). Furthermore, as a consequence of its availability and relatively low cost, most of the research has focused on recycled granular iron as the reducing agent.

During the early investigations, substantial rates of reaction were observed under ambient temperature and pressure, leading to the proposal that the technology could be implemented *in situ* (Gillham and O'Hannesin, 1992; Gillham and Burris, 1992). This was supported by the initial field demonstration at Canadian Forces Base (CFB) Borden, Ontario, as reported in O'Hannesin (1993) and O'Hannesin and Gillham (1998). Prior to this initial field test, most studies had been conducted in the laboratory on a small scale and using very pure iron materials. The field test and the experiments conducted to design the test used cuttings and grindings from a local foundry, with no pre-treatment, demonstrating that the quality of the iron and the presence of oxides that are ubiquitous on iron surfaces were not a significant limitation to the technology. The five-year duration of the test, as reported in O'Hannesin and Gillham (1998), was also encouraging with respect to the long-term performance of granular iron PRBs.

The first installation of a granular iron PRB at an industrial site was completed early in 1995 (Warner et al., 2005). This was an important step in the development of the technology, not only because it was the first commercial application, but also because in developing the project, it was necessary to locate a large quantity of granular iron. In this particular application the material was obtained from *Master Builders Inc.* of Cleveland, Ohio. Other suppliers including *Connelly GPM Inc.* of Chicago, Illinois and *Peerless Metal Powders and Abrasives Inc.* of Detroit, Michigan were subsequently identified. All three products are derived from cuttings, grindings and other waste iron materials that are collected from manufacturing facilities, passed through a rotary kiln to remove cutting oils and other surface contaminants, and ground and screened to size. Traditionally, the resulting products are used as a wear-resistant additive to concrete, as catalysts and abrasives, and for a host of other applications. A variety of other iron materials have since been identified. The availability of large quantities of the reactant, at reasonable cost, was a major factor in the early commercial development of the technology. The initial installation continues to support the development of the technology in that the initial cost analysis was based on the assumption that the iron would need to be replaced every five years. As reported in Warner et al. (2005), there has been no appreciable decline in performance ten years after installation, and operation and maintenance costs continue to be low.

Recognizing the potential importance of the technology, a Permeable Reactive Barrier(s) Working Group was established in 1995 under the Remediation Technology Development Forum of the U.S. Environmental Protection Agency (USEPA). This organization played a major role in advancing the technology through independent evaluation and transfer of information. Through demonstration projects and the development of guidance documents, other agencies, such as the Department of Defense (DoD), the Department of Energy and the Interstate Technology & Regulatory Council also contributed significantly to technology development.

There is now a substantial body of literature concerning PRBs, ranging from very fundamental research to highly applied field installations, covering a wide range of groundwater contaminants. Consistent with the focus of this monograph, discussion will be limited primarily to chlorinated solvents, and though some aspects of the basic processes will be introduced, the primary focus will be on the applied aspects of the technology.

16.2 REACTION

16.2.1 Nature of the Reaction/Processes

The addition of water containing chlorinated organic compounds to iron results in two redox reactions, reduction of water accompanied by oxidation of the iron (Equation 16.1) and reduction of the chlorinated organic (R-Cl) accompanied by oxidation of the iron (Equation 16.2).

$$\begin{array}{c} Fe^0 \rightarrow Fe^{2+} + 2e^- \\ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \\ \hline Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \end{array} \qquad \text{(Eq. 16.1)}$$

$$\begin{array}{c} Fe^0 \rightarrow Fe^{2+} + 2e^- \\ R\ Cl + 2e^- + H^+ \rightarrow RH + Cl^- \\ \hline R\ Cl + Fe^0 + H^+ \rightarrow Fe^{2+} + RH + Cl^- \end{array} \qquad \text{(Eq. 16.2)}$$

The carbon of chlorinated organic compounds is in an oxidized state, while the metallic form of iron is the most highly reduced; thus, thermodynamically, Equation 16.2 is very favorable for many contaminants. Furthermore, the metal has an abundant supply of mobile electrons. As a consequence of the reducing properties of Fe(0), redox potential (Eh) values are commonly in the range of -200 to -500 millivolts (mV). Furthermore, the release of OH^- and the formation of H_2, in Equation 16.1, as well as the consumption of H^+ in Equation 16.2, leads to pH values that are commonly in the range of 9 to 10. At the elevated pH values, Fe(II) precipitates as $Fe(OH)_2$, which is subsequently transformed to magnetite (Fe_3O_4). This has two important consequences: dissolved iron concentrations (resulting from both Equations 16.1 and 16.2), exiting the iron zone are generally very low (<2 milligrams per liter [mg/L]), and the iron surfaces become coated with a magnetite surface film of increasing thickness over time. The high pH values can further alter the natural geochemistry of the groundwater, resulting in the formation of secondary minerals, such as calcium carbonate and iron carbonate.

The reactions occur on the iron surface and thus rates of degradation depend on the available surface area density (surface area of iron per volume of solution) and on the condition of the surfaces. It should be noted that the reactions seldom occur on clean metallic surfaces. Commercial recycled iron materials, having passed through a rotary kiln, are covered with a thick high-temperature oxide double layer. The nature of the layer is variable, depending upon the conditions in the kiln, but generally includes an inner layer of magnetite and an outer layer of higher valent oxides such as hematite and maghemite (Ritter et al., 2002). Contaminants are adsorbed onto the outer surface of the oxide film and the reduction reaction occurs on the outer surface, requiring that the oxide film be conducting. While magnetite is an electron conductor, the high valance oxides are not. Fortunately however, under reducing conditions in an aqueous environment, the outer non-conducting oxides dissolve or are autoreduced to magnetite (Ritter et al., 2002, and references therein). As a semiconductor, it would be reasonable to expect rates of reaction to decline with increasing thickness of the magnetite films. This will be addressed further in Section 16.4.

16.2.2 Pathways

Various reaction mechanisms and pathways have been proposed for degradation of chlorinated aliphatic compounds. Two of the common mechanisms include hydrogenolysis and reductive β-elimination. In hydrogenolysis, a chlorine atom is replaced by a hydrogen atom, accompanied by the addition of two electrons (from the iron). In reductive β-elimination, two chlorine atoms are released, accompanied by the formation of an additional carbon-carbon bond. For chlorinated methanes, with a single carbon atom, the primary mechanism appears to be hydrogenolysis. A fraction of CT is sequentially reduced through a one-electron transfer pathway to form trichloromethane (chloroform [CF]) followed by dichloromethane (DCM), while the remainder is reduced through a two-electron transfer pathway to form methane, formate or carbon monoxide (CO) (McCormick and Adriaens, 2004).

In the case of chlorinated ethenes, the most common industrial solvents and those identified most commonly at hazardous waste sites, hydrogenolysis and β-elimination appear to proceed simultaneously. As shown in Figure 16.2, perchloroethene (PCE) can degrade sequentially by hydrogenolysis through trichloroethene (TCE), *cis*-dichloroethene (*cis*-DCE), vinyl chloride (VC) and finally ethene; alternatively, PCE and TCE can degrade through β-elimination to dichloroacetylene and chloroacetylene, respectively. Both of the chlorinated acetylenes are highly unstable and degrade rapidly, primarily through reductive dechlorination to acetylene (Arnold and Roberts, 2000). A third mechanism, hydrogenation, involves the addition of two hydrogen atoms across two carbon atoms with the removal of a C-C bond. An example is the reduction of acetylene to ethene as in Figure 16.2.

From both laboratory and field studies, for degradation of PCE and TCE, the chlorinated intermediates seldom exceed 5–10% of the initial compound. Indeed, Arnold and Roberts (2000) and Li and Farrell (2000) showed that >90% of TCE degrades through β-elimination. This is highly advantageous with respect to application of the technology in that relatively small amounts of the slower-degrading intermediates (dichloroethene [DCE] and VC) are produced. It also should be noted that both laboratory and field tests indicate that of the DCE isomers, *cis*-DCE is by far the most prevalent. The rate of degradation tends to decline with decreasing chlorine content of the compound; thus, for example, VC tends to degrade at lower rates than PCE. Thus, from practical considerations, VC could become the controlling compound in the design of a PRB, even if VC was not initially present in the contaminated water.

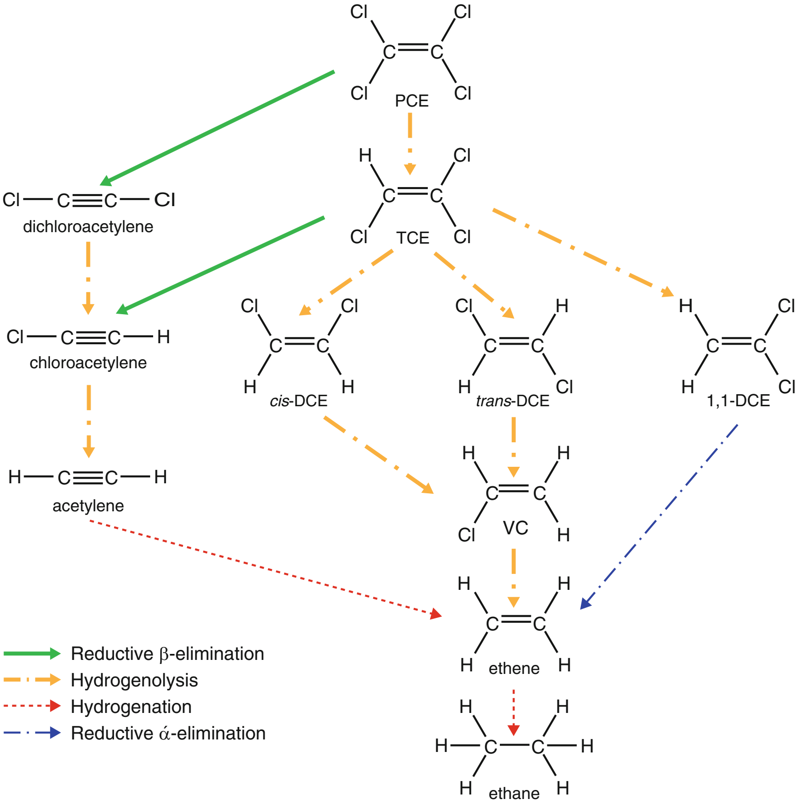

Figure 16.2. Proposed pathways for dechlorination of chlorinated ethenes. Pathways in thin lines have shown to be negligible when starting with PCE or TCE. Modified from Arnold and Roberts, 2000.

16.2.3 Kinetics of Degradation

Figure 16.3(a) shows TCE concentration versus distance along a column containing granular iron. The exponential decline in concentration suggests first-order kinetics and indeed, most laboratory tests, using both batch and column procedures, indicate the process to be first-order with respect to the concentration of the contaminant (pseudo first-order). That is,

$$C = C_o e^{-kt} \qquad \text{(Eq. 16.3)}$$

giving

$$In\left(\frac{C}{C_o}\right) = -kt \qquad \text{(Eq. 16.4)}$$

where C is the concentration in solution at a particular time (t), C_o is the initial concentration and k is the first-order rate constant. Figure 16.3(b) shows a least-squares best fit of Equation 16.4 to a semilog plot of the data in Figure 16.3(a). The excellent fit confirms consistency with the first-order equation.

The rate constant (k) is a measure of the reaction rate and can be calculated directly from Equation 16.4. Alternatively, the half life ($t_{½}$), the time required for one-half of the compound to disappear ($C/C_o = 0.5$), can be determined from Equation 16.4 to give

$$t_{1/2} = ln\ 2/k = 0.693/k \qquad \text{(Eq. 16.5)}$$

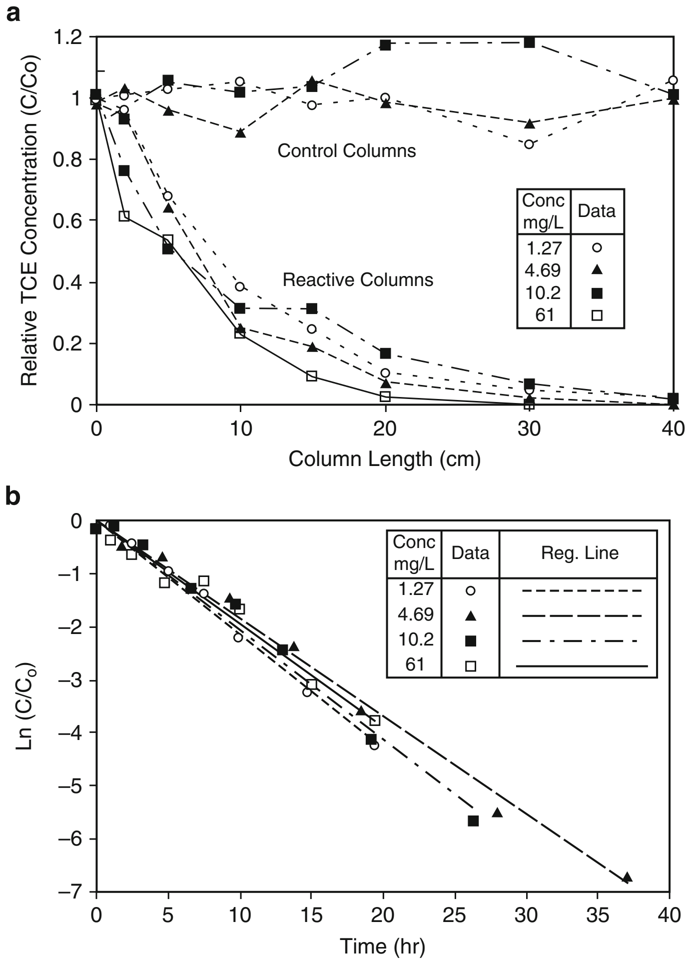

Figure 16.3. Example of steady concentration profiles in a column of granular iron in which TCE is present in the influent solution. Different lines represent different initial concentrations: (a) concentration versus distance along the column, (b) Log concentration versus residence time, including the least-square fit of the first-order kinetic model (adapted from Orth and Gillham, 1996).

The literature clearly shows that the measured rate constant (or half life) can be influenced by numerous factors:

- Available surface area of the iron,
- Type of iron,
- Inorganic composition of the groundwater,
- Temperature, and
- Concentration/competition effects.

Available Surface Area—Since the reduction reaction is a surface process, the reaction rate will depend upon the available surface area of iron. Indeed, rate constants measured in batch tests, where there is generally a small amount of iron relative to the volume of solution, are much lower than measured in column tests. Similarly, if a particular application calls for a mixture of iron and sand rather than 100% iron, the rate constant will be lower in the iron-sand mixture. Thus, in order to compare results from different methods of measurement, it is common to normalize the measured rate constant to the surface area of iron per unit volume of solution. That is, following Johnson et al. (1996),

$$k_{SA} = k_{obs}/\rho_a \quad \text{(Eq. 16.6)}$$

where k_{SA} is the normalized rate constant (L water/square meter [m^2]/k_{obs}), k_{obs} is the measured rate constant (hour^{-1} [hr^{-1}]) and ρ_a is the surface area density of the iron (m^2 iron/L water).

While the correlation reflected in Equation 16.6 provides a useful basis for comparison, it is far from perfect. The specific surface area of the iron (m^2/gram [g]) is most frequently measured by the nitrogen-BET (Brunauer-Emmett-Teller) (Brunauer et al., 1938). There is speculation that the measured surface area may be sensitive to the surface oxide coatings and therefore may not provide a true measure of the reactive surface area. Undoubtedly, further variation is caused by differences in the iron surface characteristics and in the procedures used in different laboratories for measuring k_{obs}. In addition, surface area changes over time.

From a practical perspective, Equation 16.6 also suggests that the highest reaction rates (k_{obs}) will be obtained from materials having the greatest specific surface area, which would imply improved performance from materials of finer grain size. While this is generally the case, materials of finer grain size also have lower permeability and thus optimization of reactivity and grain size needs to be considered within the context of the particular application.

Type of Iron Material—The effectiveness in degrading organic compounds has been evaluated for many types of iron materials ranging from acid-washed, high-purity iron to the oxide-coated commercial materials, as well as slag, spent foundry sand and other waste products from the iron and steel industries. From these tests, it can be concluded that if metallic iron is present, the degradation reaction is likely to proceed; in the absence of metallic iron, degradation will proceed very slowly, if at all. It is not surprising that of the metallic iron materials that have been tested, there is considerable variation in k_{SA} values, but considering the range in materials, it is perhaps surprising that there is not a greater range in reactivity. For example, using acid-washed electrolytic iron, Su and Puls (1999) obtained a k_{SA} value for TCE of $0.308 \pm 0.018 \times 10^{-5}$ L/hr m^2 while Jeen et al. (2006), using commercial Connelly material, obtained a value of 1.52×10^{-4} L/hr m^2. Similarly, considering TCE and the most commonly used commercial materials, k_{SA} values for Connelly are generally within the range of 2.0×10^{-5} L/hr m^2 to 3.4×10^{-4} L/hr m^2, while values for Peerless are normally in the range of 4.0×10^{-5} L/hr m^2 to 1.3×10^{-4} L/hr m^2. This suggests that the purity of the iron and the oxide coatings generally present on commercial materials do not have a significantly detrimental effect on reactivity. It follows that in selecting the commercial material to be used in a particular project, price is likely to be as big a factor as the reactivity of the material.

Inorganic Composition of the Groundwater—The inorganic composition of the influent groundwater can have a profound influence on the reactivity of commercial iron materials. Most of these effects concern long-term performance and will be discussed further in Section 16.4. However, there are common constituents of groundwater that influence the initial reactivity; bicarbonate is a notable example. In studies of the influence of anions on iron reactivity, several studies such as those reported in D'Andrea et al. (2005), Klausen et al. (2003) and Agrawal et al. (2002) have shown bicarbonate to significantly increase reactivity. The increased reaction rates appear to be a consequence of an increase in the corrosion rate of the iron due to its buffering property. Since most groundwater contains significant amounts of HCO_3^-, initial reaction rates in the field are likely to be higher than one would anticipate based on laboratory tests performed using deionized water. Devlin and Allin (2005) found that Cl^- and SO_4^- had relatively little effect on reactivity. More generally, for design purposes, laboratory treatability tests should be conducted using groundwater from the particular site or water with a composition very similar to that present at the site.

Temperature—While reaction rates are most commonly measured at room temperature (about 22 degrees Celsius [°C]), groundwater temperatures, depending on location, can range from 5° to 15°C or more. Various studies, including Johnson et al. (1996), Su and Puls (1999), Deng et al. (1999), and O'Hannesin et al. (2004), have shown the temperature dependence of the degradation process to be consistent with the Arhenius equation. That is,

$$In\left(\frac{k_{T2}}{k_{T1}}\right) = \frac{E_a}{R}\left(\frac{1}{T_2}\right) - \left(\frac{1}{T_1}\right) \qquad \text{(Eq. 16.7)}$$

where k_{T2} and k_{T1} are the rate constants at two temperatures (T_1 and T_2 in degrees Kelvin [°K]), E_a (kilojoules per mole [kJ/mol]) is the activation energy and R is the universal gas constant. Thus, knowing k at one temperature (T_1) and the activation energy, k can be calculated for any other temperature (T_2) or more generally, a correction factor (k_{T2}/k_{T1}) can be calculated. The values of E_a depend upon the organic contaminant, character of the iron material and undoubtedly other factors; however, based on literature values Tratnyek et al. (2003) suggest a range from 15 to 55 kJ/mol. Based on measured values, Su and Puls (1998) indicate a range from 30 to 80 kJ/mol. As an example, using degradation rates measured at different temperatures in column tests, O'Hannesin et al. (2004) calculated an activation energy for TCE of 62 kJ/mol. Using 25°C as the reference temperature and expressing the reaction rate in terms of half life, Figure 16.4 shows the correction factor over the range from 5° to 25°C. At 10°C, for example, the reaction rate is almost four times lower (half life four times greater) than at 25°C. Thus, at 10°C, the residence time in a PRB would need to be four times greater than might be expected based only on a laboratory-measured value of the rate constant. Clearly, this is a factor that needs to be considered in PRB design.

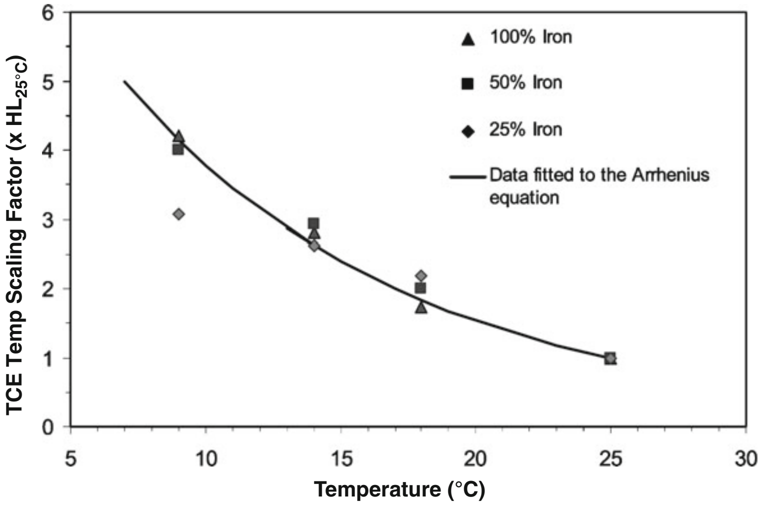

Figure 16.4. Temperature correction factor for TCE with commercial iron material. The symbols are measured data and the line is a best fit of the Arrhenius equation with an activation energy (Ea) of 62 kJ/mol. The half life at a particular temperature is obtained by multiplying the half life at 25°C by the appropriate correction factor on the vertical axis. From O'Hannesin et al., 2004.

Concentration/Competition Effects—Evidence has been presented to indicate that at high contaminant concentrations, degradation does not follow pseudo first-order kinetics; this has been attributed to saturation of reactive sites. Further, apparent non-first-order behavior has been attributed to competition between reactants for reactive sites or competitive sorption processes. A brief review of this literature and the associated kinetic models is presented in Tratnyek et al. (2003). Under the conditions presented in Orth and Gillham (1996), as shown in Figure 16.3 part b, the first-order model gave a good fit to the data over an initial concentration range of 1 to 60 mg/L TCE. Thus, there is reason to believe that at the concentrations commonly found in most contaminant plumes, first-order kinetics should apply. Furthermore, considering that most commercial iron materials are covered with a thick layer of oxides (primarily magnetite), the reactive site model becomes somewhat tenuous. For the majority of experimental results and the concentrations commonly found in contaminant plumes, the first-order model appears to be adequate for practical applications.

16.2.4 Typical Reaction Rates

After 15 years of investigation, reaction rates for degradation by Fe(0) now have been measured for many compounds; some compounds, such as CT and TCE, have been measured numerous times using a variety of methods. Preparation of a representative and meaningful table of these results has therefore become a significant challenge. Therefore, and consistent with the purpose of this chapter, the discussion will be limited to the common chlorinated solvents and will draw heavily upon summary tables produced by others.

Table 16.1. Rate Constants for Several Chlorinated Compounds. The literature values summarize the range that has been reported, and includes variation as a result of measurement method.

	Degradation Rates from Commercial Studies[a]				Literature Values[b]	
Compound	**Half life (hr)**	**k_{obs} (hr^{-1})**	**k_{SA} ($L/hr\ m^2$)**	**N**	**k_{SA} ($L/hr\ m^2$)**	**N**
TCE	1.3±0.9	0.71±0.38	$(9.5 \pm 5.9) \times 10^{-5}$	57	$(3.9 \pm 3.6) \times 10^{-4}$ (1) $(2.2 \pm 3.4) \times 10^{-4}$ (2)	12 19
***cis*-DCE**	3.4±2.2	0.34±0.28	$(4.6 \pm 4.2) \times 10^{-5}$	52	$(4.1 \pm 1.7) \times 10^{-5}$ (1)	3
VC	3.2±2.9	0.62±0.90	$(7.4 \pm 8.5) \times 10^{-5}$	34	$(5.0 \pm 1.5) \times 10^{-5}$ (1)	3
CT	0.26±0.17	3.4±1.6	$(4.1 \pm 2.2) \times 10^{-4}$	4	$(1.2 \pm 1.5) \times 10^{-1}$ (1) $(3.5 \pm 7.7) \times 10^{-3}$ (2)	11 15
TCM	2.0±1.1	0.50±0.37	$(7.7 \pm 7.8) \times 10^{-5}$	8	$(9.2 \pm 7.3) \times 10^{-4}$ (1)	3
1,1,1-TCA	0.85±0.80	1.4±1.1	$(1.8 \pm 1.5) \times 10^{-4}$	18	$(1.1 \pm 7.3) \times 10^{-4}$ (1)	3

(Average ± Standard Deviation, N= Number of Experiments)

Sources: Miehr et al., 2004; Scherer et al., 1998.

[a] Data from flow-through 100% iron columns at room temperature (provided by EnviroMetal Technologies Inc.)

[b] Data from batch tests with laboratory and commercial grade iron sources at room temperature

Table 16.1 shows rate constants for several chlorinated alkanes. The literature values summarize the range of values that have been reported. Though normalized values (k_{SA}) are shown, there is still a considerable range. This variation is undoubtedly a consequence of the different measurement methods used (batch vs. column for example), different iron materials and possibly different solution matrices. For comparative purposes, a second column of half lives is provided in Table 16.1 from a database from treatability tests using groundwater from contaminated sites and commercial iron materials. The k_{obs} values under the "Commercial Studies" heading were all obtained from column tests using 100% commercial granular iron. A typical value for ρ_a (Equation 16.6) for a granular iron column is about 7 m^2/L. To provide a basis for comparison with the literature values, the k_{obs} values were converted to k_{SA} using this value. As indicated in Table 16.1, the k_{SA} values calculated from the treatability tests generally fall within the range reported in the literature. Since the same procedures were used in the same laboratory, the range in values from the commercial database is believed to reflect, to some degree, the variation in the inorganic composition of the groundwater. For convenience, the range in half lives, calculated from the k_{obs} values, is also shown.

16.3 IRON PRB DESIGN

16.3.1 Interpretation and Application of Rate Data

A primary consideration in PRB design is the residence time required to reach objective concentrations. The objective concentration is the regulated or negotiated maximum concentration of each contaminant exiting the PRB and is commonly the Maximum Contaminant Level (MCL) as established by the USEPA. In determining the required residence time, in addition to the influent contaminant levels, the simultaneous production and degradation of intermediate products of degradation must be considered. The process is further complicated by the fact that in some cases, such as the chlorinated ethenes, there are multiple pathways. Because chlorinated ethenes are the most common industrial solvents identified at contaminated sites, they will form the basis for the following discussion.

Either through laboratory column tests, using groundwater from the particular site, or through the use of data from a site with similar geochemical conditions, degradation rate constants for the organic compounds of concern are estimated. This includes the group of compounds that may be present in the water initially, as well as potential degradation products. Because of the simultaneous production and degradation of some compounds, laboratory data is generally interpreted through the use of a multi-component kinetic model. For example, Figure 16.5 shows the possible pathways for degradation of the chlorinated ethenes.

Consistent with experimental results and Figure 16.2, there is no evidence that the pathways labeled at <1% exist and thus these will not be considered further. Each remaining pathway is characterized by a rate constant (k) and the mole fraction of the compound that follows that particular path (f). First-order rate equations can then be written for each compound; that is,

$$\partial \mathrm{PCE}/\partial t = -k_{\mathrm{PCE}}\mathrm{PCE} \qquad \text{(Eq. 16.8)}$$

$$\partial \mathrm{TCE}/\partial t = f_{\mathrm{PCE1}}k_{\mathrm{PCE}}\mathrm{PCE} - k_{\mathrm{TCE}}\mathrm{TCE} \qquad \text{(Eq. 16.9)}$$

$$\partial \mathrm{DCE}/\partial t = f_{\mathrm{TCE1}}k_{\mathrm{TCE}}\mathrm{TCE} - k_{cis\text{-}\mathrm{DCE}}\,cis\text{-}\mathrm{DCE} \qquad \text{(Eq. 16.10)}$$

$$\partial \mathrm{VC}/\partial t = f_{cis\text{-}\mathrm{DCE}}k_{cis\text{-}\mathrm{DCE}}\,cis\text{-}\mathrm{DCE} - k_{\mathrm{VC}}\mathrm{VC} \qquad \text{(Eq. 16.11)}$$

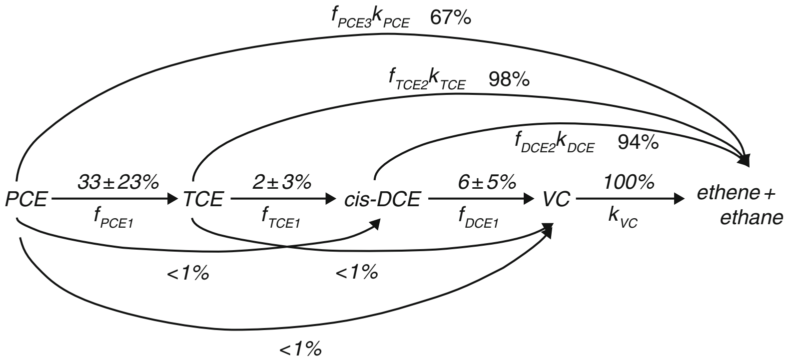

Figure 16.5. Degradation model used to determine required residence time for degradation of chlorinated ethenes (adapted from EnviroMetal Technologies Inc.).

Using commercial software, the set of equations can be fit to the results of column tests, giving estimates of all k and f values. After applying temperature correction factors to the k values, the model then can be run to give concentrations of all compounds as a function of time. From this, the residence time required to meet the objective concentration can be determined for each contaminant.

In practice, after testing a wide range of site waters, the molar conversions (f values), particularly for the major pathways, fall within a narrow range and thus are provided as input to the model (percentage values on the pathways of Figure 16.5).

Figure 16.6 shows the results of a simulation for a particular site water. In this case, initial concentrations were 10,000 micrograms per liter (μg/L) TCE and 100 μg/L *cis*-DCE. The f values were those shown in Figure 16.5 and the rate constants were determined by fitting the set of first-order rate equations to the results of column treatability tests. The objective concentrations were taken to be the USEPA MCLs (5 μg/L for TCE, 70 μg/L for *cis*-DCE and 2 μg/L for VC). The *cis*-DCE concentration increased from the initial value of 100 μg/L to about 110 μg/L, before declining to below the MCL, while VC increased from zero to about 10 μg/L before declining. In this case, even though VC was not initially present in the site water, because of the lower k value, the necessary residence time (about 46 hours) was controlled by the production and subsequent degradation of VC.

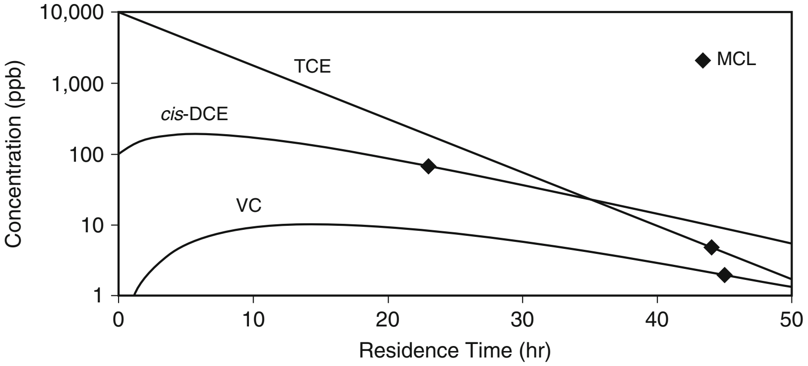

Figure 16.6. Estimation of residence time, using the model of Figure 16.5, for a hypothetical contaminant plume (provided by EnviroMetal Technologies, Inc.).

16.3.2 Treatment Zone Design

Having determined the contact time required to meet the objective concentration, the next question of critical importance concerns the thickness of the PRB that is required in order to provide the necessary residence time. Transport of contaminants through a PRB involves advection, dispersion, reaction and sorption. Because the reactive material is installed as homogeneously as possible and because the flow-through thickness is relatively small (generally <1 m), dispersion is a weak process, and at steady-state concentration distribution, sorption is also a minor process. Thus, for practical purposes, the residence time within the PRB can be calculated assuming plug flow. In this case, the required thickness in the direction of flow (l) is simply given by

$$l = V_{PRB} t_R \qquad \text{(Eq. 16.12)}$$

where V_{PRB} is the groundwater velocity within the PRB and t_R is the residence time required to meet the discharge concentration limits.

There is uncertainty in t_R associated with the degree to which laboratory k_{obs} values are applicable to field conditions, the partitioning of the degradation process between the different possible pathways (the "f" values) and the accuracy of the temperature correction factor. Furthermore, t_R values can change over time as a consequence of changing influent concentrations and gradual reductions in the reactivity of the iron (see Section 16.4). While these uncertainties should not be overlooked, in most situations the greatest uncertainty is associated with V_{PRB}.

The velocity within the PRB is related to the velocity in the aquifer (V_{AQ}) through the ratio of porosities according to

$$V_{PRB} = V_{AQ}\frac{n_{AQ}}{n_{PRB}} \qquad \text{(Eq. 16.13)}$$

where n_{AQ} and n_{PRB} are the porosities of the aquifer and PRB respectively. For unconsolidated aquifer materials, porosity values typically range from about 0.2 to 0.4, while the porosity of granular iron PRBs are generally in the range of about 0.45 to 0.5. Thus, in most situations, the velocity in the PRB will be lower than in the aquifer. Accurate determination of the aquifer velocity remains a significant challenge however.

In most PRB applications, estimates of groundwater velocity are based on the Darcy equation according to

$$V_{AQ} = \frac{q_{AQ}}{n_{AQ}} = \frac{K_{AQ}}{n_{AQ}}\mathrm{i} \qquad \text{(Eq. 16.14)}$$

where q_{AQ} is the groundwater flux (Darcy flux), K_{AQ} is hydraulic conductivity of the aquifer material and i is the hydraulic gradient. Determining K_{AQ} presents considerable difficulty with respect to both accuracy and scale. While a detailed analysis is beyond the scope of this discussion, few hydrogeologists would claim a certainty greater than a factor of two for measured hydraulic conductivity values. Furthermore, the common methods of measurement such as pump-test analyses and, to a lesser degree, single-well response tests give integrated values that may not be relevant at the scale or location of the PRB. This is particularly the case for aquifers that are highly heterogeneous. For example, relatively thin layers of high hydraulic conductivity that are not identified or represented in the hydraulic conductivity values could have a significant influence on the ultimate performance of a PRB. While there is no satisfactory means to resolve this problem, several single-well tests along the anticipated alignment of the PRB, combined with detailed stratigraphic investigations, provide the best means to reduce the uncertainty in K values. Uncertainty in hydraulic gradient (i) also can be significant, particularly in regions of low gradient, and temporal variations in gradient also can occur seasonally or in response to the pumping schedule of local production wells.

The required residence time is sensitive to the influent concentration and thus it is common to vary the thickness of the PRB according to the concentration distribution within the contaminant plume. Similarly, the required thickness of the PRB is directly proportional to the velocity. Thus, it is common to vary the thickness according to major stratigraphic features having contrasting values of hydraulic conductivity.

Because the cost of iron is generally a significant component of total construction costs (frequently in the range of 30–50%) there is clearly an incentive to keep the wall as thin as possible. On the other hand, because of uncertainty in the required residence time, and particularly in the groundwater velocity distribution, an appropriate factor of safety is generally included in the design, with the safety factor requiring professional judgment based on the level of confidence in the various parameters.

Though the deterministic approach to design, as discussed above, is used most commonly, an alternative is a probabilistic approach, as discussed in Vidumsky and Landis (2001), Hocking et al. (2001) and Christians et al. (2006). In this case, the range and distribution of transport and reaction parameters are provided, and through a Monte Carlo simulation process, a probability distribution of PRB thickness is provided as the output. One can then select the thickness that will provide the acceptable probability of success. Conceptually, this approach is appealing in that it reduces the need for arbitrary safety factors in the design and also provides a means to examine the influence of uncertainty in the various parameters on the ultimate design. However, it does not incorporate heterogeneity explicitly, and knowledge of parameter uncertainty is still required in order to arrive at defensible results.

16.3.3 Possible PRB Configurations

Various configurations of PRBs have been implemented, including continuous walls, funnel-and-gate systems, and *in situ* reactive vessels and injected treatment zones. As represented in Figure 16.1, in a continuous wall configuration, the treatment material is distributed as a wall or panel across the entire width and depth of the contaminant plume. If the grain size of the iron is selected such that the hydraulic conductivity is greater than that of the aquifer, the wall will not significantly alter the natural groundwater flow path. Thus, there is no need for the "wall" to be keyed into a low permeable zone or to extend for a significant distance beyond the lateral limits of the plume. To date, the continuous wall PRB has been the most commonly used configuration.

A funnel-and-gate configuration uses low permeability materials (funnel) to direct groundwater towards one or more permeable treatment zones (gates). Directing or funneling the groundwater towards a treatment gate will increase the groundwater flow velocity in the gate relative to background by an amount that is approximately equal to the ratio of the width of the funnel and gate to the width of the gate. Because the purpose of the impermeable funnel sections is to divert the natural flow of water, it is necessary that the lateral funnel sections extend beyond the lateral extent of the plume in order to ensure complete capture of the plume. The total length of a funnel-and-gate system may be on the order of 1.2 to 2.5 times the plume width, depending on the number of gates, and the funnel-to-gate ratio. Because the hydraulic head on the upgradient side of the funnel and gate increases, there is the possibility that the contaminants will be pushed to greater depth and thus flow under the funnel-and-gate sections. To avoid this, it is preferable that the funnel and gate be keyed into an underlying low permeability layer. Alternatively, if no impermeable layer is present, it may be necessary to extend the funnel-and-gate system well below the initial depth of the plume. Starr and Cherry (1994) present numerical simulations of flow fields associated with various funnel-and-gate configurations.

Closely related to the funnel and gate design are *in situ* reaction vessels, which use funnels or collection trenches to capture the plume and pass the groundwater, through differences in hydraulic head, through a buried vessel containing the treatment material. These vessels also can be used to control and treat groundwater exiting from otherwise completely contained source areas. The use of *in situ* vessels is usually determined by specific site conditions; examples are described in Primrose et al. (2004). A particularly novel approach is the GeoSiphon^{TM}, described in Phifer et al. (1999).

Because of the higher velocity through the treatment zone in funnel-and-gate configurations and treatment vessels, the flow-through thickness is generally greater than in a continuous wall configuration. Indeed, in principle, the same amount of iron is required to treat the same discharge of contaminated water independent of the configuration of the treatment zone. It should also be noted that the higher velocity in funnel-and-gate systems or vessels, and thus the higher flow rate per unit surface area, could result in accelerated passivation of the treatment zone relative to a continuous wall (see Section 16.4). On the other hand, having the treatment material confined to a gate or vessel makes it more convenient and less costly than in the case of a continuous wall should the reactive material require replacement at some time in the future.

16.3.4 Construction Methods

Several methods are available for construction of granular iron PRBs. The most suitable method will depend on several site-specific factors, such as the depth of installation, the nature of the geologic materials, surface/subsurface obstructions (e.g., buildings and utilities) and the required flow-through thickness. Where the minimum practical excavation width is wider than the required flow-through thickness of 100% granular iron, sand is frequently mixed with the granular iron as a bulking agent, thus reducing the amount and cost of iron. The sand is chosen to have hydraulic properties similar to those of the granular iron and if possible, to have mineralogical properties similar to the aquifer material. Below is a summary of methods used to install granular iron PRBs, the range in depth for which the method is applicable and the iron flow-through thickness that can be achieved.

16.3.4.1 Excavation Methods

Unsupported Excavation—This is the simplest and least expensive installation method and can be implemented using conventional backhoe equipment. The geologic material must have sufficient strength such that the trench remains open for a sufficient period of time to permit backfilling with granular iron or an iron/sand mixture. The method is generally limited to relatively shallow depths, and the minimum width of the trench is determined by the width of the excavator bucket, usually no narrower than about 1 foot (ft) (30 centimeters [cm]). The method has been used to install PRBs to depths of 20 ft (6 m) below ground surface (bgs) in till and highly fractured shale materials.

Continuous Trenching—Continuous trenching machines allow simultaneous excavation and backfilling without an open trench. Excavation is performed by a cutting chain immediately in front of a trench-box (boot) that extends the thickness and depth of the treatment zone. Both the cutting chain and boot are attached to the trenching machine. As the trencher advances, granular iron or an iron/sand mixture is added to the hopper and is expelled from the back of the boot, creating a continuous treatment zone. Trenchers are available for installing treatment zones from 1.5 ft (0.5 m) to 3 ft (0.9 m) in width and to depths of about 35 ft (11 m). Several passes of the trencher can be made if greater widths are required. A bench on which to operate the trencher can be excavated to near the water table to increase the depth that can be reached.

Continuous trenchers have high mobilization costs and require a period for assembly and therefore may not be cost effective for small projects. However, for large projects where the geological conditions are favorable, they provide a highly cost-effective and rapid means of installation.

Supported Excavation—Where the geologic materials do not have sufficient strength for a trench to remain open, which is normally the case, some form of mechanical trench support can be used. Temporary support methods such as trench boxes or hydraulic shoring have been used at several sites. The permeability of the soil must be sufficiently low such that dewatering is not required in order for these methods to be effective. Prefabricated trench boxes similar to those commonly used during installation of utilities and sewers can be used to maintain trench integrity during excavation and backfilling operations. The trench box is slid along the trench with excavation proceeding just ahead and backfilling occurring in the back half of the trench box. Typical trench boxes are 4 ft (1.2 m) wide, though custom trench boxes can be fabricated to smaller widths. An alternative is to use a system of temporary shoring. Generally, hydraulic shores are used to provide additional stability to the trench until it is backfilled. The temporary shores are placed in the excavation immediately after the trench is excavated to provide temporary support during the excavation and backfilling operations. Advantages of the shored excavation method are that the trench width can be as narrow as 2 ft (0.6 m) and two workers can place the hydraulic shores without the use of heavy equipment.

The trench box and hydraulic shoring methods are generally limited to depths no greater than about 20 ft (6 m).

Sheet Piling Cofferdam—Using sheet piling cofferdams is another method for providing mechanical support for open trenches. Sheet piling is driven around the perimeter of the treatment zone, and the soil within the sheet piling enclosure is excavated. Typically, internal bracing is required at greater depths. The sheet pile maintains the dimensions of the treatment zone during excavation and backfilling. After backfilling is complete, the sheet piling is removed and groundwater is allowed to flow through the treatment zone. The method is limited to minimum widths of about 3 ft (1 m) and maximum depths of about 40 ft (13 m).

A significant advantage of all of the mechanically supported trench methods is that they provide a high degree of control in placing the reactive materials and the boundaries of the treatment zones are well defined. They are, however, limited to relatively shallow depths.

Biopolymer Trenching—Installation of a treatment zone of granular iron using a biodegradable polymer (biopolymer) slurry is similar to constructing a conventional impermeable slurry wall. As the trench is excavated, a biopolymer slurry is added, and through density and viscosity effects, stabilizes the exposed trench walls. The biopolymer used is typically guar gum. Excavation continues through the biopolymer without the need for dewatering or mechanical shoring. Granular iron (or an iron/sand mixture) is placed through the biopolymer using a tremie pipe. Recirculation wells are spaced along the length of the trench to flush out the polymer slurry and to add enzyme solution to assist in breaking down residual polymer. Because of the high solubility of the biopolymer, any remaining material will be flushed out by the flow of groundwater through the treatment zone. Depths of up to 70 ft (21 m) bgs and a minimum width of 2 ft (0.6 m) or greater can be achieved using specialized backhoe equipment. Substantially greater depths could be achieved through the use of clam-shell excavators. The biopolymer is highly biodegradable and thus residual polymer can result in high levels of biological activity following installation. To minimize possible effects on performance, efforts should be made to flush as much polymer material as possible from the PRB during construction.

16.3.4.2 Injection Methods

Vertical Hydraulic Fracturing—Thin vertical treatment zones, up to 9 inches (23 cm) thick, can be installed using vertical hydrofracturing. This method uses a specialized tool that is inserted into a borehole to the required depth and oriented to control the direction of the fracture. The vertical interval of the fracture is isolated in the borehole by packers. The fluid used for fracturing consists of a biopolymer slurry similar to that used in biopolymer trenching; however, the polymer is cross-linked, resulting in a fluid of very high viscosity. The granular iron, of grain size considerably smaller than that normally used in trenching methods, is suspended in the highly viscous fluid. The fracturing fluid is pumped under low pressure (25 pounds per square inch [psi]) into the formation, which causes the subsurface material to separate, creating an iron treatment zone a few inches in thickness with a controlled vertical dimension. Several fractures propagated from boreholes located along the line of installation coalesce to create a continuous PRB. Though the maximum thickness of a single panel is about 9 in (20 cm), parallel panels can be installed to increase the total flow-through thickness of the iron zone. Using this method, PRBs have been constructed to depths of 120 ft (40 m) and technically, greater depths can be achieved. Further details concerning this method can be found in Hocking et al. (2004).

Jetting—Installation of an iron PRB by jetting is a variation of the jet-grouting procedure that is well developed for construction of impermeable barriers. The same equipment is used to inject granular iron to form an iron PRB. High pressures, of about 5,000 to 6,000 psi, are used to erode the soil and deposit fine-grained iron in the natural aquifer material. The jetting tool is advanced into the formation to the desired depth and the iron, suspended in biodegradable slurry, is injected from the nozzles as the tool is withdrawn. If the tool is rotated, a columnar iron zone is created. The diameter of injection depends on several factors, but diameters of 2 to 7 ft (0.6 to 2.1 m) can be achieved. If the tool is not rotated, and has only two opposing nozzles, a thin diaphragm treatment wall can be created. Diaphragm walls may be 2 to 3 inches (5 to 8 cm) of 100% iron near the point of injection but may be several inches of an iron-aquifer material mixture further away.

Direct Push Injection—This method typically involves hydraulic fracturing, in which a slurry solution is injected at a pressure that exceeds the combined lithostatic pressure and cohesive strength of the formation. Rods are pushed into the subsurface to the required depth, and then retracted, exposing an injection nozzle. The granular iron is suspended in a biopolymer slurry and pumped into the formation at a rate that exceeds the ability of the formation to accept the fluid. As a result, the pressure increases until fractures form along horizontal planes of weakness. The fluid invades the fractures, depositing a layer of iron. Enzymes are added to the biopolymer slurry during injection to accelerate degradation of the polymer.

Pneumatic Fracturing and Injection—Pneumatic fracturing is the injection of gas, usually nitrogen, at high pressure and flow rate in order to create fractures or fissures in the unconsolidated or rock matrix. Fractures or fissures occur when the pressure of injected gas exceeds the natural *in situ* stresses and the flow rate exceeds the natural permeability of the soils. In cohesive geologic materials, pneumatic fracturing enhances the permeability by creating fracture networks, while in rock, the effect is generally dilation and extension of existing discontinuities, thereby improving the interconnection between existing fractures. In materials with low cohesive strength, the iron can be pneumatically injected without first fracturing the formation. More commonly, however, the zone of interest is first fractured, then using the same equipment, fine-grained iron is added to the nitrogen stream and is subsequently deposited in the fracture network. Further information is provided in McCall et al. (2004).

16.3.4.3 Other Methods

Augered Boreholes—Treatment zones of iron can be constructed by an array of augered boreholes. When the required depth is achieved, the iron can be placed either through the auger stem as the augers are removed or directly into an open borehole.

Caissons—Caisson installation involves driving a large circular steel caisson into the ground and augering out the native material. The caisson is then backfilled with iron and removed. Although caissons as large as 15 ft (4.6 m) in diameter can be installed, smaller diameters are more common. Overlapping or tangential caisson-emplaced treatment zones can be used to create a larger permeable treatment zone.

Soil Mixing—Soil-mixing equipment generally uses one or more large-diameter augers to thoroughly mix iron into the soil. The iron is initially mixed with biodegradable slurry and pumped to the mixing augers while they are advanced slowly through the soil. Over time, the biodegradable slurry breaks down, allowing the groundwater to flow through the treatment zone. Alternatively, the iron can be placed in a smaller diameter borehole and mixed into the adjacent aquifer material using the soil-mixing equipment.

Mandrel (or H-Beam)—A mandrel is a hollow steel box or H-beam that is driven into the ground to create a thin continuous treatment zone. A disposable shoe at the leading edge of the mandrel prevents aquifer material from entering the cavity as the mandrel is advanced. Once the mandrel reaches the maximum depth of the treatment zone the shoe is driven from the end of the H-beam and iron is placed inside the mandrel. As the mandrel is removed, the iron fills the void that is created. The process is then repeated with the mandrel being driven adjacent to the iron zone previously installed. The mandrel can be modified for a particular site, but its open-end dimensions range from 3 to 5 in (8 to 13 cm) by 20 to 30 in (51 to 76 cm).

16.3.5 Installations in Fractured Rock

Innovative PRB designs and construction methods are being developed for groundwater remediation in fractured bedrock. If the bedrock is sufficiently weathered and can be economically excavated, possibly with the aid of a rock hammer, a PRB can be constructed using trenching methods similar to those described for unconsolidated media. As an example, a PRB was installed to a depth of 14 feet (4.2 m) in a highly weathered shale using a conventional excavator with no mechanical support of the trench walls (personal communication, EnviroMetal Technologies Inc.).

Rock trenchers are capable of excavating a continuous trench in bedrock, such as limestone. This equipment has been used for several years to install utilities in areas where bedrock is relatively shallow. Excavation is performed by a cutting chain that extends the width and depth of the finished treatment zone. A bench on which to operate the trencher can be excavated to near the water table to increase the total depth attainable with the trencher. A continuous rock trencher has been used to install a PRB in limestone bedrock to a depth of 18 feet (5.5 m).

Waterjet technology has been used extensively in the mining industry, particularly for cutting and quarrying blocks of granite and other rock types. High-pressure waterjet units can be used to cut a thin (3 to 6 in [7.5 to 15 cm]) vertical slot in the bedrock along the length of the proposed alignment, allowing a PRB to be constructed (Elmore et al., 2003).

Installation of an array of closely-spaced boreholes backfilled with granular iron also could be used to intercept fractures and provide treatment. The array of boreholes would need to be designed to capture the groundwater plume through a combination of intercepting the fractures and creating connecting pathways between fractures. Treatment would occur as the groundwater flowed through the granular iron in the boreholes.

Refractive flow and treatment (RFT) configurations rely on creating zones of relatively high hydraulic conductivity contrast to divert groundwater flow to a treatment zone. Precision blasting can be an effective means of producing highly conducting and elongated rubble zones (Dick and Edwards, 1997). Pneumatic and hydraulic fracturing also have been used as a means of emplacing iron along pre-existing planes of weakness in bedrock formations.

16.4 LONG-TERM PERFORMANCE

16.4.1 Definition and Potential Factors

The major appeal of granular iron PRBs is a reduced cost for remediation. As the capital cost of a PRB is generally comparable to that of a pump-and-treat system, the main economic advantage accrues from greatly reduced operation and maintenance costs. To realize these benefits, the PRB must perform effectively, without significant maintenance or replacement of the iron, for long periods of time. The question then is how long is long? Because of particular circumstances at the site, the first commercial installation of a PRB was shown to be economically viable even if the iron had to be replaced every five years. In that particular case, as noted previously, the PRB continues to perform adequately after 10 years of operation, without replacement of the iron (Warner et al., 2005). Taking yet another approach, net present value calculations suggest that replacement of iron in a PRB every 10 to 15 years adds very little to the total cost. Thus, for the purpose of this discussion, long-term performance will be defined as adequate treatment for a period of 10 to 15 years.

The record of field performance is encouraging, although only a small number of installations have reached the 10-year criterion and none have yet reached the 15-year criterion. It is therefore important to consider the factors that may limit long-term performance and the evidence that is available, primarily from laboratory tests, concerning their potential effects over time. Generally included among these factors are persistence of the iron, competing oxidants, precipitate formation (implications for both hydraulic and reactivity changes) and microbial effects.

16.4.2 Persistence of Metallic Iron

As indicated in Equation 16.1 and 16.2, metallic iron is not only consumed through oxidation by the chlorinated organic compounds but also by reaction with water. The reaction with water proceeds whether or not chlorinated compounds are present and except in the presence of very high contaminant concentrations, corrosion of iron will be dominated by reactions with water.

Using hydrogen evolution as a measure of the anaerobic corrosion rate of iron in water, Reardon (2005) measured values for various iron materials that ranged between 0.1 and 0.6 millimoles (mmol)/kilograms (kg) Fe/day, with a value of 0.2 mmol/kg Fe/day for a material commonly used in PRB construction (Reardon, 2005). The iron corrosion rate is strongly dependent on grain size (specific surface area), as well as on temperature and the type of iron. Furthermore, the corrosion rate depends upon the anions in solution. The literature is not entirely consistent in that Reardon (1995) showed enhancement in the order $HCO_3^- > SO_4^{2-} > Cl^-$, while Devlin and Allin (2005) showed SO_4^{2-} and Cl^- had little effect on iron reactivity. Deng et al. (1998) observed enhancement in the order $PO_4^{3-} > BO_3^{3-} > H_2SiO_4$. Reardon (1995) also observed a decline in hydrogen production (decline in corrosion rate) over time.

Using a corrosion rate of 0.3 mmol/kg Fe/day, it can readily be shown that the metallic iron in a PRB should persist for periods of up to 100 years or more. While there is considerable uncertainty in this estimate, one can reasonably expect that the iron will persist for several decades and well in excess of the 10 to 15 years used in our definition of long-term performance.

Over the past several years, there has been considerable interest in the injection of nanoscale iron for groundwater remediation. Because of the much smaller grain size and thus a vastly greater specific surface area, nano-iron corrodes at a much higher rate, and using normalized specific surface area, it can be shown that nano-iron is likely to be consumed in a matter of weeks to a few months (Liu and Lowry, 2006). Thus, it would appear that injection of nano-iron would be more appropriate in situations where high mass removal is required over short periods of time, as in source-zone treatment, rather than in the construction of PRBs for plume control and treatment.

16.4.3 Competing Oxidants

In addition to water and chlorinated solvents, other oxidants, such as dissolved oxygen, nitrate, chromate and permanganate, can be present in groundwater. Dissolved oxygen reacts quickly with iron, forming high valency iron oxides, such as hematite and maghemite. As noted previously, these are passivating oxides and therefore have the potential to adversely affect PRB performance. In laboratory column tests, Mackenzie et al. (1999) noted the formation of iron oxides near the influent end of the column, and attributed a significant decline in permeability to oxide accumulation.

Oxygen, though potentially present at concentrations of about 8 mg/L, depending upon temperature, is frequently absent in contaminant plumes and is seldom present at concentrations in excess of 1–2 mg/L. In the initial test of the PRB concept at Borden (O'Hannesin and Gillham, 1998) the dissolved oxygen concentration in the groundwater entering the PRB was about 1–3 mg/L. After five years of operation, there was only slight evidence of the formation of higher valence iron oxides, and this was restricted to the first 2–3 cm of the influent surface, with no evidence of a decline in hydraulic conductivity. While the evidence from the numerous cores from other commercial installations is generally less precise (e.g., Vogan et al., 1998), it is also the case that no evidence of declining performance as a consequence of oxygen invasion has been reported. Nevertheless, acknowledging that little high-quality field data is available, in contaminant plumes with high concentrations of dissolved oxygen (greater than perhaps 3 or 4 mg/L), a reduction in hydraulic conductivity and reactivity as a consequence of iron oxide formation should be anticipated.

Nitrate is frequently a constituent of shallow groundwater at concentrations of a few mg/L to tens of mg/L NO_3^- - N, with most of the nitrate being attributed to anthropogenic sources, such as agricultural fertilizers or disposal of septic effluent. In addition, waste streams from manufacturing processes can contain NO_3^- - N at several tens of mg/L and in some cases, these concentrations may occur as cocontaminants with chlorinated solvents. Numerous laboratory studies have shown NO_3^- to be rapidly reduced to NH_4^+ by iron, accompanied by oxidation of the iron, resulting in the formation of passivating higher valency iron oxides (Ritter et al., 2003; Lu, 2005).

Column tests show progressive passivation from the influent end, with the zone of nitrate reduction and TCE reduction progressing further into the column over time, with near complete passivation as the eventual consequence. Unfortunately, there is insufficient information to indicate if there is a threshold below which NO_3^- is not a problem; furthermore, there is no data available to indicate if the effect of nitrate in field situations is similar to observations in the laboratory. Though incomplete, the available information suggests that if nitrate mass flux is significant, special precautions should be taken. These could include running treatability tests for a sufficient period of time to ensure that any negative effects of nitrate can be evaluated.

In some cases, potential problems may be averted by constructing the PRB with added thickness to accommodate a degree of passivation by nitrate. Alternatively, and particularly in cases of very high nitrate concentration, a nitrate removal zone in advance of the iron PRB could be considered. This zone would include an organic carbon source to promote denitrification. Encouraging, but preliminary, research has shown that iron surfaces passivated by nitrate may be rejuvenated by passing water containing no nitrate over these surfaces (Lu, 2005).

Chromate frequently occurs in groundwater as a cocontaminant with chlorinated solvents, particularly in contaminant plumes associated with metal-plating facilities. There is considerable literature available concerning the removal of chromium from contaminated water using Fe(0) (Blowes et al., 1997; Pratt et al., 1997; Astrup et al., 2000). Generally, Cr(VI) is reduced to Cr(III), which precipitates as chromium hydroxides or mixed Fe(III)−Cr(III) oxides. As a consequence of the chromium precipitates, or possibly as a consequence of the formation of higher valence iron oxides, treatment of chromate has a gradual passivating effect on the iron. However, the literature concerning the effect of chromate removal on treatment of chlorinated solvents is considerably less extensive. In laboratory column tests, Yang (2006) showed that TCE did not appear to have a significant effect on the removal rate of chromate; however, the removal of chromate had a significant passivating effect on the degradation of TCE; this was attributed to the formation of chromium precipitates, as well as the formation of tri-valent iron oxides on the iron surfaces as observed using Raman spectroscopy.

An iron PRB was installed at Elizabeth City, North Carolina, for removal of both chromium and TCE. A comprehensive discussion of this project, including treatability tests, design, installation, performance monitoring and mathematical simulation, is provided in Wilkin and Puls (2003). Concentrations of chromate and TCE entering the PRB were as high as 4.7 and 4.2 mg/L, respectively (Wilkin and Puls, 2003). Performance monitoring indicated complete removal of the chromate near the influent face of the PRB and first-order decay of the TCE concentrations, with a minor discharge of *cis*-DCE at one location where the influent TCE concentration was particularly high. As reported in Wilkin and Puls (2003), the performance remained satisfactory after five years of operation. Thus, while it is clear that the precipitation of chromium can have an adverse effect on reactivity towards TCE, it appears that at moderate concentrations, there should be no difficulties in designing a PRB such that it meets the criterion for long-term performance.

In situ chemical oxidation is an emerging technology for treatment of chlorinated-solvent source zones. Of the potential oxidants, considerable attention has been directed towards permanganate, added either as $NaMnO_4$ or $KMnO_4$ (Gonullu and Farquhar, 1989; Thomson et al., 2000; Siegrist et al., 2001). With the expectation that removal of the source zone will not be complete, it has been proposed that PRB technology could be implemented as a polishing step downgradient of such a treatment area. Depending on the distance between MnO_4^- application and the PRB, in some cases MnO_4^- may not be entirely consumed and therefore may enter the PRB. Okwi et al. (2005) reported the simultaneous addition of TCE and MnO_4^- to laboratory columns containing granular iron. At the high MnO_4^- concentrations used (5,000 mg/L), the columns were quickly passivated with respect to both TCE and MnO_4^- removal. In contact with iron, the Mn(VII) of MnO_4^- is quickly reduced to Mn(II), which subsequently precipitates as various oxides/hydroxides of Mn. Furthermore, because MnO_4^- is a strong oxidant, the passivating higher valent oxides of iron were also identified. Though somewhat speculative, the authors considered the iron oxides to be the primary passivating agents, with the Mn precipitates possibly playing a secondary role. Because of the particularly high MnO_4^- concentrations used, the results cannot be readily transferred to the field, but are nevertheless of interest in that they clearly indicate that high concentrations of strong oxidants can rapidly degrade the performance of iron PRBs.

16.4.4 Formation of Secondary Minerals

Because of the low Eh and high pH characteristics of iron PRBs, secondary minerals are likely to form in virtually all groundwater environments. These have the potential to form coatings on the iron and thus reduce the reactivity; if present in sufficient quantities, they could also reduce the pore space, leading to a decline in hydraulic conductivity. Should the permeability decline sufficiently, then much of the plume could be diverted around the PRB, rendering it ineffective.

A wide range of secondary minerals have been identified in laboratory columns and in field PRBs; however, in most cases, there is insufficient information to predict the effect that these may have on long-term performance. Furthermore, it is generally not practical to perform laboratory treatability tests for a sufficient period of time to give useful information concerning the effects of secondary minerals on long-term performance, and only recently have suitable predictive models been under development.

The major mineral phases that have been identified in iron PRBs include various iron oxides, hydroxides and oxyhydroxides, intermediate products (green rusts), carbonates (aragonite, calcite and siderite) and iron sulfides (Blowes et al., 1997; Gu et al., 1999; Phillips et al., 2000; Roh et al., 2000; Phillips et al., 2003). In most cases, the primary source of dissolved iron that reacts with anions to form iron-bearing mineral phases is from oxidation of the iron metal. Bicarbonate (HCO_3^-) is present in virtually all groundwaters at concentrations ranging from a few to several hundred mg/L. Furthermore, in the PRBs that have been examined, carbonates commonly appear to be the predominant secondary minerals present as aragonite, calcite ($CaCO_3$) or siderite ($FeCO_3$). While often not observed in laboratory studies, sulfate reduction is ubiquitous in iron PRBs in the field. However, with the exception of a few isolated cases with extremely high natural sulfate (in excess of 100s of mg/L), sulfides do not appear to be a major mineral phase influencing PRB performance. Thus the following discussion will be limited primarily to secondary minerals of carbonate.

In cases where core samples have been collected, the greatest accumulation of precipitates appears very near the upgradient face of the PRB. Vogan et al. (1999) reported calcium carbonate accumulations in a funnel-and-gate system after two years of operation. Though there was no observable change in performance, core samples revealed about 6 weight (wt) % $CaCO_3$ in the sample collected from the upgradient interface, with a rapid decline with distance (1 wt % at a distance of 15 cm from the interface). The 6 wt % carbonate was calculated to be equivalent to a loss of initial porosity of almost 5% per year. From changes in inorganic chemical compositions, McMahon et al. (1999) estimated that the total porosity of a PRB was reduced by about 0.35% per year as a consequence of calcite and siderite precipitation. This estimate assumed that the precipitates formed uniformly throughout the PRB; though solid-phase analyses were not reported, visual inspection indicated a greater abundance of precipitates near the influent face.

In general, based on both laboratory and field evidence, and because the primary source of dissolved iron is corrosion by water, iron (oxy) hydroxides will form throughout a PRB. However, because these hydroxides ultimately transform to magnetite, which is electron-conducting, they do not substantially reduce the reactivity of the iron and the rate of formation does not cause a significant decline in permeability.

Projecting the empirical field evidence, it would be reasonable to expect continued precipitate formation near the influent surface of a PRB, ultimately resulting in reduced permeability and bypass of contaminated groundwater around the PRB (or the need for some form of maintenance). However, controlled experimental data indicates that precipitation may have a greater effect on the reactivity of the iron rather than on the hydraulic performance of the PRB. In long-term column tests with dissolved $CaCO_3$ in the influent solution, Zhang and Gillham (2005) observed the formation of aragonite near the influent end of the columns early in the test. With the passage of time, however, the pH near the influent end declined, suggesting reduced iron reactivity; there was no further precipitation in this region. Indeed, Ca^{2+} and HCO_3^- were carried further into the column and precipitated where the iron remained reactive, and the pH values were elevated. Thus, rather than precipitating at the influent to the degree that the iron was substantially impermeable, aragonite was deposited as a moving front that progressed through the column. The results suggested that at about 3 wt % $CaCO_3$, the iron was essentially non-reactive; at this percentage, the permeability was reduced by about half an order of magnitude. Though passivation of the iron is generally considered to be undesirable, it can be advantageous in that it prevents the continued formation of precipitates to the point that the PRB becomes impermeable. Assuming a groundwater velocity of 5 cm/day with a $CaCO_3$ concentration of 100 mg/L and using highly simplified plug-flow assumptions, Zhang and Gillham (2005) suggested that the passivating front would progress through a PRB at a rate of about 1 cm/year; this factor could be readily accommodated in the initial design of a PRB.

Various efforts have been made to develop mathematical models for predicting PRB performance. The initial attempts used geochemical equilibrium models (Schumaker, 1995; Gaveskar et al., 1998; Morrison et al., 2001) to represent the chemical changes occurring within a PRB; more recently, complex reactive transport models have been developed (Mayer et al., 2001; Yabusaki et al., 2001; Li et al., 2005). Though the reactive transport models represent a significant advance over the equilibrium models, the reactivity of the iron is assumed to be constant in all cases. If the observations of Zhang and Gillham (2005) are generally applicable, then the current models are significantly limited in terms of their ability to predict long-term performance.

Jeen et al. (2006; 2007) conducted column tests similar to those of Zhang and Gillham (2005) and obtained results showing similar patterns of precipitate formation. In addition, an empirical relationship between the iron reactivity and the amount of precipitate present was derived. The relationship was then incorporated into the multi-component reactive transport model MIN3P presented in Mayer et al. (2001). The model was highly successful in reproducing the various concentration profiles observed in the columns, as well as the distribution of precipitates. Furthermore, assuming conditions similar to those in the laboratory, a groundwater velocity of 10 cm/day with influent concentrations of 100 mg/L $CaCO_3$ and 10 mg/L TCE, modeling results indicated that a PRB of 50 cm thickness would perform effectively for periods in excess of 40 years. The model presented in Jeen et al. (2007) appears to accommodate the major factors that influence long-term performance of PRBs. However, because of its complexity and the large number of interacting parameters, its practicality and accuracy for predicting long-term performance and its usefulness as a design tool remain uncertain.

Because of the extremely wide range of geochemical conditions that can be encountered, it is difficult to arrive at generally applicable conclusions regarding long-term performance. Clearly, if high concentrations of oxidants are present, passivation of the iron must be anticipated and accommodated in the design; this could include increasing the thickness of the PRB or designing special features for removal of the oxidant. In some cases, the PRB concept may not be appropriate. It is also apparent from the empirical field evidence and experimental observations that secondary minerals will form in virtually all PRBs; their influence on performance is strongly dependent on the groundwater velocity and the concentration of precipitating species in the groundwater. The evidence suggests that precipitates are not likely to have a significantly detrimental effect on permeability but will cause a reduction in reactivity of the iron. In most groundwater, this can probably be accommodated through a modest addition to the thickness of the PRB. It appears that there are few situations where the 10–15 year criterion for long-term performance cannot be achieved with relative ease; in many environments, performance periods of 20–40 years or more are likely to be achievable.

16.4.5 Microbiological Effects

Precipitation of iron oxides in the screens of pumping wells is a well-known phenomenon that prompted initial concern regarding biofouling of iron PRBs. However, under the strongly reducing and high pH conditions of most PRBs, biofouling has not been documented and, indeed, the environment is quite hostile for most microbes. In most cases where samples have been collected for microbial analyses, populations have been no greater within the PRB than in the natural groundwater (Matheson and Tratnyek, 1994; Vogan et al., 1998). There are exceptions however; in a groundwater containing 120 mg/L of nitrate, Gu et al. (2001) found biomass in an iron PRB of one to three orders of magnitude higher than in the groundwater, with an abundance of sulfate reducers and denitrifiers. Indeed, where there is a decline in sulfate concentration across a PRB, the presence of sulfate-reducing bacteria should be anticipated. High levels of biological activity were also reported in one gate of a funnel-and-gate system installed in Denver, Colorado (Wilkin and Puls, 2003); subsequent investigation (Hart et al., 2004) showed that smearing (decreasing hydraulic conductivity) of the trench walls had caused the gate to be “sealed off” from groundwater flow, creating an essentially stagnant area within the gate. Thus, with the exception of a small number of special conditions, biofouling is not likely to be of concern with respect to the performance of iron PRBs.

There is speculation and preliminary evidence that PRBs may enhance downgradient biodegradation (Scherer et al., 2000). In particular, the dissolved hydrogen exiting the PRB may stimulate downgradient biological activity, which could promote the degradation of compounds not normally degraded by iron, such as DCM and 1,2 dichloroethane (Vidumsky, 2003; Stening et al., 2008). Other contributions to this topic include Wildman and Alvarez (2001), Weathers et al. (1997), and Sfeir et al. (2000).

16.5 CASE STUDIES

The following case studies have been selected to illustrate the deterministic approach typically used to design iron PRBs.

16.5.1 DoD Facility, New York

In 1998, the U.S. Army Corps of Engineers (USACE) installed a PRB at a DoD facility in eastern New York (Wood and Heckelman, 2002). Shallow groundwater at the site occurs in unconsolidated deposits comprising a 4 ft (1.2 m) thick fill unit and a 2 to 6 ft (0.6 to 1.8 m) thick lacustrine unit, overlying weathered bedrock (USEPA, 2001; Anderson, 2001). To examine the feasibility of PRB application at the facility, groundwater from the site was pumped through a 1.7 ft long column of 100% Connelly GPM iron at a constant flow rate. Samples collected along the length of the column were analyzed for the primary contaminants present (PCE, TCE, *cis*-DCE and VC) allowing concentration versus distance profiles to be obtained (Figure 16.7). These data were converted to concentration versus time profiles using the column flow rate (1 ft/day) and fitted with a first-order model to obtain the half lives shown in Figure 16.7. The half lives, increased by a factor of two when corrected for groundwater temperature, were then input to a first-order simulation model together with anticipated field-scale influent concentrations. It was determined (Figure 16.8) that 2.5-days would be the residence time required to reach USEPA MCLs.

Concurrent with the bench-scale design activity, a groundwater modeling study was conducted to assess a variety of PRB configurations (Gaule et al., 2000). Configurations incorporating funnel sections or reactive walls non-perpendicular to flow created underflow and reduced capture zone efficiency. A configuration with two staggered PRBs aligned perpendicular to flow was most cost-effective. At the design velocity of 0.15 ft/day (4.5 cm/day), the models indicated that a wall of 0.82 ft (25 cm) of 100% iron would provide the required residence time.

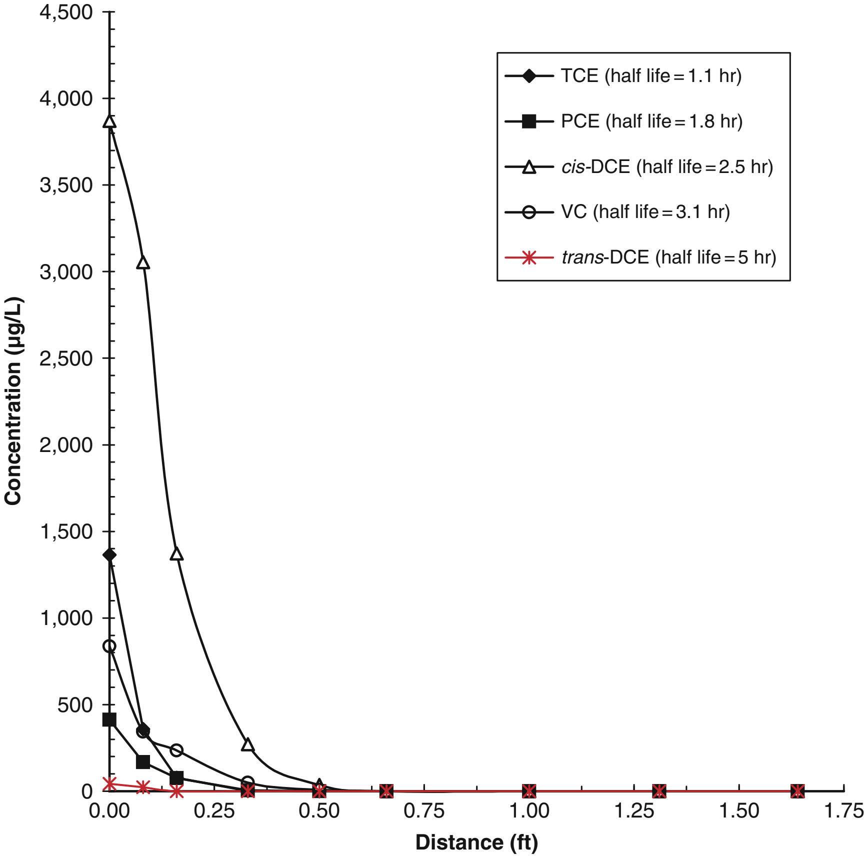

Figure 16.7. Concentration versus distance profiles obtained in column test using groundwater from U.S. DoD facility, New York, and half lives obtained from first-order model fit to these data (modified from EnviroMetal Technologies Inc., 1998).

The shallow depth of this installation meant that construction could be economically completed with a trench dug with a backhoe and maintained with temporary hydraulic shoring (Anderson, 2001). To accommodate the 2.5 ft (75 cm) width of the excavator bucket, iron was mixed at a 1:1 ratio with local sand, which created an additional safety factor in the design. An upgradient 180-ft PRB and offset downgradient 90-ft PRB were keyed into the weathered bedrock.

Construction costs, including the cost of iron, were about $300,000 U.S., and cost savings of over $3,000,000 U.S. over a 30-year life cycle were estimated by the USACE (Gaule et al., 2001). Three years of monitoring data indicated that volatile organic compound (VOC) concentrations remained below regulatory standards in groundwater exiting the PRBs.

16.5.2 Former Industrial Facility, Massachusetts

The depth of a chlorinated solvent plume migrating towards municipal supply wells from a former industrial facility in Needham, Massachusetts, necessitated the use of biopolymer trenching methods to complete the PRB installation (Richards, 2002). The PRB was designed to intercept an overburdened TCE plume, about 550 ft (165 m) wide and 57 ft (17 m) deep, to the local bedrock.

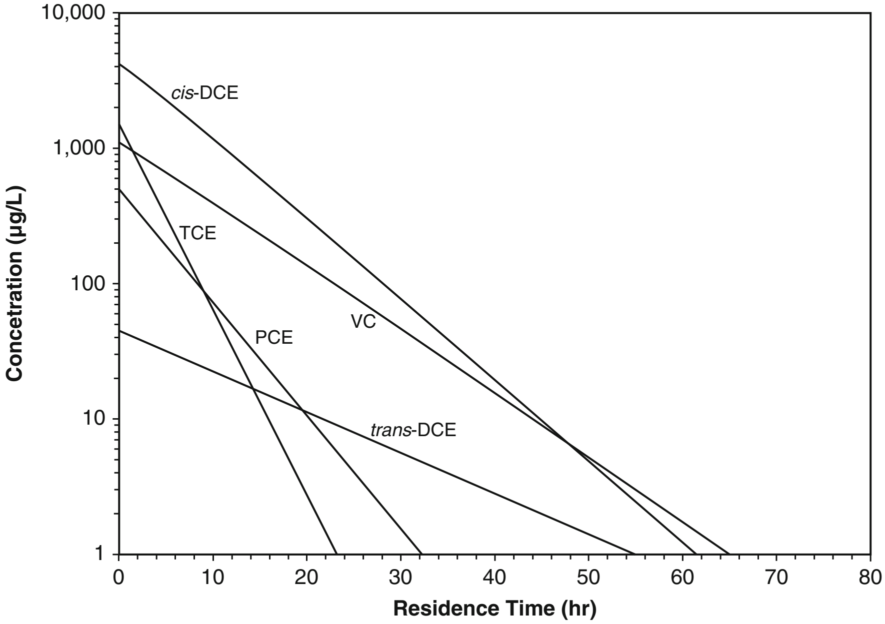

Figure 16.8. Simulation of field-scale residence time requirement based on column test results, U.S. DoD facility, New York (from Goldstein et al., 2000).

Two sources of granular iron were evaluated for use in this application, one from Connelly GPM, Inc., Chicago, Illinois, and the other from Peerless Metal Powders & Abrasives, Inc., Detroit, Michigan. The grain size of both iron sources ranged from 0.25 to 2.0 millimeters (mm) (−8 to +50 U.S. standard mesh size). Laboratory column tests were completed as described in the above case study, but in this case, each column was packed with a mixture of 68% by volume granular iron and 32% by volume sand, in order to simulate the sand/iron mixture anticipated to be implemented in the field. Biodegradable slurry was mixed into the sand/iron mixture to simulate the construction technique. Groundwater was collected from the site, and laboratory grade TCE was added to the groundwater to increase the concentration to about 500 µg/L of TCE. A flow velocity of 78 cm/day was selected to simulate actual field conditions. All column experiments were performed at room temperature.

The TCE concentration versus residence time data from the columns (Figure 16.9), fitted using a first-order kinetic model, resulted in a TCE half life of 1.0 hour for the Peerless iron and 1.1 hours for the Connelly iron (Duchene and Jacobson, 2002). The degradation rates were increased by a factor of three to account for the temperature difference between the laboratory test and the expected *in situ* temperature.

In situ permeability tests and a range of hydraulic gradients were evaluated to determine suitable groundwater flow velocities for design. The design influent TCE concentrations were determined from historic water quality data. First-order simulations (Figure 16.10) indicated that a residence time of 13 hours was required for the PRB placed in the core of the plume to degrade the TCE to below the USEPA MCL of 5 µg/L.

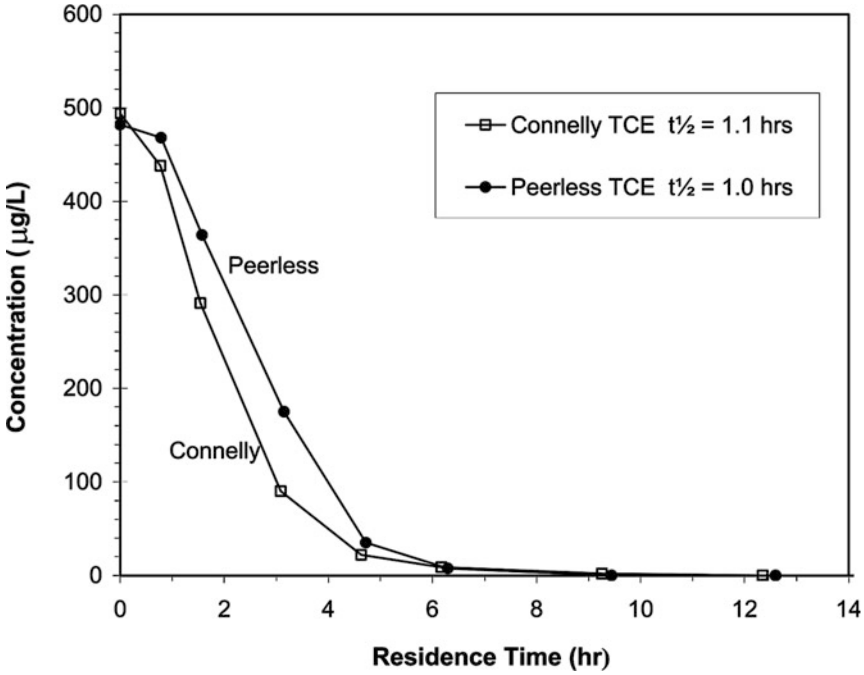

Figure 16.9. Concentration versus time profiles obtained in column test using groundwater from a former industrial facility in Massachusetts, and half lives obtained from first-order model fit to these data (modified from Duchene and Jacobson, 2002).

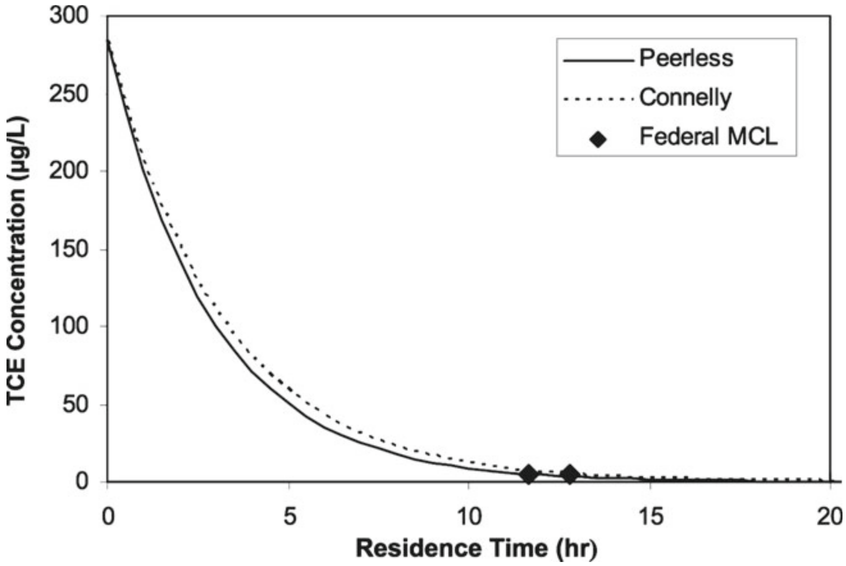

Figure 16.10. Simulation of field-scale residence time requirement based on column test results from a former industrial facility in Massachusetts (modified from EnviroMetal Technologies., 2000).

The flow-through thickness of iron required was obtained by multiplying the residence time by the groundwater flow velocity. As the TCE concentration and groundwater flow velocity varied throughout the plume, the plume was divided into two areas for design, Zone A and

Zone B, were assigned according to the differences in expected TCE mass flux. The design thickness in the central portion of the plume with higher TCE flux was 1.7 ft (50 cm) of 100% iron (Zone A); the remainder of the PRB had a design thickness of 0.5 ft (15 cm) of 100% iron (Zone B). Sand was used as a bulking agent to enable a 2-ft wide trench to be excavated and backfilled. A cross-section of the installation is shown in Figure 16.11, modified from Duchene and Jacobson, 2002.

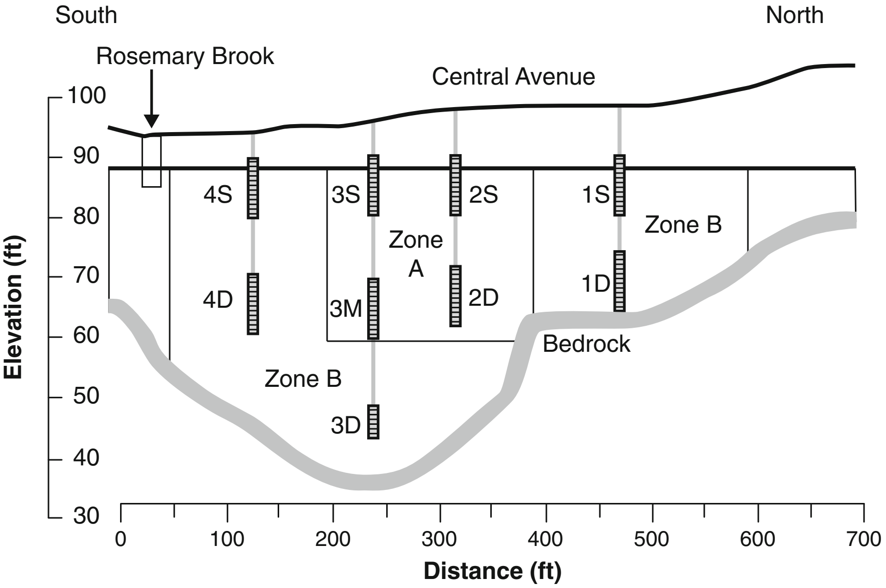

Figure 16.11. Cross-section of PRB showing the two iron zones and monitoring well network; Zone A = 1.7 ft iron plus sand, Zone B = 0.5 ft iron plus sand (modified from Duchene and Jacobson, 2002).

Construction of the PRB was completed below a two-lane residential street. Biodegradable slurry was used as liquid shoring and was added as the trench excavation proceeded to provide stability for the trench walls. Soda ash and a biostat are frequently added to the slurry to slow microbial breakdown. Adding the biostat raised regulatory concerns about the potential to contaminate groundwater, so the biostat was not used (Huber et al., 2001). The contractor modified the construction process to account for the fact that there was no additional protection against premature microbial breakdown of the mixture.

The iron/sand mixture was prepared in an off-site pugmill and delivered to the site in trucks. The iron/sand mixture was placed through the slurry by the tremie method, which displaces the biodegradable slurry. After placement of the backfill was completed, residual slurry in the PRB was broken down through circulation of an enzymatic breaker fluid and natural biological degradation, allowing groundwater to flow through the PRB.

Monitoring of PRB performance was accomplished using monitoring wells arranged in nine transects of two wells that intersect the PRB in the direction of groundwater flow. Groundwater samples are analyzed for pH, Eh, dissolved oxygen and VOCs. The contractor performed the initial monitoring to provide evidence that the biopolymer had not affected the iron reactivity. To the authors' knowledge, routine groundwater monitoring of VOCs has shown that the PRB has performed essentially as designed for several years following installation.

16.6 STAGE OF TECHNOLOGY DEVELOPMENT

16.6.1 Number of Sites and Performance

Iron PRB technology for chlorinated solvents was commercialized by the University of Waterloo, Waterloo, Ontario, through EnviroMetal Technologies Inc. (ETI), founded in 1992. When introduced in the early 1990s, the PRB concept was a significant departure from conventional treatment technologies and was therefore greeted with considerable skepticism. Through the efforts of the research community, the scientific basis of the technology has evolved, and through numerous pilot-scale demonstrations by "arms-length" agencies such as USEPA and DoD, considerable confidence in the practical viability of the concept has been developed. ETI currently lists over 200 applications of the technology, approximately 40 of which are demonstration projects, with over 150 full-scale commercial applications. The largest number of applications is in the United States, with several in Europe and 15 in Japan. Thus, it is reasonable to classify iron PRBs as "an accepted standard practice."

Of the sites listed by ETI, most continue to perform in a manner consistent with the initial design. Of the approximately 10 sites that have not met expectations, insufficient design information concerning the characteristics of the plume (size, groundwater velocity, and/or concentration distribution) has been the major cause of compromised performance. In these cases, the problem was generally resolved by increasing the length of the PRB or the thickness at particular locations. A small number of cases of insufficient performance can be attributed to construction artifacts, such as smearing of the trench wall, that have impeded flow through the PRB. The need for careful and thorough site characterization prior to the design and installation of a PRB cannot be overemphasized. To this point, a PRB has not failed as a consequence of lower-than-expected performance of the iron material.

Although a substantial number of PRBs have been installed and the record of performance is enviable, relative to the many thousands of sites for which the technology could be applicable, the number of installations remains small. This could be due in part to low incentives for cleanup and in part to the high initial capital cost. This situation may change as the record of performance at existing installations lengthens, leading to more demonstrable evidence of the economic benefits.

16.6.2 Future Developments

Even though the iron PRB technology is firmly established, numerous opportunities to improve the technology exist. Some of these are addressed very briefly below.

Installation Methods—While numerous methods for installing PRBs are available, continued improvement and development, particularly with a view to reducing cost, would be beneficial. This is particularly the case for installations at depths of greater than 80–100 ft (24–30 m) and for bedrock plume applications.

Prediction of Performance—Though the empirical evidence and experimental results are encouraging, or even convincing, with respect to long-term performance, predicting a reasonable expectation for the period of performance in a wide range of geochemical conditions continues to be an elusive goal. The model presented in Jeen et al. (2007) may prove to be a useful step in this direction. As the period of record for several installations now approaches (or exceeds) ten years, these sites could provide useful data for testing and improving predictive models.

Sequential Treatment—Many contaminant plumes include several contaminants, not all of which can be adequately treated by iron; in some cases, while iron treats the parent compound, it may not treat degradation products, which may also be toxic. Sequential treatment systems that include different reactive materials to treat the different contaminants may be a useful and practical approach in these situations. Work is proceeding in this area (Fiorenza et al., 2000, for example), and significant developments can be expected over the next few years.

PRB–Monitored Natural Attenuation—Iron PRB technology has been combined with monitored natural attenuation (MNA) at only a few sites. Because of the first-order kinetics associated with granular iron, large amounts of mass are removed very quickly at high concentrations, while at low concentration, rates of mass removal become very low. Thus, in aquifers where natural attenuation is an active process, a relatively thin, and thus less costly, PRB could be used to remove much of the mass, relying on downgradient natural attenuation as a polishing process to meet MCLs.

Iron-Clay Combinations for Source-Zone Treatment—PRBs were developed for plume control; however, granular iron has been applied using various emplacement methods for source-zone treatment (ITRC, 2005). In particular, a granular iron/clay slurry can be mixed into a dense nonaqueous phase liquid (DNAPL) source zone using mixing augers or by some other suitable means. The clay acts as a lubricant during injection and further reduces the permeability in the source zone, reducing the potential for discharge of dissolved contaminants. Following mixing, the DNAPL will be distributed as small droplets. As the iron degrades contaminants in the dissolved phase, the droplets will continue to dissolve, eventually consuming the DNAPLs. Because of the mixing process, this technology should be relatively immune to the effects of geologic heterogeneity, a significant limitation to several of the other proposed methods for source zone treatment. The viability of this concept has been demonstrated in numerous laboratory studies and in field applications (Wadley et al., 2005; Shackleford et al., 2005; Olson, 2005).

Bimetals—There is considerable evidence (Sweeney and Fischer, 1972, Odziemkowski et al., 1998) that plating a very small amount of a more noble metal, such as palladium or nickel, onto the surface of iron can increase the degradation rates of many chlorinated compounds by a factor of ten or more. Use of such plating could reduce the amount of reactive material required in a PRB by a factor of ten, with possible cost reductions and a greater range of options for installation, particularly at greater depths. Unfortunately, the noble metal acts as a catalyst and as in most catalyzed reactions, the catalyst becomes poisoned over a period of time (Lin et al., 2004; Odziemkowski et al., 1998), requiring reactivation or replacement at intervals of a few weeks to a few months. Thus, there appears to be little potential for using these materials in PRBs, though if cost-effective methods for reactivation can be developed, they may have application in aboveground treatment systems.

Nano-iron—Interest in iron having particle sizes in the nanometer (nm) range (generally 10–100 nm) was stimulated by the early work of Wang and Zhang (1997). Because of the small particle size and correspondingly high specific surface area, nano-iron is substantially more reactive than the iron materials normally used in PRB applications; the reactivity can be increased even further by plating a more noble metal onto the iron. In addition to the higher reactivity, it has been proposed that because of the small particle size, nano-iron could be injected and transported well beyond the point of injection by natural groundwater flow. Because of the high reactivity, even with water, it is unlikely that nanoparticles will persist in the subsurface for periods of greater than a few weeks to months (Liu and Lowry, 2006), and because of their high cost, repeated injections may not be practical. In addition, no record was found of tests where the nanoparticles have been shown to migrate significant distances from the injection point (e.g., Tratnyek and Johnson, 2006; Liu and Lowry, 2006). Based on the current state of the technology, the use of nano-iron is probably most appropriate in situations where high rates of mass removal are required over short periods of time, as may be the case in source zone treatment.

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CHAPTER 17

ELECTROLYTIC REACTIVE BARRIERS FOR CHLORINATED SOLVENT REMEDIATION

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Dedication:
David M. Gilbert, a key driving force behind the development of e-barriers, unexpectedly passed away in May of 2008. Our friend and colleague will be forever missed by all who knew him.

17.1 INTRODUCTION

The e-barrier is an emerging technology that applies fundamental electrochemical principles to a permeable reactive barrier (PRB). The e-barrier consists of closely spaced (e.g., 1 centimeter [cm]) permeable electrodes installed in a trench that intercepts a plume of contaminated groundwater (Figure 17.1). Low-voltage direct current (DC) sufficient to drive the degradation reactions of interest is applied to the electrodes. If sufficient electrical potential is applied, oxidizing conditions develop at the anode (positive electrode) and reducing conditions develop at the cathode (negative electrode). Since a complete electrical circuit is present, the dissolved contaminants are subject to sequential oxidation-reduction or reduction-oxidation, depending on the sequence of charges applied to the electrode set. This sequence can be altered depending on the contaminant of interest and the chemistry of the local groundwater. Through sequential oxidation-reduction (or reduction-oxidation), an aqueous phase chlorinated compound is degraded into thermodynamically favored carbon dioxide or methane and chloride.

The e-barrier requires relatively little power (e.g., 10 watts per square meter [W/m^2]) compared to electrically based remediation technologies, such as thermal heating. Treatment is achieved through electrochemical transformation of the contaminant compound into thermodynamically favored forms. The applied voltage can be adjusted to completely degrade the target compound, as well as any intermediate compounds that may pose an environmental risk.

This chapter is intended to provide the information necessary for potential end-users to evaluate e-barrier technology for site-specific applications. It is organized to provide a general understanding of the principles of operation, the materials of construction and the methods of installation and operation. Unlike other PRB technologies, the e-barrier does not have a long record of commercial application. Information presented in this chapter is therefore limited to the cumulative experience gained from several laboratory- and field-based projects.

As an emerging technology, installation methods and long-term performance of the e-barrier technology have yet to be fully demonstrated. Three field pilot studies have been conducted to date; through each of these field-based demonstrations, significant advances in design, installation, and operation have been made. The most advanced e-barrier is currently operating at the Pueblo Chemical Depot (Pueblo, Colorado) for the treatment of energetic compounds in groundwater (see Section 17.2.2.3 and Section 17.2.3.1). Since the e-barrier is an emerging technology, discussion of the contaminants treated to date, costs of application, and a

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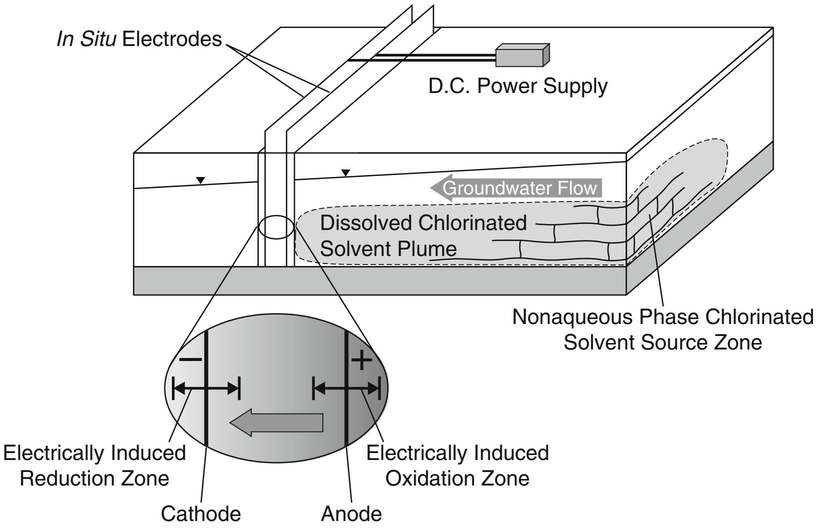

Figure 17.1. Conceptual e-barrier for treatment of a chlorinated solvent plume (after Sale et al., 2005).

case study for a trichloroethene (TCE) plume at F.E. Warren Air Force Base (AFB) (Cheyenne, Wyoming) are included to assist in the evaluation of e-barriers for site-specific use.

17.1.1 Advantages and Limitations

An electrolytic approach to *in situ* degradation of groundwater contaminants has several promising attributes:

- Both oxidation and reduction reactions are induced in a single PRB.
- Since both oxidative and reductive steps are included, the need for a "treatment train" approach may be reduced or eliminated.
- The power cost is low, given that only the reactions of interest need to be induced.
- The approach is environmentally benign since the electrodes deliver and recover electrons without the need to introduce chemical reactants into the subsurface.
- The induced reaction conditions can be manipulated to achieve the desired downstream water quality after the system has been emplaced by adjusting the applied potential difference between the electrodes.
- Undesired precipitates (e.g., calcium carbonate ($CaCO_3$)) that can lead to electrode plugging and eventual fouling can be removed by periodically reversing the electrode polarity.
- More than one pair of electrodes can be used to improve performance.

Limitations of an e-barrier approach include the following:

- The initial capital cost may be higher than that of other PRBs.
- Unwanted compounds (e.g., chloroform ($CHCl_3$)) can form at the electrode surfaces under extreme operating conditions.
- The depth of the contaminant plume may limit the number of sites where e-barriers can be applied, as installation of an e-barrier deeper than 60 feet (ft) (approximately 20 meters [m]) below ground surface may not be economically feasible.

17.2 TECHNOLOGY DESCRIPTION

17.2.1 Principles of Operation

A schematic of an e-barrier is presented in Figure 17.1. In this example, the groundwater initially encounters the anode. Oxidizing conditions are imposed by the transfer of electrons from the solution constituents to the anode. By advection, the groundwater then encounters the cathode. Reducing conditions are imposed at the cathode as electrons from the cathode are transferred to the chemicals in solution. Hence, the groundwater is subjected to sequential oxidation and reduction. The net effect of these reactions is to reduce the contaminant concentration, thereby reducing the contaminant flux.

Reactions occurring in an e-barrier can be categorized as one of the following:

- Direct electrolytic degradation of the target compound at the electrode surfaces (heterogeneous electron transfer)
- Reaction of the target compound with oxygen or hydrogen generated electrolytically at the anode or cathode, respectively (homogeneous reaction)
- Reaction of the target compound with free radicals formed through the reduction of dissolved oxygen at the cathode surface (homogeneous reaction) (Bunce et al., 1997). Although reactions are specific to the conditions in native groundwater, possible reaction mechanisms depend on the anode-cathode configuration sequence.

17.2.1.1 Reactions near the Anode

The reactions that occur at or near the anode include direct electrolytic oxidation of the target compound, such as TCE, to the corresponding mineralization products (Reaction 17.1) and the oxidation of water to form oxygen and hydronium ions (Reaction 17.2). Hydronium ions generated through Reaction 17.2 lower the pH around the anode. Carbon dioxide, which is generated through both Reaction 17.1 and through an induced equilibrium shift with dissolved carbonic acid salts under acidic conditions (Reaction 17.3), may exceed its solubility limit and off-gas (Reaction 17.4). Likewise, oxygen may also off-gas (Reaction 17.5). Lastly, cations (such as calcium) may combine with oxygen to precipitate on the anode as metal oxides (Reaction 17.6).

$$C_2HCl_3 + 13H_2O \rightarrow 2CO_{2(aq)} + 6e^- + 3Cl^- + 9H_3O^+ \qquad \text{(Rx. 17.1)}$$

$$\tfrac{3}{2}H_2O \rightarrow \tfrac{1}{4}O_{2(aq)} + e^- + H_3O^+ \qquad \text{(Rx. 17.2)}$$

$$HCO_3^- + H_3O^+ \rightarrow CO_{2(aq)} + 2H_2O \qquad \text{(Rx. 17.3)}$$

$$CO_{2(aq)} \rightarrow CO_{2(g)} \qquad \text{(Rx. 17.4)}$$

$$O_{2(aq)} \rightarrow O_{2(g)} \qquad \text{(Rx. 17.5)}$$

$$Ca^{2+} + 3\,H_2O \rightarrow CaO_{(s)} + 2H_3O^+ \qquad \text{(Rx. 17.6)}$$

17.2.1.2 Reactions near the Cathode

Products from the initial oxidation reactions are advected onto the cathode, where reduction reactions occur. The two prominent reactions are direct electrolytic reduction of the target compounds (for example TCE) at the surface of the cathode (Reaction 17.7) and the reduction of water (Reaction 17.8). Reaction 17.7 indicates complete reduction of TCE into methane and chloride, however, under field conditions this reaction may not go to completion. Like oxygen and carbon dioxide near the anode, hydrogen generated from water may be off-gassed

(Reaction 17.9). Several possible reactions at the cathode consume hydronium, meaning that pH can increase to a level where inorganic salts may precipitate (Reaction 17.10). Reactions 17.6 and 17.10 have the potential to plug the electrodes. Since most groundwater contains dissolved calcium or other polyvalent cations, controlling precipitate formation on the surface of the electrodes is critical and is discussed later in this chapter.

$$C_2HCl_3 + 10e^- + 7H_2O \rightarrow 2CH_{4(aq)} + 3\,Cl^- + 7OH^- \qquad \text{(Rx. 17.7)}$$

$$H_2O + e^- \rightarrow \tfrac{1}{2}H_{2(aq)} + OH^- \qquad \text{(Rx. 17.8)}$$

$$H_{2(aq)} \rightarrow H_{2(g)} \qquad \text{(Rx. 17.9)}$$

$$Ca^{2+} + OH^- + HCO_3^- \rightarrow CaCO_{3(s)} + H_2O \qquad \text{(Rx. 17.10)}$$

Several reactions that may occur at the cathode utilize chemical species generated at the anode. When dissolved oxygen generated at the anode is transported to the cathode, it can react with hydrogen generated at the cathode (Reaction 17.11), although a catalyst is likely required.

$$O_{2(aq)} + 2H_{2(aq)} \rightarrow 2H_2O \qquad \text{(Rx. 17.11)}$$

In other cases, conditions near the cathode may generate radical species that can react with the target contaminant. For example, the combination of acidic conditions (e.g., $pH<4$) and the presence of dissolved oxygen and iron or manganese can promote Fenton's type reactions (Reactions 17.12 and 17.13) (Gözmen et al., 2003; Oturan and Pinson, 1995; Oturan et al., 2000).

$$O_{2(aq)} + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad \text{(Rx. 17.12)}$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{2+} + OH^- + OH^\bullet \qquad \text{(Rx. 17.13)}$$

The hydroxyl radicals generated in Reaction 17.13 are non-specific oxidizing agents and may react to degrade the target contaminant.

17.2.1.3 Downgradient Effects

Products of reduction at the downgradient cathode surface (e.g., hydrogen ($H_{2(aq)}$)) may be transported downstream into the formation by advection. Reduced constituents can subsequently react with chlorinated compounds such as TCE (Reaction 17.14) or with solids such as iron hydroxides present in the aquifer matrix (Reaction 17.15). As observed above for Reaction 17.7, Reaction 17.14 may not go to completion under field conditions.

$$C_2HCl_3 + 5H_{2(aq)} + 3H_2O \rightarrow 2CH_{4(aq)} + 3Cl^- + 3H_3O^+ \qquad \text{(Rx. 17.14)}$$

$$Fe(OH)_3 + \tfrac{1}{2}H_{2(aq)} \rightarrow Fe^{2+} + 2OH^- + H_2O \qquad \text{(Rx. 17.15)}$$

Reaction 17.14 may be a major dechlorination process when an appropriate catalyst is present (e.g., anaerobic microorganisms that utilize H_2 as an electron donor and TCE as the electron acceptor) (Matheson and Tratnyek, 1994).

17.2.2 Materials of Construction

The e-barrier consists of three integrated components: the electrode material, the e-barrier assembly (consisting of electrodes and geonet-geotextile spacers) and the assembly support.

The electrode material is the system's reactive component. The electrode assembly ensures that the physical environment in which the electrodes are placed allows for flow through the barrier while still maintaining electrode spacing. The assembly support provides the structure necessary for the e-barrier's installation and prevents contaminated groundwater from by-passing the electrodes. Details of each component are discussed below.

17.2.2.1 Electrode Materials

In principle, there are several materials that could be used as electrodes in an e-barrier. Ideally, electrode materials should be inert (low aqueous solubility), stable over a wide range of electrical potentials and cost effective. Materials tested in laboratory studies include titanium, titanium-mixed metal oxide (Ti-mmo), gold, stainless steel, carbon (glassy and felt), carbon black and copper. The efficacy of iron (Farrell et al., 2000; Li and Farrell, 2000; Scherer et al., 1997), silver (Criddle and McCarty, 1991), platinum (Chen et al., 2003) and nickel (Liu et al., 2000) electrodes has been reviewed.

Only expanded Ti-mmo has been tested in field demonstrations (Eltech Systems, Chardon, Ohio). It was chosen for its structural and chemical stability over a wide range of applied electrical potentials. In the field demonstrations conducted to date, expanded Ti-mmo has been used for both anodes and cathodes. This allows for flexibility in the polarity configuration during normal operation (oxidation-reduction or reduction-oxidation) and precipitate control strategies (such as periodic polarity reversal). Laboratory studies show that expanded Ti-mmo electrodes (Figure 17.2) are stable under both positive and negative polarization. Studies also estimate that the Ti-mmo electrode's lifetime exceeds 50 years (Gilbert et al., 2008). Additional information regarding use of Ti-mmo electrodes for e-barriers is presented in Petersen et al. (2007).

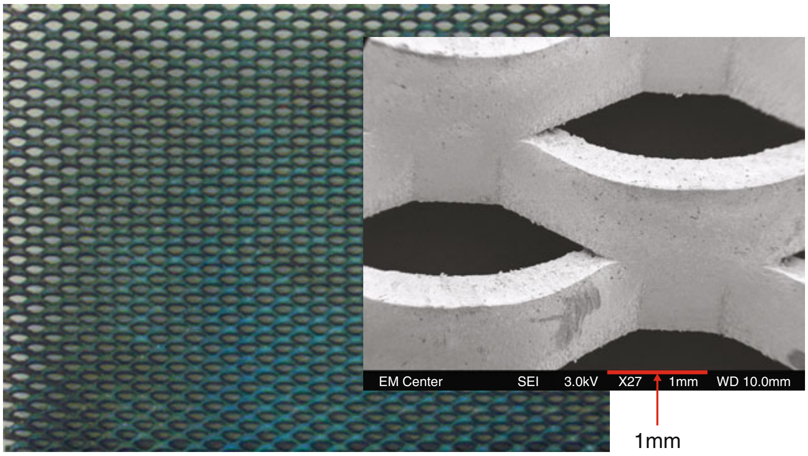

Figure 17.2. Expanded titanium-mixed metal oxide (Ti-mmo) electrodes used in the e-barrier (Eltech Systems, Chardon, Ohio) and a scanning electron microscopy (SEM) image of an electrode in the inset.

17.2.2.2 e-barrier Assembly

The e-barrier consists of a composite electrode assembly using geonet (e.g., Tenax Corp., Maryland) as the electrode spacer with geotextile fabric on the external surfaces to prevent infiltration of backfill into the barrier. The geonet between the electrodes provides very high porosity and permeability within the active area of the e-barrier. It also serves several other functions:

- Seepage velocities through the e-barrier will likely be lower than that of the formation, allowing for greater residence time and improved treatment.
- The relatively high permeability allows H_2 and oxygen (O_2) gases to escape the system in a safe manner.

Electrode spacing can be varied depending on site-specific conditions (e.g., specific conductivity of groundwater). Typical spacing ranges from 1–2.5 cm.

17.2.2.3 Assembly Support

The most convenient approach to fabrication and installation of an e-barrier is to use a modular design for the supporting structure. Individual modules can be fabricated using several different materials. Examples include vinyl sheet pile, fiberglass sheet pile, polyvinyl chloride (PVC) framing and high-density polyethylene (HDPE) sheeting. Materials used for the assembly supports should be non-conductive (electrically and hydraulically), compatible with the contaminants present, have sealable joints between individual modules and be cost-effective.

The two types of assembly supports that have been tested in field demonstrations are PVC framing and vinyl sheet piles. PVC framing proved to be effective but limited in application because fabrication was labor-intensive and the sealing between individual modules was challenging. Use of vinyl sheet piles resulted in significantly lower cost of fabrication, reliable sealing between modules, and a panel with greater robustness (Figure 17.3).

17.2.3 e-Barrier Operation

17.2.3.1 Power Supply

Direct current can be supplied to the e-barrier through line service using a rectifier or through a remote power source, such as solar photovoltaic cells. The e-barrier requires between 3–10 W/m^2 of power to operate. This low power requirement makes solar power an attractive alternative, especially for remote locations, but line power is likely the least expensive option where available. Several considerations should be made when selecting a power source. The preferred equipment when utilizing line power is a DC rectifier capable of variable applied voltage. Depending on the size of the e-barrier, more than one rectifier may be necessary to meet the system current requirement. The field demonstration at F.E. Warren AFB indicates that a maximum 6 amps per square meter (A/m^2) of active area would provide sufficient current for a TCE plume.

DC rectifiers are commonly used in impressed current cathodic protection, which uses direct current to supply electrons to a metallic structure in order to limit oxidation. These rectifiers are available from several vendors. Solar photovoltaic or battery power supply can be used in areas where line power is unavailable. Battery banks are also required, since power should be applied continuously to the e-barrier (Figure 17.4).

17.2.3.2 Applied Voltages

The e-barrier's performance depends on the applied electrical potential (voltage) and the resultant current. A variable voltage power supply allows for applied voltage adjustment and fine-tuning of the treatment in order to optimize downstream water quality versus power requirements.

Figure 17.3. Individual electrode panel mounted to vinyl sheet pile sections forming a single e-barrier module. 15 e-barrier modules were installed at the Pueblo Chemical Depot for management of a groundwater plume containing energetic compounds.

Figure 17.4. Solar photovoltaic powered e-barrier for treatment of energetic compounds at the Pueblo Chemical Depot.

17.2.3.3 Polarity Reversals

Periodically reversing electrode polarity removes unwanted precipitates (e.g., $CaCO_{3(s)}$) from the electrode surfaces. Polarity reversals change the local pH conditions, which dissolves the solids that precipitate on the electrode surface under normal operating conditions. The frequency and duration of polarity reversals are dependent on the site-specific groundwater geochemistry and the operating voltage of the e-barrier. Polarity reversals can be conducted automatically using a programmable logic controller and a series of DC contactors.

17.2.4 Installation Methods

To date, traditional excavation using trench-box shoring has been used for e-barrier installation in field demonstrations. In large part, this reflects the scale and rigorous monitoring requirements of a small-scale field demonstration. Other methods of shoring (e.g., guar) could be used for installation of an e-barrier, but this method has not yet been demonstrated. Installation methods used for other PRBs, such as continuous trenching, would not be suitable for installation of an e-barrier since individual panels need to be placed without damaging the electrode sets or wiring.

17.2.5 Contaminants Treated

The degradation of several dissolved phase chlorinated compounds using e-barriers has been tested in both laboratory- and field-scale experiments. Laboratory experiments have mainly consisted of flow-through column reactors (Figure 17.5), which are one-dimensional analogs of a field-scale system. Field-scale experiments have been conducted on a narrower range of chlorinated solvents. Laboratory experiments have evaluated e-barrier technology to illustrate the range of contaminants that can be degraded under different operating conditions including TCE (Petersen, 2003; Sale et al., 2005) and energetic compounds (Gilbert and Sale, 2005).

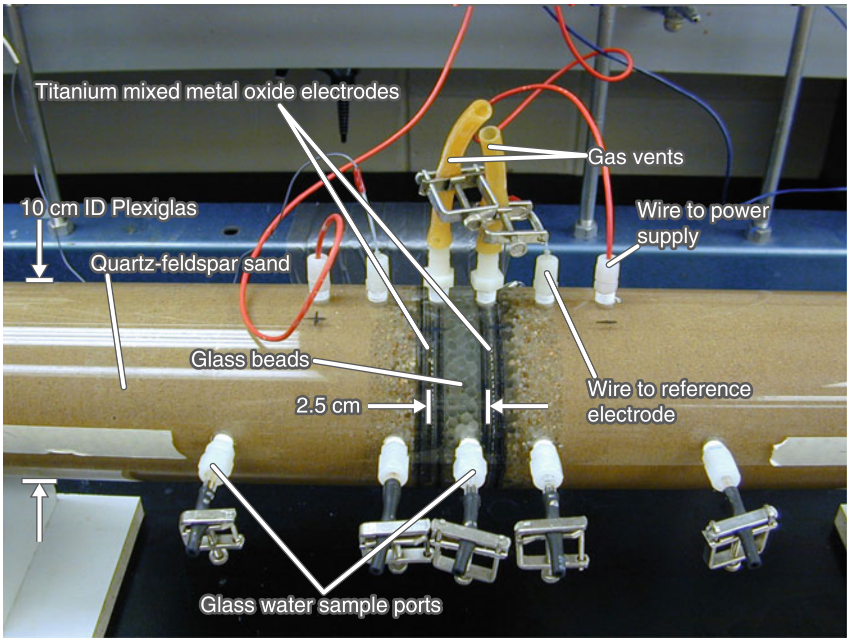

Figure 17.5. Experimental setup of the flow-through column electrolytic reactor.

17.3 PERFORMANCE

17.3.1 Laboratory Studies

Chlorinated ethanes and ethenes were degraded in a laboratory column e-barrier that was operated in a sequential oxidation-reduction sequence. The two contaminants used to illustrate treatment efficacy were 1,1,1-trichloroethane (1,1,1-TCA) and perchloroethene (PCE). The influent concentrations of 1,1,1-TCA and PCE were approximately 50 and 3 milligrams per liter (mg/L), respectively. These chemicals were dissolved in a simulated groundwater solution (calcium-bicarbonate type water) flowing through a column at an interstitial velocity of 1 ft/day (0.3 m/day).

Applied potential differences ranging from 0 to 40 volts (V) were evaluated. Steady-state effluent concentrations indicated a relationship between the extent of dechlorination and the applied potential difference (Figure 17.6). At 10 V, 98% of the 1,1,1-TCA and 50% of the PCE were transformed to lesser or completely dechlorinated products. Degradation products included 1,1-dichloroethane (1,1-DCA), ethene, and ethane, which are the result of reduction reactions similar to Reaction 17.7.

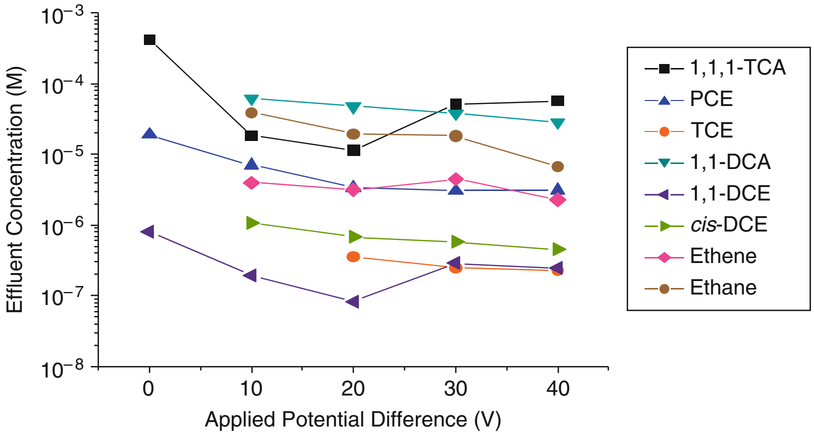

Figure 17.6. Steady-state effluent concentrations from flow-through electrolytic reactors as a function of the applied potential difference (V). The 0 V experiment served as the no power control case. Unpublished research conducted by the authors at Colorado State University.

Initially, increasing the applied potential difference decreased effluent concentrations of all observed species, but at 30 V and greater, 1,1,1-TCA concentrations were no longer reduced. However, PCE effluent concentrations continued to decline to a level of 0.5 mg/L, an 85% reduction in mass flux through the system. Although the suite of reaction intermediates/products indicate that dechlorination occurred primarily through reductive processes, vinyl chloride (VC) was not formed at detectable levels. Column experiments were also performed in the cathode-anode electrode sequence (reduction-oxidation), but in all cases, the chlorinated solvent flux reductions in this mode of operation were less than those achieved in the anode-cathode sequence.

These results illustrate the relationship between applied potential and effluent water quality. Nonetheless, increasingly extreme conditions may not necessarily lead to decreasing contaminant fluxes. Consequently, the optimum operating conditions are likely site-specific and dependent on factors such as seepage velocity, geochemistry and contaminant concentrations.

17.3.2 Field Studies

A prototype e-barrier in a 4.5-m^2 (48-ft^2) capture area was installed at the Canadian Forces Base Borden in an existing contaminant plume containing PCE and TCE. Influent contaminant concentrations were spatially non-uniform (Figure 17.7), varying by more than an order of magnitude in distances less than 1 m (3 ft). The average groundwater velocity was between 0.2 and 0.3 m/day (0.5 and 1 ft/day), and local groundwater direction fluctuated by approximately 30 degrees. The combination of these two site characteristics resulted in a complex setting to evaluate mass flux reduction through the system.

The changes in downstream water quality reflected the occurrence of multiple reaction processes. Collectively, these processes had the effect of dechlorinating the target compounds. At 5 V applied between the electrodes, PCE and TCE were both dechlorinated by a reductive mechanism such as that shown in Reaction 17.7 at the electrode surface (Figure 17.7). However, the rate of the reductive mechanism was not sufficient to completely dechlorinate the influent mass. Consequently, a significant amount of TCE was measured downstream of the system at this operating condition. The formation of *cis*-1,2-dichloroethene (*cis*-DCE) occurred concomitant with a decline in TCE concentrations downstream of the e-barrier. This transformation likely proceeded through a microbial pathway that utilized electrolytically generated H_2 as the electron donor, in the mechanism illustrated by Reaction 17.14. This capability was later confirmed in separate laboratory microcosm experiments (Ballaban, 2003).

Chlorinated ethanes and ethenes were degraded by multiple electrolytically induced mechanisms in laboratory and field proof-of-concept studies. These results provided the technical basis for further large-scale evaluations of the technology. In another ongoing demonstration project, e-barriers are being evaluated to treat compounds such as dissolved explosives and other emerging contaminants in a variety of system configurations (Gilbert and Sale, 2005; Wani et al., 2006). The ability to treat a wide variety of compounds is an appealing attribute, given that mixtures of contaminants are often found in the environment (Monosson, 2005).

17.3.3 Cost Comparison with Other Reactive Barrier Technologies

At present, the most comprehensive cost analysis of e-barrier implementation is based on the F.E. Warren AFB field demonstration (Sale et al., 2005; Gilbert et al., 2008). At this site, the cost for design and construction of the demonstration scale e-barrier was \$4,390/m^2 of intercepted plume (Table 17.1). Costs associated with operations and monitoring were \$113/m^2/year. Table 17.2 indicates that the e-barrier demonstration had a higher capital cost than the full-scale field applications. The F.E. Warren Spill Site 7 zero-valent iron PRB was 32% less expensive than the demonstration scale e-barrier. However, advances in e-barrier design and operation subsequent to the F.E. Warren AFB demonstration have lowered the cost per cross sectional area of intercepted plume and made the cost of full-scale e-barriers more competitive with zero-valent iron PRBs.

17.3.4 Potential Side Effects

There has been some concern that e-barrier technology could lead to undesirable side effects, such as increasing the mobility of other compounds (e.g., metals naturally present in the subsurface) or causing the formation of other contaminants of concern. The results of the field demonstrations conducted to date indicate that normal e-barrier operation does not result in increased mobility of metals or anionic species. However, at high operating potentials, chloroform was detected in the effluent groundwater during one of the field demonstrations. Follow-up laboratory studies suggested that chlorine, generated from the oxidation of background chloride, reacted with the acetone-based PVC cement used in the construction of the e-barrier to form chloroform. Chloroform generation was minimized during the demonstration by decreasing the imposed potential difference. In future implementations, avoiding acetone and methyl-ketone based construction materials and minimizing applied voltage will help mitigate the occurrence of by-products typical of disinfection processes.

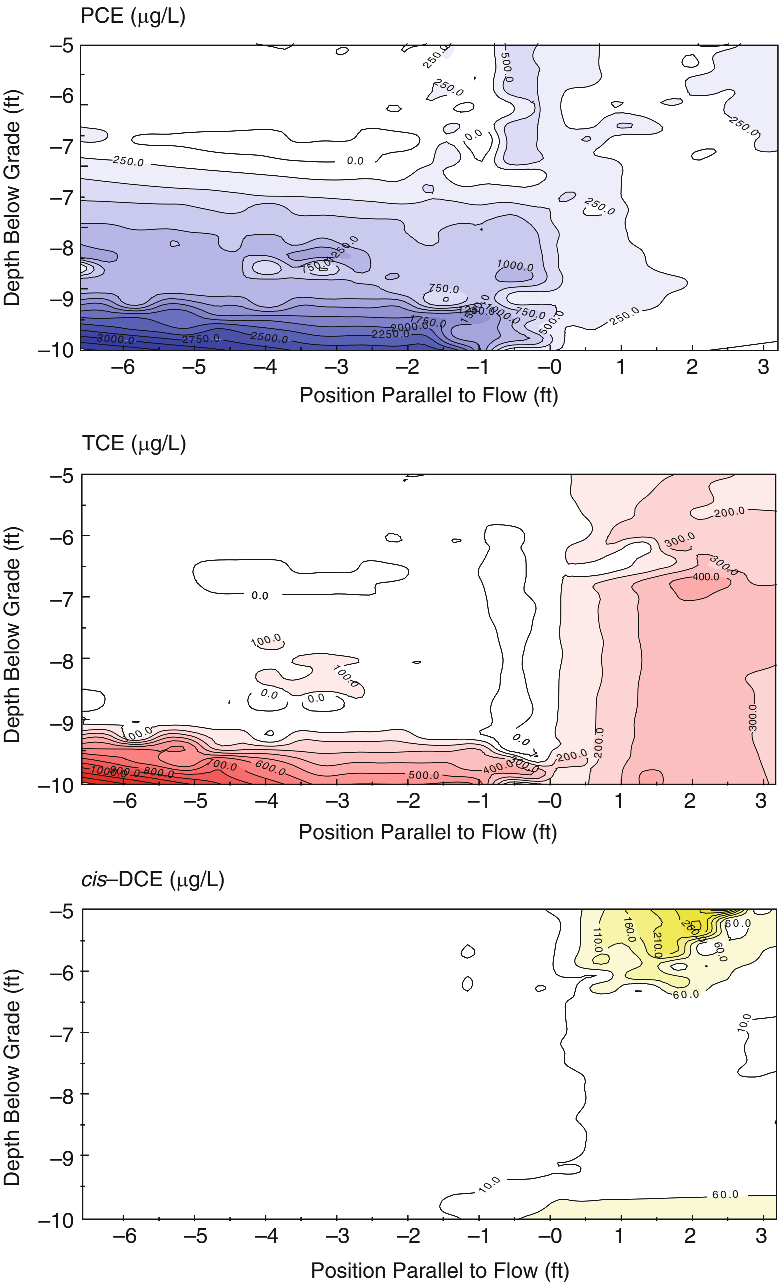

Figure 17.7. Concentration maps of PCE, TCE, and *cis*-DCE (micrograms per liter [μg/L]) from a plane parallel to groundwater flow through the Borden e-barrier midpoint at an applied potential difference of 5 V. Contours were generated from 45 discrete sample points within the plane. Unpublished research conducted by the authors at Colorado State University in collaboration with the University of Waterloo.

Table 17.1. Costs for the F.E. Warren Air Force Base Demonstration e-Barrier

Category	Cost ($/ft^2)	Cost ($/m^2)
Barrier Installation	126	1356
Electrodes	66	710
Panel Fabrication	38	409
Miscellaneous Barrier Components Subtotal	22	237
Hydrogeologic Investigation	21	226
Rectifier	20	215
Design (5% of construction)	19	204
Construction Oversight (5% of construction)	19	204
Data Logger	17	183
Demobilization	16	172
Utility Conduits	12	129
PVC Pipe Frame	10	108
Drilling for Monitoring Points	10	108
Geonet	9	97
Reference Electrodes	3	32
Subtotal—Design and Construction Costs	**408**	**4390**
Performance Monitoring (Annual Basis)	7.00	75
Tracking Electrical Performance (Annual Basis)[1]	2.40	26
Cell Phone Connection (Annual Basis)	0.68	7.3
Power (Annual Basis)	0.43	4.6
Subtotal—Operations and Monitoring Costs	**11**	**113**
Total	**419**	**4503**

[1] Assumes annual sampling/reporting for two wells up and downgradient per 100 ft of barrier length, given a 10 ft saturated thickness, at a cost of $3,500/well/year.

At applied potentials above approximately 1.5 V, the e-barrier will generate gaseous hydrogen and oxygen. Under normal operating conditions, rates of gas generation are low. To date, significant concentrations of these gases have not been observed in gas samples. Nevertheless, site-specific conditions will vary and testing should be considered to verify that adverse conditions are not present.

17.3.5 Lessons Learned

- Sustainable operation of e-barriers can be achieved by using solar photovoltaic power supplies.
- Fabrication can be simplified by using commercially available off-the-shelf vinyl or fiberglass sheet pile for electrode assembly support.
- Precipitates that may form on electrode surfaces can be controlled using a polarity reversal strategy.
- Chloroform formation can be minimized through control of applied potential and selecting construction materials that do not contain acetone.

Table 17.2. Capital and Year-One Expenditures for the F.E. Warren AFB e-Barrier Compared to Several Zero-Valent Iron PRBs (USEPA, 2002)

Site	Capital Cost	Annual O & M	Depth (ft)	Active Area (ft^2)	Capital Cost/ft^2	O&M Cost/ft^2
Industrial Site, SC	$400,000		29	9425	$42	
Somersworth Landfill SF Site, NH	$2,515,000		40	32000	$79	
Cape Canaveral, FL	$760,150		45	6300	$121	
Industrial Site, NY	$1,000,000		18	6600	$152	
Pease AFB, NH	$750,000	$35,000	33	4950	$152	$7.07
Watervliet Arsenal, NY	$387,000	NA	10	1900	$204	
USCG Support Center, NC	$835,000	$85,000	24	3648	$229	$23.30
Former Manufacturing, Fairfield, NJ	$875,000	$25,000	25	3175	$276	$7.87
Warren AFB Spill Site 7, WY	$2,350,000		15	8520	$276	
Kansas City Plant , MO	$1,300,000		39	3900	$333	
e-barrier at F.E. Warren AFB, WY	**$75,000**	**$2,700**	**6**	**183**	**$409.84**	**$14.75**

17.4 CASE STUDY: F.E. WARREN AFB FIELD DEMONSTRATION

Building on past work, three demonstration-scale e-barriers have been installed as of August 2006. Two of the barriers were applied to dissolved chlorinated solvents (Canadian Forces Base Borden, Ontario, and F.E. Warren AFB, Wyoming), and the third to dissolved energetic compounds (Pueblo Chemical Depot, Pueblo, Colorado). The demonstration-scale e-barrier applied to chlorinated solvents at F.E. Warren AFB will be discussed in this case study. Additional details can be found in Petersen (2003), Sale et al. (2005) and Gilbert et al. (2008).

17.4.1 Site Description

F.E. Warren AFB is about 7,000 acres in area. Surficial geology consists of shallow eolian and fluvial deposits underlain by the Ogallala Formation, which consists of interbeds of gravel, sand and silts with varying clay content. Through historical maintenance and disposal activities, chlorinated solvents (primarily TCE) have been released to the subsurface. The demonstration e-barrier was installed through a TCE plume (approximately 300 µg/L) to a depth of approximately 6 m (20 ft) below ground surface (Figure 17.8). Formation properties and other information is included in Table 17.3.

Figure 17.8. Installation of the e-barrier at F.E. Warren AFB.

Table 17.3. F.E. Warren AFB Site Characteristics

Parameter	Value	Units
Formation Porosity	0.25	
Hydraulic Conductivity	4.3	ft/day
Formation Seepage Velocity	0.37	ft/day
TCE Concentration	301	μg/L
Total Dissolved Solids	670	mg/L
pH	7.2	std. units
Chloride	78	mg/L
Nitrate	33	mg/L
Sulfate	56	mg/L
Bicarbonate	225	mg/L as $CaCO_3$
Calcium	140	mg/L
Potassium	3.7	mg/L
Magnesium	20	mg/L
Sodium	42	mg/L

17.4.2 Installation, Operation, and Monitoring

The demonstration e-barrier consisted of 17 individual modules (2 m by 0.3 m [6.6 ft by 1 ft]), each containing 3 Ti-mmo electrode panels (Figure 17.9). The three-electrode design was intended to allow polarity reversals without compromising electrode sequence. The approximately 17 m^2 (183 ft^2) e-barrier was installed using conventional trenching/trench-box methods (Figures 17.9 and 17.10). Backfill consisted of uncontaminated quartz-feldspar sand from a local source. This backfill had a hydraulic conductivity greater than that of the surrounding formation to ensure flow through the barrier.

Power was supplied to the e-barrier using line power and a variable voltage, 200 A single phase DC rectifier (Figure 17.11). The rectifier was intentionally oversized to allow testing of a wide range of applied potentials. Maximum current density measured during the demonstration was 6 A/m^2 (approximately 100 A total system requirement). Polarity reversals were conducted on a 12-hour per week (hr/week) schedule using a programmable logic controller (ABB, Cady, NC) and 180 A DC contactors (Albright, United Kingdom).

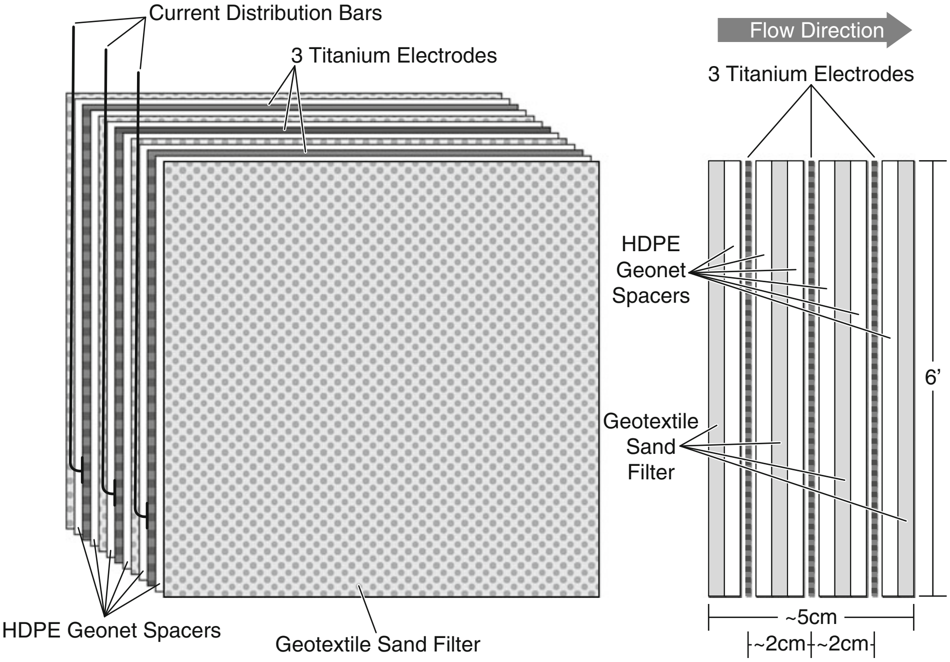

Figure 17.9. Schematic of the electrode assembly (from Sale et al., 2005).

Figure 17.10. Nine e-barrier modules prior to installation (from Sale et al., 2005).

Figure 17.11. Rectifier used for power to the e-barrier (Corrpower, Inc., Chardon, Ohio) (from Sale et al., 2005).

17.4.3 Performance Results

Effects on groundwater quality were defined using 144 sampling points located upgradient and downgradient of the e-barrier. TCE flux was reduced by 90–95% over the 18-month evaluation period (Figure 17.12), and flux reduction was shown to be dependent on applied potential. No adverse reaction intermediates were observed, with the exception of the apparent formation of chloroform at the center of the e-barrier. Plausible explanations include highly oxic conditions developed at the e-barrier and/or unanticipated reactions with the PVC pipe cement, which can be easily excluded from future systems. Additional information regarding this project, the e-barrier demonstration for energetic compounds in groundwater, and the e-barrier in general can be found at the ESTCP website (Project CU-0112: www.estcp.org).

17.5 CONCLUSIONS

Electrolytic reactive barriers are an emerging PRB technology that can be effective for treatment of aqueous chlorinated solvents and other groundwater contaminants. A field demonstration of e-barrier technology indicated that over 90% degradation of TCE can be achieved without formation of DCE or VC. A currently operating e-barrier is showing high levels of removal for energetic compounds. Costs associated with implementation and operation of the e-barrier are similar to those of other barrier technologies such as zero-valent iron PRBs. The sequential and modular nature of the e-barrier allows for treatment of a wide range of groundwater contaminants, including mixtures.

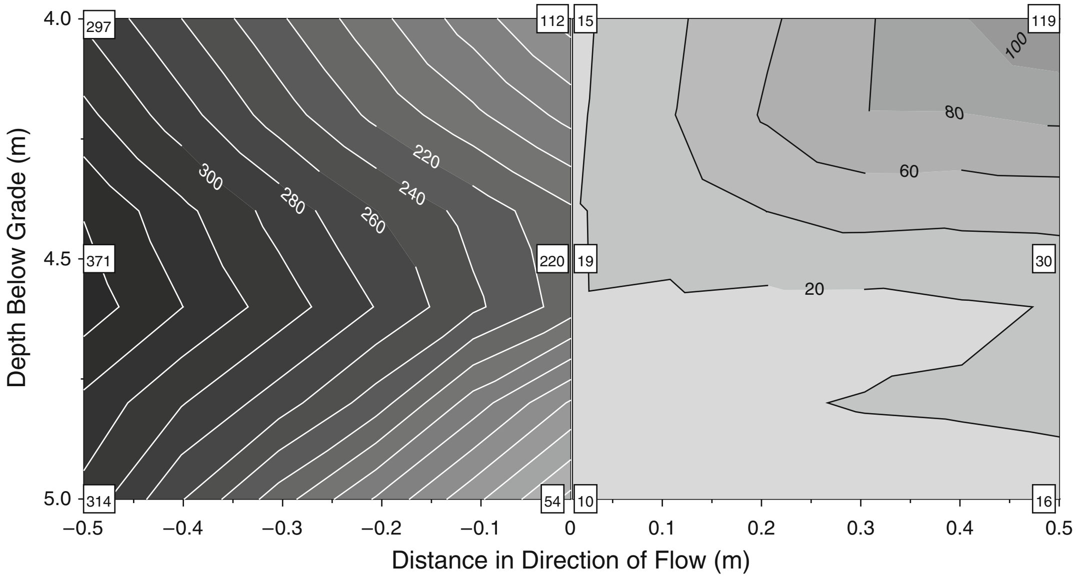

Figure 17.12. TCE concentration (μg/L) reduction through an e-barrier at 6.5 V applied voltage. The e-barrier is located at position 0 (from Sale et al., 2005).

The emerging nature of e-barriers as a plume treatment technology requires careful consideration of site-specific conditions (e.g., depth to plume, groundwater quality, availability of power, and treatment goals) prior to application of e-barrier technology. As new field demonstrations and applications are undertaken, the growing body of knowledge is expected to provide additional insights into the optimal installation methods and operational procedures, the contaminants that can be treated, and the long-term costs and performance of e-barriers.

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CHAPTER 18

IN-WELL TREATMENT FOR CHLORINATED SOLVENT REMEDIATION

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18.1 INTRODUCTION

The goal of this chapter is to provide an introduction to in-well technologies including the history of development, the basic principles of operation of groundwater circulation and in-well treatment processes, and the applicability and limitations of this class of technologies. In-well treatment technologies include a number of well configurations in which contaminants are removed from groundwater within the confines of the well as the water is pumped through the well. For most configurations, this is accomplished without pumping the water above ground for treatment. These systems mostly fall into the grouping of technologies termed groundwater circulation wells (GCWs) and most share a common design characteristic that includes at least two screened sections separated by a blank riser section. Groundwater enters the well through one or more screened sections, is treated, and then discharged back into the formation through the other screen(s), creating a circulation pattern within the aquifer that facilitates transport of contaminant to the well.

It does not make sense, for several reasons, to design in-well treatment systems for applications where the water is to be used for aboveground purposes, including (1) the inherent constraints of space limitations in the confines of the well, (2) difficulties in monitoring, optimizing and controlling the treatment process and (3) difficulties in achieving treatment goals because of short hydraulic residence times within the well casing. Currently, out-of-well treatment makes more sense for these cases; however, this may change as advances in catalytic systems continue to improve the kinetics of contaminant destruction.

The in-well technologies discussed herein represent a subset of the GCW technologies. Systems designed to deliver remedial agents to the aquifer to support *in situ* treatment will be discussed in a separate volume in this series (Kitanidis and McCarty, 2010).

In-well treatment is applicable at sites where groundwater can be circulated within/across a targeted contaminated volume of the aquifer, and for contaminants that are soluble and subject to advective transport during groundwater circulation. Chlorinated solvent plumes meet these criteria. In general, in-well treatment is not suitable for treating high molecular weight compounds or hydrophobic contaminants that strongly adsorb to aquifer solids, such as petroleum hydrocarbons and other oil-like substances.

In-well treatment has been successfully implemented for treating chlorinated solvents, including the chlorinated ethenes, ethanes and methanes. Successful applications have ranged from single well pilot-scale demonstrations to full-scale operations where designs ranged from single well configurations to nested systems with multiple wells placed and operated in opposing and/or complimentary modes. The selection of the appropriate configuration and the associated design criteria are dependent on site specific conditions and the negotiated remedial objectives.

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Two case histories are presented to provide real world information on system designs, performance, and costs. The information is focused on the predominant in-well treatment GCW configurations that have been deployed in the field at chlorinated solvent sites.

18.1.1 Background/History

In-well treatment technologies first entered the commercial market in the mid 1980s when IEG Technologies introduced their Unterdruck-Verdampfer-Brunnen (UVB) systems (Herrling et al., 1991a; Herrling et al., 1991b). These systems combined mechanical pumping with vacuum driven in-well air sparging (stripping) to pull water from the aquifer, remove volatile organic compounds (VOCs) from the water inside the well casing, and reinject the water back to the formation without bringing it above ground. The first systems were deployed at sites in Europe, and then introduced into the U.S. market in the early 1990s.

Simultaneous to the introduction of UVB technologies to the U.S., Stanford University was developing an air-lift in-well treatment system that would become the NoVOCs™ technology (Gvirtzman and Gorelick, 1992; Gvirtzman and Gorelick, 1993). The system was licensed to EG&G in late 1995. Around the same time Wasatch Environmental Inc. in Utah introduced a simplified air-lift in-well treatment technology known as the Density Driven Convection (DDC) technology (Schrauf et al., 1993). Both the NoVOCs™ and DDC systems injected air below the static water level in the well, which decreased the specific gravity of the fluid in the well relative to the water in the formation. This in turn caused the water in the well to rise, pulling water in from the formation through the lower section of the well. This method of pumping water, known as air-lift pumping, had been around for a long time and was frequently used for dewatering aquifers during construction (Powers, 1992). The use of the process to simultaneously strip contaminants was innovative. IEG Technologies followed with the development of their Koaxiale Grundwasserbeluftung (KGB) air-lift system (Battelle, 1995).

During the 1990s these four GCW configurations underwent extensive pilot-scale testing, which resulted in a better understanding of the underlying principles governing the performance of in-well treatment and the mechanics of groundwater circulation in aquifers using dual screen designs. The radius of influence and the single pass treatment performance were not as great as expected. Early "rules of thumb" design practices were gradually replaced by more sound engineering principles as the technologies matured. Intensive aquifer characterization, groundwater and contaminant transport modeling, tracer testing, and extensive sampling and contaminant analyses became crucial to effective implementation. The earlier demonstrations helped the development of more reliable designs and defined the bounds for the application of the technologies based on various contaminant and hydrogeologic conditions. Development and maturation of in-well treatment continued through the later part of the 1990s and into the early 2000s.

Since the early years of development and testing, several new in-well system configurations have entered the market. Reactive well technologies introduced in 1998 by the Department of Energy (DOE) Pacific Northwest National Laboratory evolved from the work done with zero-valent and pallidized iron (Gilmore et al., 1998a; Gilmore et al., 1998b). Researchers at the DOE Lawrence Livermore National Laboratory (LLNL) and Stanford University developed an in-well treatment technology based on the NoVOCs™ well design that incorporated catalytic reductive dehalogenation (CRD), using dissolved hydrogen as a reducing agent in the presence of a palladium-on-alumina catalyst (McNab et al., 2000; Lowry and Reinhard, 2001). The rapid reduction reaction kinetics of the CRD process allowed for the development of compact reactor designs that fit within the well bore. The technology was successfully pilot tested at a site at LLNL (McNab et al., 2000). However, in a second demonstration funded by the Department of Defense (DoD) Environmental Security Technology Certification Program (ESTCP) and conducted at

Edwards Air Force Base (AFB), California, the system was never placed *in situ* presumably due to higher maintenance costs (ESTCP, 2007). The performance of the catalyst was verified and the technology holds promise, but at this time, the well design may require improvement to reduce maintenance costs and effectively incorporate the process into a reliable *in situ* application.

18.1.2 Current Status of the Technology

Although in-well treatment technologies continue to be modified and improved, they are currently being applied at full scale to treat a wide variety of VOCs, including chlorinated solvents, and site closures are being reported (Wasatch Environmental, 2005; IEG Technologies, 2008). In-well technologies are being marketed by the developers or through engineering firms that are licensed by those developers. Additionally, simpler air-lift systems, such as the configuration tested at Tyndall AFB, can be deployed that do not require licensing agreements, provided that the patents held by the packaged systems are not violated (Battelle, 1995).

18.1.3 Well System Designs

In-well treatment systems can be divided into two broad classifications, air-lift and mechanically pumped systems, based on the way they move water. Figure 18.1a shows a schematic view of a mechanically pumped system. This class of system includes submersible pumps to move the water, and configurations are available that include an air stripping reactor or one of the other treatment processes discussed later in this chapter. A typical air stripping configuration is shown in Figure 18.1b. As previously discussed, air-lift systems inject air to decrease the density of the water in the well casing relative to the water in the formation, which causes the water in the well to rise, pulling in water through the bottom of the well. Air stripping provides the majority of the treatment within the well and additional treatment in the formation is possible if the contaminants are susceptible to aerobic biodegradation, as may be the case for *cis*-1,2-dichloroethene (*cis*-DCE) and vinyl chloride (VC). More detailed information on these two pumping methods is provided in Section 18.2.1.

While numerous in-well treatment configurations have been reported during development of the technology, and custom designs can be developed for a given site, the UVB/KGB and related configurations, the DDC, and more recently Accelerated Remediation Technologies ART In-Well Stripping Technology (Pucke et al., 2004), are currently the most commonly applied technologies. The reactive well systems appear to hold promise but, to date, these systems have not been deployed at full-scale. However additional field deployments should lead to increased acceptance of this innovative configuration. Table 18.1 lists several of the more commonly deployed in-well systems currently on the market, along with some of the key features and design/operating characteristics that make the systems unique.

18.1.4 Patent/Licensing Issues

Since the inception of in-well treatment technologies, developers have filed numerous patent applications to protect specific features of their designs and/or aspects of their processes that are considered unique. However, the methods for moving groundwater (i.e., air-lift or mechanical pumping) are not patented processes, nor are most of the in-well treatment processes. Most patents cover specific components/features of the specific design, which the developers determined improves their system's performance and makes their system unique. Patent infringement must be considered when using non-licensed vendors and/or when designing an in-well treatment system for a given site without paying the royalties associated with the standard and patent protected configurations.

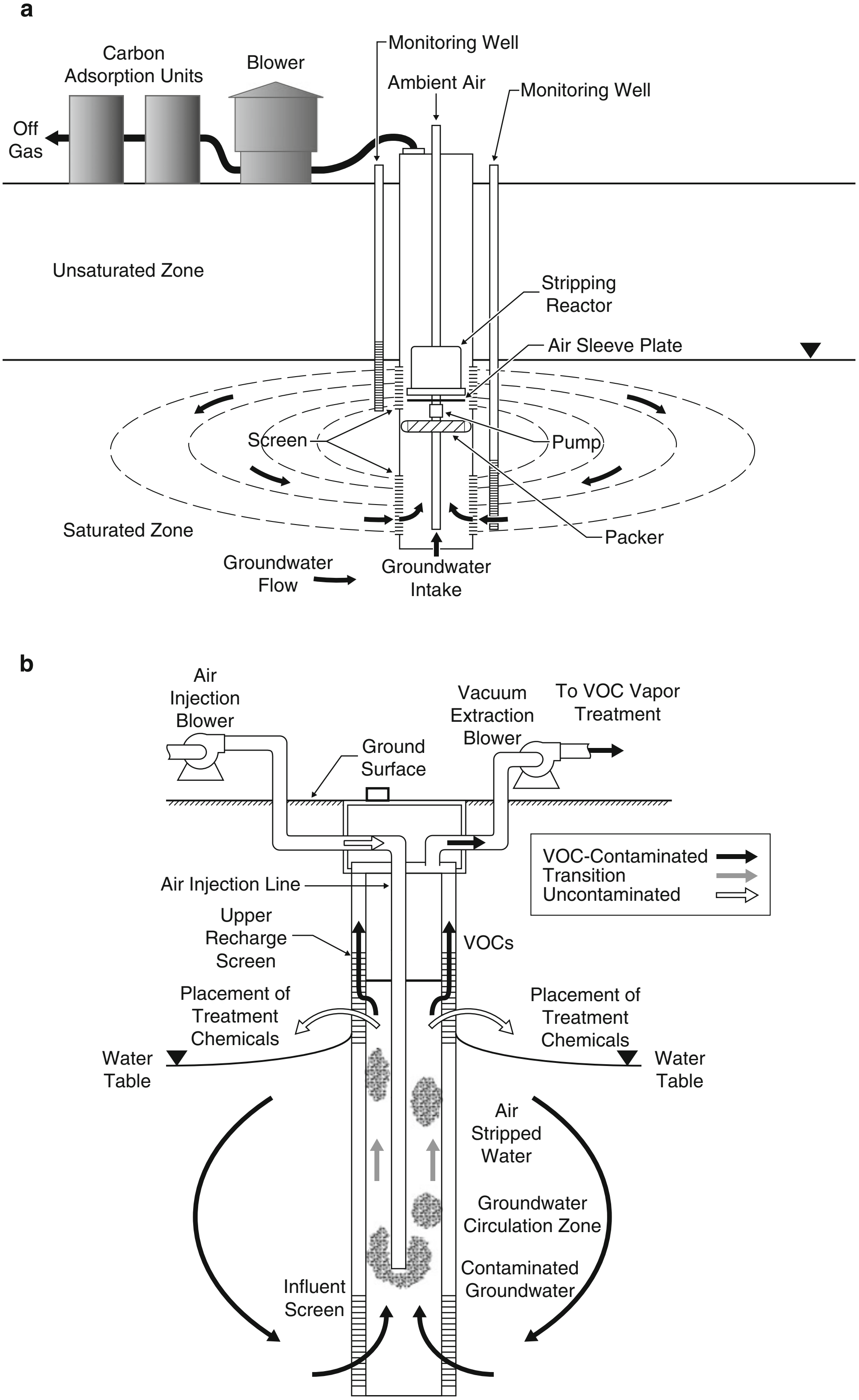

Figure 18.1. Schematics of (a) a mechanical pump configuration and (b) an air-lift configuration (Van Deuren et al., 2002; USEPA, 1999).

Table 18.1 Selected In-Well Treatment System Configurations and Key Features

Treatment System	Key Features
UVB Adventus Americas, Inc. 2871 W. Forest Road - Suite 2 Freeport, IL 61032	Typical system includes a double-screened well with a submersible pump and packer assembly to move groundwater and create a circulation pattern in the aquifer, a negative pressure air stripping reactor to remove VOCs as the groundwater passes through the well, an aboveground blower to power the stripper, and an off-gas treatment system such as activated carbon filters. UVB configurations include wells with more than two screens to create more than one circulation cell. UVB systems are referred to as "vacuum vaporizer wells" because the pressure in the well is kept below ambient during operation.
mGCW-R Adventus Americas, Inc. 2871 W. Forest Road - Suite 2 Freeport, IL 61032	Incorporates controlled release carbon material (EHC™) and zero-valent iron. The media are placed in filter packs inside of the intake well screen, outside the inner well casing and inside an outer well casing at the discharge end of the well, and in optional infiltration trenches if increased treatment capacity is needed. Groundwater is drawn from the formation through the influent screen filter pack and discharged back to the formation through the effluent screen and associated infiltration trenches without being brought above the ground surface.
DDC Wasatch Environmental, Inc. 2410 West California Ave. Salt Lake City, UT 84104	Air-lift system that typically includes a two-screen well with an air injection tube inserted below the water level, a blower, and aboveground off-gas treatment system. For aerobically biodegradable contaminants, the off-gas is discharged directly into the vadose zone through the upper well screen. Applications for chlorinated solvents most commonly require off-gas collection and treatment.
ART Accelerated Remediation Technologies, LLC. 10100 W 87th Street, Suite 204 Overland Park, KS 66212	A combined air-lift and mechanically pumped system that includes a two-screen well and incorporates vapor extraction. The air-lift pumping draws water in through a lower screen and recharges water through an upper screen. A submersible pump placed at the bottom of the well pumps water to a spray head located above the water level inside the well. Contaminants are stripped by both the air lift and the spraying action combined with the countercurrent air flow imparted in the well headspace by the vapor extraction component. The negative pressure exerted by the vapor extraction creates additional water lift.
NoVOCs™ There is no current license holder for this technology	Air-lift system that typically includes a two-screen well with an air injection tube, a deflection plate near the water table to induce coalescence of the bubbles, and an aboveground off-gas treatment system to remove stripped contaminants prior to atmospheric discharge of the vapors from the well. NoVOCs™ systems inject air into the well at depth, which creates an airlift pumping action that serves to move groundwater while simultaneously stripping volatile contaminants from the water passing through the well.

18.2 PRINCIPLES OF OPERATION

Currently, in-well treatment systems employ some form of groundwater circulation well to pull groundwater in through one screened section of the well and discharge the treated water through a separate screened section. This establishes a 3-dimensional (3-D) circulation pattern in the aquifer without pumping water above the ground surface. The geometry of the circulation pattern depends on the operational modes of the individual wells, the placement of nested or multiple wells, and the hydrogeologic properties of the aquifer.

In-well treatment systems can be configured with upward in-well flow (upflow) or downward in-well flow (downflow) depending on site requirements, including the type and distribution of contaminants. Figure 18.2 is a generalized schematic showing the flow schemes for each operating mode in a single dual screen well. Background groundwater flow tends to distort the circulation patterns, with the degree of distortion a function of the groundwater velocity. Figure 18.3 illustrates this effect on an upflow system (Herrling et al., 1991a). Figures 18.3b and 18.3c suggest that increasing background flow velocities can cause a decrease in the radius of the flow field. This has a direct impact on the GCW-induced circulation cell and dictates the GCW spacing required for effective system design. The effect of groundwater flow on downflow systems would be similar to those illustrated.

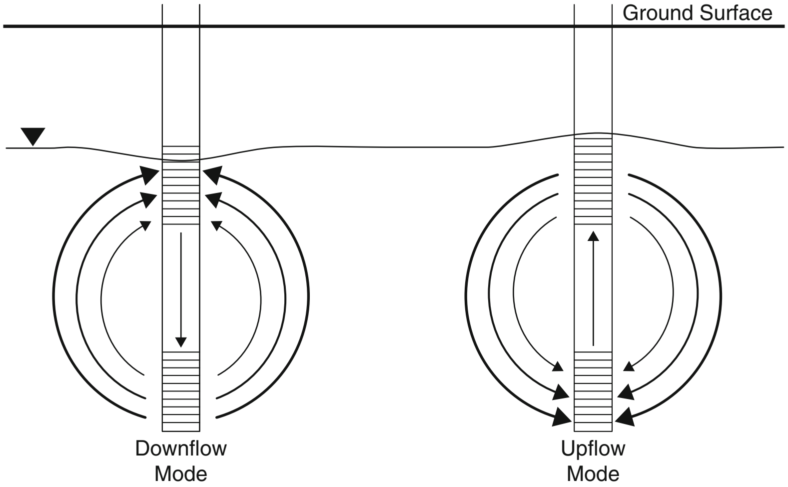

Figure 18.2. Generalized schematic of downflow and upflow groundwater circulating wells.

Figure 18.4b illustrates results from numerical simulations showing the effect on the circulation pattern with two GCW systems operating in the same mode and placed close enough to affect each other (Herrling et al., 1994). This type of well placement may be necessary to treat a volume of aquifer that is greater than the volume that could be effectively circulated/treated by a single well (Figure 18.4a), or to develop an effective capture zone for controlling plume migration. The strong vertical circulation between the two wells may prove beneficial for highly contaminated areas near a source if the water moving in the vertical direction crosses less permeable strata to pick up and transfer contamination to the treatment well that strictly horizontal flow would circumvent (Herrling et al., 1994).

18.2.1 Methods of Pumping Groundwater

As discussed in Section 18.1.3, the majority of in-well treatment systems utilize one of two methods for inducing groundwater circulation: mechanical or air-lift pumping.

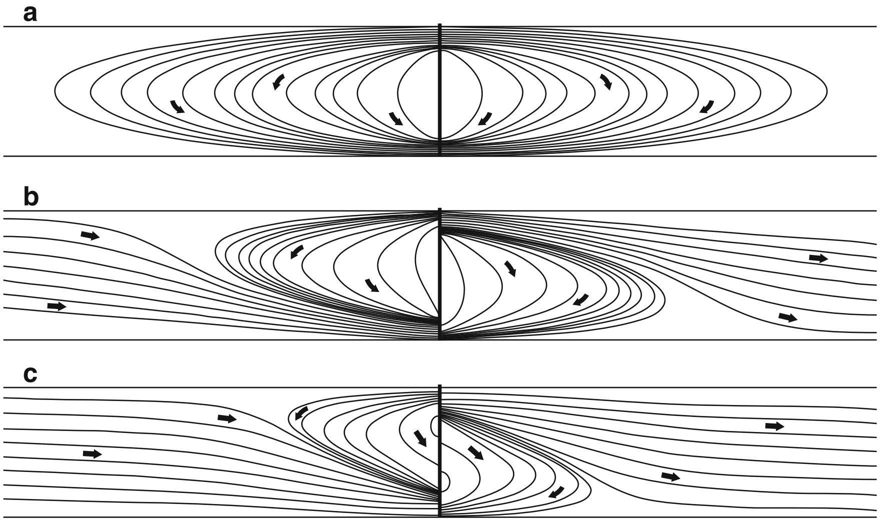

Figure 18.3. Idealized circulation pattern around an upflow GCW system with horizontal groundwater velocities of (a) 0.0 meters/day (m/day), (b) 0.3 m/day, and (c) 1.0 m/day (from Herrling et al., 1991a).

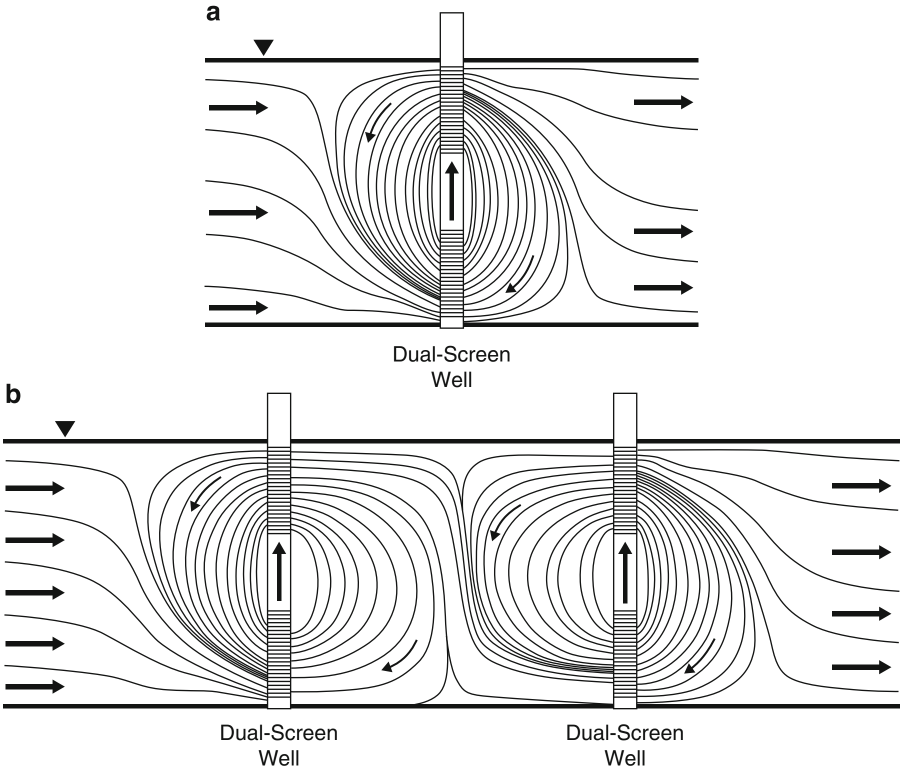

Figure 18.4. Numerical simulation showing the circulation pattern around (a) a single GCW system and (b) two GCW systems (adapted from Herrling et al., 1994).

18.2.1.1 Mechanical Pumping

Certain in-well designs incorporate centrifugal groundwater pumps in their designs to move groundwater through the wells. These systems often include packers placed within the well to hydraulically separate the two screens and prevent short circuiting within the well volume. Mechanical pump systems can move groundwater with minimal impact on geochemistry compared to their air-lift counterparts. These designs can operate in either an upflow or downflow mode by reversing the pumps or orienting them accordingly during well construction).

18.2.1.2 Air-Lift Pumping

Air-lift designs incorporate an air line that extends to some depth below the water level in the well. Air or gas mixtures without oxygen are injected through the line depending on the type of treatment for which the system is deployed. The injected gas mixes with the water and causes a decrease in the specific gravity of the fluid (Powers, 1992). The difference between the weight of the air-water fluid within the well and the water in the formation outside the well causes the water in the well to rise. As the water rises, the displaced water in the bottom of the well is replaced by water drawn in from the formation. Air-lift systems are operated exclusively in an upflow mode. More detailed information on air-lift pumping is available from other sources (Stepanoff, 1965; Govier and Aziz, 1972; Clark and Dabolt, 1986; Morrison et al., 1987; Gvirtzman and Gorelick, 1992; Alimonti and Galardini, 1992; Francois et al., 1996).

18.2.2 Treatment Methodologies

In-well treatment processes that have been used to treat chlorinated solvent contaminants include air stripping, activated carbon adsorption, biodegradation, chemical oxidation and reactive media decomposition using either zero-valent iron- or palladium-based catalysts. Effective in-well treatment requires that contaminants are adequately soluble and mobile to facilitate transport from the aquifer to the well during groundwater circulation. Selection of the in-well treatment method is contaminant, site, and system-configuration specific. Contaminants that cannot be mobilized effectively to the well must be treated in the aquifer.

18.2.2.1 Air Stripping

The most commonly applied in-well treatment methods are some form of air stripping. Air stripping long has been used effectively for aboveground treatment of water and wastewater containing volatile contaminants. Several in-well system configurations use mechanical pumping with in-well air stripping, while others inject air at depth below the static water level to both drive groundwater circulation using air lift, and to simultaneously strip volatile contaminants. Systems that couple air-lift pumping with in-well air stripping balance the operation of these two mechanisms for optimum performance. Systems that utilize mechanical pumping can effectively optimize groundwater pumping and air stripping separately. The air stripping process removes volatile organic compounds and aerates the water prior to discharge from the well system.

Air stripping is a phase transfer process where volatile contaminants are transferred from the aqueous phase to the vapor phase. The transfer effectiveness is a function of the temperature of the two phases, the total pressure in the system, and molecular interactions occurring between the contaminants and the water (Montgomery, 1985). Henry's Law describes the partitioning of a contaminant between the water and gas phases at equilibrium. The partitioning can be calculated by combining Henry's Law with Dalton's Law according to Equation 18.1 (Montgomery, 1985):

$$Y_i = \frac{X_i H_i}{P_T} \qquad \text{(Eq. 18.1)}$$

where: Y_i = the mole fraction of compound in the gas phase
X_i = the mole fraction of compound in the water phase
H_i = the Henry's Law constant
P_T = the total system pressure

In general, compounds with a higher Henry's Law constant are more easily stripped from water than compounds with lower Henry's Law constants. Table 18.2 contains Henry's Law constants for a list of organic compounds that can be readily air stripped. If the Henry's Law constant for a given contaminant and the total system pressure are known, the above relationship can be used to determine the equilibrium partitioning between gas and water phases during air stripping. Equilibrium is constrained by the laws of mass transfer and the residence time; bubble sizes associated with in-well treatment systems often result in lower vapor phase concentrations than Equation 18.1 would indicate.

Table 18.2. Henry's Law Constants (atm·m^3/mol) for Selected Organic Compounds

Compound	Henry's Law Constant	Compound	Henry's Law Constant
Chloroform	0.0029[1]	Perchloroethene	0.023[2]
Carbon Tetrachloride	0.0302[1]	Trichloroethene	0.0103[2]
Chlorobenzene	0.00445[1]	1,1-Dichloroethene	0.0154[2]
1,2-Dichlorobenzene	0.0024[1]	*cis*-1,2-Dichloroethene	0.0075[2]
1,3-Dichlorobenzene	0.0047[1]	*trans*-1,2-Dichloroethene	0.0066[2]
1,4-Dichlorobenzene	0.00445[1]	Vinyl Chloride	0.695[2]

Sources: [1]Montgomery and Welkom, 1990; [2]Arthur D. Little, Inc., 1987

Typical air stripper performance is controlled and optimized by adjusting the air-to-water ratio, which is easily controlled in systems that operate the pump and the stripper independently. Optimizing the treatment efficiency of in-well systems that utilize air-lift pumping to drive groundwater circulation and VOC stripping requires balancing the two processes. The air injection rates and bubble size to optimize air-lift pumping may not be the same as needed to maximize air-stripping efficiency. As a result, air-lift systems may not have the same treatment efficiency for a single well pass as the mechanical pump systems that can incorporate higher air to water ratios and utilize more optimal bubble sizes, although air-lift systems may afford other operational and design advantages over mechanically pumped in-well treatment designs under site-specific circumstances. More detailed information on the theory of air stripping and design procedures for air stripping systems can be found in Canter and Knox (1986), Montgomery and Welkom (1990) and Gvirtzman and Gorelick (1992).

18.2.2.2 Activated Carbon Adsorption

Activated carbon is commonly used in water and wastewater treatment, usually as a polishing step, and also for vapor phase treatment of off-gas from phase transfer treatment unit processes such as air strippers. Most times, the use of activated carbon with in-well treatment systems is for off-gas treatment; however, there are configurations that deploy aqueous phase carbon filters inside the well (Allmon et al., 1999). Contaminated groundwater enters the well, flows through the filter and contacts the carbon, and then is discharged back to the formation.

Activated carbon adsorption, like air stripping, is a phase transfer process in which a contaminant is transferred from the aqueous phase to the solid phase (i.e., the surface of the carbon substrate). Adsorption is the physical/chemical process of accumulating contaminant molecules at a solid/liquid interface. For in-well treatment, the contaminant is referred to as the "adsorbate" and the activated carbon as the "adsorbent."

Adsorption is driven by attractive forces between the adsorbate and the surface of the adsorbent. These forces can result in two types of adsorption, termed "physical" or "chemical" adsorption. Physical adsorption is promoted by weaker electrostatic forces such as hydrogen bonding and London-van der Waals forces and by hydrophobic interactions. Often, physical adsorption is a reversible process and a "feedback" phenomenon can occur if the adsorbate concentration in the aqueous phase decreases to below the equilibrium concentration.

Chemical adsorption, often referred to as "chemisorption," is promoted by stronger electrostatic forces that resemble covalent or electrostatic bonding between two atoms (Montgomery, 1985). Chemisorption typically occurs at specific sites on the surface of the activated carbon, and may be strongly influenced by specific functional group types and densities. In general, chemisorption is less reversible than physical sorption.

The adsorptive capacity of activated carbon is dependent on the properties and concentration of the adsorbate and on temperature and pH (Metcalf and Eddy, 1991). The adsorptive properties of activated carbon for a given contaminant are modeled using isotherm approaches that fit different equations to empirically derived data. The most commonly applied isotherm model used to describe activated carbon adsorption of chlorinated solvents is the Freundlich isotherm (Equation 18.2).

$$C_s = K_f C_e^{1/n} \qquad \text{(Eq.18.2)}$$

Where:

C_s = mass of adsorbate per unit weight of carbon at equilibrium
C_e = the equilibrium concentration of contaminant remaining in the water at equilibrium
K_f and n = empirical constants

K_f and n are determined using Equation 18.3 by plotting C_s versus C_e.

$$\mathrm{Log}(C_s) = \log(K_f) + 1/n(\log(C_e)) \qquad \text{(Eq.18.3)}$$

Table 18.3 lists Freundlich isotherm parameters for selected chlorinated organic compounds and indicates their relative sorptive capacity. In general, activated carbon adsorption is an effective treatment process for all of the compounds listed in Table 18.3. For more in-depth information on activated carbon adsorption theory and design, see Montgomery (1985) and Metcalf and Eddy (1991).

18.2.2.3 Biodegradation

In-well treatment systems that incorporate bioreactors in their designs have been deployed in the field (Buermann and Bott-Breuning, 1994; Lakhwala et al., 1995; Lakhwala et al., 1998; USEPA, 1998). The reactors are fixed-film configurations, available in either a spiral wound membrane or an activated carbon support medium configuration. The indigenous microorganisms from the aquifer colonize the reactor as groundwater is circulated through the well, or the reactors can be inoculated with a culture of organisms with a specific degrading capability. For indigenous organisms, once a sufficient population of the microorganisms develops, biodegradation occurs as the water passes through the reactor.

Table 18.3. Relative Sorption Capacity and Freundlich Isotherm Constants for Chlorinated Solvent Compounds

Sorption Capacity	Compound	Freundlich Constants[(1)]	
		K (mg/g)(L/mg)$^{1/n}$	1/n
High	Perchloroethene	51	0.56
	Trichloroethene	28	0.62
	trans-1,2-Dichloroethene	14	0.45
	cis-1,2-Dichloroethene	12	0.59
	Carbon Tetrachloride	11	0.83
	1,1,2,2-Tetrachloroethane	11	0.37
	1,1,2-Trichloroethane	5.8	0.60
	1,1-Dichloroethene	4.9	0.54
	1,2-Dichloroethane	3.6	0.83
	Chloroform	2.6	0.73
	1,1,1-Trichloroethane	2.5	0.34
	1,1-Dichloroethane	1.8	0.53
Moderate	Vinyl Chloride	Not Reported	
	Methylene Chloride	1.3	1.16

[1] USACOE, 2001

18.2.2.4 Reactive Media Catalyzed Decomposition

The most recent in-well treatment advances are the reactive media catalyzed systems that include placement of a catalyzing medium into the well design. Two reactive media have been tested at small scale including palladized zero-valent iron and hydrogen/palladium (Gilmore et al., 1998a; Gilmore et al., 1998b; McNab et al., 2000; Lowry and Reinhard, 2001). The latter technology uses electrolytically generated hydrogen to chemically reduce the halogenated compounds in the presence of the catalyst. Hydrogen is generated in the well by placing a direct current across sets of electrodes. Hydrogen is generated at the cathode and oxygen at the anode. Groundwater mechanically pumped into the well is “hydrogenated” by electrolysis, then passes through the catalyst bed, and passes the anode prior to reinjection. The in-well reactor configuration is a packed bed of catalyst material contained in a cylinder. Chlorinated solvents are catalytically dehalogenated by the hydrogen, resulting in a non-halogenated backbone and chloride ion. Additionally, electrosomatic transport of contaminants toward the cathode contributes to contaminant removal. The wells can be placed in arrays in pairs, or one anode well may be used with a plurality of cathode wells. The direct current flow between electrode wells may be periodically reversed to control the formation of mineral deposits and to rejuvenate the catalysts.

18.2.2.5 Ozonation

Ozone (O_3) is a strong oxidant that has proven effective for oxidizing chlorinated solvents (Nimmer et al., 2000; Siegrist et al., 2000). Ozone can directly oxidize organic contaminants, or ozone can “decompose” and form free radicals, such as hydroxyl radicals, that are nonselective oxidizers that rapidly attack certain organic contaminants. Ozone sparging has been demonstrated effective for treating chlorinated solvents in groundwater. Incorporating ozone into in-well treatment systems is recognized as possible (USEPA, 1998). The Kerfoot Technologies, Inc. C-Sparge™ system is an air-lift in-well treatment system that has the option of incorporating aquifer ozone sparging. Because the sparging takes place outside the well, this system is not considered a true in-well system and hence is not covered in this chapter. Incorporating ozonation into air-lift in-well treatment systems may not be practical due to the inherent inefficiencies of mass transfer in the well and the need to ensure destruction of unreacted ozone before discharge to the atmosphere, but should be considered and evaluated on a case-by-case basis. Consideration must be given to the need to generate ozone on site. Generation requires an air/oxygen source and electrical power, and the corrosive properties of ozone gas require resistant materials for well construction.

18.3 APPLICABILITY AND LIMITATIONS

In-well treatment for dissolved phase chlorinated solvent plumes may be appropriate provided that the contaminant(s) can effectively be transported to the well. All of the configurations listed in Table 18.1 have been field demonstrated to be effective for chlorinated solvents; however, there are general limitations on the applicability of all in-well designs that must be taken into account when considering their implementation at a given site. In general, the following factors may limit the applicability and effectiveness of in-well treatment processes.

- Air-lift and air-stripping systems transfer the contaminants from the aqueous phase to the gas phase in the well. Further treatment in the formation may or may not occur depending on the aerobic biodegradability of the specific contaminant(s), the availability of cometabolites, the presence of necessary microorganisms, and other geochemical and microbiological requirements.
- Air stripping is more effective for contaminants with higher Henry's Law constants, and for higher contaminant concentrations. Low cleanup goals and low Henry's Law constants will likely require multiple passes and longer remediation times.
- Air stripping systems can suffer catastrophic fouling due to precipitation of oxidized metals and/or biofouling. Catalytic systems can suffer fouling of the catalyst surface, premature passivation, and/or biofouling. In either case, it is necessary to understand the geochemistry and microbiology of the aquifer to predict how the system will be affected by potential changes over time.
- Shallow aquifers may require an excessive number of wells, as the extent of influence from each well is a function of both well screen length and separation.
- The nature of the circulation patterns imparted by multi-screened wells can result in spreading or smearing of the contamination. This can cause problems at sites containing nonaqueous phase liquids (NAPLs), and consideration should be given to removing the NAPL prior to implementing in-well treatment of the dissolved phase part of the plume.
- Effective circulation is generally limited to sites with horizontal hydraulic conductivities (K_H) greater than 10^{-5} centimeters per second (cm/sec) (0.028 feet per day [ft/day]). Sites with low-conductivity lenses may not achieve the desired vertical component of circulation with a single well system or multiple wells operating under the same mode, but these sites may benefit from nested wells that operate in opposing modes.
- In-well treatment systems may not be efficient at sites with high groundwater velocities due to groundwater flowing through and/or around the capture zone.

In-well treatment systems that rely on groundwater circulation to transfer contaminants to the well require detailed site characterization to define the expected flow field, accurately model contaminant transport to the well(s), and predict cleanup timeframes. Figure 18.5 is a generalized flow diagram that considers several site characteristics that are crucial for successful implementation of in-well treatment systems. The decisions focus on aquifer and plume characteristics that affect the ability to achieve groundwater circulation with the dual-screened well systems. It is important to note that this generalized approach is designed to indicate caution more that to serve as a final screening tool. Those decisions necessarily rely on site-specific conditions and considerations and are best made by qualified environmental professionals. The following discussion describes the variables in Figure 18.5 as well as some of the more relevant site characteristics and system operating parameters that must be taken into account in determining site characterization data requirements for technology selection and design purposes.

The effectiveness and rate of contaminant transport from the aquifer to the well depends on the volume and rate at which groundwater can be circulated by the well system, on physical properties of the aquifer including permeability, hydraulic conductivity, and heterogeneity, and on specific properties of the contaminant including its water solubility and sorptive capacity (degree of partitioning) onto the aquifer solids. The pumping rate determines the groundwater recirculation rate, and thereby the rate of mass transfer to and from the well. Site-specific considerations that determine the applicability of in-well treatment systems include:

- Hydraulic conductivity determined in both the horizontal (K_H) and vertical (K_V) directions
  - Impermeable soils will result in slow, restricted groundwater recirculation, while highly permeable soils may result in short circuiting.
  - Anisotropic soils where $K_H > K_V$ are desirable to promote horizontal groundwater flow.
  - Impermeable layers (aquitards) between the upper and lower well screens could hinder or prevent the flow of groundwater between the upper and lower well screens but could facilitate communication between nested wells.
- Depth to water table and thickness of the aquifer
  - The submergence (the ratio of the well depth below the water table to the total depth below the ground surface) must meet the minimum requirements to ensure adequate groundwater circulation.
- Pumping rate through each well
  - Well-induced groundwater recirculation flow rates must overcome background groundwater flow.

Each of these parameters, the horizontal and vertical hydraulic conductivities, the length of the screens and the spacing between the sections, and the pumping rate combine to determine the volume of aquifer that can be treated, and the rate at which water can be moved to the well. These values and other design criteria are determined from site-specific tests, not estimated values.

Geochemistry also has an effect on the long-term operation and success of in-well treatment systems, with the degree of impacts dependent on the physical, chemical, or biological processes being employed. For example, if water entering a well contains little or no oxygen and groundwater constituents are in their reduced state, air lift pumping and/or air stripping could result in oxidation and precipitation reactions which could adversely impact the continued operation of the system. One of the more common problems for in-well treatment technologies that aerate groundwater is reduced iron, which when oxidized can precipitate and clog well screens and other well components. Added to this is the potential for biological fouling due to aerobic growth, which can cause similar clogging problems. Systems that do not aerate the water have a lower potential for such clogging.

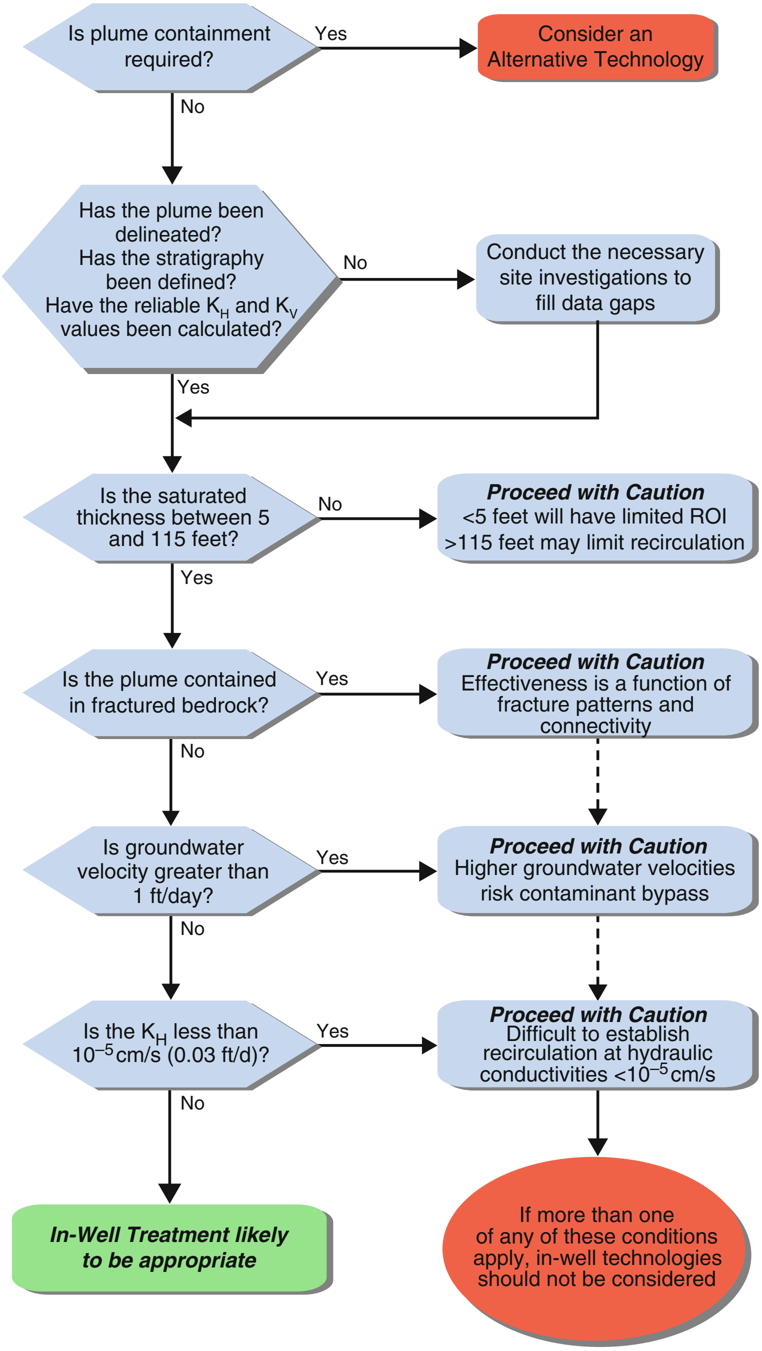

Figure 18.5. Generalized flow diagram for screening in-well treatment implementation based on key aquifer and plume characteristics.

Another example of how the geochemistry can affect in-well treatment system performance is the reduction in infiltration capacity caused by the salinity and/or sodium content of the water commonly encountered in arid environments. The higher the sodium content of the water, the more likely soil particles will separate and cause plugging issues. In these cases, the reinjection zones around the treatment wells should be chemically treated with calcium, which will displace the sodium and minimize plugging. This practice is used in irrigation in arid regions where infiltration is promoted by adding gypsum.

Each in-well treatment process has inherent advantages and limitations. In-well air stripping has the advantage of being able to be deployed in a variety of well sizes and thus relatively small, inexpensive wells can be used. However, in-well air stripping effectiveness is limited by the volatility of the contaminants and the air/water contact within the well. Air stripping is most efficient when fine bubbles are used, while air-lift pumping is most efficient when larger diameter bubbles are used. The use of larger air bubbles to meet the need of the air-lift pump reduces the air stripping capacity, and a larger well size may be required to meet the air stripping requirements. The coalescence of finer air bubbles as they rise in the well can decrease the stripping efficiency. In addition, the contaminated air stream must be treated with granular activated carbon (GAC) or alternative methods, or be injected into the vadose zone where the contaminants can be biologically degraded before reaching the atmosphere. GAC treatment of the off-gas usually is conducted above ground and adds to the capital and operating costs of the in-well process. *In situ* off-gas treatment in the vadose zone requires (1) that the contaminant be aerobically biodegradable and (2) that there is sufficient depth in the vadose zone to provide the required residence time.

In-well GAC treatment generally requires larger well diameters to provide the space (i.e., hydraulic residence time) required to meet the kinetic constraints of adsorption. The GAC must be able to be easily removed and replaced. GAC disposal and replacement will add to the long-term operating costs of in-well treatment.

18.3.1 Biological Treatment

In-well biological treatment, as with any bioreactor technology, requires that the hydraulic residence time in the bioreactor be sufficiently long enough to meet degradation kinetic constraints. Depending on the specific bioreactor configuration, which in turn dictates the amount of viable biomass retained, larger well diameters are often required. If contaminants are not effectively treated within the hydraulic residence time, multiple passes will be required, which can add to the operating costs and/or the time required to achieve the cleanup goal.

18.3.2 Short Circuiting of Groundwater Flow

The potential for short circuiting of groundwater flow, either within the well or between the screened sections in dual-screen configurations is a physical constraint of in-well treatment systems. Short circuiting will significantly decrease radial flow from the well in the formation, which will decrease the contaminant transfer rate/efficiency and increase the time required to achieve the remedial objective. Leaking packers and improperly grouted or packed boreholes can cause short circuiting within the well or in the formation within the immediate vicinity of the well, respectively.

Well construction and adequate grouting in the borehole are essential to the physical and hydraulic separation of the injection and withdrawal portions of the well. A continuous sand pack in the borehole would provide no physical or hydraulic separation between these two areas, allowing water to be transmitted within the borehole without traveling through the aquifer matrix. Short circuiting may also occur due to isotropic conditions in the aquifer, in which the vertical permeability of the aquifer materials is the same as the horizontal permeability. In this situation, the driving force for horizontal flow away from the treatment well is limited and flow is likely to proceed directly from the area, or screen, of injection to the area, or screen, of withdrawal.

Short circuiting can be evaluated by measuring the "communication time" between injection and extraction points, through the use of conservative tracers. Communication times even between screens within the same well can range from minutes to days, depending on the site anisotropy/stratigraphy, the distribution of the injected water within the formation, and the integrity of the seal in the annulus between the screens. The rapid appearance of tracers at extraction points can indicate significant short circuiting. For example, in a study at Tyndall AFB, Florida, conducted to evaluate the feasibility of coupling the GCW technology with bioventing, Battelle (1995) reported a communication time of less than 2 minutes between the upper and lower screens in an air-lift system with 1.5 m (5 ft) of separation between the upper and lower screens placed in homogeneous coarse sand. The communication time along the outer flow lines of the circulation cell was on the order of weeks. This difference in times means that the water close to the well was treated many times before the water towards the outer fringes of the circulation cell was treated once.

18.4 HEALTH AND SAFETY CONSIDERATIONS

In addition to the health and safety issues associated with working at sites with elevated concentrations of chlorinated solvents, in-well treatment systems introduce additional considerations that are configuration specific and must be considered in the development of the site Health and Safety Plan.

Air-lift systems produce off-gas containing the stripped chlorinated solvents, which is most commonly treated above ground. Depending on the aqueous concentrations entering the well and the stripping efficiency, contaminant concentrations in the off-gas can exceed the allowable exposure limits. Care must be taken to protect workers near the well and to ensure that people working or living nearby are not exposed to levels above permissible exposure limits.

Activated carbon systems concentrate contaminants on the carbon surface. Safety procedures must be used to minimize worker exposure during removal of exhausted carbon from wells in preparation for shipping for disposal/regeneration. When a carbon filter is removed from the well, contaminants can volatilize to create a breathing hazard, and direct contact with the carbon can result in dermal exposure. Proper personal protective equipment should be worn when changing out the carbon filters.

Biological systems are not pure culture systems and there is always the potential that the reactor has promoted the growth of pathogens. As such, any work on the well system where the workers might be exposed to biomass from the bioreactor should be done to minimize the potential for inhaling, ingesting or contacting cuts or abrasions. Worker awareness is critical to avoid exposure. For example, an unusual odor may prompt people to hold their nose close to the source to investigate the odor. This could result in inhalation of a pathogen, which could lead to illness. Workers should be trained in the proper handling procedures for biological materials.

Ozone is a corrosive gas that can cause severe irritation of the respiratory tract if inhaled, as well as irritation to the eyes. Ozone injection creates a positive pressure in the well, which must be allowed to dissipate before the well or plumbing system is opened to minimize worker exposure to unreacted ozone and/or unreacted contaminants or their byproducts. Additionally, because the system is under pressure, there is always the potential for leaks. The system should be checked for such leaks to protect workers from exposure and to ensure that the ozone is delivered to the groundwater where it can react.

18.5 SITE CHARACTERIZATION REQUIREMENTS AND SYSTEM SELECTION

Existing site data from monitoring wells and soil borings provide useful information for the initial phase of site characterization. Additional wells and/or borings may be needed to fill data gaps. Existing monitoring wells should be resampled if the data from the last sampling event is older than 3 to 6 months. Intact formation samples should be collected to provide an accurate assessment of geological conditions and to identify or estimate hydrogeological properties of the aquifer. Samples can be collected to chemically characterize the saturated soils and to measure the physical and geochemical properties of the aquifer. Groundwater samples are collected and analyzed to characterize the nature and extent of contamination, and other general groundwater quality parameters that may be impacted by, or impact, the operation of the in-well treatment process (e.g., pH, dissolved oxygen, and ferrous iron).

Aquifer hydraulic property data needed to model the operation of in-well systems for design and placement of the treatment wells can be obtained from pump tests, dipole tests, and/or conventional slug tests conducted in target areas of the plume.

18.5.1 Pump Tests

In single-well pump tests, water is pumped and both discharge from and drawdown in the well over time is measured. In multiple-well pump tests, drawdown in monitoring wells and/or piezometers at known distances from the pumping well is monitored.

The interpretation of pump test results is typically accomplished by graphical analysis of drawdown versus time. The data are typically plotted as log drawdown versus log time, and curve-fitting techniques are commonly used to characterize the data.

Interpretation of the characteristic curves fit to the data varies by method, but usually involves comparison of test data to template curves that represent various aquifer parameter values. The information typically produced by these analysis methods includes aquifer hydraulic conductivity, transmissivity (product of hydraulic conductivity and saturated thickness) and storativity. Some methods yield both the horizontal and vertical hydraulic conductivity of the aquifer. A complete description of the theory and application of pumping tests can be found in Domenico and Schwartz (1990) and Fetter (2001). Pumping tests and the various methods that can be used in the analysis of data collected during a pumping test are provided in Kruseman and de Ridder (1990). A guide is available to aid in the selection of the proper aquifer test techniques for a given aquifer type (ASTM, 2004).

18.5.2 Dipole Tests

The dipole test was developed to provide information on the local vertical distribution of horizontal and vertical hydraulic conductivities and the vertical distribution of the specific storativity (Kabala, 1993). The test is applicable to in-well treatment systems that circulate groundwater because during the test, groundwater is circulated in the formation much like during system operation. Another advantage of the dipole test is that water is not withdrawn from the ground, thus eliminating disposal requirements.

The dipole test is conducted in a single well where a vertical section of the well is isolated using two inflatable packers. The isolated section is divided into two chambers with a third inflatable packer modified to allow water to be pumped from one chamber to the other. It is critical that the packer is installed properly to provide a tight seal between the two chambers. A bentonite seal is required in the annulus of the well adjacent to the middle packet to prevent interference from the "skin" effect. A submersible pump is placed in one of the chambers. Pressure transducers are placed in each chamber to measure the pressure developed during pumping and above and below the two outside packers to monitor for leaks. During the test, groundwater is pumped between the two chambers at a constant rate. This causes groundwater to enter the first chamber and leave the well through the second chamber. The net result is circulation of the water in the formation just outside the well. During pumping, pressure readings from the four pressure transducers are recorded. Data loggers are used to rapidly collect the data through the transient and up to steady state conditions.

The data from the test is used to calculate the horizontal and vertical hydraulic conductivities, and the storativity. The pressure (drawdown) data are graphed against time. Three points are selected from different phases of the drawdown curve to define a system of three nonlinear equations. The three equations are solved through application of the Newton-Raphson algorithm for three unknowns. If any of the parameters are known from previous aquifer tests, a simpler computational method based on the Newton-Raphson iterative algorithm for one or two unknowns can be applied to find the remaining parameters. More detailed description of the test and data analysis procedures can be found in Kabala (1993).

18.5.3 Slug Testing

Slug withdrawal or injection tests are commonly used as alternatives to pumping tests to determine the hydraulic conductivity in the region around a well. One key advantage of slug tests is their relatively short duration, only minutes to at most a few hours are required. In addition, no pumping is required, minimizing the volume of investigation derived waste generated by the aquifer investigation. Wells operating near a site where a pump test would normally be performed can interfere with pump test results. However, since slug tests indicate aquifer conditions in the immediate vicinity of the test well, the interference of nearby operating wells is minimized.

Slug testing involves adding or removing a "slug" of known volume to (or from) a well and monitoring the water level in the well as it falls (or rises) back to the equilibrium water level. The slug may consist either of water or a solid object (usually a cylinder) of known volume. If a water slug is removed, the test is sometimes referred to as a "bail test." In any case, the displaced water imposes a temporary hydraulic gradient around the well, which motivates water flow in the direction that will result in restoration of the equilibrium water table level.

18.6 SYSTEM DESIGN REQUIREMENTS

In-well treatment system design is based on site specific geologic and hydrogeologic conditions, on results of the field testing described above, and results from flow and transport modeling. Design considerations include the volume and dimensions of the aquifer requiring treatment, general well configuration and in-well treatment process, required/achievable pumping rates, well-screen lengths and placement, well diameter, and monitoring requirements. Design and installation of an independent in-well treatment system must take patent restrictions into consideration.

Effective design of in-well treatment systems relies heavily on high quality groundwater modeling, using actual site data for input parameters. The ability to effectively circulate groundwater is very sensitive to anisotropy and in many cases there can be too much or too little anisotropy to develop an adequate circulation cell. In practice, very small variations in hydraulic conductivity can have a significant effect on the circulation. Modeling based on site-specific properties is used to design, optimize and monitor the system.

Several numerical modeling programs/approaches have been used for designing and/or evaluating the flow patterns around in-well treatment systems. Philip and Walter (1992) developed a semianalytical method for predicting the steady-state hydraulic head and flow field around an arbitrary number of GCWs operating in a homogeneous anisotropic aquifer. They compared the approach with a fully analytical solution and found the two approaches to match very well closer to the well locations, with some discrepancy appearing towards the stagnation point at the leading edge of the capture zone. McCaulou et al. (1995) employed a simple mass transport model to predict the zone in an aquifer that would be biologically remediated by operating a GCW to deliver terminal electron acceptors. Stallard et al. (1996) developed a numerical model coupling the solutions of a 2-D unsaturated/saturated flow equation and a 2-D contaminant transport equation to predict the long-term performance of a GCW. Data from groundwater simulation tank experiments were input into the model, which was solved using a finite difference approach. The model output was compared to output generated by the 3-D finite element models 3DFEWATER and 3DLEWASTE. The comparison found numerical models effective in estimating the shape of the plume and the capture efficiencies in the 2-D simulation.

White and Gilmore (1996) performed numerical analyses of an in-well treatment well at Edwards AFB in California with the Subsurface Transport over Multiple Phases (STOMP) simulator, a very sophisticated program specifically designed to model multidimensional flows. The simulations showed close agreement with the hydraulic and contaminant reduction data from the field. More information on the use of STOMP, including a copy of the User's manual, additional references, and instructions for acquiring the simulator, can be found at http://stomp.pnl.gov/.

18.7 PERFORMANCE MONITORING REQUIREMENTS

Performance monitoring includes periodic collection of data to evaluate the status of the operating in-well treatment system, and the remedial progress in the aquifer outside the well. Monitoring is essential to optimize system performance, to detect impending failures and unwanted effects, and to demonstrate removal of contaminants from the site. Without monitoring, an in-well treatment system could continually function significantly below its potential removal and economic efficiencies, wasting both time and money. While there are costs associated with performance monitoring, those costs are easily recovered by optimizing energy and removal efficiencies, and by reliably documenting cumulative contaminant mass removal.

18.7.1 In-Well Treatment Process Monitoring

In-well process monitoring is conducted to determine the treatment process effectiveness and to adjust any operating parameters to optimize the performance. Standard in-well monitoring parameters include:

- Concentration of contaminant(s) in groundwater entering the well.
- Concentration of contaminant(s) in the treated water leaving the well.
- Water flow rate through the well.

These measurements are required for mass removal calculations and, as a system performance check, can be compared to the predicted values generated during the modeling and design phases of the project. Additional parameters that should be measured are specific to the treatment process. For example, if a bioprocess is used, respiratory gases and/or substrate concentrations might be monitored to ascertain the level of biological activity. Conversely, monitoring respiratory gases in an air-lift well system using aboveground carbon adsorption to treat the off-gas would provide no benefit for assessing treatment performance. Air-lift system-specific monitoring parameters include the air flow rate and the concentrations of contaminants in the influent gas and the off-gas.

18.7.1.1 Measuring Contaminant Concentrations

In-well treatment systems should be designed with the capability to collect representative samples of the influent to, and effluent from, the well. This could include a sample line located at a point within the well that pulls water before it encounters any treatment, and a sample line located within the discharge screened section. A monitoring well located immediately adjacent to the outside of the influent screen may not provide a representative sample due to contaminant plume and aquifer heterogeneities (Battelle, 1995). A well located outside and adjacent to the upper screen may provide a representative sample of the treated water leaving the well if there is sufficient mixing of the water as it passes through the well.

18.7.1.2 Measuring Flow Rates

For any in-well system configuration, the in-well flow rates must be known in order to perform mass removal calculations and thus are important for process and operational performance monitoring. The groundwater pumping rate refers to the volume of water passing through the well in a unit of time. Hydraulic heads are measured at the well to determine the gradient imposed on the aquifer by the system. The vapor flow rate is important for systems that utilize air lift, air stripping, and/or soil vapor extraction. The flow rates are needed to perform mass balances on contaminants.

18.7.2 Remedial Progress Monitoring

The ultimate goal of in-well treatment is to reduce contaminant concentrations in the aquifer to achieve cleanup goals. Remedial progress monitoring is conducted in the aquifer to determine the volume of aquifer undergoing treatment and to assess the mass of contaminant removed and remaining. Because in-well systems impart a 3-D flow in the aquifer, subsurface monitoring should include wells completed at multiple depths and at various distances from the treatment well. Hydraulic head measurements, aquifer tests, tracer tests and *in situ* flow sensors all have been used with varying degrees of success to assess the movement of groundwater in aquifers around in-well treatment systems (Johnson and Simon, 2007). Groundwater sampling and analysis for contaminant concentrations is the most direct tool for assessing remedial progress and will ultimately be the indicator that the remedial objective of reaching the cleanup goal(s) has been achieved.

18.7.2.1 Aquifer Volume of Influence Measurements

A key design parameter is the radius of influence (ROI) around a treatment well. The ROI represents the lateral area of the aquifer that can be impacted by the treatment well over the project lifetime. The term ROI can be misleading, since the 2-D shape of the circulation cell is not likely to be perfectly circular (due to spatial heterogeneities and background groundwater flow), and the vertical influence is generally much less than the lateral affect. However, the ROI is a critical parameter that can have a large influence on the costs and feasibility of the technology, because it largely determines well spacing.

Despite its importance, it can be difficult to define the ROI with precision, particularly for GCWs. For example, in-well treatment requires contaminant transport to the well as the groundwater moves through the aquifer and is drawn to the well. This process relies on desorption of contaminant from the aquifer solids, which will be mass transfer limited, and it may take many cycles for the "flushing" action to reduce the contaminant concentrations to target levels. Therefore, it may be more appropriate to use the term "effective ROI" to describe the portion of the overall circulation cell within which the remediation goals can be met during the project lifetime.

When in-well systems are used for plume interception, the ROI is defined as the distance from the well at which the plume is effectively "captured" into the circulation cell. Accurately determining this ROI requires the application of a groundwater model, using the design pumping rate to determine the expected hydraulic gradients and imparted groundwater flow field. The modeling results show how the background groundwater flow will affect the dimensions of the circulation cell and provide an estimate of achievable effective ROI. Knowing the effective ROI is extremely important for proper placement of wells, to ensure that the plume does not "pass by" the treatment system.

Once the system is operating in the field, the actual ROI must be determined, which can be accomplished using any of several approaches. The following sections discuss several of the more common of these approaches. Johnson and Simon (2007) conducted an extensive evaluation of the flow patterns around an in-well treatment system at a site in Florida that included hydraulic and tracer testing combined with flow and transport modeling. Based on their findings, they developed a cost effective sequential protocol that allows for selecting the tools that are appropriate for defining the flow field at a given site.

Water Level/Pressure Measurements. Measuring water levels in the treatment well(s), in piezometers placed adjacent to the influent and effluent screened sections of the treatment well(s), and in monitoring wells placed around the zone of influence, can provide a good estimate of the ROI, provided that the aquifer is well characterized with respect to hydraulic conductivity and heterogeneity. Unfortunately, this is frequently not the case and hydraulic head measurements alone cannot overcome the uncertainties of a poorly characterized site (Johnson and Simon, 2007). Although the drawdown observed with groundwater withdrawal is offset by recirculation of the groundwater, water level and pressure-head differences are observable and if the aquifer is sufficiently characterized, the data are useful for measuring the ROI and for monitoring changes over the course of operating the treatment well(s).

A variety of tools are available to measure water levels in treatment and monitoring wells. These include wetted tape, electric tape, electronic pressure transducers, sounding (acoustical) devices, oil/water interface probes and airline pressure apparatus. A mechanical water level chart recorder can be installed to measure relative changes in the water level for a predetermined time interval. This can prove useful at system startup and during the dynamic phase of operation. Pressure transducers can be installed in a network of monitoring wells to provide continuous measurements of water levels. The output from the transducers can be recorded and transmitted or saved by a data logger, then downloaded to an electronic file in the field.

Pressure transducers can be difficult to install in the pumping zone, since it is necessary to feed the transducer lines through or alongside the treatment unit inside the circulating well. Problems can arise when trying to feed these lines around packers or other in-well components. Turbulence in airlift systems can interfere with pressure transducer readings. Incorporating a stilling tube into the well design to isolate a column of water in the well from the rising air bubbles and imparted turbulence could overcome this problem.

In Situ Sensors. *In situ* flow and flux sensors have been used to evaluate groundwater flow with varying degrees of success. These devices are installed directly in the aquifer at selected points around the treatment well. The sensors measure the thermal gradients of flow/flux, and depending on the specific sensor type and its orientation, both a horizontal and vertical flow component can be measured. Johnson and Simon (2007) evaluated thermal groundwater velocity sensors and found that they provide more representative measurements of the horizontal flow than the vertical component.

Dye/Tracer Tests. Sites with few monitoring wells may not produce sufficient data to evaluate the ROI or the dimensions of the circulation cell. Systems with low pumping rates may induce only a very shallow head gradient around the treatment well, making it difficult to determine the circulation radius. Hydraulic head and water level measurements taken in monitoring wells may be insufficient to characterize the treatment area. In these cases, tracer or dye testing can be conducted to determine the actual ROI. These tests also can be used to compare and confirm head measurements from sites with extensive monitoring networks.

Tracer and dye tests are performed to determine groundwater flow paths and velocities in the aquifer during operation of an in-well system. Tracers can be thermal (water temperature), or can consist of particles such as biological solids (yeast, bacteria, spores), ions, organic acids, dyes, and radioactive isotopes. The selection of a particular tracer is dependent on the data objectives and on the natural system into which the tracer will be introduced. The ideal tracer will have the following characteristics:

- No interaction with the aquifer matrix,
- No chemical reactivity in the site groundwater,
- No toxicity,
- Migration only at the rate of groundwater movement,
- Easy to detect, and
- Similar physical and/or chemical properties to the material being traced.

Inorganic ionic compounds (such as chloride, bromide, sulfate and iodide) and organic compounds such as fluorobenzoate have been used extensively as groundwater tracers. The inorganic ionic compounds are easily detected in the field using ion-specific electrodes, or by measuring changes in the groundwater specific conductance (electrical conductivity) as the tracer moves past a monitoring point. The disadvantages of ions as tracers include chemical dispersion, interference from background ions, and sorption by microorganisms or soil particles.

Various organic, fluorescent dyes are also widely used groundwater tracers. Fluorescent dyes are relatively inexpensive to use and are easily detected. Natural groundwater factors such as suspended solids, hardness, salinity, pH and temperature can interfere with the movement and detection of the dyes. Both ionic detectors and fluorimeters (for quantification of fluorescent dyes) can be installed in a well or can be operated at ground surface to analyze collected samples.

Two distinct tracer test approaches include the divergent test and the convergent test. The divergent test is conducted by injecting a tracer compound or dye into the treatment well and then periodically collecting groundwater samples from monitoring wells or points at different depths and distances from the well. The data are used to determine the travel time of the tracer from the point of injection to the monitoring locations.

With the convergent approach, a dye or tracer is injected into the groundwater via monitoring wells or injection points at some distance from the treatment well, and the influent to the well is monitored for arrival of the tracer. The selection of a tracer and tracer testing method is specific to the contaminant characteristics and GCW design and should be performed on a site-specific basis. It should be noted that regulations pertaining to the injection of materials into groundwater vary and should be investigated thoroughly to ensure compliance.

Johnson and Simon's (2007) flow field evaluation method includes a volatile tracer test using sulfur hexafluoride (SF_6) to evaluate short circuiting between the two well screens of a dual screen in-well system, and a divergent tracer test using fluorescein to evaluate groundwater flow in the aquifer further from the well. The volatile tracer results showed a 1- to 2-day travel time between screens. It is not clear how the tracer was added to the water leaving the well and hence it is not clear if this is a true measure of the communication time between the screens. The fluorescein test results effectively show the heterogeneity in the flow field around the treatment well, with tracer traveling further in the shallower zones than the medium and deeper zones.

18.7.2.2 Treatment Performance

Groundwater samples are collected from monitoring wells, remediation/recovery wells, and/or production wells and analyzed for the contaminants and other parameters of interest. The data generated from these samples is the ultimate measure of the system's treatment performance and can serve to demonstrate to a regulatory agency that the site has met the remedial objectives. Monitoring wells specifically designed and installed to monitor system performance will yield the most reliable and representative groundwater samples. Understanding the site hydrogeology and the plume configuration is necessary to effectively place monitoring wells within the volume of influence from the well(s).

The number and frequency of groundwater sampling events for characterization purposes is inversely proportional to the quality and quantity of groundwater data developed during the background investigation. If little is known about the concentration and location of the contaminated groundwater, further sampling will be required to characterize the contaminant plume. The money spent characterizing a site is usually recoverable over the life of a project.

Collected samples are analyzed for the contaminant of interest, as well as any other water parameters that may affect either the current contaminant concentration or the effectiveness of the GCW, once operations commence. For example, if a degradation product of a primary contaminant has been determined to inhibit or compete with the degradation of the parent compound, then the daughter species must be characterized initially and monitored (along with the primary contaminant) throughout the project.

18.8 SITE CLOSURE ISSUES

Achieving site closure with in-well treatment systems requires that the previously agreed upon remedial objectives are met. Most frequently closure will require achieving a target concentration in groundwater samples collected from across the contaminated volume of aquifer. The closure strategy is worked out with the overseeing regulatory agency at the initiation of the project. It should be noted that the efficiency of an in-well treatment system can decline over time as the concentrations in the influent are diluted by the treated water recirculating closer to the well. A point of diminishing returns can be reached when the cost of operating the well exceeds the benefit from additional removal of contaminant. Proper design and placement of treatment wells can minimize this potential, but a contingency should be worked into the closure plan to address this potential issue.

18.9 CASE STUDIES

In-well treatment systems have been applied at pilot and/or full scale at numerous sites but applications for dissolved chlorinated solvent plumes are more limited. Complete documentation including site characterization, system design, operation, performance and cost is even more limited. Table 18.4 summarizes selected applications where in-well treatment systems were deployed for treating dissolved phase chlorinated solvent plumes.

Two detailed case histories are presented below. Case History #1 is included to illustrate a successful application of an in-well treatment technology, not as an endorsement of the specific technology described. Case History #2 describes an implementation that encountered several problems, which ultimately resulted in failure caused by site characteristics, not necessarily the specific configuration tested. This case history is included to illustrate the importance of careful and thorough upfront site characterization to collect the site-specific data needed to select and design an appropriate in-well treatment system that can efficiently and cost effectively achieve the remedial objectives.

18.9.1 Case History #1: UVB Demonstration at March AFB, California

The UVB technology was evaluated under the U.S. Environmental Protection Agency (USEPA) Superfund Innovative Technology Evaluation (SITE) program between April 1993 and May 1994 for treating TCE at Site 31, March AFB located near Riverside, California (USEPA, 1995; USEPA, 1999). The demonstration was designed to provide potential users of the technology with the necessary information to assess the applicability of the UVB system at other contaminated sites. The demonstration was conducted over a 12-month period during which data were collected in three phases: baseline sampling, long-term sampling and dye tracer sampling. Baseline and long-term sampling included collection of groundwater samples from eight monitoring wells, a soil gas sample from the soil vapor monitoring well, and air samples from the three UVB process air streams both before UVB system startup and monthly thereafter. In addition, a dye tracer study was conducted to evaluate the radius of the system's circulation cell. This study included introducing fluorescent dye into the groundwater and subsequent monitoring of 13 groundwater wells three times a week over a 4-month period for the presence of dye.

Site Description. Site 31 was within an alluvial filled valley that consisted of poorly consolidated deposits of clay, silt, sand and cobble-sized particles. The upper 12.2 m (40 ft) consisted predominantly of interbedded silt and silty sand. A "clean" and laterally continuous layer of sand extended from 12.2 to 15.2 m (40 to 50 ft) bgs. The sand interval was underlain by a layer of silty sand that extended to approximately 19.8 m (65 ft) bgs. A discontinuous layer of relatively clean sand extended from approximately 19.8 to 22.9 m (65 to 75 ft) bgs and pinched out to the north and south toward the UVB well and outer cluster wells. Below the sand were interbedded silts and sands, and minor clays. A prominent clay layer encountered at 36.6 m (120 ft) bgs acted as a confining layer beneath the site. Bedrock was found at depths ranging from 29.0 to 30.5 m (95 to 100 ft) bgs in the northern and eastern portions of the Site 31 and 45.7 to 50.3 m (150 to 165 ft) bgs in the southern and western portion of the site.

Site 31 was characterized with an upper unconfined aquifer and a lower semi-confined aquifer. The depth to groundwater in the upper zone was approximately 12.2 m (40 ft). The average hydraulic conductivity was calculated at 4.26 x 10^{-3} cm/sec (12.1 ft/day) with an effective porosity of 27.2% and transmissivity of 2.2 x 10^{-4} cm/sec (0.62 ft/day). Groundwater flow was to the southeast at a gradient of approximately 0.014 and a maximum velocity of 2.65 x 10^{-4} to 2.72 x 10^{-4} cm/sec (0.75 to 0.77 ft/day).

Contaminants. TCE and *cis*-DCE concentrations up to 2,000 micrograms per liter (µg/L) and 210 µg/L, respectively, had been detected in groundwater samples at Site 31 prior to the UVB demonstration with the highest TCE concentrations found immediately south of Building 1211. A second area of elevated TCE concentrations was located northeast of the UVB system. Vertical distribution of TCE appeared to be stratified with the highest concentrations detected approximately 12.2 to 24.4 m (40 to 80 ft) bgs and the lowest concentrations detected approximately 27.4 to 32.0 m (90 to 105 ft) bgs.

System Description. Figure 18.6 is a plan view schematic representation of the system layout showing the locations of the treatment well and associated monitoring wells and Figure 18.7 is a cross sectional view showing the relative depths of those same system components. A single-well UVB consisting of a 40.6 cm (16 inch) diameter dual screen well was installed in a 66.0 cm (26 inch) diameter bore hole. The well was installed to a depth of 25.5 m (83.7 ft) bgs. The lower (influent) screen was 3.7 m (12 ft) long and composed of steel bridge-slot casing. The upper (effluent) screen was 4.2 m (13.8 ft) long and constructed from 1.2 m (4 ft) of bridge-slot casing and 3.0 m (9.8 ft) of double-cased stainless steel screen filled with 1.0 cm (3/8 inch) Teflon™ beads. The two screen sections were separated by 4.5 m (14.7 ft). Completion of the well included placement of a gravel pack around the screened sections and a bentonite and cement slurry between the screens and above to ground surface.

An inflatable packer was installed at 20.3 m (66.7 ft) bgs to separate the upper and lower screened sections. An intake pipe passed through the packer and provided flow from the lower screened section to the stripping reactor, which was located in the upper section of the well. The stripping system consisted of a submersible pump, a pinhole (diffuser) plate, a double-wall stripper reactor, internal centralizers and leveling ballast, and an air intake pipe. The discharge throat of the pump was equipped with a 15 millimeter (mm) (0.59 inch) orifice flow restrictor to maintain a constant flow of approximately 83.3 L/min (22 gallons per minute [gpm]). The stripping unit components were constructed of high density polyethylene or aluminum. Aboveground components included a blower, moisture separator, process air stream piping, electrical supply, and two 816.5 kg (1,800 pound) vapor phase carbon adsorption units.

The monitoring system consisted of six groundwater monitoring wells and one soil gas well to evaluate the UVB system. The groundwater monitoring wells were placed in two clusters that each included a shallow-, intermediate- and deep-screened well. A preliminary estimate of a 15.2 m (50 ft) radius of the circulation cell resulted in placement of the monitoring well clusters at approximately 12.2 to 27.4 m (40 and 90 ft) from the UVB well. The cluster farthest from the UVB well served as the control set for comparison with inner cluster results. Two additional shallow-screened monitoring wells were installed based on results from a dye-tracer test and were located approximately 12.2 m (40 ft) from the UVB well. The soil gas well was located approximately 19.8 m (65 ft) from the UVB well.

Table 18.4. Selected In-Well Treatment System Application for Dissolved Phase Chlorinated Solvent Contamination

Contaminant	Site	System Configuration	Geologic Setting	Depth to Groundwater/ Depth of Well Completion m bgs (ft bgs)	K_H cm/sec (ft/day) K_V cm/sec (ft/day) Gradient	Pre-treatment Contaminant Concentrations (µg/L)	Post-treatment Contaminant Concentrations (µg/L)	Treatment Efficiency	Cost ($) (total unless otherwise noted)
PCE	Dry Cleaning Site in Hutchinson, KS (1)(4)	Single-well NoVOCs™ (5-month demonstration)	Unconsolidated sands, silts and clay	4.3–4.9 (14 -16) 11.6 (38)	0.176–0.272 (500–770) NR (NR) 0.001	30–600	5–39	NR	95 K
TCE	Edwards AFB, CA (1)	Single-well NoVOCs™	Alluvial sands and gravel	7.6 (25) 15.2 (50)	3.53×10^{-3} (10) 3.53×10^{-4} (1) 0.1	Avg: 300 Max: 502	$<$ 5 to 173	90% per pass	817 K
	March AFB, CA (1)	Single-well UVB™	Fine-grained sand and silt	12.2 (40) 26.7 (87.5)	10^{-4} (0.283) NR (NR) 0.007	3.4–1,000 Avg: 500	47–270 Avg: 250	90–95% per pass	297 K ($260/1000 gal)
	Massachusetts Military Reservation, MA (1)(5)	Two 3-screen UVB™ wells (2)	Fine to coarse sands and silts	4.6–13.7 (15 to 45) 83.8 (275)	$5.1\text{x}10^{-2}$–$8.1\text{x}10^{-2}$ (144-230) NR (NR) 0.002	Max: 2,800 Mid zone: 600 Upgradient: 400 Low zone: 200	Effluent: 100 Mid zone: 180 Upgradient: 150 Lower zone: 200	95.5% per pass ~40 kg removed (3)	NR
	Massachusetts Military Reservation, MA (1)(5)	Two dual-screen NoVOCs™ wells (2)	Fine to coarse sands and silts	74.7 (245) NR (NR)	$5.1\text{x}10^{-2}$–$8.1\text{x}10^{-2}$ (144-230) NR (NR) 0.002	Max: 2,800 Reinjection zone: 2,700 Extraction zone: 1,300	Reinjection zone: 100 Extraction zone: 1,300	91% per pass ~84 kg removed (3)	NR
PCE, TCE	Westinghouse Savannah River, SC (1)	Two Airlift Recirculation Wells	Fine to medium grained sands	30.5 (100) 53.3 (175)	$9.1\text{x}10^{-3}$ (25.8) $5.0\text{x}10^{-4}$ (1.43) NR	Variable and up to and greater than 10,000	Reduced 30 to 80% over 14 months	1 to 2 lbs/day removed	100 K/well
PCE, TCE, *cis*-DCE	Sweden-3 Chapman Superfund Site, NY (1)	Single-well UVB (5-month pilot)	Silty clays, sand and gravels	2.4–3.0 (8–10) 7.9 (25.9)	$7.0\text{x}10^{-6}$–$1.0\text{x}10^{-4}$ (0.02-0.029) NR (NR) NR	Avg PCE: 653 Avg TCE: 2,245 Avg *cis*-DCE: 2,322	Decreases observed, data not available	NR	153 K
	Maxwell AFB, AL(4)	Single DDC well	Sandy clay, poorly graded fine-grained sand and medium to fine-grained sand, and gravelly sand	8.2 (27) 11.6 (38)	NR (NR) NR (NR) 0.003	PCE and TCE: $<$ 100	Decreases between 75 and 96%	30–50% TCE 42–61% PCE per pass	NA

PCE, TCE, *cis*-DCE, CF	Uniform Processing Facility, Minneapolis, MN	Single ART well	Silty sand	9.1 (30) 16.8 (55)	NR (NR) NR (NR) NR	PCE: 2,700 TCE: 3 *cis*-DCE: 0.57 CF: 3.2	170 BDL BDL BDL	93% PCE (70 days of operation)	NR
TCE, *cis*-DCE	Naval Air Station (NAS) North Island, CA (5)	Single NoVOCs™ well	Artificial fill (fine-grained sand),	2.4 (8) 23.8 (78)	$4.3x10^{-3}$ (12) NR (NR) 0.0008	Avg TCE: 1,650 Avg *cis*-DCE: 45,000 Avg 1,1-DCE: 3,530	Avg TCE: 32 Avg *cis*-DCE: 1,400 Avg 1,1-DCE: 27	93% TCE 95% *cis*-DCE 98% 1,1-DCE 92.5 lbs total VOCs removed over 1056 hrs operation	Capital 190K O&M 160K/yr (1st yr), 150K/yr thereafter
CT, PCE	Brookhaven National Laboratory, NY (4)	Seven UVB wells (18 month full scale)	Fine to coarse sand, trace clay, silt and gravel lenses	45.7 (150) 58.8–74.1 (193–243)	$3.0x10^{-2}$–$5.3x10^{-2}$ (84.7–149) NR (NR) 0.001	Max CT: 1,540 Max PCE: 330 Max total VOC: 1,900	88–96.5% total VOCs	Avg 92.8% per pass 300 lbs removed	4,990 K (total cost including 8 yrs of operation)
PCE, TCE, *cis*-DCE, CF, CT, 1,2-DCA	Lawrence Livermore National Laboratory, CA (6)	Single Reactive Well	Unconsolidated alluvial deposits	20–30 (65.6–98.4) 42.5 (139.4)	NR (NR) NR (NR) NR	Total CVOC: 4,000 to 5,000 Influent PCE: 366–370 TCE: 3612–3777; 1,1-DCE: 130–180 *cis*-DCE: 0.6–0.7 VC: <0.4 1,2-DCA: 26–28 CF: 167–235 CT: 18–21	Effluent PCE: <0.4 TCE: <0.4–0.8 1,1-DCE: <0.4 *cis*-DCE: <0.4–0.9 VC: <0.4 1,2-DCA: 19–27 CF: 6.5–36 CT: <0.4	PCE: >99% TCE: >99% *cis*-DCE: – VC: – 1,2-DCA: 0% CF: ~ 91% CT: >98%	NR

[1] USEPA, 1998: [2] Systems pilot tested for 5 months, continued operation for a total of 18 months: [3] After 18 months of operation: [4] USDOE, 2002: [5] USEPA, 2000a; b: [6] McNab et al., 2000.

Note: 1,2-DCA–1,2-dichloroethane; 1,1-DCE–1,1-dichloroethene; Avg–average; BDL–below detection limit; bgs–below ground surface; CF–chloroform; *cis*-DCE–*cis*-1,2-dichloroethene; CT–carbon tetrachloride; K–thousand dollars; kg–kilogram; K_H–horizontal hydraulic conductivity; K_V–vertical hydraulic conductivity; lb–pound; Max–maximum; µg–microgram; O&M–operation and maintenance; PCE–perchloroethene; NR–not reported; TCE–trichloroethene; VC–vinyl chloride; VOC–volatile organic compound.

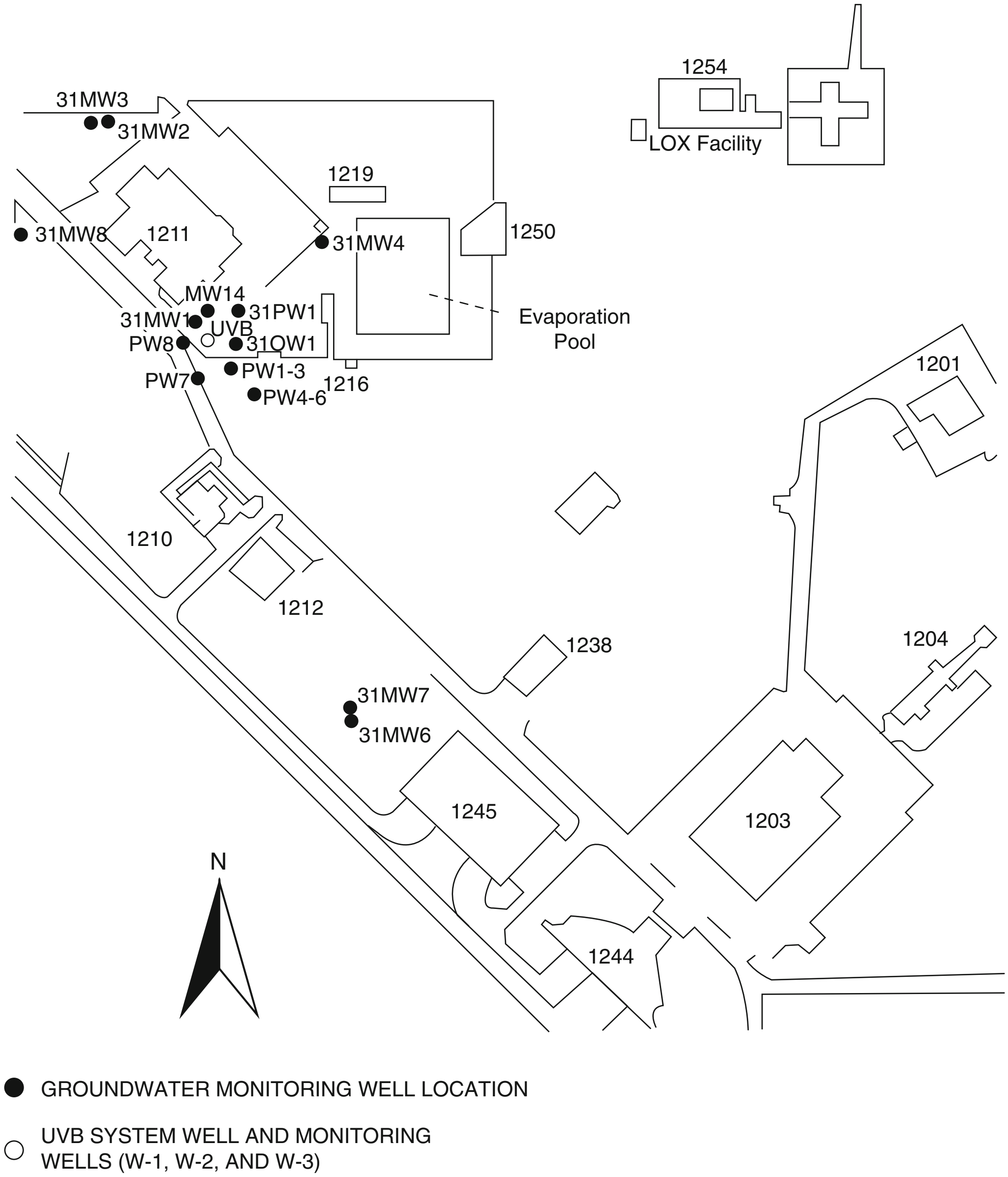

Figure 18.6. Plan view showing the layout of the UVB system demonstrated at March AFB (USEPA, 1995).

System Operation. The system was operated in an upflow mode for a period of 12 months. During this time, the air flow ranged from 2.83 to 25.4 m^3/min (100 to 898 ft^3/min) at a velocity ranging from 338 to 3048 m/min (1,109 to 9,999 ft/min). The water flow rate was maintained at 83.3 L/min (22 gpm). The vacuum in the well ranged from 95.2 to 103.6 kilopascals (kPa) (13.81 to 15.03 pounds per square inch [psia]). The temperature of the internal monitoring ports ranged from 18.5 to 44.7 °C and the relative humidity ranged from 27 to 100%.

System Monitoring. System performance was monitored by sampling eight groundwater monitoring wells and one soil gas monitoring well. Baseline groundwater samples were collected before system start-up and analyzed for VOCs, dissolved metals and general chemistry parameters. The soil gas sample was analyzed for VOCs and fixed gases–oxygen (O_2), nitrogen (N_2) and carbon dioxide (CO_2). Groundwater, soil gas and air samples from the UVB process air streams were collected monthly for six consecutive months after system start-up. Groundwater samples were analyzed for VOCs, dissolved metals and general chemistry parameters. System air samples were analyzed for VOCs and the soil gas samples were analyzed for VOCs and fixed gases to evaluate the potential for increasing microbiological activity in the vadose zone. Samples from the ambient air and contaminated air before treatment were also analyzed for fixed gases. Soil gas and system air stream sampling was terminated after six months and groundwater monitoring continued every month for an additional six months and included collecting groundwater samples from the shallow and intermediate depth monitoring wells only for VOC analysis.

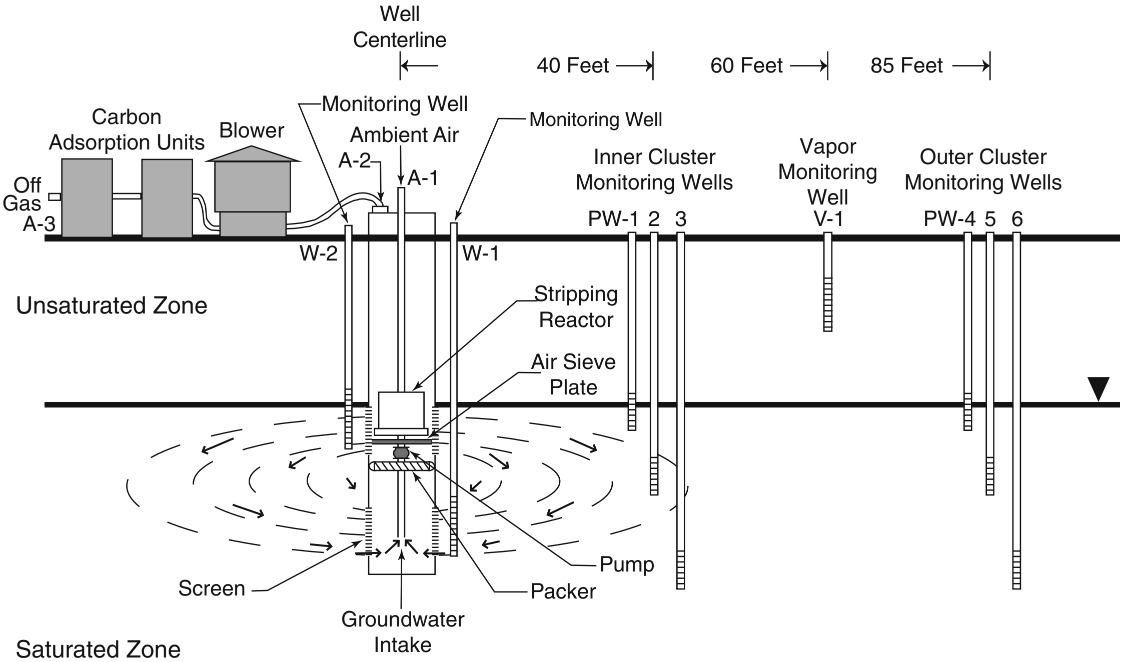

Figure 18.7. Cross-sectional view of the UVB system demonstrated at March AFB (USEPA, 1995).

A 4 month long dye-tracer test was conducted to assess the radius of the circulation cell. Fluorescent dyes were injected into the circulation cell and groundwater samples were collected three times per week from 13 wells for both qualitative and quantitative analysis of fluorescence.

Results. TCE concentration data showed that the UVB system had an average single pass efficiency of greater than 94%. Over the course of the demonstration, TCE concentrations in samples from the influent well ranged between 14 and 220 µg/L, with an approximate arithmetic mean of 56 µg/L. The TCE concentration in the discharged water was below 5 µg/L for nine out of 10 monthly monitoring events during which the system operated without apparent maintenance problems. The mean TCE concentration in the water discharged from the system was approximately 3 µg/L with a 95% upper confidence of 6 µg/L. *cis*-DCE concentrations in the discharge water were consistently below 1 µg/L; however, it was not meaningful to assess the system's ability to remove *cis*-DCE because the influent concentrations were consistently below 4 µg/L.

The circulation cell radius was estimated to be at least 12.2 m (40 ft) in the downgradient direction based on the results of the dye-tracer test. However, no dye was observed in wells located 12.2 m (40 ft) upgradient or cross gradient of the UVB system. Groundwater flow modeling indicated a radius of the circulation cell of 25.3 m (83 ft). Aquifer pump test data indicated the radius of circulation of approximately 18.3 m (60 ft).

Groundwater TCE concentrations were reduced approximately 52% within the radius of the circulation cell during the 12 month demonstration. TCE concentrations in samples from the shallow and intermediate zone wells were reduced both vertically and laterally except in the intermediate outer cluster well, which showed an increase in concentration. Lateral TCE concentration reductions averaged approximately 52%. No reduction of TCE concentrations was observed in samples collected from the deep zone. This was attributed to the short duration of monitoring in that zone.

Costs. The estimated capital costs for the single treatment unit were $180,000. Annual operation and maintenance costs were estimated at $72,000 for the first year and $42,000 for each of the subsequent years. Based on these estimates, the total cost for operating the single UVB system for 1 year was calculated to be $260,000. Extrapolated over time at an annual inflation rate of 4%, the cost to operate a single UVB system was calculated to be $340,000 for 3 years, $440,000 for 5 years, and $710,000 for 10 years. Treatment costs per 1,000 gallons of groundwater were estimated to be $260 for 1 year, $110 for 3 years, $88 for 5 years, and $71 for 10 years.

18.9.2 Case History #2: NoVOCs™ Demonstration at Naval Air Station North Island, California

The NoVOCs™ technology was evaluated at Installation Restoration Program Site 9 on Naval Air Station (NAS) North Island in San Diego, CA under the USEPA SITE Program and in conjunction with the USEPA Technology Innovation Office, Naval Facilities Engineering Command Southwest Division, Navy Environmental Leadership Program, and Clean Sites, Inc. (USEPA 2000a; USEPA 2000b). The objective was to assess the technology's effectiveness for treating groundwater contaminated with high levels of chlorinated and aromatic hydrocarbons.

Site Description. Site 9 is comprised of a 16.2-hectare (40-acre) former chemical waste disposal area located on the western end of NAS North Island. The site encompassed three major waste disposal areas: a shallow pit used for disposal of liquid wastes, four parallel trenches containing different types of wastes (solvents, caustics, acids, and semi-synthetic ceramic and metallic compounds), and a drum disposal area. It was estimated that between 30,283 and 90,850 m^3 (8×10^6 and 2.4×10^7 gallons) of waste were disposed at Site 9. Site 9 posed significant challenges because the groundwater contained total dissolved solids (TDS) ranging from 18,000–41,000 mg/L, considerably higher concentrations of TDS than typical drinking water aquifers.

Site 9 was underlain by artificial fill that consisted of fine-grained, loose sand extending to a depth of approximately 4.6 m (15 ft) bgs in the vicinity of the NoVOCs™ well. The Bay Point Formation, poorly consolidated, fine- and medium-grained fossiliferous sandstone, underlies the fill. Two thin silt and clay layers were present in the subsurface at the site and were likely to be continuous in the vicinity of the site. The first fine-grained layer was a 0.6 to 1.5 m (2 to 5 ft) thick clay, silt, and clayey sand layer found at approximately 10.7 to 12.2 m (35 to 40 ft) bgs and continuous beneath the NoVOCs™ location. A sandstone layer was encountered at approximately 27.4 m (90 ft) bgs. The second clay layer was located at approximately 32.0 m (105 ft) bgs and appeared to be continuous in the vicinity of the NoVOCs™ placement. A soil boring (S9-SB-34) advanced near the location of the NoVOCs™ well found mostly sand and silty sand with a clay/silt layer encountered at 10.8 m (35.5 ft) bgs, dense sands encountered between 18.3 and 18.6 m (60 and 61 ft) bgs and 19.8 and 20.6 m (65 to 67.5 ft) bgs, and a thin, cemented sandstone layer encountered at 24.1 m (79 ft) bgs. The sand and silty sands layers contained various quantities of shell fragments.

Groundwater at NAS North Island is saline, with salt concentrations ranging from 18,000 to 41,000 mg/L. The depth to groundwater was approximately 2.4 m (8 ft) bgs with the upper 33.5 m (110 ft) of the saturated zone containing an unconfined aquifer characterized with a thin 1.5 to 6.1 m (5 to 20 ft) discontinuous freshwater lens, a brackish mixing zone 9.1 to 30.5 m (30 to 100 ft) thick, and a saltwater wedge that was intruding inland. The horizontal hydraulic conductivity was estimated at 4.2 x 10^{-3} cm/sec (11.9 ft/day) and the hydraulic gradient was measured at 0.0008 toward the west over most of the site and 0.006 near the shoreline. The aquifer transmissivity was estimated to be 12.8 cm^2/sec (1,195 ft^2/day), the specific yield was 3.2 x 10^{-1} (dimensionless), and the effective porosity was 0.25 (dimensionless).

A constant discharge rate pumping test was conducted to characterize shallow zone aquifer hydraulic properties by pumping the recharge chamber of the NoVOCs™ well. The constant discharge pumping test data indicated that the shallow aquifer zone was fairly transmissive in the horizontal direction. The upper and lower aquifer zones were well connected with the vertical hydraulic conductivity approximately one-fifth of the horizontal conductivity value (i.e., the anisotropy ratio, K_H/K_V is about 5).

Contaminants. Groundwater at Site 9 contained chlorinated solvents, chlorinated solvent breakdown products, petroleum hydrocarbons and metals. The predominant chlorinated solvents included PCE, TCE and 1,1,1-TCA. Breakdown products detected in the groundwater included DCA, *cis*-DCE and VC. High concentrations of chlorinated solvent compounds above the lower clay layer suggested the presence of dense nonaqueous phase liquid (DNAPL).

System Description. The NoVOCs™ system consisted of a single treatment well and ten groundwater monitoring wells placed as shown in Figure 18.8. The treatment well was constructed from (1) a 20.3 cm (8 inch) diameter, Schedule-80 PVC casing with two screens, (2) a 12.7 cm (5 inch) diameter, Schedule 40 PVC eductor pipe, (3) a 5.1 cm (2 inch) diameter, Schedule 40 PVC airline fitted with a flow meter, and (4) a wellhead fixture with a deflector plate for measuring flow rate. The aboveground components included a control trailer and an off-gas treatment system. The control trailer contained the air injection blower, electrical control panel, a Remote Telemetry Unit programmable logic controller, an inlet moisture separator system, and an air system that included an inlet filter, air intake valve, vacuum relief valve, inlet and discharge pressure sensors, an outlet temperature sensor, an outlet high pressure relief valve and air supply flow sensors. The off-gas was passed through a flameless oxidation system for removal of VOCs prior to atmospheric discharge.

The NoVOCs™ well design included a recharge zone located beneath the upper clay/silt layer; the extraction screen was installed above a cemented sandstone layer encountered at 23.8 m (78 ft) bgs. Two piezometers were installed within the sand pack of the NoVOCs™ well-one adjacent to the NoVOCs™ recharge screen and one adjacent to the NoVOCs™ intake screen (Figure 18.9). Seven cross gradient monitoring wells were installed at four distances from the NoVOCs™ well: a three-well cluster at 9.1 m (30 ft), a well pair at 18.3 (60 ft), and single monitoring wells at 27.4 and 32.0 m (90 and 105 ft). A pair of downgradient monitoring wells were installed approximately 30.5 m (100 ft) from the NoVOCs™ well, and a single monitoring well was installed 30.5 m (100 ft) upgradient of the NoVOCs™ well. The monitoring wells were screened at one of three intervals: at the top of the treatment zone between about 12.5 and 14.3 m (41 and 47 ft) bgs, in the middle of the treatment zone between about 14.9 and 18.9 m (49 and 62 ft) bgs, and at the bottom of the treatment zone between about 20.4 and 23.8 m (67 and 78 ft) bgs.

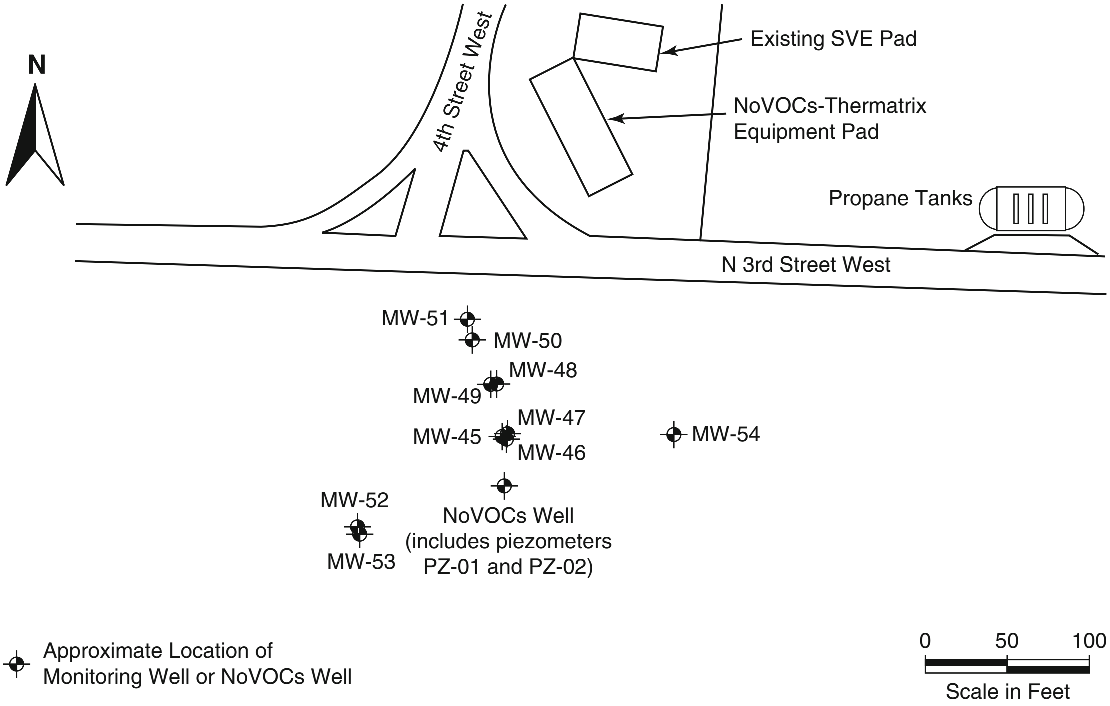

Figure 18.8. Layout of the NoVOCs™ treatment system at NAS North Island (USEPA, 2000b).

System Operation. The geochemical properties of the aquifer posed significant challenges for the operation of the NoVOCs™ system. Operation and maintenance problems causing shutdown of the NoVOCs™ system were primarily related to well fouling, pH problems in the NoVOCs™ well, and maintenance problems with the off-gas treatment system. As a result, the system's operating conditions varied throughout the evaluation resulting in four different operating periods: system startup and shakedown that ran from February 26 through March 26, 1998, early system operation that ran from April 20 through June 19, 1998, reconfiguration operation that ran from September 24 through October 30, 1998, and final configuration operation that ran from December 4, 1998 through January 4, 1999. During these operating periods, NoVOCs™ operation underwent modification including varying configurations of the well internal components and various settings of operating parameters including supply air flow, pressure, and pH. The later operating periods included biocide addition (to control biological fouling of the well) and addition of two different chemical treatments to control iron fouling. For the period of April 28 through June 8, 1998, the NoVOCs™ system operated approximately 70% of the time at an estimated pumping rate between 37.9 and 90.8 L/min (10 and 24 gpm).

System Monitoring. System operating parameters including blower suction, blower temperature, air flow rate, wellhead pressure, pumping rate, and pH in the groundwater discharged from the system were monitored on a regular basis. System performance was based on VOC analysis of groundwater samples collected before and after system startup. Baseline sampling was repeated due to the reconfiguration of the NoVOCs™ system with the first baseline sampling conducted in April 1998, and the second conducted in September 1998. Performance samples were collected weekly for the first month of the demonstration and then monthly thereafter. Because of system operational difficulties during the evaluation, long-term sampling was limited to six weeks instead of the planned six-month monitoring period.

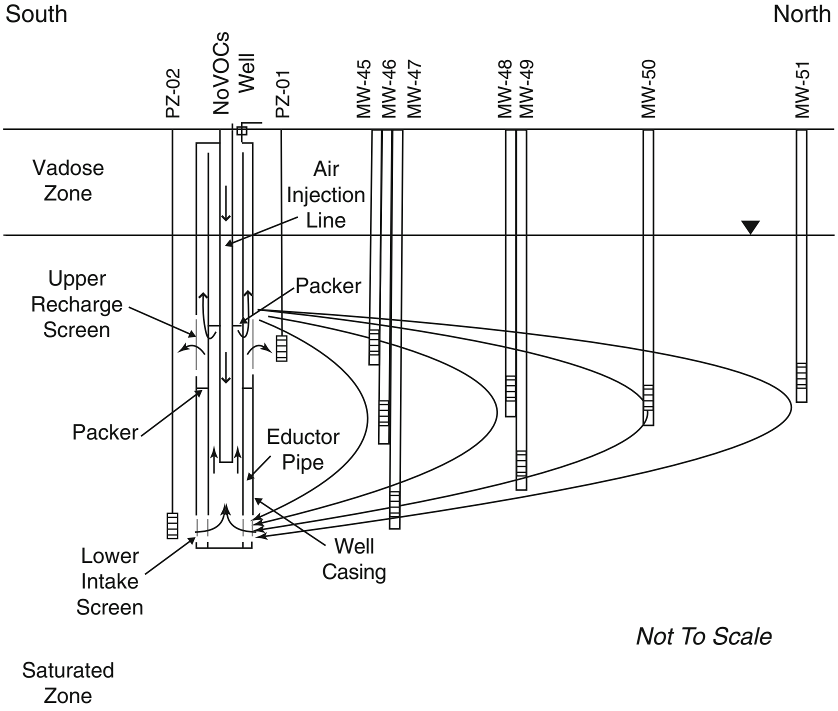

Figure 18.9. Cross section of the NoVOCs™ treatment system at Site 9, NAS North Island (USEPA, 2000b).

Groundwater samples collected from piezometers PZ-01 and PZ-02 were analyzed for VOC concentrations to evaluate the removal efficiency of the system. Groundwater samples were collected from the monitoring wells to evaluate the change in contaminant concentrations within the treatment cell. Dissolved oxygen, specific conductance, temperature, oxidation-reduction potential (ORP) and pH were measured in the field during each sampling event. The results of these analyses were used to evaluate changes in aquifer chemistry caused by the NoVOCs™ system.

VOC concentrations were measured in air samples collected from the influent and effluent of the NoVOCs™ and off-gas treatment systems in Summa canisters by EPA Method TO-14. Air samples were collected weekly during the first month of the evaluation (four events) and monthly thereafter for one month (one event). The data were used to evaluate contaminant mass removal of the NoVOCs™ system and to assess the effectiveness of the flameless oxidation process. Air sampling was terminated because of operational problems with the NoVOCs™ system.

Results. VOC analyses of influent and effluent from the NoVOCs™ system showed that in-well treatment performance for 1,1-DCE, *cis*-DCE, and TCE achieved 98, 95, and 93%, respectively. The mean concentrations of 1,1-DCE, *cis*-DCE, and TCE entering the well were approximately 3,530, 45,000, and 1,650 µg/L, respectively. The mean concentrations of 1,1-DCE, *cis*-DCE, and TCE after in-well treatment were 27, 1,400, and 32 µg/L, respectively.

The intermittent operation of the NoVOCs™ system prevented direct evaluation of the radius of the NoVOCs™ treatment cell. During the constant discharge rate (flow [Q] = 20 gpm) pumping test, measurable drawdown [+/-0.3 cm (0.01 ft)] was observed at different depths and at approximately 30.5 m (100 ft) from the NoVOCs™ well, indicating a potential radius of influence of up to 30.5 m (100 ft). Dipole flow testing was performed to measure pressure changes in the aquifer under NoVOCs™ operation. Dipole testing involves the use of three packers in a single well to isolate two discrete sections of the well, pumping water from one section to the other to establish a circulatory pattern in the adjacent formation, and measuring the steady state head difference between the two chambers and at locations in the formation (Kabala, 1993). Depending on the setup of the test, the data can be used to estimate the horizontal and vertical hydraulic conductivity values within the zone of influence of the well as well as to determine the dimensions of that zone. The test at NAS North Island involved pumping the lower section of the NoVOCs™ well while simultaneously injecting water into the upper section at different rates and at different step intervals. The data generated showed measurable pressure responses at cross gradient locations 9.1 m (30 ft) from the NoVOCs™.

Operational problems with the NoVOCs™ system resulted in intermittent operation for less than the planned six-month period. VOC mass removal was calculated for the time when the system was running by measuring the air flow rate and concentration of VOCs in air entering and exiting the NoVOCs™ system. The average total VOC mass removal of the NoVOCs™ system ranged from 4.5 to 63.6 grams per hour (g/hr) (0.01 to 0.14 lb/hr) with an average of 45.4 g/hr (0.10 lb/hr). The total VOC mass removed during the entire operation period from April 20, 1998 to June 19, 1998 was estimated to be approximately 42.0 kg (92.5 lb).

Costs. An economic analysis of the NoVOCs™ technology based on the demonstration showed a one time capital cost for the well and associated equipment estimated at $190,000. Annual O&M costs were estimated to be $160,000 per year for the first year and $150,000 per year for each subsequent year. Cost estimates for operation of a single well NoVOCs™ system over a range of time calculated based on these estimates and an annual inflation rate of 4% were $350,000 for the first year, $670,000 for 3 years; $1,000,000 for 5 years; and $2,000,000 for 10 years. The cost of treatment per unit volume of water was not calculated because of the number of assumptions required to make such a calculation. Additionally, costs per unit volume of water were not calculated for this project because of the site specific nature of treatment costs.

18.10 TECHNOLOGY DOCUMENTS

Several technical documents have been published that provide guidance on implementing in-well treatment technologies or that describe detailed evaluations of these technologies under highly monitored conditions. Three key documents are described below.

18.10.1 ESTCP Protocol

In 1997, ESTCP produced a guidance document titled “Technical Protocol for Implementing the Groundwater Circulating Technology for Site Remediation,” which describes the underlying principles of in-well treatment systems, the designs of several configurations

(UVB, NoVOCs™ and DDC) and requirements for site characterization, system O&M, and performance evaluation (ESTCP, 1997).

18.10.2 USEPA Site Program Reports

The USEPA evaluated NoVOCs™ and UVB systems under the SITE program. The NoVOCs was tested at NAS North Island, CA (USEPA, 2000a; b), and the UVB at March AFB, CA (USEPA, 1995; Bannon et al., 1995; USEPA, 1999). The results of these evaluations have been published in Technology Evaluation Reports (TERs) and in SITE Technology Capsules, which are abbreviations of the TERs. These documents include descriptions of the technologies, their applicability and limitations, results from the demonstrations, lessons learned during the demonstrations, and an economic analysis.

18.10.3 Air Force Massachusetts Military Reservation Documents

The Air Force Center for Environmental Excellence (now the Air Force Center for Engineering and the Environment) has supported demonstrations of GCW configurations at the Massachusetts Military Reservation located on Cape Cod, MA. The demonstrations included intensive monitoring and several reports have been published that provide valuable insight to the design and performance of those systems (Parsons Engineering Science, Inc., 1997a, 1997b; Smith, 2001; Kavanaugh et al., 1999; USEPA, 2002).

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CHAPTER 19

PHYTOREMEDIATION OF CHLORINATED SOLVENT PLUMES

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19.1 INTRODUCTION

Increasing knowledge of bioremediation has demonstrated the self-remediation potential of water, sediments and soil in natural ecosystems. While abiotic processes can be involved to some extent, biological systems play the major role in natural remediation of organic pollutants. Living organisms are commonly exposed to natural and xenobiotic toxic compounds. As a consequence, these organisms have developed multiple detoxification mechanisms to prevent harmful effects from exposure to these compounds. Environmental biotechnologies exploit the natural potential of living organisms, such as bacteria, plants and fungi, to detoxify human-made pollutants discharged into the environment. Bacteria are extremely versatile organisms, more so than higher life forms. As a consequence, bacteria constantly develop new metabolic pathways for the degradation of a large range of xenobiotic pollutants (Limbert and Betts, 1996). While less versatile and adaptive, higher organisms such as plants also possess detoxification mechanisms to counteract the harmful effects of exposure to toxic contaminants (Sandermann, 1994). Often, symbiotic bacteria living in association with plants also play an important role in the degradation process (Chaudhry et al., 2005). Phytoremediation seeks to use the natural and adaptive capabilities of plants, and their associated organisms, to treat a wide range of pollutants including chlorinated solvents.

19.1.1 The Phytoremediation Concept

Phytoremediation is defined as the use of vascular plants to remove or mitigate the impact of pollutants in soil, sediment and water. Phytoremediation technology has been reviewed in numerous documents, including Meagher (2000), Schnoor (2000), Dietz and Schnoor (2001a), Garbisu and Alkorta (2001), Davis et al. (2002), McCutcheon and Schnoor (2003a), Newman and Reynolds (2004), Arthur et al. (2005) and Pilon-Smits (2005). It offers a promising alternative for the treatment and containment of shallow contamination at numerous polluted sites. Widespread dispersion of environmental contamination renders bioremediation strategies a cost-effective alternative to more traditional technologies (Schnoor et al., 1995). Phytoremediation has been shown to efficiently reduce environmental hazards associated with various classes of pollutants, including heavy metals, explosives and energetic compounds, pesticides, petroleum products and polycyclic aromatic hydrocarbons (PAHs), and chlorinated solvents (Salt et al., 1998; Meagher, 2000; Newman and Reynolds, 2004). An extensive review of the potential applications of phytoremediation can be found in McCutcheon and Schnoor (2003b).

Higher plants are able to efficiently take up pollutants from soil, sediment, surface water and groundwater. Following the uptake into plant tissues, pollutants can undergo degradation, immobilization, volatilization or photolysis (Schnoor et al., 1995; Salt et al., 1998). Plants have

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been shown to metabolize organic compounds through processes that share many characteristics with the mammalian liver, leading to the *green liver* concept (Sandermann, 1994). Phytoremediation also involves indirect plant-mediated mechanisms, such as the enhancement of microbial activity and biodegradation in the root zone (Limbert and Betts, 1996), and the hydraulic control of contaminant plumes through the transpiration of large amounts of water (Ferro et al., 2003).

19.1.1.1 Historical Background

While phytoremediation is a relatively new concept, the name phytoremediation was first introduced in the early 1990s (Raskin, 1996). The biodegradation of xenobiotic compounds by plants has been known for a long time (Castelfranco et al., 1961). Land-farming of wastewaters has been a treatment technology for at least 300 years, and wetland treatment of wastewater and the use of plants to control air pollution have been used for several decades (McCutcheon and Schnoor, 2003b). Plant-mediated bioremediation of metal-contaminated soils was proposed first in the 1970s even though metal toxicity was believed to limit the process until the discovery of hyperaccumulator plants (Brooks et al., 1977).

The idea that plants can detoxify and metabolize organic compounds emerged in 1977 with the metabolism of 1,1,1-trichloro-2,2-*bis*-(4'-chlorophenyl) ethane (DDT) and benzo(*a*)pyrene (Cole, 1983; Sanderman, 1994; Coleman et al., 1997). During the 1980s and 1990s, phytoremediation acquired the status of a proven bioremediation technology for the treatment of both heavy-metal and organic pollutant-contaminated soil and groundwater (Shimp et al., 1993; Cunningham et al., 1995; McCutcheon et al., 1995; Schnoor et al., 1995; Salt et al., 1998; Schnoor, 2000).

19.1.1.2 Heavy Metal versus Organic Compounds

Elemental metals cannot be degraded and they typically accumulate in plant tissues, which then have to be harvested and safely disposed (Salt et al., 1998). Historically, a large part of phytoremediation technology focused on the treatment of heavy-metal contamination: *Phytoextraction* refers to the removal of metals from soil and their accumulation in aboveground plant parts; *rhizofiltration* refers to the sorption, concentration and/or precipitation of metals in or on the root tissues (Salt et al., 1995; Chaney et al., 1997; Raskin et al., 1997). Another important difference between metals and toxic organic pollutants is that metals occur naturally in the environment (in addition to anthropogenic sources).

As a consequence, certain plant species native to natural metal-contaminated soil, known as "hyperaccumulators", are able to take up and accumulate metals in their tissues at very high concentrations (Brooks et al., 1979). Unlike heavy metals, organic pollutants, such as chlorinated solvents, theoretically can be transformed into innocuous constituents. As a consequence, processes like phytotransformation and rhizosphere biodegradation are more important since they can lead to a complete breakdown of toxic pollutants (Alkorta and Garbisu, 2001).

19.1.1.3 Phytoremediation as a Cost Effective Alternative for the Treatment of Polluted Soils

Numerous bench-scale or greenhouse investigations have proven the efficiency of plants for taking up and transforming environmental pollutants (Newman and Reynolds, 2004). However, phytoremediation has not yet been recognized by the U.S. Environmental Protection Agency (USEPA) as an approved bioremediation technology, and only a few documented full-scale phytoremediation projects have been conducted (Schnoor et al., 1995; Schnoor, 1997).

Although phytoremediation is not a cleanup panacea, it has been proven effective for the treatment of a range of soil and groundwater contaminants (Schnoor, 1997). Overall, phytoremediation effectiveness depends largely on the nature of the contaminants (chemical speciation), the architecture of the contamination (depth, concentration), the site characterization (type of soil, climate, groundwater), and the degree of cleanup required. Advantages and limits of phytoremediation have been reviewed in several documents, including Cunningham et al. (1995), Schnoor et al. (1995), Schnoor (1997), Macek et al. (2000), Gordon et al. (2003), Marmiroli and McCutcheon (2003), Grandel and Dahmke (2004) and Pilon-Smits (2005).

Advantages of Phytoremediation. Phytoremediation is a promising and attractive remediation technology that has several advantages over more traditional processes because it:

- Is relatively inexpensive because of the absence of complex and energy-consuming equipment and the limited maintenance requirements.
- Is an *in situ* process, which is recognized as "environmentally friendly" (not destructive for soil or natural habitats), and it is also applicable to large areas contaminated with low concentrations of pollutants.
- Relies on the use of green plants and trees for cleaning up pollution, making it an attractive green technology.
- Can be used to achieve many different objectives, including pollution cleanup and control, erosion control, site maintenance, and biomass production; it is well adapted for the remediation of urban or industrial brownfields (Marmiroli and McCutcheon, 2003).
- Can be used, in some cases, as a "polishing treatment" after the application of other cleanup technologies (Schnoor et al., 1995).

Limitations of Phytoremediation. There are several recognized limitations in the application of phytoremediation:

- Phytoremediation can be used only on shallow contamination not extending much deeper than the root zone, even though effects from hydraulic control and rhizosphere changes can extend beyond the root depth (Schnoor et al., 1995).
- Phytoremediation typically is not a rapid process. Uptake and phytotransformation mechanisms are slow, planted trees need several years to reach mature size, and in temperate regions, plants have limited transpiration during the dormant season (Schnoor et al., 1995; Schnoor, 1997).
- Phytoremediation of organic pollutants is limited to those compounds considered "moderately hydrophobic." There are biological barriers that are more or less selective for the uptake of both organic and inorganic compounds (Burken and Schnoor, 1998b) (see Section 19.1.2.1).
- Plants have only limited metabolic capabilities to transform most organic recalcitrant pollutants, such as polychlorinated biphenyls (PCBs), PAHs, and explosives, which accumulate inside plant tissues (Schnoor et al., 1995), and plants are living organisms that are sensitive to toxic contaminants (see Section 19.1.2.12).
- Phytoremediation can lead to non-desirable effects. Pollutants or toxic metabolites that accumulate in plant tissues may be released in the environment (Yoon et al., 2006); immobilized, relatively innocuous toxic compounds in soil can be mobilized by phytoremediation processes (acidification, organic complexants) and introduced in the food chain (Schnoor, 1997); volatile toxic compounds (such as mercury or chlorinated solvents) can be volatilized into the atmosphere (Newman et al., 1997).

- The most important constraints to the development and application of phytoremediation are not of a technical nature. Current regulatory policies may not be consistent with the use of phytoremediation, phytoremediation may not be competitive with other remediation technologies, and patents and proprietary rights can limit the use of phytoremediation (Miller, 1997; Marmiroli and McCutcheon, 2003).

Despite these drawbacks, phytoremediation may be well suited for treating chlorinated solvents. Chlorinated solvent plumes often are shallow and at concentrations low enough that no phytotoxicity effect is observed. Chlorinated solvents can be efficiently taken up inside plant tissues, and they are known to be biodegradable by both microbes in the rhizosphere and by plant enzymes. Finally, chlorinated solvents and their transformation products are susceptible to volatilization into the atmosphere, but at levels that do not constitute a threat to living organisms (Schipper, 2003; Newman and Reynolds, 2004).

19.1.2 Processes Involved in Chlorinated Solvent Phytoremediation

19.1.2.1 Phytoremediation as Plant-Mediated Remediation

Phytoremediation encompasses a range of processes beyond direct plant uptake and metabolism, and it is best described as plant-mediated remediation (Cunningham et al., 1995; Schnoor et al., 1995; Schnoor, 1997; Macek et al., 2000; McCutcheon and Schnoor, 2003b). While definitions and terminology vary, the different processes involved as part of phytoremediation are illustrated in Figure 19.1.

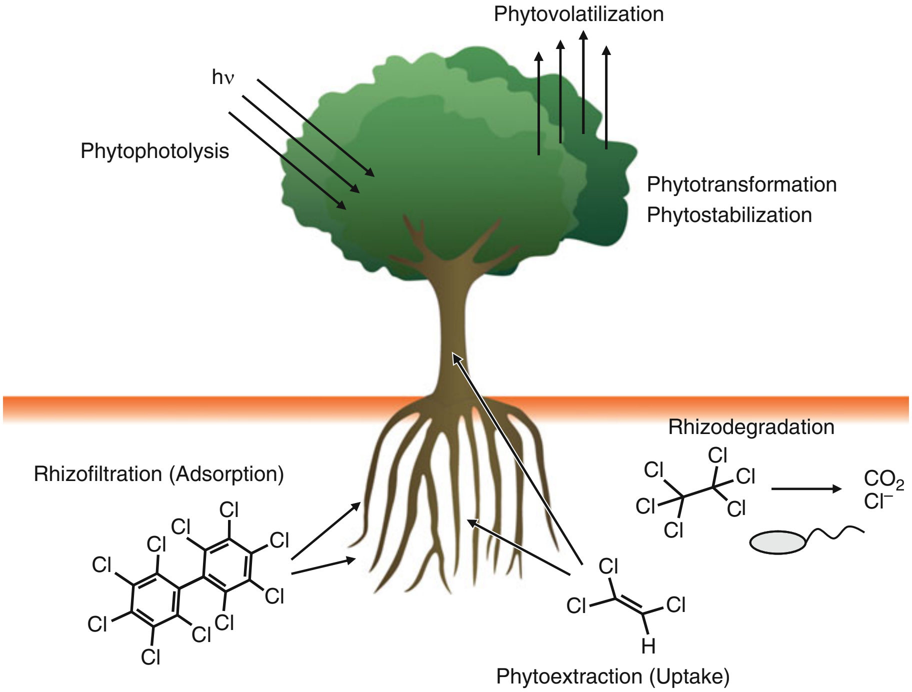


Figure 19.1. Phytoremediation involves several processes. Pollutants in soil and groundwater can be taken up inside plant tissues (*phytoextraction*) or adsorbed to the roots (*rhizofiltration*), pollutants taken up inside plant tissues may undergo transformation by plant enzymes (*phytotransformation*) or may be incorporated into plant structures (*phytostabilization*), they may be volatilized to the atmosphere (*phytovolatilization*) or exposed to light-mediated degradation (*phytophotolysis*). Pollutants in soil also may be degraded by microbes associated with the root zone (rhizodegradation).

Pollutants in soil and groundwater are first taken up (*phytoextraction*) or adsorbed to the roots (*rhizofiltration*). Pollutants then can be translocated to different parts of the plant, where they can be transformed by plant enzymes (*phytotransformation*), can volatilize to the atmosphere (*phytovolatilization*) or can undergo light-mediated degradation (*phytophotolysis*) (Schnoor et al., 1995; Salt et al., 1998; McCutcheon and Schnoor, 2003b). Alternatively, toxic pollutants or their transformation products can be sequestrated in cell organelles or incorporated within the plant structure (*phytostabilization*) (Salt et al., 1995). Another important mechanism is related to the bacterial activity in the rhizosphere. Plants release organic matter in soil that promotes microbial activity in the root zone, which can result in an enhancement of both biodegradation and immobilization of toxic pollutants (*rhizodegradation*) (Anderson et al., 1993; Limbert and Betts, 1996). In addition, large phreatophytic trees transport considerable volumes of groundwater through transpiration, thus modifying groundwater flux (*hydraulic control*). Hence, trees can be used to limit off-site migration of contaminants (Ferro et al., 2003).

19.1.2.2 Chlorinated Solvent Properties Relevant to Phytoremediation

Chlorinated solvents, such as perchloroethene (PCE) and trichloroethene (TCE), are the most frequent contaminants of concern in groundwater in the United States (Norris et al., 1994; Ajo-Franklin et al., 2006). While chlorinated solvents are known to be biodegradable, they can persist in groundwater for decades (Bradley, 2003). Chlorinated solvents are characterized by low water solubility; however, their solubility is four or five orders of magnitude greater than the USEPA's maximum contaminant level (MCL) (Ajo-Franklin et al., 2006). Also, much of the chlorinated solvent contamination in the subsurface occurs in the form of dense nonaqueous phase liquids (DNAPLs), which can be particularly difficult to remediate. As a consequence, phytoremediation usually does not result in a significant reduction in the concentration of chlorinated solvents in aquifers. Another problem associated with phytoremediation of chlorinated solvents is the need for large planted surface areas to achieve treatment objectives (Matthews et al., 2003) (see Section 19.1.2.10).

However, phytoremediation is often a good technology for treatment of chlorinated solvent contamination in groundwater, both because of the nature of the contamination and the chemical and physical properties of the contaminants (Newman et al., 1997, 2003). Chlorinated solvent contamination of aquifers, when present as shallow and slow moving DNAPLs, allows plant roots to reach contaminated zones and sufficient time for phytoremediation processes to be effective, by both contaminant uptake and rhizosphere degradation. As moderately hydrophobic compounds, most chlorinated solvents have octanol-water partition coefficient (K_{ow}) values that predict them to be efficiently taken up inside plant tissues, where they can be further degraded by plant enzymes (Newman et al., 1997; Burken and Schnoor, 1998b). Chlorinated solvents are also susceptible to reductive and oxidative degradation by bacteria, processes that can occur sequentially in saturated soil where reductive anoxic conditions prevail, and in the vadose zone where oxidative aerobic conditions prevail (Bradley, 2003). Finally, as most chlorinated solvents have a relatively high vapor pressure and low boiling point, they can be easily volatilized to ambient air from plant leaves or directly from soil.

Laboratory experiments and field demonstrations have proven highly efficient removal of chlorinated solvents by plant uptake and/or by rhizodegradation from both hydroponic solutions and soil. Together, these reports show that phytoremediation can be effective for the treatment of shallow groundwater contamination by chlorinated solvents (Newman et al., 1997). Table 19.1 summarizes a number of publications on the phytoremediation of chlorinated solvents.

Table 19.1. Non-comprehensive List of Publications on Phytoremediation of Chlorinated Solvents by Compound

System	Metabolites	Mechanism	Reference
***cis*-1,2-dichloroethene (*cis*-DCE); Trichloroethene (TCE)**			
Bald cypress (*Taxodium distichum*) Tupelo (*Nyssa aquatica*) Sweet gum (*Liquidambar stryaciflua*) Oak (*Quercus* spp.) Sycamore (*Platanus occidentalis*) Loblolly pine (*Pinus taeda*)		• Phytoextraction • Inter-species variation	Vroblesky et al., 1999
2,4-dichlorophenol (2,4-DCP)			
Brassica napus hairy root cultures		• Removal from solution • Peroxidase oxidation (suggested)	Agostini et al., 2003
Ethylene dibromide (EDB); TCE			
Hydroponic *Leuceana leucocephala*	Trichloroethanol Bromide	• Phytoextraction • Oxidative transformation • Dehalogenation	Doty et al., 2003
Hexachloroethane (HCA); Carbon tetrachloride (CT)			
Aquatic plants *Eloeda canadensis* and *Myrophyllum aquaticum* Macrophytic algae *Spirogyra* spp. and *Nitella* spp.	TCE, 1,1,2,2-Tetrachloroethane, 1,1,2-Trichloroethane, Trichloroacetic acid, and Dichloroacetic acid from HCA. Chloroform from CT	• Phytotransformation by oxidative and reductive transformation • Sequestration • Sorption	Nzengung et al., 1999a; 1999b; 2003
HCA; Perchloroethene (PCE); TCE; Pentachlorophenol; 1,3,5-Trichlorobenzene; 1,4-Dichlorobenzene; CT; Toxaphene; 1,1,1-Trichloro-2,2-bis-(4-chlorophenyl)ethane (DDT)			
Canadian waterweed (*Elodea canadensis*) plants and cell-free extracts		• Dehalogenation of aliphatic compounds by dehalogenases (suggested)	Wolfe and Hoehamer, 2003
PCE			
Trees on the field Hybrid poplar trees		• Phytoextraction by transfer from soil vapor phase to roots	Struckhoff et al., 2005
PCE; TCE			
Hydroponic cottonwood Willow trees	Trichloroacetic acid Dichloroacetic acid	• Phytoextraction • Phytotransformation by oxidative transformation • Volatilization • Mineralization	Nzengung and Jeffers, 2001

(*continued*)

Table 19.1. (continued)

System	Metabolites	Mechanism	Reference
TCE			
Rhizosphere soil	*cis*-DCE *trans*-1,2-dichloroethene (*trans*-DCE)	• Adsorption on soil • Diffusional loss • Anaerobic rhizodegradation by dehalogenation	Brigmon et al., 1998
Hybrid poplars cuttings Cell cultures	Trichloroethanol Trichloroacetic acid Dichloroacetic acid	• Phytotransformation by oxidative transformation • Volatilization • Mineralization	Gordon et al., 1998
Alfalfa in growth chambers		• Transfer from saturated to vadose zone • Volatilization	Narayanan et al., 1999
Hybrid poplars	Trichloroethanol Trichloroacetic acid Dichloroacetic acid	• Phytotransformation by oxidative transformation	Doucette et al., 1999
Artificial aquifer with trees	Trichloroethanol Trichloroacetic acid Dichloroacetic acid	• Phytotransformation by oxidative transformation • Volatilization • Mineralization	Newman et al., 1999
Bald cypress (*Taxodium distichum*)		• Phytoextraction, seasonal variation	Nietch et al., 1999
Transgenic tobacco		• Phytotransformation by oxidative transformation	Doty et al., 2000
Tobacco Poplar	Trichloroethanol Trichloroacetic acid Dichloroacetic acid Glucosyl conjugate (β-D-glucoside of trichloroethanol)	• Phytotransformation by oxidative transformation • Conjugation by glycosylation	Shang et al., 2001
Cottonwood trees	*cis*-DCE Vinyl chloride	• Rhizodegradation • Reductive dehalogenation	Godsy et al., 2003
Deep-rooted trees		• Hydraulic control (modeling)	Matthews et al., 2003
Hybrid poplar trees		• Volatilization, involving transport and diffusion through the transpiration stream	Ma and Burken, 2003; 2004
TCE; 1,1,1-Trichlorethane (1,1,1-TCA)			
Alfalfa		• Rhizodegradation • Volatilization	Narayanan et al., 1995
TCE; 1,1,2,2-Tetrachloroethane (1,1,2,2-TeCA); CT			
Hybrid poplar trees from contaminated soil		• Phytoextraction • Partitioning	Ma and Burken, 2002

(*continued*)

Table 19.1. (continued)

System	Metabolites	Mechanism	Reference
^{14}C-Trichloroethene (^{14}C-TCE)			
Vegetated and non-vegetated soils (*Paspalum notatum, Lespedeza cuneata, Pinus taeda, Solidago* sp.), TCE-contaminated	^{14}C-Carbon dioxide	• Rhizodegradation • Mineralization	Walton and Anderson, 1990
Vegetated and non-vegetated soils (*Lespedeza cuneata, Pinus taeda, Solidago* sp., *Glycine max*), TCE-contaminated	^{14}C-Carbon dioxide	• Rhizodegradation • Mineralization • Uptake	Anderson et al., 1993 Anderson and Walton, 1995
Hybrid poplar hydroponic Hairy root cultures	Trichloroethanol Dichloroacetic acid Trichloracetic acid Carbon dioxide	• Phytoextraction • Phytotransformation by oxidative transformation • Mineralization • Sequestration • Volatilization	Newman et al.,, 1997
Edible garden plants (carrots, spinach, and tomatoes)		• Phytoextraction • Volatilization • Sorption to soil • Accumulation • Sequestration	Schnabel et al., 1997
Hydroponic hybrid poplar in growth chambers		• Phytoextraction • Volatilization	Orchard et al., 2000a; b
Hybrid poplar cell suspension		• Phytoextraction • Incorporation in cell wall and in large biomolecules	Shang and Gordon, 2002
^{14}C-TCE, pentachlorophenol, 1,2,4-trichlorobenzene			
Hydroponic poplars		• Phytoextraction, relationship between uptake and translocation and K_{ow} • Volatilization	Burken and Schnoor, 1998b

19.1.2.3 Overview of Phytoremediation Processes

The different processes that may be active during phytoremediation have generated a variety of different names and definitions; to date, no general agreement on terminology can be found in the literature. An extensive list of these physiological processes and their multiple names is presented in McCutcheon and Schnoor (2003b). The simplified descriptions below are based on the recognition of five major mechanisms: *phytotransformation*, *rhizodegradation*, *phytostabilization*, *phytoextraction*, and *rhizofiltration* (Schnoor, 1997). In addition, three processes that are also part of phytoremediation technology will be discussed: *phytovolatilization*, *phytophotolysis*, and *hydraulic control*. These processes are briefly described below.

Greater detail on these processes and their roles in chlorinated solvent plume treatment are provided in the following sections.

Phytotransformation—or phytodegradation in a more restricted sense—refers to the metabolism of organic pollutants inside plant tissues. In a broader sense, it refers to the uptake, transformation and/or the storage of organic contaminants by and inside plants (Schnoor, 1997; McCutcheon and Schnoor, 2003b). The process involves first the uptake of pollutants from soil, sediment, surface water or groundwater by plant roots. The potential for uptake by plants depends largely on the hydrophobicity of the chemical, represented by the log K_{ow}. Experimental relationships based on log K_{ow} can be used to predict the sorption of specific chemicals to the roots (root concentration factor [RCF]) and the uptake and translocation of chemicals inside plant tissues through the transpiration stream (transpiration stream concentration factor [TSCF]). Typically, moderately hydrophobic organic compounds (with a log K_{ow} between 0.5 and 4.5) can be significantly taken up by plants (Briggs et al., 1982; Burken and Schnoor, 1998b).

Besides the physical-chemical properties of organic pollutants, additional factors affecting the uptake include chemical speciation and the concentration of the contaminants in the environmental matrix. In addition, a variety of ecological and environmental factors can play a role in contaminant uptake, such as plant species, soil characteristics, bacterial activity and climatic conditions (Schnoor, 1997; Burken and Schnoor, 1998b; Marmiroli and Cutcheon, 2003). Typical applications for phytotransformation include sites contaminated by organic biodegradable contaminants, such as explosives and energetic compounds, petrochemicals and PAHs, chlorinated solvents, pesticides and fertilizers, and landfill leachates (Schnoor et al., 1995; Macek et al., 2000; Meagher, 2000; Newman and Reynolds, 2004).

An important mechanism of phytotransformation is the chemical degradation and detoxification of organic compounds inside plant tissues. Enzymatic reactions that can be performed by plants are highly diverse, and can be summarized according to the green liver model (Figure 19.2). Based on early observations that plants were capable of metabolizing organic xenobiotic pollutants (pesticides), Sandermann (1994) introduced the green liver concept, which typically occurs in three phases.

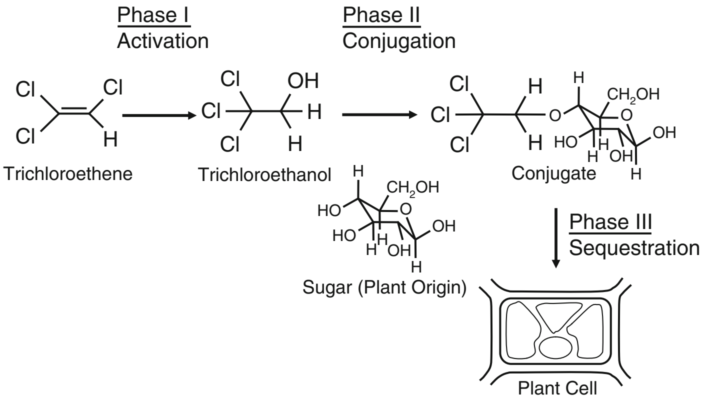


Figure 19.2. The green liver model. Hypothetical pathway representing the metabolism of TCE in plants: Phase I—oxidation of TCE to trichloroethanol (TCEth), Phase II—conjugation with a sugar molecule, Phase III—sequestration of the conjugate in plant cells.

Initial activation, or *Phase I*, consists of the oxidation, reduction or hydrolysis of the xenobiotic compound, which is transformed into a more reactive metabolite. Examples of

Phase I reactions include oxidation or hydroxylation by cytochrome P450 monooxygenases and reduction of nitro groups by nitroreductases. In *Phase II*, the resulting activated product undergoes a transferase-catalyzed conjugation with a molecule of plant origin, forming an adduct less toxic and more soluble than the parent pollutant. Transferases may involve glutathione *S*-transferase or glycosyltransferases. *Phase III* involves the sequestration of the conjugate, which can be stored in plant organelles such as vacuoles, incorporated into biopolymers such as lignin, or excreted in the case of wetland plants (Cole, 1983; Sandermann, 1994; Coleman et al., 1997; Schroder et al., 2001; Burken, 2003) (see Section 19.1.2.10).

From an environmental viewpoint, phytotransformation must lead to a significant detoxification of toxic compounds. Without further transformation, pollutants and toxic metabolites that accumulate inside plant tissues will eventually return to the soil or groundwater and may enter the food web, resulting only in pollution transfer (Schnoor et al., 1995, Schnoor, 1997).

Rhizodegradation—also known as phytostimulation, rhizosphere biodegradation, or plant-assisted bioremediation—refers to the enhanced microbial activity and biodegradation of pollutants that occurs in the root zone (Anderson et al., 1993; Limbert and Betts, 1996). Root exudates and root turnover increase soil organic carbon, which is beneficial both for microbial growth and cometabolic biodegradation. By buffering the pH and through biosorption of toxic metals, plants create ecological niches that promote microbial growth (Anderson et al., 1993; Shimp et al., 1993; Schnoor, 1997).

Root exudates contain organic acids, alcohols, and phenolic compounds that increase contaminant bioavailability and biodegradation, both by solubilization of hydrophobic pollutants and by complexation of heavy metals (Chaudhry et al., 2005). Roots also excrete catabolic enzymes directly involved in biodegradation, such as dehalogenases and nitroreductases, which are known to be active in close proximity to the roots (Schnoor, 1997; Gianfreda and Nannipieri, 2001; Gianfreda and Rao, 2004). Specific compounds in root exudates have been suggested to induce microbial enzymes and to stimulate specific biodegradation capabilities (Fletcher and Hedge, 1995). Finally, roots introduce oxygen in the rhizosphere, which is necessary for oxidative biodegradation (Anderson et al., 1993; Shimp et al., 1993; Chaudhry et al., 2005).

Phytostabilization is the use of vegetation to hold soil and sediments in place and to immobilize toxic contaminants in soil or stabilize dissolved phase plumes in order to mitigate their impact on the environment (Salt et al., 1995; Schnoor, 1997). These processes are also referred to as biomineralization, phytosequestration or lignification. Phytostabilization is especially useful for metal contaminants and radionuclides that are not amenable to biodegradation and it will not be considered further here.

In a sense, the transpiration of large amounts of water by vigorously growing trees is also a stabilization technology, because it prevents the migration of plumes of toxic pollutants towards groundwater or receiving waters, but this usually is referred to as *hydraulic control* (see below). Finally, the enhanced microbial activity and higher carbon content in the root zone promote the sequestration of some toxic contaminants by humification, mineralization, and sorption to soil particles. It is noteworthy that Phytostabilization also refers to the sequestration of toxic contaminants taken up inside plant tissues (or their metabolites) by storage into cell organelles or incorporation into cell structures (Phase III of the green liver model).

Phytoextraction—also known as phytoaccumulation, phytoconcentration or hyperaccumulation—refers to the use of plants to take up, translocate and accumulate contaminants from the soil or groundwater to the roots and aboveground parts (Chaney et al., 1997). It is typically more important to elemental contaminants (metals) not susceptible to biodegradation than to organic contaminants, such as chlorinated solvents. However, solvents must first be "phytoextracted" before degradation within the plant or transpiration from the aboveground tissues can occur.

Rhizofiltration is the term for the use of plant roots to sorb, concentrate or precipitate metal contaminants from surface water or groundwater (Salt et al., 1995). Other terms for this process include blastofiltration, phytosorption or biofiltration. Metals that are not easily taken up by plants and therefore are not suitable for phytoextraction, such as lead, chromium, and radionuclides, may be good candidates for rhizofiltration. However, rhizofiltration is not a significant process in the phytoremediation of relatively water-soluble compounds such as chlorinated solvents.

Phytovolatilization describes the volatilization of contaminants from the plant to the atmosphere. Some contaminants can be volatilized through the leaves after uptake and translocation (McCutcheon and Schnoor, 2003b). Leaves of trees exhibit a very large surface area that can potentially volatilize significant amounts of chemicals. Volatilization depends not only on the physical and chemical properties of the contaminants, but also on the physiological state and morphological characteristics of the plants (cuticle, stomata opening), and on meteorological conditions that determine the transpiration rate (temperature, humidity) (Davis et al., 2002; Pilon-Smits, 2005). Volatile organic compounds (VOCs), such as solvents and other chlorinated organic chemicals, are susceptible to volatilization into the atmosphere (Newman et al., 1997; Burken and Schnoor, 1998a; McCutcheon and Rock, 2001).

Phytophotolysis refers to the degradation of contaminants in the leaves due to exposure to light (McCutcheon and Schnoor, 2003b). The ability of energetic ultraviolet (UV) radiation from sunlight to degrade a range of organic molecules has been recognized for a long time (Dubbleman and Shuitmaker, 1992; Burrows et al., 2002). In addition, an indirect effect of sunlight is the generation of free radicals and reactive oxygen species (ROS) that can react with organic molecules (DeRosa and Crutchley, 2002). Light-mediated degradation of explosives (e.g., RDX) in plants has been documented in the literature (Just and Schnoor, 2004; Van Aken et al., 2004). However, photolysis of chlorinated solvents seems to be insignificant under ambient illumination (Sato et al., 1997; Feiyan et al., 2002).

Hydraulic control (or hydrologic control) of contaminant plumes is one of the most recognized mechanisms of phytoremediation. Large phreatophytic trees such as poplars and willows transpire considerable volumes of groundwater and can modify or reverse the direction of groundwater flow, preventing contamination of surrounding areas by capturing plumes prior to off-site migration (Ferro et al., 2003). By extracting large amounts of water, they can lower the water table level and create a cone of depression centered on the vegetated area (Eberts et al., 2003; Eberts et al., 2005).

The efficacy of hydraulic control depends largely on the transpiration rate, which in turn is determined by the physiology of the plant (the size of the plant, its root system and depth, and its leaf surface area). However, other factors are also important including external parameters related to soil texture and hydrology, notably soil permeability and the recharge rate of the aquifer, and on meteorological parameters, including temperature, solar irradiation, wind conditions, humidity, and rainfall distribution. One important feature of hydraulic control is that the phytoremediation process can be effective below the root zone. Furthermore, hydraulic control is not dependent on the ability of the plant to take up contaminants (Ferro et al., 2003).

19.1.2.4 Rhizodegradation

Several reports have compared the degradation of chlorinated solvents in both vegetated soil (rhizosphere) and non-vegetated soil (edaphosphere). For example, Walton and Anderson (1990) studied soil samples from unvegetated soil at a chlorinated solvent contaminated site, as well as from the root zone of four plant species (*Paspalum notatum, Lespedeza cuneata*, *Pinus taeda*, and *Solidago* sp.) at the same site. After incubating the soil samples, they found more microbial biomass, greater TCE disappearance from the headspace, and enhanced mineralization of ^{14}C-TCE into $^{14}CO_2$ by microflora from the vegetated soil samples. Anderson et al. (1993) and Anderson and Walton (1995) also observed increased mineralization of ^{14}C-TCE in soil vegetated with different plant species (*Lespedeza cuneata*, *Pinus taeda*, *Solidago* sp., and *Glycine max*). Greater than 26% of the ^{14}C-TCE was mineralized in the vegetated soil, compared with 15% for non-vegetated soil and less than 9% for sterile soil. Enhanced TCE mineralization also was observed in soil containing *P. taeda* seedlings with root-ectomycorrhizae associations, which raises the question of the involvement of mycorrhizae in TCE degradation.

Godsy et al. (2003) measured TCE degradation by microbes from the rhizosphere of cottonwood trees located at a chlorinated ethene contaminated site. Their results showed that only microbes from the rhizospheres of mature trees (about 22 years old) were capable of dechlorinating TCE to *cis*-1,2-dichloroethene (*cis*-DCE) and vinyl chloride (VC), whereas microbes associated with newly planted trees were not. The authors suggested that mature rhizosphere soil was rich in organic material and contained microniches with low oxygen concentrations that allowed for increased TCE respiration.

Using laboratory-scale chambers planted with alfalfa (*Medicago sativa*), Narayanan et al. (1995) reported a significant decrease of TCE and trichloroethane (TCA) in groundwater, which was attributed largely to microbial activity in soil (although volatilization and plant uptake also likely contributed to the process). Evidence for anaerobic dechlorination of the chlorinated solvents included chloride accumulation and methane production during the incubations.

Conversely, other phytoremediation experiments conducted with poplar trees have shown no enhancement of TCE and carbon tetrachloride (CT) mineralization in vegetated soil compared to unvegetated controls (Newman et al., 1999; Wang et al., 2004). Studies on natural attenuation in four TCE-contaminated rhizosphere soils concluded that sorption to soil and diffusional losses were the dominant mechanisms of TCE attenuation in the aquifer (Brigmon et al., 1998). The addition of methane, oxygen and methanol to stimulate TCE biodegradation by methanotrophic or methanogenic activity was unsuccessful. Although detection of *cis*-DCE and *trans*-DCE indicated anaerobic reductive dechlorination, these products represented less than 5% of the initial TCE.

19.1.2.5 Phytoextraction

Uptake and translocation of organic chemicals in plants are measured by the TSCF (transpiration stream concentration factor). The TSCF can be used as a measure of the efficiency of uptake and translocation of organic chemicals from a hydroponic solution (i.e., the ratio of the concentration in solution relative to that in the transpiration stream of the xylem flowing up the shoots of the plant). A TSCF value of 1.0 indicates that there is perfect uptake and translocation of the organic contaminant at a concentration equal to that in solution, i.e., there is no membrane selectivity nor rejection of the chemical at the root-water interface. The opposite, a TSCF value of 0.0, would indicate that the plant fully excludes the chemical contaminant from uptake and translocation or alternatively, that the chemical is bound so strongly to roots that it is not translocated. It is noteworthy that the TSCF assumes equilibrium between nonreactive phases and does not allow for physical and chemical reactions. Therefore, it is important to realize that transformation of chlorinated solvents inside the plant can modify the prediction based on the TSCF.

Briggs et al. (1982) developed an experimental relationship to predict the uptake of herbicide-related chemicals (e.g., phenylureas) by crop plants (barley) on the basis of the log K_{ow}. Burken and Schnoor (1998b) developed a similar relationship to predict the uptake of common organic pollutants by hybrid poplar plants. Polar compounds, such as phenol or aniline (log $K_{ow} < 0.5$), do not pass the organic membranes (i.e., endodermis) of the roots, while hydrophobic compounds, such as pentachlorophenol (log $K_{ow} > 4.5$), tend to sorb on root tissues. Only compounds with "intermediate hydrophobicity" are efficiently taken up and translocated in plant tissues. Based on this relationship, TCE with a log K_{ow} of 2.33, is predicted to be significantly taken up by plants.

The RCF (root concentration factor) is a measure of the tendency of organic chemicals to sorb to root tissues, and as such is the ratio of the organic chemical sorbed to the roots (milligrams per kilogram [mg/kg] fresh tissue) to the concentration in solution (mg per liter [mg/L]). The slope of the linear sorption isotherm gives the RCF value (in units of L/kg). Briggs et al. (1982) and Burken and Schnoor (1998b) developed these relationships for various chemicals and plants. They described an organic partitioning phenomenon whereby "like dissolves like"—that is, organic chemicals tend to partition into soil organic matter or into the organic structure of the hemicellulose cell wall or the lipid bilayer of the cell membrane.

Experimental data show a general increase of RCF with log K_{ow}, which again predicts good uptake of TCE by the roots. As with the TSCF, the RCF assumes an equilibrium and does not account for transformation or translocation of contaminants inside plant tissues, which may modify the predictions based only on the RCF. Burken and Schnoor (1998b) also showed that VOCs such as benzene and TCE are readily transpired through the leave tissues. Concentrations of TCE measured in plant tissues were usually very low. Often TCE was not detected in exposed plants (Narayanan et al., 1995; Schnabel et al., 1997) or only traces were measured (Nzengung and Jeffers, 2001). Burken and Schnoor (1998b) reported a 2% accumulation of TCE in bottom stems and less than 1% in other plant compartments.

In phytoremediation experiments using hybrid poplar plants, Newman et al. (1997, 1999) observed the highest TCE levels in stems, lower levels in roots, and even lower or undetectable levels in the leafs. The low concentrations in the leaves probably are a result of the high transpiration rates through the foliage (Shang et al., 2003). Based on the diffusive loss in the trunk of trees, Davis et al. (1999) concluded that radial diffusion of TCE can explain the rapid disappearance from the stem. Conversely, Anderson et al. (1993) and Anderson and Walton (1995) observed the incorporation of ^{14}C into plant tissues ranging from 1 to 21% of the original ^{14}C-TCE, depending on the plant species. It was unclear, however, whether the recovered ^{14}C represented the original TCE or microbial or plant metabolites.

Analyzing the trunk of several tree species (bald cypress, *Taxodium distichum*; tupelo, *Nyssa aquatica*; sweet gum, *Liquidambar stryaciflua*; oak, *Quercus* spp.; sycamore, *Platanus occidentalis*; and loblolly pine, *Pinus taeda*) growing on a chlorinated solvent-contaminated site, Vroblesky et al. (1999) detected low concentrations of TCE and *cis*-DCE, which varied depending on the tree species. The authors also observed a significant decrease in concentration with the height of the trunk samples.

In greenhouse experiments, Nietch et al. (1999) observed that bald cypresses were capable of extracting TCE from groundwater with efficiencies correlated with the plant activity (decreasing from day to night and from August to December). In phytoremediation experiments using edible garden plants (carrots, spinach, and tomatoes) in air-flow bioreactors, Schnabel et al. (1997) detected only low amounts of ^{14}C-TCE in plant tissues, accounting for 1 to 2% of the TCE added to the nutrient solution. Concentrations of TCE in plant tissues were higher than in soil, with concentration factors ranging from 2.6 (tomato) to 32 (spinach). A correlation was observed between the concentrations of TCE, 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA), and CT in tree tissues and in groundwater underneath the trees (Ma and Burken, 2002). Extraction from groundwater and distribution in tree tissues was shown to depend on the partitioning coefficients of chlorinated solvents.

Orchard et al. (2000a, 2000b) studied the uptake and volatilization of TCE by hydroponic hybrid poplars using a dual-chamber plant growth system designed to minimize experimental artifacts. They observed concentrations of TCE in the shoot tissues ranging from 2 to 168 mg/kg, depending on transpired water and exposure concentration. On the other hand, the experimental TSCFs were much lower than those previously reported or predicted. Recently, Struckhoff et al. (2005) observed a relationship between soil and tree core concentrations of PCE. The authors hypothesized a transfer by diffusion of PCE from the soil vapor phase to the roots by experimentally determining the partitioning coefficients of PCE between the plant tissues and vapor phase, as well as between the plant tissues and soil.

19.1.2.6 Phytotransformation

Beside rhizodegradation, uptake, translocation, and volatilization, experimental evidence indicates that plants are able to metabolize TCE. Using hybrid poplar plants and root cell cultures, Newman et al. (1997) first demonstrated oxidative metabolism of TCE, similar to that observed in mammal livers. TCE oxidation products were detected, including trichloroethanol (TCEth), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA) (Figure 19.3). They also observed a limited mineralization of TCE accounting for 1 to 2% of the applied TCE. The authors detected the same metabolites in axenic hybrid poplar cell cultures, showing that they resulted primarily from plant metabolism and not from microbial degradation in the rhizosphere. Similar metabolites were found in subsequent experiments using hydroponic and soil-grown poplars and cell cultures (Gordon et al., 1998), poplars in field conditions (Newman et al., 1999), poplar and tobacco plants (Shang et al., 2001), hydroponic cottonwood and willow trees (Nzengung and Jeffries, 2001), poplar cell suspensions (Shang and Gordon, 2002), and a hydroponic tropical leguminous tree, *Leuceana leucocephala* (Doty et al., 2003). DCAA and TCAA also were detected as metabolites during oxidation of TCA, 1,1,2,2-TeCA, and 1,1,2-trichloroethane (1,1,2-TCA) by aquatic plants and algae (see below, Nzengung et al., 1999a, 2003). Based on mass balances (99% removal and 9% transpiration) and the release of chloride ions over the three years of a field trial using poplar trees, Newman et al. (1999) concluded that a large amount of TCE was metabolized inside plant tissues.

In addition to oxidative metabolism, reductive dehalogenation of chlorinated solvents similar to microbial anaerobic respiration has been reported to occur within plants. Using aquatic plants (Canadian waterweed and axenic parrot feather) and macrophytic algae (*Spirogyra* spp.), Nzengung et al. (1999a) showed that plant cells were able to reduce CT into chloroform, which was hypothesized to be further mineralized via carbene formation to carbon dioxide (CO_2) and hydrochloric acid (Figure 19.4). The same organisms also were able to reductively dechlorinate hexachloroethane (HCA) to pentachloroethane (PCA) and PCE, with the subsequent formation of small amounts of TCE, tetrachloroethane (TeCA), and TCA. Similar metabolites were detected using dead plant material, suggesting the persistence of dehalogenase activity even in the absence of living cells.

Wolfe and Hoehamer (1993) showed that both aquatic plants and cell-free extracts from Canadian waterweed (*Elodea canadensis*) can perform rapid dehalogenation of a range of aliphatic halogenated compounds, including HCA, PCE and TCE, while aromatic chlorinated solvents were not metabolized. Nzengung et al. (1999a, 2003) conducted phytoremediation experiments with aquatic plants (*E. canadensis* and *Myrophyllum aquaticum*) and macrophytic algae (*Spirogyra* spp. and *Nitella* spp.) that showed transformation and mineralization of several common halogenated contaminants, including TCE, PCE, HCA and CT. Metabolites from HCA dechlorination included PCA and PCE, with subsequent formation of small amounts of TCE and traces of 1,1,2,2-TeCA and 1,1,2-TCA. Complete mineralization to carbon dioxide was also observed (Figure 19.5). The authors concluded that highly chlorinated compounds, such as HCA and PCE, underwent reductive metabolism, whereas less chlorinated compounds, such as TCE, underwent oxidative metabolism.

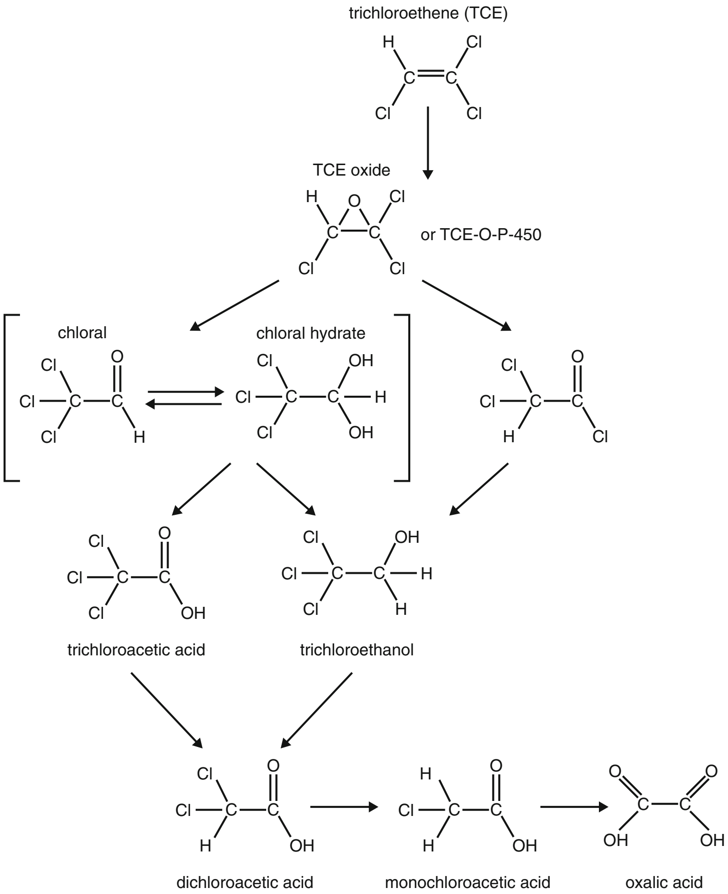


Figure 19.3. Oxidative metabolism of TCE (adapted from Shang et al., 2003).

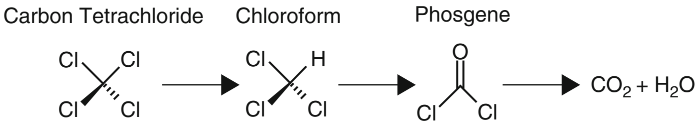


Figure 19.4. Reductive metabolism of carbon tetrachloride in plants (adapted from Nzengung et al., 2003).

Shang et al. (2001) reported further glycosylation of TCEth (generated from TCE oxidation) in both TCE-exposed tobacco and poplar tissues (Figure 19.6). Glycosylation of toxic compounds (conjugation with a hexose) is an important plant detoxification mechanism (Pflugmacher and Sandermann, 1998). Because neither TCEth nor its glucoside persisted in plant tissues, the authors concluded that they were likely further metabolized through incorporation into plant carbohydrate polymers (Shang et al., 2001).

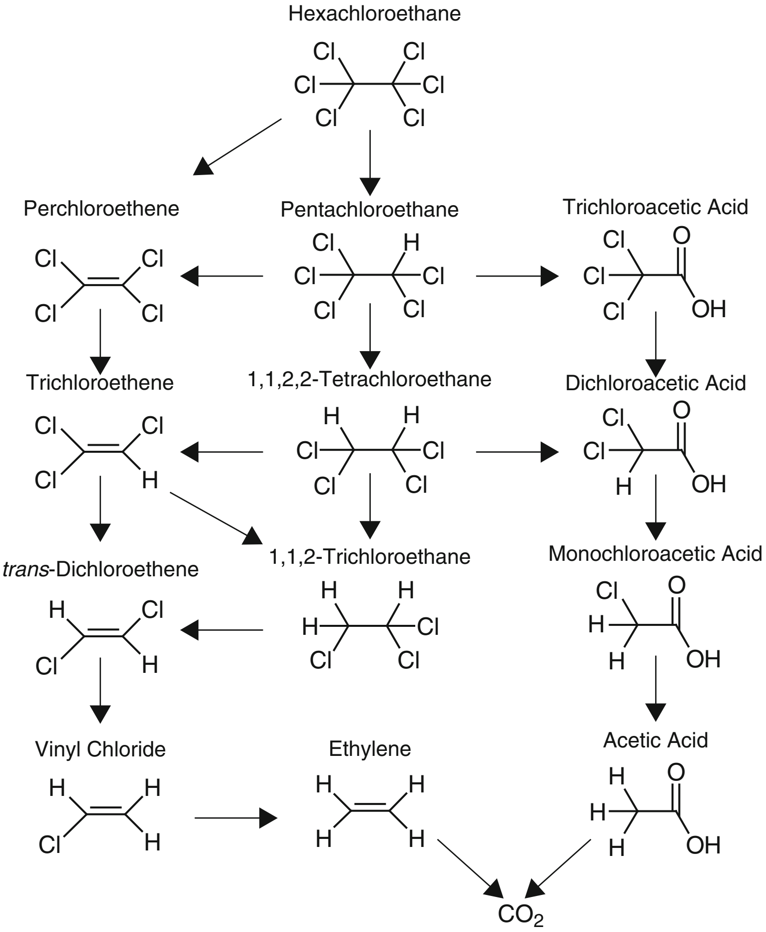


Figure 19.5. Reductive metabolism of hexachloroethane in plants (adapted from Nzengung et al., 2003).

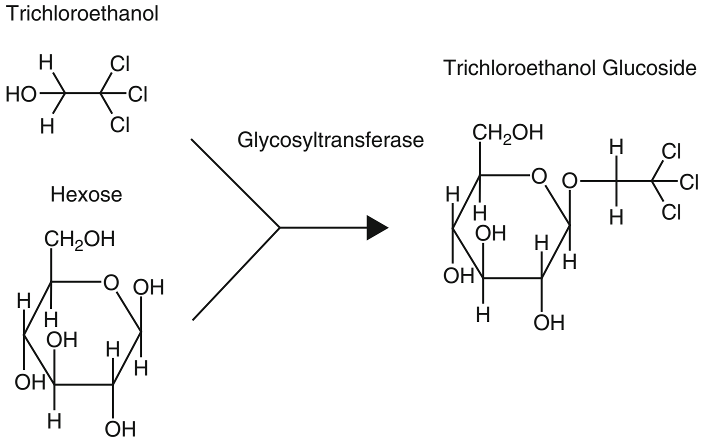


Figure 19.6. Conjugation of trichloroethanol with a plant hexose (adapted from Shang et al., 2001).

19.1.2.7 Phytovolatilization

Several studies have shown that plants are capable of transpiring chlorinated solvents into the atmosphere, though volatilization losses seem to be minor compared to overall plant consumption (Anderson and Walton, 1995; Narayanan et al., 1995, 1999; Burken and Schnoor, 1998; Davis et al., 1998; Gordon et al., 1998; Orchard et al., 2000b; Nzengung and Jeffries, 2001; Wang et al., 2004). In an early report, Narayanan et al., (1995) reported volatilization of small amounts of TCE and TCA in plant chambers vegetated with alfalfa.

Generally speaking, a high variability has been observed in the amount of TCE transpired. For instance, Burken and Schnoor (1998a) reported 20% transpiration by hydroponic poplar plants, while Orchard et al. (2000b) reported only 1% transpiration. In their experiment using edible garden plants in air-flow bioreactors, Schnabel et al. (1997) observed that 74 to 95% of the ^{14}C-TCE in the nutrient solution was volatilized to the atmosphere. It is noteworthy that often in these experiments, it was not clearly discerned whether volatilization occurred directly from soil or through plant transpiration.

In the experiment previously cited, Newman et al. (1997) observed limited volatilization from hybrid poplars exposed to TCE. The much lower level of TCE observed in leaf tissues by comparison to stem and root tissues was attributed to volatilization into the atmosphere. In a field trial using hybrid poplar trees, Newman et al. (1999) showed that 9% of applied TCE was transpired. In a similar phytoremediation experiment, Gordon et al. (1998) used mass balance data to estimate that 70 to 90% of the TCE was transpired under laboratory conditions, while less than 5% of the TCE taken up by the plants was transpired in the greenhouse and field studies. Anderson and Walton (1995) reported a high variability of TCE transpired across different species.

Several factors may explain the observed differences in the amounts of chlorinated solvent transpired by leaves, including sorption to the roots and/or the plant tissues and metabolism inside plant tissues (Shang et al., 2003). Ma and Burken (2003, 2004) showed that volatilization of TCE from hybrid poplars occurred through transport via the xylem transpiration stream and radial diffusion along the transpiration pathway. As a consequence, volatilization flux decreased with the height above ground level. Although significant concentrations of chlorinated solvents were detected in leaf bags on exposed plants, chlorinated solvents were not detected in ambient air surrounding exposed plants, suggesting that natural air diffusion and mixing are sufficient to ensure that transpiration of these compounds during phytoremediation does not constitute an environmental threat (Davis et al., 1998; Newman et al., 1999; Vroblesky et al., 1999; Doucette et al., 2003).

Cho et al. (2005) showed that under non-saturated conditions, volatilization of TCA, TCE and PCE from soil was the predominant mechanism of dissipation and that, in the early stage of the experiment, the presence of plants can limit dissipation. However, the authors suggested that the presence of plants can enhance removal either by direct uptake or by stimulating microbial degradation. Studying the phytoremediation of CT by poplar plants, Wang et al. (1999, 2004) similarly observed insignificant volatilization/diffusion from the leaves and trunks of exposed plants.

It is useful to note that although UV-mediated photodegradation of chlorinated solvents has been reported in the literature, reaction rates are slow under ambient conditions and photolysis products are often toxic (Sato et al., 1997; Feiyan et al., 2002).

Finally, climatic conditions are likely to exert a strong influence on the amount and rate of chlorinated solvents volatilized from exposed vegetation. For example, TCE uptake by trees grown on TCE-contaminated sites was higher at a dry site (in Utah) than at a wetter one (in Florida), reflecting the fact that the plants used a higher fraction of the contaminated groundwater for transpiration under the drier conditions (Doucette et al., 2003).

19.1.2.8 Phytostabilization

A common detoxification mechanism in plants is to sequester xenobiotic compounds, their metabolites or conjugates by storage in cell compartments, such as vacuoles, or by incorporation into plant structures such as lignin or cellulose (Phase III of the green liver model). However, only a few sources have reported the incorporation of radiolabeled chlorinated solvents into plant structures. Newman et al. (1997) observed that 0.1 to 0.2% of radioactivity from applied ^{14}C-TCE was non-extractable from plant tissues. Similarly, the small amounts of radioactivity from ^{14}C-TCE detected by Schnabel et al. (1997) in exposed edible garden plants (1-2%) were found to be non-extractable, leading the authors to conclude that TCE was taken up and transformed, and the subsequent metabolites were sequestered within plant tissues. The authors also observed that 5 to 21% of the original ^{14}C-TCE was sorbed to soil particles.

19.1.2.9 Hydraulic Control

A number of studies have shown that plants can efficiently take up chlorinated solvents from the subsurface by extracting contaminated groundwater through the transpiration stream (Burken and Schnoor, 1998a; Gordon et al., 1998; Newman et al., 1998; 1999; Wang et al., 1999). Strictly speaking, hydraulic control relies on the capacity of plants to contain a contaminated plume by modifying or reversing the groundwater flow through transpiring large amounts of water. The process is therefore independent from the capacity of the plant to take up contaminants from groundwater.

Because of the scale of the process (large surface areas), hydraulic control only can be demonstrated through modeling or from field-scale experimentation. Using a numerical groundwater-flow model (MODFLOW, U.S. Geological Survey, Reston, Virginia), Matthews et al. (2003) showed that the minimum area needed to capture a contamination plume was positively correlated with several soil and seasonal parameters, including aquifer horizontal hydraulic conductivity, saturated thickness, groundwater gradient, plume width, aquifer anisotropy, and the duration of the growing season. The study also demonstrated that evapotranspiration fluxes from plantations established to contain the plume were significantly higher than the groundwater flux through the plume itself.

Several large-scale, long-term experiments have been conducted that clearly demonstrate that large plants (and particularly poplar trees) transpire sufficient amounts of water to affect natural groundwater flow and therefore can intercept or contain shallow chlorinated solvent-contaminated plumes (Compton et al., 1998; Tossell et al., 1998; Jones et al., 1999; Thomas and Krueger, 1999; Quinn et al., 2001). This research will be discussed in greater detail at the end of this chapter (see Section 19.3) (Eberts et al., 2003; Hirsh et al., 2003).

19.1.2.10 Plant Enzymes Involved in the Metabolism of Chlorinated Solvents

The metabolism of TCE by both mammals and bacteria has been studied extensively. TCE is metabolized by three main processes: oxidation, reduction, and conjugation (Shang et al., 2003). Biodegradation pathways of chloroethenes depend on the degree of chlorination. Higher chlorinated congeners such as TCE undergo reductive dechlorination, while lower chlorinated congeners such as VC undergo oxidative degradation (Bradley, 2003). It is noteworthy that TCE is susceptible to both reductive and oxidative metabolisms.

Like many other toxic compounds, TCE in mammals is metabolized primarily in the liver. Hepatic cytochrome P450 dependent monooxygenases oxidize TCE by the addition of one atom of oxygen from dioxygen (O_2) to produce chloral, which in turn is transformed into TCEth and

TCAA (Lash et al., 2000). TCEth typically forms conjugates with reduced glutathione, while TCAA tends to decompose into chloroform or is sequentially dechlorinated to produce oxalic acid. Following another very common detoxification mechanism, TCE can undergo conjugation with reduced glutathione to produce a glutathionyl adduct that is enzymatically broken down into various toxic and mutagenic products (Lash et al., 2000). Bacterial degradation of TCE can follow either an oxidative or reductive pathway. Oxygenases can incorporate one or two oxygen atoms from O_2 into the TCE molecule, resulting in metabolites similar to those observed in mammals; for example chloral, TCEth, trichloro-, dichloro-, and monochloroacetic acid, and oxalic acid (Bradley, 2003). Reductive metabolism of TCE involves dehalogenase-catalyzed sequential dechlorination into DCEs, VC and ethene.

In comparison to mammals and bacteria, little information is available about plant metabolism of chlorinated solvents. Most biochemical data are derived from detection of metabolites in plant tissues. As far as we know, no purified or characterized plant enzyme involved in chlorinated solvent metabolism, such as cytochrome P450 monooxygenase, glutathione *S*-transferase or dehalogenase, have been reported. Complications arise from the difficulty in separating microbial metabolism in the root zone or in the hydroponic solution from plant-mediated transformation.

Plant enzymes potentially involved in the metabolism of chlorinated solvents can be classified according to the green liver model (Figure 19.2). Considering Phase I of this model (activation), detection of oxidized TCE metabolites resulting from the addition of −OH groups, such as TCEth and TCAA, suggests the action of a plant cytochrome P450 monooxygenase (Newman et al., 1997; Doucette et al., 1999; Nzengung et al., 2001; Nzengung and Jeffries, 2001; Shang et al., 2001; Doty et al., 2003). Wang et al. (2002) showed that specific cytochrome P450 inhibitors decreased the transformation of CT by axenic poplar cell cultures, which strongly suggests the involvement of this enzyme in CT poplar metabolism. Similar to mammals, cytochrome P450 enzymes are known to play a key role in plant metabolism of pesticides and other toxic xenobiotic compounds (Sandermann, 1994; Komossa et al., 1995; Coleman et al., 1997).

Other oxidative enzymes have been hypothesized to catalyze oxidative transformation of chlorinated solvents, such as peroxidases and laccases (Agostini et al., 2003; Nzengung et al., 2003). On the other hand, while plant-mediated reductive dehalogenation is well documented, no plant dehalogenase has been identified so far (Nzengung et al., 1999a; Doty et al., 2003; Wolfe and Hoehamer, 1993).

For Phase II of the green liver model (conjugation), it is commonly assumed that glutathione *S*-transferase catalyzes the conjugation of activated (hydroxylated) xenobiotic compounds, including chlorinated solvents, with reduced glutathione, thereby forming more soluble and less toxic conjugates (Sandermann, 1994; Komossa et al., 1995; Marrs, 1996; Schroder and Collins, 2002). However, no such glutathionyl conjugate has been identified in plant tissues. Shang et al. (2001) reported that an activated metabolite of TCE, TCEth, was glycosylated in tobacco and poplar tissues. Plant glycosyltransferase-mediated conjugations also have been reported in the detoxification of chlorophenols and DDT metabolites (Pflugmacher and Sandermann, 1998).

Sequestration of chlorinated solvent metabolites (Phase III of the green liver model) was suggested by Shang and Gordon (2002) based on evidence that ^{14}C from radiolabeled TCE was incorporated into the cell wall and into large biomolecules. However, the nature of the enzymes potentially involved was not deduced. Several authors have reported small amounts (1–2%) of ^{14}C-TCE mineralization (i.e., release of $^{14}CO_2$) in plant tissues, suggesting further metabolic transformation (Newman et al., 1997; Gordon et al., 1998; Nzengung and Jeffers, 2001).

19.1.2.11 Genetically Modified Plants for Chlorinated Solvent Phytoremediation

The efficiency of phytoremediation potentially can be improved by using genetic engineering technologies. Genetic transformations of plants for enhanced phytoremediation typically is achieved by introducing new external genes or by inducing overexpression of genes involved in detoxification processes, such as metal uptake and transport, or degradation of organic pollutants (Cherian and Oliveira, 2005; Eapen and D'Souza, 2005). Transgenic plants have been produced for phytoremediation of heavy metals and organic pollutants (Pollard et al., 2002). Examples include tobacco plants expressing a yeast metallothionein gene and showing a higher tolerance to cadmium (Misra and Gedamu, 1989), *Arabidopsis thaliana* overexpressing a zinc transporter protein and showing a twofold higher accumulation of zinc in roots (van der Zaal et al., 1999), and tobacco plants expressing bacterial reductases (pentaerythritol tetranitrate [PETN] reductase and nitroreductases) and showing a higher tolerance to the explosive trinitrotoluene (TNT) (Hannink et al., 2001).

Similarly, research has been conducted to improve the ability of plants to metabolize chlorinated solvents. Mammalian cytochromes P450 2E1 are known to be involved in the oxidation of a wide range of toxic halogenated compounds, including TCE, CT, and chloroform. Tobacco leaf tissues were transformed with a nopaline-type *Agrobacterium tumefaciens* strain containing a binary vector with a P450 2E1 complementary DNA (cDNA) (Doty et al., 2000). Whole plants were regenerated from the transformed tissues and the resulting transgenic plants were able to metabolize TCE 640-fold faster than wild type plants. Transgenic plants also exhibited an increased uptake and debromination of ethylene dibromide (EDB).

In similar research, Banerjee et al. (2002) developed transgenic hairy root cultures of *Atropa belladonna* by introducing a rabbit cytochrome P450 2E1. The transformation of hairy root cultures was realized using *A. rhizogenes* containing a binary vector with a full-length rabbit P450 2E1 cDNA. Transgenic cultures were shown to metabolize TCE more rapidly than non-vector plants (as measured by the production of the metabolites chloral and TCEth).

19.1.2.12 Phytotoxicity of Chlorinated Solvents

While phytotoxicity of some target pollutants can affect the feasibility of a phytoremediation system, most research has focused on the uptake and metabolism of xenobiotics by plants instead of phytotoxicity (Medina et al., 2003). Plants have detoxification mechanisms that help protect them against numerous toxic compounds. These mechanisms involve exclusion by roots, degradation, conjugation, sequestration, and excretion through volatilization (see the green liver model in Section 19.1.2.3 and Figure 19.2).

While many toxic xenobiotic compounds have specific modes of action (e.g., inhibition of metabolic enzymes), others such as chlorinated solvents are believed to be toxic through more general mechanisms, such as disruption of membrane functions. Low concentrations of TCE (< 1 micromolar [μM]) have been shown to increase ion leakage from cultured soybean seedlings. Similarly, several plant species undergo inhibition of gravitropic response when exposed to submillimolar concentrations of TCE (Ryu et al., 1996), which suggests an impairment of membrane function (Buchanan et al., 2000). Inderjit et al. (2003) found that the growth of carrot (*Daucus carota* L.) seedlings was inhibited by TCE concentrations as low as 1 mg/L.

In toxicity experiments based on the germination of tobacco pollen exposed to six chlorinated solvents (di-, tri-, and tetrachloroethane, and di-, tri-, and tetrachloroethene), Schubert et al. (1995) demonstrated that phytotoxicity increased as the degree of chlorination increased (presumably because higher chlorinated compounds partitioned more strongly to plant membranes). Similarly, Dietz and Schnoor (2001b) observed that the growth of hybrid poplar cuttings in hydroponic culture was inhibited by 2 millimolar [mM] of 1,1,1-TCA, by 0.9 mM of TCE, and by only 0.3 mM of PCE, indicating an inverse relationship between toxicity and log K_{ow}. A similar relationship was observed between the decrease of transpiration rate and log K_{ow}. Newman et al. (1997) also observed that hybrid poplar trees exposed for eight months to 50 mg/L TCE were only 85% of the size of non-exposed control trees.

However, using fourier transform infrared (FTIR) to analyze the steady state CO_2 concentration surrounding hybrid poplars, Davis et al. (1998) reported that exposure of the roots to 1 mM of TCE (which corresponds to a steady-state concentration of 0.1 mM in the gas phase surrounding the plants) did not affect photosynthesis. In other phytoremediation experiments using hybrid poplar trees, Burken and Schnoor (1998b) did not observe toxic effects after exposure to TCE at 50 mg/L for over one week.

While mechanisms of solvent toxicity are not fully understood, it is likely that solvents like TCE act primarily by the disruption of cell membrane integrity. Calculations based on log K_{ow} suggest that at equilibrium, a cell membrane exposed to millimolar concentrations of chlorinated solvents in the aqueous phase would contain a much higher concentration in the lipid phase that is susceptible to disrupting normal side chain interactions and membrane fluidity (Davis et al., 2002). Alternatively, solvents also may interact with the lipophilic fraction of membrane proteins, impairing their normal function. Supporting this hypothesis is the observation that many solvents, such as TCE and diethyl ether, whose mode of action is believed to be by interaction with membrane proteins, such as potassium channels or membrane ATPases, were once used as anesthetics for humans (Davis et al., 2002).

19.2 IMPLEMENTATION

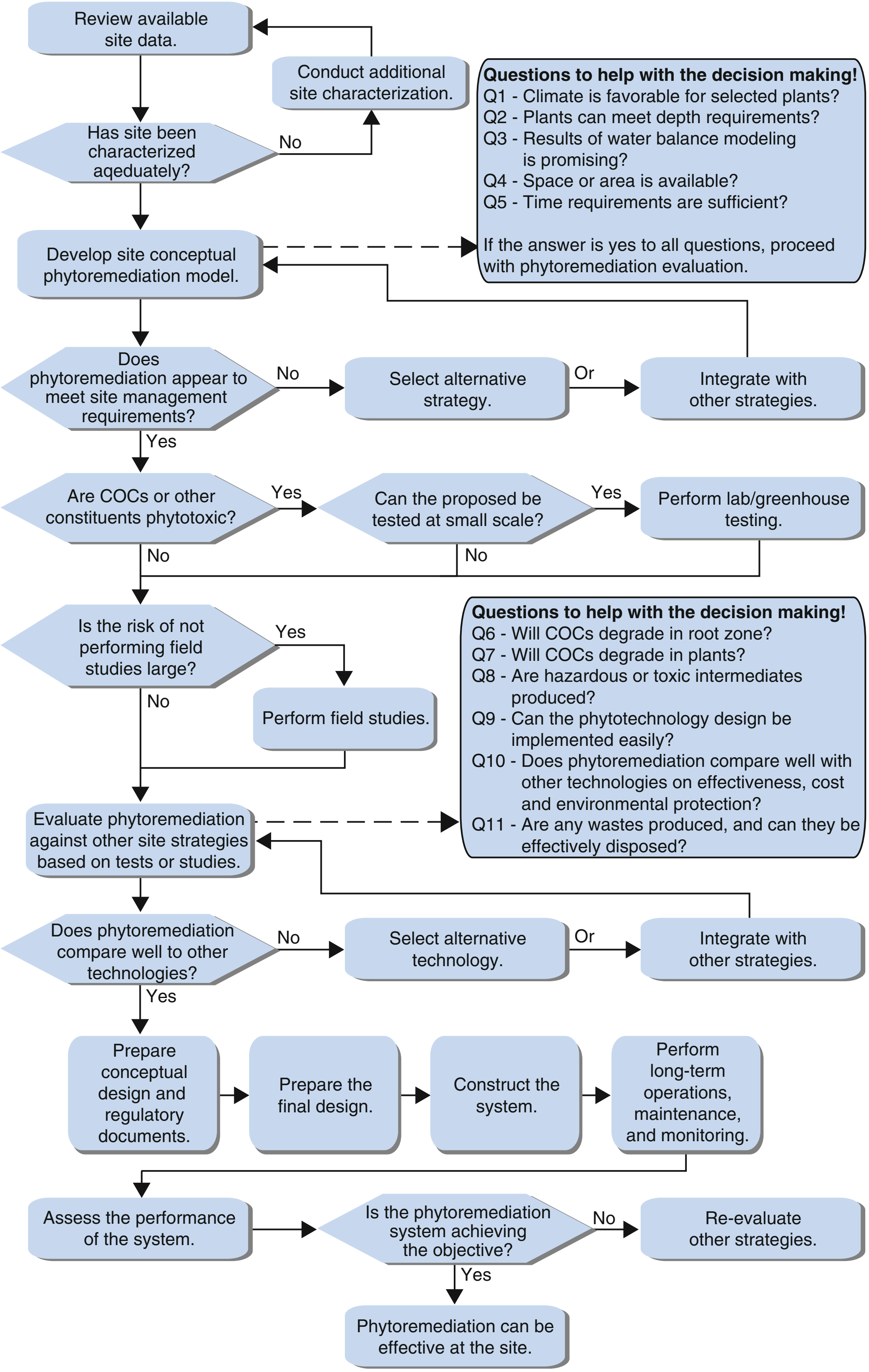
Several general sources of guidance exist to aid in developing a phytoremediation system for treating chlorinated solvents in groundwater. For example, the Remediation Technologies Development Forum (RTDF) (2005) has developed a technical protocol for site selection, field-site design and monitoring, and the Interstate Technology & Regulatory Council (ITRC) (2001; 2009) has published a decision tree that can be used to evaluate the suitability of a site for phytoremediation. Ferro et al. (2003) have addressed the maintenance of hydraulic control with the use of deep-rooted trees.

19.2.1 Assessing the Applicability of Phytoremediation

19.2.1.1 Phytoremediation Goals

The first step in assessing the applicability of phytoremediation of chlorinated solvents in groundwater is to determine the goals of the project. These goals are developed based on site conditions, the overall site management objectives and the regulatory requirements. As discussed in Section 19.1.2, phytoremediation of groundwater impacted by chlorinated solvents includes two processes: reductions in the contaminant concentrations in the groundwater and hydraulic control of the groundwater plume. The first process relies on the ability of plants to degrade, sequester, and/or take up chlorinated solvents, thus reducing the concentrations and mass flux of contaminants beyond the treatment zone. The second process relies on the direct effects of plants on site hydrology. As is discussed in Section 19.3, these two processes are interrelated.

The design, implementation and monitoring of a phytoremediation system depends on many factors. The ITRC has developed a decision tree to aid in this process (ITRC, 2001; 2009). The RTDF modified the ITRC decision tree (Figure 19.7) to be more specific for treating chlorinated solvents in groundwater (RTDF, 2005).



Questions to help with the decision making!
Q1 - Climate is favorable for selected plants?
Q2 - Plants can meet depth requirements?
Q3 - Results of water balance modeling is promising?
Q4 - Space or area is available?
Q5 - Time requirements are sufficient?

If the answer is yes to all questions, proceed with phytoremediation evaluation.

Questions to help with the decision making!
Q6 - Will COCs degrade in root zone?
Q7 - Will COCs degrade in plants?
Q8 - Are hazardous or toxic intermediates produced?
Q9 - Can the phytotechnology design be implemented easily?
Q10 - Does phytoremediation compare well with other technologies on effectiveness, cost and environmental protection?
Q11 - Are any wastes produced, and can they be effectively disposed?

Figure 19.7. Phytoremediation decision making tree (COC-contaminant of concern) (RTDF, 2005).

19.2.1.2 Review of Site Characteristics

The first step in determining the feasibility of phytoremediation for a chlorinated solvent plume is a review of historical site information. Favorable site characteristics include the following:

- Climate favorable for plants suitable for phytoremediation,
- Absence of nonaqueous phase liquids or areas where the contaminant concentrations may be toxic for the plants,
- Depth to the contaminated aquifer that is not too great to preclude root contact and significant transpiration,
- A water balance that predicts transpiration by the plants can achieve hydraulic control of the groundwater,
- Sufficient space for a full-scale phytoremediation project, and
- Sufficient time for a phytoremediation project to achieve its goals.

19.2.1.3 Site Management Goals

If the site characterization process indicates phytoremediation can be effective, then performance goals must be established. The effectiveness of phytoremediation in meeting these goals should be compared with other remedial strategies. In addition, phytoremediation may be better implemented in conjunction with one or several other remedial technologies. Stakeholders should be informed that phytoremediation systems for groundwater plume control are space- and time-intensive. Often a bench-scale or pilot-scale study will be required to assess the feasibility of the phytoremediation application.

19.2.2 Design Considerations

The design of a phytoremediation system encompasses plant selection based on climate and agronomic properties, planting techniques and site maintenance. During the design phase, a performance monitoring program should be established, providing the remedial action goals and the methods that will be used to determine whether the goals have been achieved. A more detailed discussion of the design of a phytoremediation system can be found in ITRC (2009).

19.2.2.1 Plant Selection

To date, the most commonly used plants for chlorinated solvent plume treatment have been the *Populus* species. A review of phytoremediation or other plant-based projects conducted within the same region should be made to determine the types of plants that could be most efficient for the phytoremediation project. The RTDF's Phytoremediation of Organics Action Team has created a Phytoremediation Bibliography. This comprehensive bibliography includes peer-reviewed journal articles, presentations and posters from conferences, book chapters and articles from newspapers and magazines, and it is updated quarterly (http://www.rtdf.org/public/phyto/phytodoc.htm).

It should be noted that plants grown under many climatic conditions will show yearly variations in metabolic activity and hence transpiration. The design of the phytoremediation system should take this into account, as hydraulic control will be the highest during the growing season but may be nonexistent during the winter months when plants are dormant.

19.2.2.2 Planting Techniques

There are many different methods for planting trees used for groundwater control. Larger trees planted in boreholes or trenches will generally mature at a faster rate than small saplings or cuttings. However, the cost of installation increases with tree size and complexity of planting. If time is not a factor, then the least expensive (smallest) cuttings or saplings can be used. However, if site conditions require that plant roots have a minimal contact with the vadose zone and a maximum exposure to groundwater, then it may be necessary to drill boreholes prior to planting.

Plant spacing should be optimized for the conditions at the site to ensure rapid growth. Adequate space should be left between trees to permit sampling and mowing equipment to move through the site. When the goal is hydraulic control of a contaminated plume, a critical parameter is the surface area that is planted. Numerical simulations based on groundwater-flow models, such as MODFLOW and MODPATH (U.S. Geological Survey, Reston, Virginia) have been proven to be useful for predicting the minimum area needed to capture a contamination plume and the impacts of soil, hydraulic and climatic factors (Matthews et al., 2003).

19.2.2.3 Agronomic Considerations

The objective of a phytoremediation system is to optimize the growth of plants to achieve canopy closure to maximize transpiration and uptake and to provide sufficient substrate for aerobic or anaerobic microbial biodegradation processes within the treatment zone. Agronomic soil tests should be conducted to determine the need for fertilizers or other soil amendments such as lime to control pH or mulch to control surface temperatures and weed growth. An agronomist should be consulted to aid in these determinations. Seedbed preparation through plowing or rototilling where boreholes or trenches are not used is important because these activities can reduce soil bulk density and therefore promote more rapid plant growth.

19.2.2.4 Maintenance

Maintenance activities include inspecting and repairing equipment used to monitor the site, as well as regularly inspecting the health of the plants responsible for remediation. Acceptable levels of plant survival should be determined during the study design and if plant survival falls below acceptable levels, replanting part of the plantation may be necessary.

19.2.3 Monitoring

Technologies for monitoring groundwater, soil, plants and air continue to evolve. Monitoring should be designed to evaluate both the progress towards the performance objectives and the needs for maintenance to ensure continued effective treatment. Generally, chlorinated solvent concentrations and groundwater flux are the most important parameters to measure. In addition, the effect of plants on rhizodegradation and rhizostabilization, contaminant uptake into the plants, phytodegradation within the plants, and volatilization from the plants may be important parameters to measure. As with all environmental technologies, a complete conceptual site model, which includes all potential exposure pathways and receptors, should be developed. The development of this type of model will help to determine parameters that should be monitored.

19.2.3.1 Groundwater Flux

There are many monitoring techniques available for assessing the effects of plants on groundwater and chlorinated solvent plumes. The most commonly used is the measurement of depth to groundwater upgradient, within the plantation, and downgradient of the site. These measurements, combined with standard hydrologic determinations of aquifer characteristics, will enable calculations of the direct effect of plants on groundwater flux. These measurements should be taken across the entire growing season, and the annual contribution of plants to hydraulic control should be averaged across all seasons of the year. As stated before, future predictions of the effect of the phytoremediation system on groundwater flux can be made through modeling (Eberts et al., 2003; Hirsh et al., 2003; Matthews et al., 2003) (see Section 19.2.2.2).

19.2.3.2 Soil Sampling

There is inherent variability in soil properties, which is usually compounded by a heterogeneous distribution of contaminants within the soil. A statistically valid soil sampling design should be developed to minimize parameter variability to acceptable levels. It is suggested that a statistician be consulted prior to the installation of the project to develop such a plan, as the soil sampling plan should ensure that the effectiveness of a phytoremediation system will be able to be distinguished from inherent variability in other soil properties. If possible, the creation of a prepared bed to help evenly distribute contaminated soil prior to installing the phytoremediation system will aid in reducing variability. The proper implementation of agronomic considerations, as outlined in Section 19.2.2.3, will also ensure good plant growth and reduce variability.

19.2.3.3 Air Monitoring

Tillman et al. (2003) developed a method for estimating the volatilization flux of TCE from unsaturated soil to the atmosphere based on a vertical flux chamber (VFC). Although the results obtained with the VFC have been shown to correlate with predictions based on a gas flow and transport model, the authors suggest that the VFC may be a preferred method because of its ease of use and lack of need for *a priori* site knowledge and accuracy, compared with the requirements for running a data-intensive flow and transport model.

One of the concerns with the growth of plants above chlorinated solvent plumes is the potential release of these compounds to the atmosphere. This release can occur by volatilization through the leaves after uptake and transport within the plant, as well as by volatilization from the vadose zone directly to the atmosphere. The results from the Aberdeen Proving Ground case study (Section 19.3.2) indicate that volatilization of these compounds produces concentrations in the ambient air that are well below risk based levels. However flux from groundwater through the vadose zone to ambient air also occurred at this site. If volatilization is a concern at a site, then ambient air monitoring may be necessary, along with an assessment of the contribution of the phytoremediation system to the ambient air concentrations.

19.3 CASE STUDIES

In this section, three case studies are presented to highlight the effects of plants on chlorinated solvent plumes. These case studies focus on the reduction of groundwater flow through hydraulic control, with experimentation to further assess the direct effect of plants on the removal and/or remediation of chlorinated compounds from the groundwater. Principal features of the three case studies have been summarized in Table 19.2.

Table 19.2. Case Study Summary by Site

Goals	Site Conditions	Results	Cost
Naval Air Station Joint Reserve Base (NAS-JEB), Fort Worth, TX			
Determine the effectiveness of eastern cottonwood (*Populus deltoides*) in abating the aquifer mass flux of dissolved TCE through a combination of hydraulic control of the contaminant plume and *in situ* microbial degradation by reductive dechlorination of chlorinated solvents	• Depth to groundwater 2.5 to 4.0 meter (m) (8.2–13.1 feet [ft]) • Average hydraulic gradient just over 2% • Groundwater velocity ~ 0.5 m/day (1.6 ft/day) • Aquifer underlain by a relatively impermeable layer of shaley limestone • Aquifer contaminated by TCE (203 to 970 mg/L) and *cis*-DCE (24 to 141 mg/L) • Annual precipitation ~ 80 centimeters (cm) (31.5 inches [in]) • Annual groundwater recharge ~ 6 cm (2.4 in) • Oxygen recharge of groundwater from precipitation results in aerobic conditions in the aquifer	• During the first three years of the study, transpiration (hydraulic control) was the predominant phytoremediation process • After six growing seasons, *in situ* biodegradation was becoming the dominant phytoremediation process controlling TCE mass flux • Modeling showed that transpiration removed about 20 to 30% of the volumetric flow of water	• Project total cost was $445,200: $193,200 in capital costs and $252,000 in total annual operations and maintenance (O&M) costs • Cost estimate for a full-scale phytoremediation project of 18,600 m^2 is $466,000, with a unit cost of $25 per m^2
J-Field Superfund Site, Aberdeen Proving Ground, Edgewood, MD			
Determine the effectiveness of hybrid poplar trees (*Populus deltoides* × *trichocarpa*) to intercept and reduce dissolved-phase VOC mass loading to a nearby marsh by hydraulic containment of the VOC plume	• Contamination between 1.5–12.2 m (5–40 ft) below ground surface (bgs) • Groundwater flow is slow due to the fine sand and clayey silt of the aquifer, and silt and clay lenses exist throughout the surficial aquifer • Even distribution of rainfall throughout the year (114 cm per year [45 inches per year]) · • Approximately 38% of precipitation infiltrates to the surficial aquifer • Seasonal variation in groundwater recharge creates large fluctuations of the water table (up to 1.5 m) that result in changes in groundwater gradient and flow direction • Major contaminants are chlorinated VOCs, mainly 1,1,2,2-TeCA, TCE, and *cis*-DCE	• Tree plantation transpiration reached about 4,130 L/day after 3 months • Modeled estimates of transpiration of 7,600 L/day after 30 years, with individual trees removing approximately 49 L/day of water and up to 163 kg of dissolved-phase VOCs • Between 0.1 and 75 mg TCE/g plant dry weight were detected in trees growing near the DNAPL area • The analyses of tree tissue showed that VOC concentrations decreased with the sampling elevation from the roots to the branches	• Project total cost was $115,000: $85,000 in capital costs and $30,000 in O&M costs

(*continued*)

Table 19.2. (continued)

Goals	Site Conditions	Results	Cost
	• Highest concentrations: 4,400 mg/L for 1,1,2,2-TeCA, 240 mg/L for TCE, and 280 mg/L for *cis*-DCE		
Solvents Recovery Service of New England (SRSNE) Superfund Site, Southington, CT			
Pump and treat contaminated groundwater, and reduce the need for mechanical pumping and treatment, in a contained DNAPL source area through the use of hybrid poplar trees	• The contaminant source was a DNAPL containing primarily TCE, PCE, 1,1-dichloroethane (1,1-DCA), *trans*-DCE, *cis*-DCE, 1,1,1-trichloroethane (1,1,1-TCA), ethylbenzene, toluene, and *sec*-butanol in both the overburden and bedrock aquifers. • The source area was contained by a sheet pile barrier wall (0.32 hectares [ha] or 0.8 acres [ac]) • Overburden and bedrock aquifers are hydraulically connected; the overburden aquifer exists at a depth of 1.2–1.5 m [4–5 ft] bgs	• Estimated transpiration of 9 gpm, compared to a maximum pumping rate using mechanical pumps of approximately 25 gpm • Equates to 1.9 million gal over the course of the growing season (May to September) for the entire 0.8-acre plantation • Removal rate of VOCs was 340 kg/yr (estimated from the volume of groundwater pumped by the trees and the VOC concentration in groundwater)	• Project total cost was $281,900, with $70,000 for O&M • Estimated that a net cost saving over the use of the mechanical pump-and-treat system of $97,000 would occur during the 7th year, and by the end of the 11th growing season, an estimated cost savings of $470,000 was projected • The tree stand was self-sustaining by the end of the 6th growing season, and no significant project costs were expected past that time

19.3.1 Treatment of TCE-Contaminated Groundwater by Eastern Cottonwood Trees, Naval Air Station Joint Reserve Base, Fort Worth, Texas

Eastern cottonwood trees were planted to control both hydraulic and TCE fluxes in TCE contaminated groundwater at the Naval Air Station Joint Reserve Base (NAS-JEB) located in Fort Worth, Texas. This five-year study was based on short term rotation woody crop planting techniques. The study concluded that the primary process responsible for TCE removal was the *in situ* hydraulic control of the contaminant plume, although there was some attenuation of TCE in groundwater due to enhanced microbial reductive dechlorination of TCE in the root zone and uptake and enzymatic transformation of TCE within the leaves.

This project was jointly funded through the USEPA Superfund Innovative Technology Evaluation (SITE) Program, the Environmental Security Technology Certification Program (ESTCP), and the Air Force Center for Environmental Excellence (AFCEE: now the Air Force Center for Engineering and the Environment). More detailed descriptions of the phytoremediation project can be found in Eberts et al. (2003), USEPA (2005a), and ESTCP (2006).

19.3.1.1 Site Description

The site is located on the Carswell Golf Course at the former Carswell Air Force Base. Releases of TCE occurred from Air Force Plant 4, which was built in 1942 to produce aircrafts during World War II, and where large quantities of TCE were used to clean metal surfaces. Releases of TCE resulted in shallow contamination of groundwater in a plume extending 1.5 km (0.93 mile) downgradient of Plant 4 (Figure 19.8).

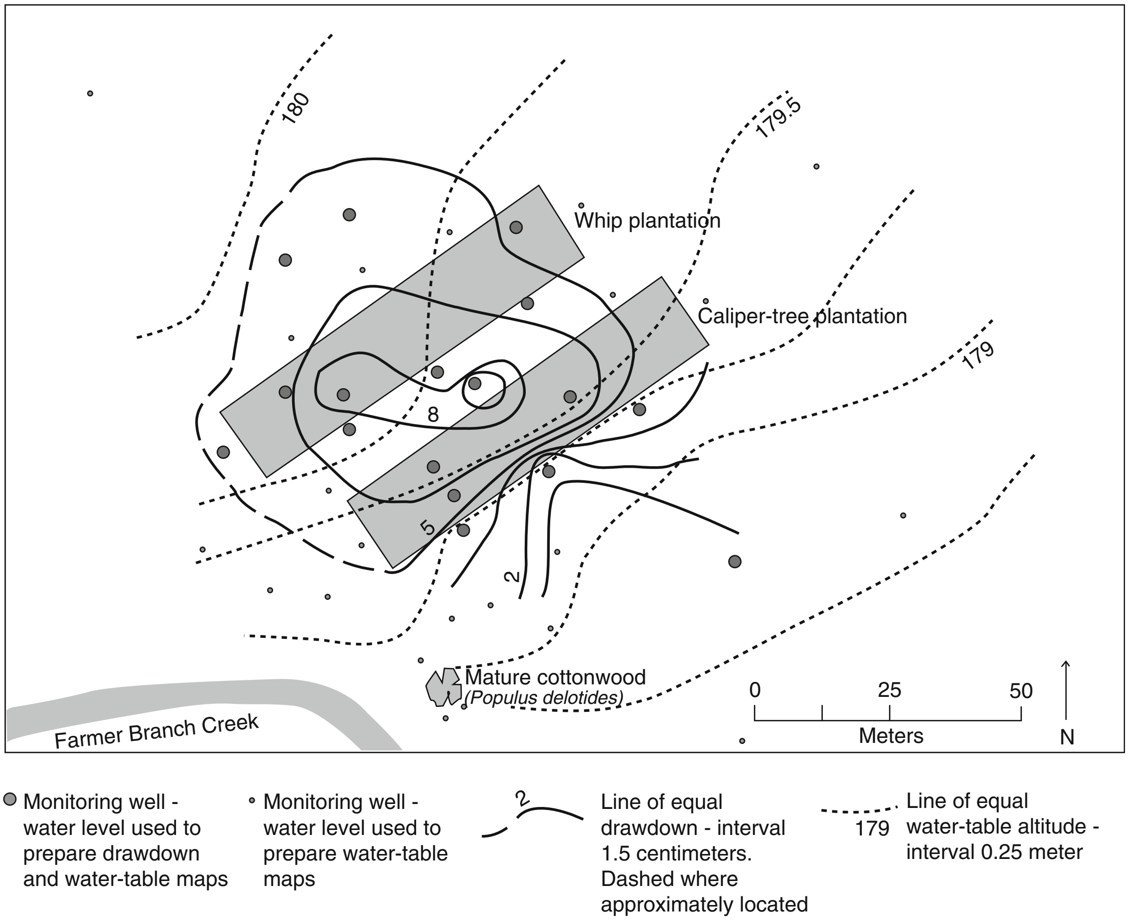


Figure 19.8. Layout of the phytoremediation site in Fort Worth, TX. Drawdown at the water table attributed to planted trees and water-table altitude are shown (peak of growing season, June 1998). From Eberts et al., 2003 (reprinted with permission of John Wiley and Sons, Inc.).

The depth to groundwater at the site ranged from 2.5 to 4.0 m (8.2 to 13.1 ft), and the thickness of the alluvial aquifer ranged from 0.5 to 1.5 m (1.6 to 4.9 ft). The average hydraulic gradient was just over 2%, and the groundwater velocity was approximately 0.5 m/day (1.6 ft/day). The aquifer is underlain by a relatively impermeable layer of shaley limestone and discharges into Farmers Branch Creek downgradient of the site. The aquifer is contaminated primarily by TCE (ranging from 203 to 970 micrograms per liter [μg/L]) and *cis*-DCE (ranging from 24 to 141 μg/L).

The site receives annual precipitation of about 80 cm (31.5 in), with an annual groundwater recharge of about 6 cm (2.4 in). The aquifer is aerobic, with dissolved oxygen concentrations in the plume above 5 mg/L, and total organic carbon (TOC) below the 1.5 mg/L detection limit. Based on these data, the site is characterized as a Type 3 by the USEPA (USEPA, 1998a). Type 3 plumes have low concentrations of native and/or anthropogenic carbon, and concentrations of dissolved oxygen that are greater than 1.0 mg/L. Under these conditions, reductive dechlorination is not expected to occur. The most significant natural attenuation mechanisms for chlorinated compounds are advection, dispersion and sorption. One of the project expectations was that poplar trees would increase the TOC levels in the aquifer, consuming oxygen and stimulating reductive dechlorination by native bacteria in the subsurface.

19.3.1.2 Phytoremediation Project

The primary objective of the project was to determine the effectiveness of eastern cottonwood (*Populus deltoides*) in abating the aquifer mass flux of dissolved TCE downgradient of the planted area. Treatment mechanisms included both hydraulic control of the contaminant plume (removal of contaminated water through the transpiration stream) and *in situ* microbial degradation by reductive dechlorination of chlorinated solvents. Secondary objectives were to elucidate the biological, hydrological and biogeochemical processes resulting from the presence of the trees by collecting long-term data on plant growth, transpiration rates and effects on the aquifer, contaminant uptake in tree tissues, subsurface redox conditions, and microbial dechlorination in groundwater.

The experimental site consisted of two 15- by 75-m (49- by 246-ft) rectangular areas planted perpendicular to groundwater flow to serve as barriers to subsurface contaminant movement from the source to its discharge to surface water. The first area was planted with whips, consisting of one-year old stems harvested from dormant branches, and the second area was planted with one-year old seedlings of 2.5-3.8 cm (1.0-1.4 in) caliper trunk diameter.

The planting method was based on the short-rotation woody crop technique, which was originally developed for bioenergy production. Preparation for planting involved installing irrigation lines and vegetative material in the trenches. Based on an agronomic assessment of micro- and macronutrients and soil characteristics, slow-release Osmacote$^{\text{TM}}$ 14-14-14 was placed around each tree. Irrigation was required to supplement precipitation and support root development during the first two growing seasons.

19.3.1.3 Monitoring Phytoremediation Performance

Phytoremediation performance was monitored through 67 wells, three water level recorders, nine tensiometers, a weather station, a stream gauge on a nearby creek (to measure stream stage), and three collars or tree probes installed periodically on selected trees (to measure sap flow).

Changes in the TCE mass flux across the planting areas were estimated from the volumetric flux of groundwater (calculated by Darcy's Law) multiplied by the average TCE concentration measured in the row of wells immediately downgradient of the site. After the fourth growing season the cone of influence of the planted trees expanded beyond the well network, preventing application of the TCE flux formula, so the volumetric flux of groundwater was estimated by using a groundwater flux model.

There was considerable variation in TCE mass flux during the first three seasons, corresponding to variations in groundwater volumetric flux and climatic conditions. The stability of the TCE concentration relative to groundwater flux indicated that the primary mechanism for the measured reductions in TCE mass flux was hydraulic control by the trees and not microbial reductive dechlorination. Similar results have been observed at other sites (Newman et al., 1999). Based on the groundwater-flow model, the amount of contaminated groundwater removed from the aquifer by transpiration accounted for approximately 20% of the initial volumetric flux across the site.

Tree Growth Rates. Initial differences were observed between the caliper and whip plantations. After the first three years of growth, caliper trees had higher root biomass and trunk diameters than whips. By the end of the fifth growing season, the caliper plantation had reached canopy closure, which was not observed in the whip plantation. The growth of the caliper trees varied predictably with depth to groundwater, a trend that again was not observed in the whip tree plantation. It was suggested that external factors may have masked differences in the trees' capabilities to access groundwater, such as irrigation, differences between calipers and whips or the extreme drought of the 2000 growing season (fifth year).

During the 2000 drought, trees growing in areas where the water table dropped below 3.5 m (11.5 ft) showed severe stress, which suggests that the use of more deeply rooting trees, as well as planting techniques encouraging deep rooting, may constitute an improved strategy for phytoremediation at this site.

Tree Transpiration Rates. Transpiration rates from trees were estimated from sap flow data obtained by sap flow gauges and thermal dissipation probes. A mean daily transpiration rate of 9.2 kg (20.3 pounds [lb]) per tree for whips and 14.7 kg (31.5 lb) per tree for calipers was estimated in June 1997 (second growing season). Adjusting for the twofold higher planting density of whip trees, the stand-level estimates were very similar for caliper and whip plantations, at 15,600 and 16,600 kg/ha/day (13,900 and 16,000 lb/ac/day) respectively (Vose et al., 2000). However, by the fifth growing season, the caliper trees showed significantly higher transpiration rates, reaching 80 kg (176 lb) per tree per day, compared to 20 kg (44 lb) per tree per day for whip trees.

Because the plantations were not expected to reach maturity over the evaluation period, future transpiration rates of the plantations were modeled based on climatic, sap flow, soil moisture, and tree root data using the PROSPER model. Estimated stand-level transpiration rates for the phytoremediation system with a closed canopy ranged from 25 to 48 cm (9.8 to 18.9 in) per growing season. Diurnal fluctuation of the water table was recorded in the second growing season, indicating the first visible effects of tree transpiration on the aquifer. A monthly estimate for the third, fourth and fifth growing seasons showed an increase in transpiration from the contaminated aquifer from May to August. It also showed a lag of groundwater transpiration by comparison with total transpiration, which reflected a decrease of soil moisture with the advance of the growing season. Higher groundwater transpiration occurred from trees planted in sand-gravel soil compared to those in clay-rich soil.

Contaminant Uptake by Trees. TCE, the reduction metabolite *cis*-DCE, and the oxidation metabolites TCAA and DCAA were detected in root, stem and leaf samples. Microbial dehalogenation of TCE was indicated by a decrease of the ratio of TCE/*cis*-DCE with time, suggesting that planted trees promoted the development of anaerobic conditions in soil. Dehalogenase activity measured directly in plant extracts also suggested that reductive dechlorination of TCE might occur inside plant tissues. In addition, detection of TCAA and DCAA in plant tissues indicated TCE oxidation metabolism. The higher concentration of TCAA and DCAA in leaf tissues suggested that the oxidation metabolism was located primarily in these organs.

Oxidation/Reduction and Microbial Dechlorination in Groundwater. Soil analyses showed that aerobic conditions prevailed in the aquifer before planting (dissolved oxygen [DO] > 5 mg/L) and were more reductive beneath a mature cottonwood adjacent to the site (1 mg/L DO). The ratios of TCE/*cis*-DCE detected in groundwater were lower in soils with lower oxygen levels, about 5 mg/L DO beneath planted areas and 0.5 mg/L DO beneath the mature cottonwood, suggesting microbial dehalogenation under more reducing conditions. By the second year of the project, no appreciable reductive dechlorination of TCE had occurred in groundwater beneath the planted area, although dissolved organic carbon (DOC) increased and the redox potential approached iron-reducing conditions.

During the fifth growing season, an inverse relationship was observed between DO and DOC concentration beneath the planted area, suggesting that aerobic degradation of organic material released from roots contributed significantly to oxygen depletion in the groundwater. Similarly, a positive relationship was found between oxygen concentration and TCE/*cis*-DCE ratios, suggesting that the combination of reduced conditions and increased DOC enhanced the reductive dehalogenation of TCE by anaerobic bacteria in the subsurface (Lee et al., 2000).

Reducing conditions also were observed locally beneath and downgradient of the planted area, suggesting that trees planted on the site stimulated microbial activity and thereby caused depletion of dissolved oxygen and creation of reducing conditions conducive to reductive dehalogenation of chlorinated solvents. A study of the microbial activity after the second growing season (1998) showed that the numbers of anaerobic organisms, including methanogens, were higher beneath the planted area, suggesting that anaerobic conditions were beginning to develop.

VC, a toxic reduction product of TCE dechlorination, had been detected in the aquifer beneath a mature cottonwood. However, according to Eberts et al. (2003), this VC accumulation does not constitute a concern because the presence of surrounding aerobic conditions ensures rapid aerobic biodegradation of VC before it poses any unacceptable risk. It is useful to note that the reductive dechlorination of TCE into the toxic compounds *cis*-DCE or VC does not constitute a remediation process if not followed by further degradation to non-toxic end products.

19.3.1.4 Modeling Phytoremediation Performance

Effects of Transpiration on Site Hydrology. The current and future effects of transpiration on the aquifer were investigated with the groundwater flow model MODFLOW. The model was calibrated to steady-state conditions with water level measurements and an estimate of the discharge to the Farmers Branch Creek. The storage coefficients of the aquifer and the average monthly recharge of the aquifer from precipitation were determined. During the third growing season, the maximum observed drawdown at the center of the cone of influence was 10 cm, while the modeled drawdown was 9 cm (Figure 19.8). The future influence of the trees was predicted from estimated transpiration of groundwater derived from a sap-flow model. Simulated drawdown at the center of the cone of influence ranged from 12 to 25 cm (5 to 10 inches) at the peak of the growing season under a closed canopy, with a lateral extension of a 3 cm (1 inch) or greater drawdown area from 140 to 210 m (459 to 689 ft). A reduction of 20 to 30% of the before-planting volumetric flow downgradient of the planted area was estimated based on these calculations.

The predicted reduction in TCE mass flux was lower than that observed for the volumetric flow because of the reduced efficiency of the trees to uptake TCE, reflected by the TSCF of 0.74 for TCE (Schnoor, 1997). The model also predicted an absence of hydraulic control of the contaminated plume during the dormant season. A larger plantation would result in more hydraulic control, although the release of water from storage in the aquifer would prevent a full hydraulic control of the TCE plume.

19.3.1.5 Conclusions

The objective of this field demonstration was to reduce TCE mass flux to a pre-specified level within three years. That estimate of time was optimistic. The results of the study indicate that during the first three years of the study, transpiration (hydraulic control) was the predominant phytoremediation process, whereas after six growing seasons, *in situ* biodegradation was becoming the dominant process controlling TCE mass flux. The detection of toxic metabolites from TCE dechlorination raised some concern about the efficacy of microbial dechlorination as a remediation process.

19.3.1.6 Cost Estimates

The total cost of the phytoremediation project was $445,200; $193,200 in capital costs and $252,000 in total operations and maintenance (O&M) costs over 5 years. Capital costs included $24,000 for preparatory work (site design and characterization); $159,100 for site work (monitoring, plantation development, installation of the weather station, and site survey); $2,100 to purchase the trees; and $10,000 to install the irrigation system. The O&M costs included landscaping ($2,000) and environmental monitoring ($250,000).

Based on the results from this field test, a cost estimate was prepared for full-scale phytoremediation of a plume with a total area of 18,600 m^2 (200,200 ft^2). The estimated cost was $466,000, corresponding to a unit cost of $25 per m^2 ($2.3 per ft^2).

19.3.2 Treatment of Halogenated Volatile Organic Compounds by Hybrid Poplars, J-Field Superfund Site, Aberdeen Proving Ground, Edgewood, Maryland

A phytoremediation field experiment was conducted using hybrid poplar trees to treat a mixture of halogenated VOCs in groundwater at the J-Field Superfund Site, Aberdeen Proving Ground, Edgewood, Maryland. This 5-year study showed that vegetation was able to control plume migration, mainly through groundwater transpiration. In addition, contaminants were significantly degraded in the rhizosphere and inside plant tissues, while detectable concentrations of halogenated VOCs were transpired into the atmosphere.

The phytoremediation system was proven to control halogenated VOCs through several mechanisms including hydraulic control, rhizodegradation, phytodegradation and volatilization. This project was initiated under a joint program of the U.S. Army Directorate of Safety, Health, and Environment, USEPA Region III and the USEPA Environmental Response Team Center. More detailed descriptions of this project can be found in USEPA (1998b, 2002) and Hirsh et al. (2003).

19.3.2.1 Site Description

The J-Field site was used for military weapons testing and disposal activities for many years, resulting in releases of chemicals to soil and groundwater. The main source of contamination was the former Toxic Burning Pits that consisted of several trenches that were used for disposal activities and were highly contaminated by VOCs. The Toxic Burning Pits rest on a topographic high area, resulting in a radial flow of VOC-contaminated groundwater, which eventually discharges into a freshwater marsh (Figure 19.9). The contamination exists between 1.5 and 12.2 m (5 and 40 ft) bgs. Groundwater flow is slow due to the fine sand and clayey silt of the aquifer, and silt and clay lenses exist throughout the surficial aquifer. The aquifer discharges into a floating mat-type freshwater marsh approximately 152 m (500 ft) downgradient of the site. The flow is aided by an even distribution of rainfall throughout the year (114 cm [45 in] per year). Approximately 38% of the precipitation infiltrated to the surficial aquifer during one monitoring period. Seasonal variations in groundwater recharge create large

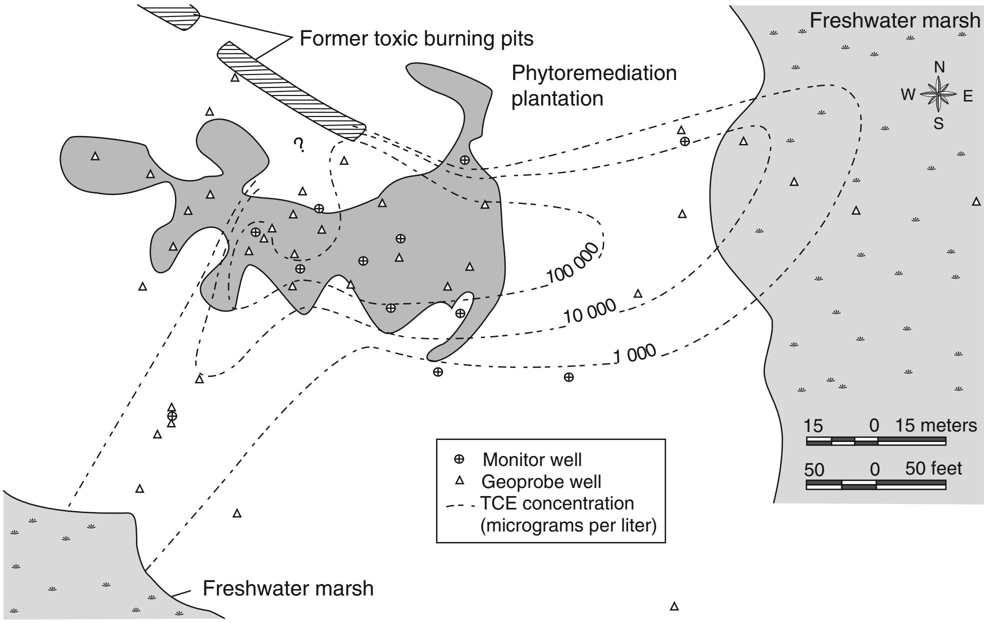


Figure 19.9. Layout of the phytoremediation site in Aberdeen Proving Ground, MD. Distribution of TCE in surficial aquifer is shown, July 2001. From Hirsh et al., 2003 (reprinted with permission of John Wiley and Sons, Inc.).

fluctuations of the water table (up to 1.5 m) that result in changes in groundwater gradient and flow direction.

The major contaminants identified at the site were chlorinated VOCs, mainly 1,1,2,2-TeCA, TCE, and *cis*-DCE. The highest concentrations detected in the Toxic Burning Pits in 2001 were 4,400 mg/L for 1,1,2,2-TeCA, 240 mg/L for TCE, and 280 mg/L for *cis*-DCE. Chlorinated VOC concentrations in groundwater showed a decrease with distance from the Toxic Burning Pits, but remained significant at the point where the plume contacts the freshwater marsh (1.0 to 10 mg/L for TCE, Figure 19.9).

Several conventional remediation technologies have been evaluated at the site, including soil washing, soil-vapor extraction, groundwater pumping and groundwater circulation wells. However, remediation of the site was hindered by several factors, including the presence of unexploded ordnance (UXO), the low permeability of the aquifer and the presence of free-phase DNAPL as a persistent VOC source. In addition, seasonal fluctuations of the water table created short-term shifts in the hydraulic gradient and flow direction.

19.3.2.2 Phytoremediation Project

In 1996, 186 hybrid poplar trees (*Populus deltoides* × *trichocarpa*) were planted in a U-shaped configuration surrounding the Toxic Burning Pits to provide hydraulic control of the VOC plume and reduce the contaminant loading to the marsh. The area of the study was approximately 0.4 ha (1.0 ac). Some of the trees were replanted in 1999 to replace those that had died. These included hybrid poplars as well as two native tree species, tulip tree (*Liriodendron tulipifera*) and silver maple (*Acer saccharinum*).

The original trees were planted on 1 m (3 ft) centers, and had plastic sleeves placed around the roots prior to planting to encourage downward root growth. During the second year of the study (1998), it was observed that the plastic sleeves, along with the heavy texture of the soil, restricted root growth. Therefore, the replacement tree roots were not encased in plastic sleeves. In addition, boreholes of various diameters and depths were used in the replacement planting. It was found that loosening the soils surrounding the boreholes allowed for optimal root development.

19.3.2.3 Monitoring Phytoremediation Performance

Hydraulic Control. Both hydraulic control and phytotransformation of chlorinated VOCs (uptake and plant degradation) depend on plant transpiration rates. Transpiration rates were estimated based on sap flow data: after three years of growth, tree plantation transpiration reached about 4,130 L/day. Future estimates indicated that transpiration would reach about 7,600 L/day after 30 years of growth, with individual trees removing approximately 49 L/day. The effects of tree transpiration were assessed by monitoring the water table elevation in wells. These data showed that during the seasonal lull in growth, the hydraulic gradient was downward to the marsh, whereas during the growing season the hydraulic gradient was reversed, with groundwater flowing towards the tree roots. During the growing season, the combination of high transpiration rates and reduced groundwater recharge created a discernible cone of depression in the center of the plantation. The aquifer response was observed as deep as 7.6 m (24.9 ft) bgs.

Rhizosphere Effect. Rhizodegradation was assessed using membrane dialysis samplers from discrete vertical zones both inside and outside the phytoremediation area. Parameters measured included VOC contaminants and degradation products, dissolved gases, TOC, and root exudates (Pardue et al., 2000). Results indicated that reductive dechlorination was the primary degradation pathway in groundwater and that areas of the rhizosphere have been rendered less reductive because of the introduction of carbon dioxide by the trees. However, it was shown that the trees did not significantly increase TOC contents in the rhizosphere. No conclusive data was obtained to assess TCE rhizodegradation within the hybrid poplar plantation.

Phytotransformation and Volatilization. Several attempts were made to determine tree concentrations of VOCs and degradation products. Core, leaf, and other tree tissues were analyzed by gas chromatography (GC) either in sample vial head-space gases or after solid-phase microextraction (Vroblesky et al., 1999; Burken, 2001). Groundwater contaminants were observed in tree tissues: between 0.1 and 75 mg TCE per gram plant dry weight were detected in trees growing near the DNAPL area. However, only a poor correlation was found between groundwater concentration and tree tissue concentration. The analyses of tree tissues also showed that VOC concentrations decreased with sampling elevation from the roots to the branches, suggesting transformation or volatilization of VOC within or from the trunk. Transpiration of VOC was measured using Tedlar bags placed over branches and sealed around the stem. GC analysis revealed the presence of only traces of 1,1,2,2-TeCA and TCE in a limited number of trees, suggesting that volatilization through the leaves was not the primary fate of VOCs taken up by trees.

Volatilization in Ambient Air. To evaluate the potential impact of VOCs on human health and the environment, VOC emissions were analyzed in the ambient atmosphere. FTIR spectrometer analyses within the phytoremediation area revealed concentrations of target compounds (i.e., 1,1,2,2-TeCA, TCE, TCA, PCE, and *cis*-DCE) below the detection limit of the instrument. Flux-chamber analyses of air emissions directly from the groundwater plume to ambient air showed traces of TCE in three of the eight chambers ranging from 9.4 to 38 parts per billion (ppb), suggesting volatilization directly from the vadose zone. These analyses indicated that VOCs released into the air through evaporation and transpiration did not approach concentrations that would pose a threat to human health or the environment. As stated previously (see Section 19.1.2.7), UV photolysis of chlorinated solvents has been reported but is unlikely to be significant under ambient conditions (Sato et al., 1997; Feiyan et al., 2002).

19.3.2.4 Modeling Phytoremediation Performance

A three-dimensional numerical groundwater flow model (MODFLOW) was updated several times to predict the effect of a pump-and-treat system on site hydrology and to integrate and support feasibility studies of the technology for dissolved VOC mass removal (Hughes, 1995; Quinn et al., 1996). Plume movement and the lateral and vertical extent of VOC contamination were analyzed using a three-dimensional geospatial model constructed using Earth Vision® (Schneider and Wrobel, 1998).

The MODFLOW model was updated with hydrostratigraphic data in the geospatial model. The model was designed to incorporate various remediation technologies screened during previous site feasibility studies (Quinn et al., 1996). Particularly, the long term, steady-state effect of hybrid poplars on groundwater hydraulics was simulated using a module designed to predict a well capture zone. Based on the maximum predicted transpiration rates of mature trees (7,600 L/day), the model showed a well-developed zone of capture centered at the Southeastern part of the plantation, with the most evident effect in the aquifer located where the flow path transitioned upward to discharge into the marsh. The zone of maximum influence was shown to be in the upper 4.6 m (15.1 ft) of the aquifer, decreasing with the depth.

Contaminant Transport Modeling. The objective of modeling contaminant transport at J-Field was to compare dissolved phase mass removal rates expected for several remedial technologies. At the time modeling was designed, the presence of the mobile DNAPL had not been detected. The fate and transport of 1,1,2,2-TeCA, TCE, and their transformation products were simulated using the multispecies reactive transport model RT3D (WESTON, 2000). Mass removal by hybrid poplars was based on the application of the uptake efficiency (TSCF) described in Burken and Schnoor (1998b).

Results from the MODFLOW-RT3D model indicated that containment of the VOCs released to the freshwater marsh was not significant, mainly due to the low permeability of the aquifer. However, the model showed that the hybrid poplars were able to capture and transpire contaminated water, removing up to 163 kg (359 lb) of dissolved VOCs after 30 years.

19.3.2.5 Conclusions

Research conducted at the J-Field over 5 years demonstrated that phytoremediation was an efficient process for containment of VOC contamination through hydraulic control. The efficiency of the technology depended on the unique conditions of the site, including its remote location (no groundwater usage), the low groundwater velocity, a VOC plume under steady-state conditions, and anoxic conditions in the freshwater marsh (stimulating microbial biodegradation of contaminants).

Hybrid poplar trees planted at J-Field contributed to remediation of the VOC plume by several processes. The most important was the transpiration of large amounts of groundwater, resulting in hydraulic containment of contaminated groundwater. Weather and length of the growing season were the most influential factors affecting the efficacy of the phytoremediation system. Peak transpiration was estimated to occur approximately 10-15 years after planting. While contaminant uptake was minimal at the time of measurement, it was expected to increase as the trees mature. Tree uptake was estimated to be 4.1 L/day (1.1 gal/day) after 5 years of growth, and was expected to increase to 7.6 L/day (2.0 gal/day) after 30 years. It was observed that the trees were also capable of biotransformation of VOCs taken up in plant tissues and releasing VOCs through volatilization to the atmosphere. However, these effects were not significant in terms of reducing the concentrations of VOCs reaching the marsh.

19.3.2.6 Cost Estimates

The total cost of the phytoremediation system was $115,000, which consisted of $85,000 in capital costs ($5,000 for site preparation, $80,000 for UXO clearance of soil during planting, and $80 per tree [approximately $15,000 for 183 trees]) and $30,000 in O&M costs. There was no established monitoring technique cost included in this estimate (USEPA, 2002).

19.3.3 Treatment of Chlorinated Volatile Organic Compounds by Hybrid Poplars, Solvents Recovery Service of New England, Southington, Connecticut

The contaminant source at this Superfund Site was a DNAPL containing primarily PCE, TCE, 1,1-DCA, *trans*-DCE, *cis*-DCE, 1,1,1-TCA, ethylbenzene, toluene, and *sec*-butanol in both the overburden and bedrock aquifers. The source area was contained by a sheet pile barrier wall, with pump-and-treat as the primary remediation technology. In order to reduce the amount of groundwater removed using the traditional pumping technology, a hydraulic control phytoremediation system was implemented at the site. More detailed descriptions of the phytoremediation project can be found in USEPA (2005b, 2006a, 2006b) and Ferro et al. (2005).

19.3.3.1 Site Description

The site encompasses the Solvents Recovery Service of New England (SRSNE) area, as well as neighboring properties. From 1955 to 1991, SRSNE reclaimed spent industrial solvents. Chemical releases of VOCs occurred from storage lagoons, drum and tank areas and a processing area. The site was declared a Superfund Site by the USEPA in 1983.

Remediation of the site consisted of a containment area within a 213 m long by 9 m deep (700 ft by 30 ft) sheet-pile wall installed to the top of bedrock. A network of 12 groundwater recovery wells was installed in both the overburden and bedrock aquifers, with the intent of creating an inward hydraulic gradient across the barrier wall. These wells pumped at a rate of 72 L/min (19 gal/min) year round. It should be noted that the overburden and bedrock aquifers are hydraulically connected at the site, and the overburden aquifer exists at a depth of 1.2-1.5 m (4-5 ft) bgs. The remediation system was a non-time critical removal action system which controlled the migration of the most highly contaminated groundwater since 1995. Recovered groundwater was treated on-site by UV oxidation, which removed approximately 850 kg (1,874 lb) of VOCs per year at an annual O&M cost of $500,000 (which equates to approximately $0.0125 per L [$0.05 per gal] of treated water).

19.3.3.2 Phytoremediation Project

A 0.32 ha (0.8 ac) stand of hybrid poplar trees was established within the containment area with the objective to pump and treat contaminated groundwater from the overburden aquifer, and to reduce the need for mechanical pumping and treatment, at least on a seasonal basis.

Preliminary Greenhouse Study. A preliminary greenhouse experiment was conducted to evaluate the potential toxicity of the dissolved VOCs in groundwater to hybrid poplar trees (*P. deltoides* × *nigra*). Three different concentrations of VOCs, ranging from 45 to

170 mg/L, were used to water the poplar saplings in 189 L (50 gal) barrels packed with alternating layers of pea gravel and sandy loam soil. Phytotoxicity was evaluated by measuring the following physiological parameters: stomatal conductance, shoot elongation, biomass production, leaf area and root growth. No significant effect on the physiological parameters was noted, indicating that a full-scale installation at the SRSNE site was feasible (Ferro et al., 1999).

Site Phytoremediation System Installation. A total of 1,000 hybrid poplar (*P. deltoides* × *nigra*) saplings were planted in 1.2 to 1.5 m (4 to 5 ft) deep trenches within the containment area in late May 1998. The trenches were backfilled with a sand/compost mix. Only 60% of the poplars survived, possibly due to the late planting date and the effect of high temperatures on the newly planted saplings. In early April 1999, 400 willow cuttings (*Salix alba*) were planted within boreholes drilled to the bottom of the original backfilled trenches. The willow cuttings were deeply planted, and the holes were backfilled with a sand/compost mix. In May 2002, the remaining hybrid poplar trees were removed, due to a Canker infestation caused by *Cryptodiaporthe populea*. By the summer of 2004 (fifth year) the willows attained canopy closure, with 370 trees surviving on the 0.32 ha (0.8 ac) tract.

19.3.3.3 Monitoring Phytoremediation Performance

Groundwater Pumping Efficiency. Groundwater pumping efficiency was estimated by calculating the rate of water consumption (Vt) through the use of thermal dissipation probes (TDPs) that measured sap velocity. The TDPs were installed into 5-7 trees during the growing season in years 2000 through 2003. The TDPs were composed of two needle-like sensors which were inserted into holes drilled into the xylem of the tree. The upper needle is heated, and the temperature difference between the two needles is measured. The sap velocity is empirically related to the change in temperature between the two needles. Sap flow was calculated as the product of sap velocity by the cross sectional area of the stem. The stand water use was calculated as the product of sap velocity by the basal area of the trees.

Using this method, the stand water use was estimated to reach 34 L/min (9 gal/min) during the 2005 growing season, which, when applied to the entire 0.32 ha (0.8 ac) tree stand, equates to 7.2 million liters (1.9 million gallons) over the course of the growing season. The highest pumping rate using mechanical pumps was approximately 95 L/min (25 gal/min). Therefore, pumping of groundwater by mature willow trees accounted for a large proportion of the water to be pumped, at least during the active growing season (which at this site is May through September).

Chlorinated Solvent Removal. VOCs were detected in the xylem core samples obtained from several trees at the site. The removal rate of VOCs was estimated from the volume of groundwater pumped by the trees in 2004 and the VOC concentration in groundwater. The estimated removal mass of VOCs using this method was 340 kg (750 lb) in that growing season. Data were not collected to determine the pathway by which the VOCs were removed (phytovolatilization, rhizodegradation or transformation within the tree).

19.3.3.4 Cost Estimates

The total cost of the remediation system was $281,900, comprised of $15,500 for the design, $40,400 for the greenhouse studies, $115,300 for installation, $40,700 for replanting with willows, and $70,000 for O&M. A net cost savings of $97,000 compared to the existing mechanical pump-and-treat system was estimated for the 2006 growing season (i.e., the seventh year). By the end of the 2010 growing season, an estimated cost savings of $470,000 was projected. The phytoremediation tree stand was selfsustaining by the end of the 2005 growing season, and no significant project costs were expected past that time.

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CHAPTER 20

COST ANALYSES FOR REMEDIAL OPTIONS

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20.1 INTRODUCTION

The economic analysis of remedial options is a key activity in any remedial selection process. It is typically employed in the feasibility study phase of remedy selection to aid in selecting the optimal remedial option for a site, in concert with a number of other criteria. In this case, for dissolved phase chlorinated solvent contaminated groundwater, the capital and recurring costs of various alternatives are compared, typically using a net present value (NPV) calculation. In addition to the ability to compare remedial options, detailed economic analysis also allows the design engineer to determine which cost elements of a specific remedy drive the cost of that remedy. Understanding the primary cost drivers improves the potential for cost optimization and therefore can lead to more cost effective remedial designs.

This chapter provides a basic approach to generating cost information for several remedial technologies that are often used to treat dissolved phase chlorinated aliphatic compounds in groundwater. Cost information for each technology is derived for one or more template site situations to illustrate the process and broken down into design elements, capital expenditures, operation and maintenance (O&M), and monitoring costs to help understand the primary cost drivers for each technology.

This chapter does not provide definitive cost information for each remedial technology since these are highly site specific. Rather, this chapter gives the design engineer a general process to use in estimating costs when applying select technologies to specific sites.

20.2 COST ANALYSIS PROCESS

20.2.1 Template Site Descriptions

The economic analysis presented here is based on a method first used by DuPont to compare *in situ* remediation technologies on a consistent economic basis (Quinton et al., 1997). That approach, involving detailed costing for hypothetical template sites, will be used in this chapter to cost remedial technologies for a residual source area and two downgradient groundwater plumes containing trichloroethene (TCE) and its daughter products. The template sites have been divided in this manner because source areas and plumes are typically addressed independently in many feasibility studies.

The template residual source area (Case 1) consists of an area of 250 square meters (m^2), or 2,690 square feet (ft^2). This source area contains 200 kilograms (kg), or 440 pounds (lb) of TCE that is either adsorbed to the soil or present as a dispersed residual phase in the aquifer matrix. This situation is typical of many small TCE source areas. The depth to groundwater is 1.5 m (4.9 ft), and it is 4.5 m (14.8 ft) to a clay aquitard that underlies the saturated zone, providing a saturated thickness of 3 m (9.8 ft). The groundwater velocity across this area is 10 m (32.8 ft) per year (yr). The groundwater in this area contains 20 milligrams per liter (mg/L) of both TCE

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and *cis*-dichloroethene (*cis*-DCE), along with 5 mg/L dissolved iron and 100 mg/L sulfate. Table 20.1 summarizes these and other characteristics of the subsurface matrix and groundwater for all three cases considered in this chapter.

Table 20.1 Description of Template Site Cases

Parameter	Case 1	Case 2	Case 3
Location	Source Area	Plume	Plume
Area (m^2)	250	–	–
Width (m)	–	75	75
Depth to Groundwater (m)	1.5	1.5	3.0
Depth to Aquitard (m)	4.5	4.5	12.0
Saturated Thickness (m)	3.0	3.0	9.0
Hydraulic Conductivity (cm/sec)	1×10^{-4}	1×10^{-4}	1×10^{-4}
Groundwater Gradient (m/m)	3×10^{-3}	3×10^{-3}	9×10^{-3}
Groundwater Velocity (m/yr)	10	10	30
Porosity	0.3	0.3	0.3
Effective Porosity	0.2	0.2	0.2
Fraction Organic Carbon	0.002	0.002	0.002
Injection Rate (L/min)	10	10	10
NOD[1] (permanganate) (g/kg solids)	2	2	2
EVO[2] Adsorption (g/kg solids)	1	1	1
Residual TCE (kg)	200	–	–
Groundwater Concentrations (mg/L)			
TCE	20	0.1	0.1
cis-DCE	20	2.0	2.0
VC	–	0.2	0.2
Dissolved Oxygen	–	–	–
Nitrate	–	–	–
Dissolved Iron	5	5	5
Sulfate	100	100	100

[1] NOD - natural oxidant demand
[2] EVO - emulsified vegetable oil

The first downgradient groundwater scenario (Case 2) consists of a plume that extends off-site. The width of the plume at the site boundary is 75 m (246 ft). The depth to groundwater is 1.5 m (4.9 ft), and it is 4.5 m (14.8 ft) to a clay aquitard that underlies the saturated zone, providing a saturated thickness of 3.0 m (9.8 ft). The groundwater velocity across this area is 10 m (32.8 ft) per year. The groundwater in this area contains 0.1 mg/L of TCE, 2 mg/L *cis*-DCE, and 0.2 mg/L vinyl chloride (VC), along with 5 mg/L dissolved iron and 100 mg/L sulfate.

The second downgradient groundwater scenario (Case 3) consists of a plume that extends off-site. The width of the plume at the site boundary is 75 m (246 ft). In this case the depth to groundwater is 3 m (9.8 ft), and it is 12 m (39.4 ft) to a clay aquitard that underlies the saturated zone, providing a saturated thickness of 9 m (29.5 ft). The groundwater velocity across this area is 30 m (98.4 ft) per year. The groundwater in this area contains 0.1 mg/L of TCE, 2 mg/L *cis*-DCE, and 0.2 mg/L VC, along with 5 mg/L dissolved iron and 100 mg/L sulfate. This combination of contaminant concentration, saturated thickness, and groundwater velocity gives a contaminant groundwater flux that is nine times higher than the previous scenario (Case 2).

20.2.2 Cost Categories and Components

The remedies applied at these template sites include enhanced *in situ* bioremediation (EISB), *in situ* chemical oxidation (ISCO), zero-valent iron (ZVI) barriers, air sparging, in-well air stripping, phytoremediation and monitored natural attenuation (MNA). Each remedy has been applied only for template site cases where it would be an appropriate technology for the site conditions. For each remedy, the costs were divided into general categories, including design, capital, O&M, and monitoring. It has been assumed that basic site data derived from remedial investigation activities are available prior to the design phase. Specific cost components in each cost category are identified in Figure 20.1.

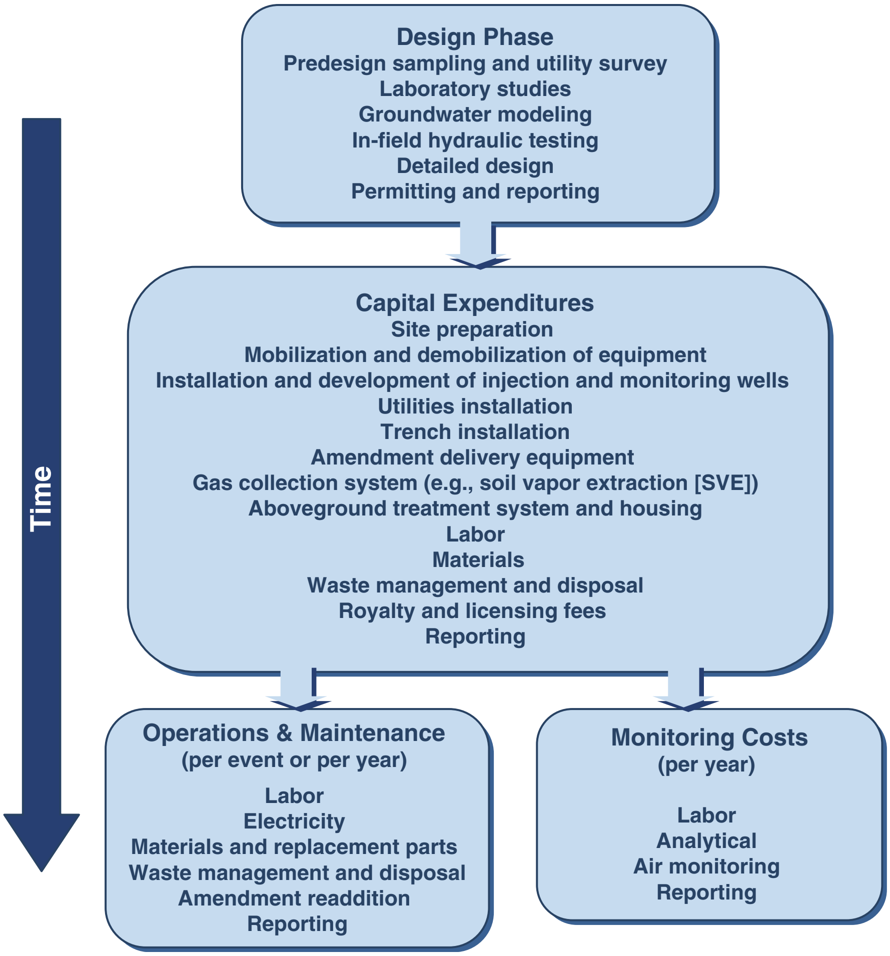

Figure 20.1. Components of cost analysis

The design activities considered in this cost analysis include any predesign sampling and surveying that is specific to the remedy applied. For example, some technologies may require laboratory studies, groundwater modeling, or on-site hydraulic testing prior to implementation. Detailed design, permitting and reporting costs are also included in this category.

The capital activities include site preparation and all implementation costs incurred during the initial application of a technology in the designated area. These may include mobilization and demobilization of equipment, installation and development of amendment injection wells, installation of a trench, installation of a vapor collection system, installation of aboveground or below ground amendment delivery equipment, installation and housing for an aboveground vapor treatment system, and installation of supporting utilities. These components may be used in various combinations, depending upon the technology applied. Other capital costs include labor, materials (e.g., amendments), waste management and disposal, and reporting. Finally, there are licensing and royalty fees associated with some technologies.

O&M activities include labor, materials, replacement parts, waste management and disposal, electricity usage and reporting required to keep the remedy operating as designed. Some technologies (e.g., ISCO and EISB) will require multiple amendment applications to be effective. These applications have been included as O&M costs when appropriate. In these cases, an average O&M cost will be calculated in order to integrate the cost of periodic amendments with annual O&M expenses. It has been assumed that the contractors performing periodic maintenance are located near the site so that travel costs are not significant relative to the time spent on site.

Monitoring costs include the labor, equipment, chemical analysis, and reporting associated with monitoring the performance of the remedy. The monitoring network used was roughly similar in each case and typically consists of five monitoring wells for the source area (Case 1) and shallow plume (Case 2) and seven monitoring wells for the deeper plume (Case 3). The exception to this monitoring well design is the MNA remedy, which consists of either 10 monitoring wells (Case 2) or 14 monitoring wells (Case 3). For most technologies the monitoring network is specific to the area containing the remedy. However, since MNA extends across the entire plume, it generally requires a more comprehensive monitoring network. It has been assumed that groundwater sampling will occur quarterly for the first five years that the remedy is active and semiannually thereafter. Air monitoring costs for aboveground treatment systems are also included in this category.

All economic comparisons have been made on a net present value basis, assuming the total lifetime of the remediation project is 30 years and using a discount rate of 3% for annual costs. This discount rate is derived from Department of Defense guidance on using economic analyses in decision making (DoD, 1995). This discount rate is based on current Office of Management and Budget data and assumes a 5% nominal return is available on U.S. Treasury Notes and Bonds and an annual inflation rate of roughly 2%. This real discount rate is appropriate for government entities, while a higher discount rate may be more appropriate for private parties who can obtain higher returns on investments.

20.3 REMEDIATION OPTIONS EVALUATED

20.3.1 Case 1: Residual Source Area

The remedial technologies applied to this area included EISB, ISCO using permanganate, and air sparging. In-well air stripping was not considered because the saturated zone is not thick enough for this technology to be effective. The objective in each case was to reduce the flux coming from the source area by 90-95%. It was assumed that three to five years of treatment will be required to reduce the flux to this level, depending upon the treatment technology. The costs also include the installation of five 5-centimeter (cm) (2-inch [in]) diameter monitoring wells for each option.

20.3.1.1 Enhanced *In Situ* Bioremediation

For the purposes of this analysis, emulsified vegetable oil (EVO) will be used as the electron donor to promote reductive dechlorination of TCE to ethene in the residual source area. The advantages of this donor include longevity and ease of distribution in the subsurface relative to other slow release donors. A laboratory biotreatability study will be used, as it is typically needed to verify that EISB will be effective at a site and that EVO is a suitable donor.

The EVO will be applied through a series of 15 injection wells spaced on 5 m (16.4 ft) centers distributed across the 250 m^2 (2,690 ft^2) source area. A groundwater model will be utilized in the design phase to help specify the injection sequence and ensure that the amendment will contact the entire source zone. The 5-cm (2-in) diameter injection wells will be screened across the saturated zone and developed prior to EVO injection. Predesign injection testing is included in the cost analysis to establish the injection rate, which is assumed to be 10 liters per minute (L/min) (2.6 gallons per minute [gpm]). The costs include addition of 185 kg (407 lb) of a commercial EVO solution to each injection point, along with 9,000 L (2,376 gallons [gal]) of fluid (dilute EVO and chase water) to ensure complete distribution of the EVO. The EVO will be metered through a dosimeter pump connected to a nearby water source, and a manifold will be used to allow injection into as many as five injection wells simultaneously. Each injection line will contain a pressure gauge and flow totalizer to allow accurate measurements of the fluid injections into each well. The injections will be performed by a two person crew requiring 11 days of labor, including setup and breakdown.

It was assumed that it will take five years to reach remedial goals using EISB. Each application of EVO will support dechlorination for two to three years, so that a second application of EVO will be required in Year 3. The second application will deliver 100% of the initial EVO loading utilizing the same injection well network. No other O&M is required with this remedial option. Quarterly monitoring will be performed for the first five years, followed by semiannual monitoring thereafter. The quarterly monitoring will include parameters specific to the remedy, such as total organic carbon (TOC) and other relevant MNA analytes. The semiannual sampling will include only volatile organic compounds (VOCs).

20.3.1.2 *In Situ* Chemical Oxidation

Potassium permanganate will be used as the oxidant to promote degradation of TCE and its daughter products in the residual source area. The advantages of this oxidant include longevity and ease of distribution in the subsurface. Laboratory natural oxidant demand (NOD) testing will be used to estimate the background NOD of the soil. In this case, it is assumed the NOD of the soil is 2 grams (g) permanganate per kg of soil.

The permanganate will be applied through the same network of 15 injection wells spaced on 5 m (16.4 ft) centers used in the EISB cost analysis. A groundwater model will be used in the design phase to help specify the injection sequence and ensure the amendment will contact the entire source zone. The 5-cm (2-in) diameter injection wells will be screened across the saturated zone and developed prior to permanganate injection. Predesign injection testing will be used to establish the injection rate, which is assumed to be 10 L/min (2.6 gpm). Potassium permanganate (220 kg [484 lb]) will be added to each injection point, along with 9,000 L (2,376 gal) of fluid (dilute permanganate and chase water) to ensure complete distribution of the oxidant.

Permanganate will be mixed in aboveground tanks prior to injection. A manifold will be used so that injection can take place in up to five injection wells simultaneously. Each injection line will contain a pressure gauge and flow totalizer so that fluid injection into each well can be accurately measured. The injections will be performed by a two person crew and will require 11 days, including setup and breakdown.

It is assumed that it will take three years to reach remedial goals using ISCO. ISCO applications are subject to rebound, so that a second and third application of oxidant will be required in Years 2 and 3. Each subsequent application will deliver 50% of the initial permanganate loading utilizing the same injection well network. No other O&M is required with this remedial option. Because ISCO is subject to rebound, quarterly monitoring will be performed for the first five years, followed by semiannual monitoring thereafter. The quarterly and semiannual sampling will include only VOCs.

20.3.1.3 Air Sparging

The air sparging application will utilize the same network of 15 injection wells spaced on 5 m (16.4 ft) centers used in the previous applications. In this case the 5-cm (2-in) diameter wells will be screened at the bottom of the saturated zone. A groundwater model will be utilized in the design phase to verify the well spacing and ensure that the sparge gas will contact the entire source zone. An in-field pilot test will be used to establish the design airflow rates and distribution. Air will be delivered to each sparge point at 560 L/min (20 cubic feet per minute [cfm]) using two 2,800 L/min (100 cfm) blowers. A series of manifolds will be used so that the air injection can be cycled between three injection points, such that air is sparged into each point 33% of the time. Each sparge point will contain a pressure gauge and flow totalizer so that air injection into each well can be accurately measured.

A soil vapor extraction (SVE) system will be required to collect vapors coming off of the treatment area (Pedersen and Curtis, 1991; USACE, 2002). The SVE system will consist of four extraction points spaced on 4.5 m (14.8 ft) centers, screened in the unsaturated zone. Vapors will be collected using two 2,800 L/min (100 cfm) blowers and treated by an aboveground system consisting of activated carbon (USEPA, 2006; Prakash et al., 1994). The aboveground system will be housed in a trailer. Labor costs for this remedy will include both system installation and start up and will require six days for a two person crew; these costs also include setup of the carbon system by the vendor.

It is assumed that it will take three years to reach remedial goals using air sparging. The O&M required for this system will involve weekly checks of system operation, with semiannual maintenance on injection wells, blowers, and the aboveground treatment system. Air monitoring of the off gas produced by the carbon treatment system will occur monthly while the system is in operation, with weekly sampling performed during the first month of operation (AFCEE, 2001). Because air sparging is subject to rebound, quarterly monitoring will be performed for the first five years, followed by semiannual monitoring thereafter. The quarterly and semiannual sampling will include only VOCs.

20.3.2 Case 2: Shallow Barrier

The remedial technologies applied to this area will be EISB, ZVI, air sparging, phytoremediation and MNA. In-well air stripping will not be applied because the saturated zone is not thick enough for this technology to be effective. All of the technologies will be applied as barriers, with the objective of reducing the contaminant concentrations by 90-95% before leaving the site. It is assumed the barrier will need to operate for 30 years. Five 5-cm (2-in) diameter monitoring wells will be installed with each option, with the exception of MNA, where 10 wells will be required.

20.3.2.1 Enhanced *In Situ* Bioremediation

EVO will be used as the electron donor to promote reductive dechlorination of chlorinated VOCs within the zone of influence of the shallow barrier. The long-life advantages previously described for this donor are particularly important in barrier applications. A laboratory biotreatability study will be used to verify that EISB will be effective at the site and that EVO is a suitable donor.

The EVO will be applied through a single row of 15 injection wells spaced on 5 m (16.4 ft) centers along the length of the shallow barrier. A groundwater model will be utilized in the design phase to verify well spacing and to ensure that flow will pass through the barrier. The 5-cm (2-in) diameter injection wells will be screened across the saturated zone and developed before the EVO is injected. Predesign injection testing will be used to verify the injection rate, which is assumed to be 10 L/min (2.6 gpm). EVO (185 kg [407 lb]) will be added to each injection point, along with 9,000 L (2,376 gal) of fluid (dilute EVO and chase water) to ensure complete distribution of the EVO. EVO will be added in the same manner described in Case 1. The injections will be performed by a two person crew and will require 11 days, including setup and breakdown.

Each application of EVO will support dechlorination for two to three years, so that an additional application of EVO will be required every third year. These subsequent applications will deliver 100% of the initial EVO loading, utilizing the same injection well network. No other O&M is required with this remedial option. Quarterly monitoring will be performed for the first five years, followed by semiannual monitoring thereafter. Both the quarterly and semiannual monitoring will include parameters specific to the remedy, such as TOC and other relevant MNA analytes.

20.3.2.2 ZVI Barrier

Granular iron will be used to promote the abiotic reduction of chlorinated VOCs within the shallow barrier. The barrier thickness can be calculated based on known degradation half lives for the target compounds, so that no laboratory or field testing is required. Granular iron (32.5 metric tons) will be applied as an iron and sand mixture along the length of the barrier using a continuous trenching technique. This technique allows the iron and sand to be added in a single pass without use of trench boxes or other shoring techniques. The trench will be 0.3 m (1.0 ft) thick and extend down to the aquitard at 4.5 m (14.8 ft). A groundwater model will be utilized in the design phase to verify that flow will pass through the barrier.

Extended lifetimes of ZVI barriers are currently not known, but several are still operational 10 years after installation. In this case, it is assumed that complete barrier replacement will not be necessary over this 30-year period. However, maintenance will be performed on the wall every ten years to regenerate the iron in place (ITRC, 2005). The cost of each maintenance event is estimated to be 25% of the initial capital cost. Quarterly monitoring will be performed for the first five years, followed by semiannual monitoring thereafter. The quarterly and semiannual sampling will include only VOCs.

20.3.2.3 Air Sparging

The air sparging application will utilize a single row of 15 injection wells spaced on 5 m (16.4 ft) centers along the length of the shallow barrier. In this case, the 5-cm (2-in) diameter wells will be screened at the bottom of the saturated zone. A groundwater model will be utilized in the design phase to verify well spacing and to ensure that flow will pass through the barrier. An in-field pilot test will be used to establish air flow rates and distribution. Air will be delivered to each sparge point at 560 L/min (20 cfm) using two 2,800 L/min (100 cfm) blowers. A series of manifolds will be used so that the air injection can be cycled between three injection points, such that air is sparged into each point 33% of the time. Each sparge point will contain a pressure gauge and flow totalizer so that air injection into each well can be accurately measured.

An SVE system will be required to collect vapors coming off of the treatment area. The SVE system will consist of nine extraction points spaced on 4.5 m (14.8 ft) centers, screened in the unsaturated zone. Vapors will be collected using three 2,800 L/min (100 cfm) blowers and treated by an aboveground activated carbon system. The aboveground system will be housed in a trailer. Labor costs for this remedy will include both system installation and start up and will require eight days for a two person crew; these costs also include setup of the carbon system by the vendor.

The O&M required for this system will involve weekly checks of system operation, with semiannual maintenance on injection wells, blowers, and the aboveground treatment system. Air monitoring of the off gas produced by the carbon treatment system will occur monthly while the system is in operation, with weekly sampling performed during the first month of operation. Quarterly monitoring will be performed for the first five years, followed by semiannual monitoring thereafter. The quarterly and semiannual sampling will include only VOCs.

20.3.2.4 Phytoremediation

Poplar trees will be used for hydraulic control and to promote the transpiration and degradation of chlorinated VOCs along the site boundary. The phytoremediation barrier will consist of five rows of 25 trees planted on 3 m (9.8 ft) centers, covering a total footprint of 15 x 75 m (49 x 246 ft) (USEPA, 2003). A groundwater model will be utilized in the design phase to verify tree spacing and to estimate residence time in the barrier. The trees will be planted as cuttings, and fertilizer and soil conditioners will be added at the same time. An irrigation system will be installed to provide water in the first five years as the root systems become established (ESTCP, 2006).

It is assumed that most of the trees will survive and remain active over this 30-year period. O&M will involve ground maintenance, periodic fertilization and application of insecticide, operation of the irrigation system during the first five years, and replacement of any trees that die. Quarterly monitoring will be performed for the first five years, followed by semiannual monitoring thereafter. The quarterly and semiannual sampling will include only VOCs. Other sampling, including tree height, canopy width, trunk diameter, sap flow and water level measurements, will be completed semiannually during the first five years and annually thereafter (ESTCP, 2006).

20.3.2.5 Monitored Natural Attenuation

MNA relies on natural attenuation mechanisms (predominantly biodegradation) to reduce contaminants to acceptable levels over long periods of time. One year of monitoring data and the creation of a comprehensive groundwater fate and transport model for the site is incorporated into the design phase for this remedy. Other than the installation of additional monitoring wells, no other capital investment is required.

No O&M is required with this remedial option. Ten 5-cm (2-in) diameter monitoring wells will be installed. The higher number of wells than used in the other options is associated with the more intense monitoring typically required for MNA. Quarterly monitoring will be performed for the first five years, followed by semiannual monitoring thereafter. The quarterly and semiannual sampling will include both VOCs and traditional MNA parameters.

20.3.3 Case 3: Deep Barrier

The remedial technologies applied to this area will be EISB, ZVI, air sparging, in-well air stripping and MNA. Phytoremediation will not be applied because the saturated thickness is too deep for this technology to be effective. All of the technologies will be applied as barriers, with the objective of reducing the contaminant concentrations by 90–95% before leaving the site. It is assumed the barrier will need to operate for 30 years. Seven 5-cm (2-in) diameter monitoring wells will be installed with this option, with the exception of MNA, where more wells will be required.

20.3.3.1 Enhanced *In Situ* Bioremediation

EVO will be used as the electron donor to promote reductive dechlorination of chlorinated VOCs within the deep barrier. A laboratory biotreatability study will be used to verify that EISB will be effective at the site and that EVO is a suitable donor.

The EVO will be applied through a single row of 15 paired injection wells spaced on 5 m (16.4 ft) centers along the length of the deep barrier. A groundwater model will be utilized in the design phase to verify well spacing and ensure flow will pass through the barrier. Each set of paired wells will consist of two 5-cm (2-in) diameter injection wells, one screened across the upper 4.5 m (14.8 ft) of the saturated zone and the second screened across the lower 4.5 m (14.8 ft). All of the wells will be developed prior to EVO injection. Predesign injection testing will be used to verify the injection rate, which is assumed to be 10 L/min (2.6 gpm). Commercial EVO solution (280 kg or 616 lb) will be added to each injection point, along with 13,500 L (3,564 gal) of fluid (dilute EVO and chase water) to ensure complete distribution of the EVO. The EVO will be added in the same manner described in Case 1. The injections will be performed by a two person crew and will require 24 days, including setup and breakdown.

Each application of EVO will support dechlorination for two to three years, so that an additional application of EVO will be required every third year. These subsequent applications will deliver 100% of the initial EVO loading utilizing the same injection well network. No other O&M is required with this remedial option. Quarterly monitoring will be performed for the first five years, followed by semiannual monitoring thereafter. Both the quarterly and semiannual monitoring will include parameters specific to the remedy, such as TOC and other relevant MNA analytes.

20.3.3.2 ZVI Barrier

Granular iron will be used to promote the abiotic reduction of chlorinated VOCs within the deep barrier. The barrier thickness was calculated based on known degradation half lives for the target compounds, so that no laboratory or field testing is required. Granular iron (288 metric tons) will be applied as an iron and sand mixture along the length of the barrier utilizing standard trenching and shoring. Guar gum will be used to maintain the stability of an open trench while the iron and sand mixture is placed using a tremie pipe. The trench will be 0.6 m (2 ft) thick and extend down to the aquitard at 12 m (39.4 ft). A groundwater model will be utilized in the design phase to verify that flow will pass through the barrier.

Extended lifetimes of ZVI barriers are currently not known, but several are still operational 10 years after installation. In this case, it is assumed that complete barrier replacement will not be necessary over this 30-year period. However, maintenance will be performed on the wall every 10 years to regenerate the iron in place (ITRC, 2005). The cost of each maintenance event is estimated to be 25% of the initial capital cost. Quarterly monitoring will be performed for the first five years, followed by semiannual monitoring thereafter. The quarterly and semiannual sampling will include only VOCs.

20.3.3.3 Air Sparging

The air sparging remedy will utilize a single row of 15 paired injection wells spaced on 5 m (16.4 ft) centers along the length of the deep barrier, similar to the EISB application. A groundwater model will be utilized in the design phase to verify well spacing and to ensure that flow will pass through the barrier. Each set of paired wells will consist of two 5-cm (2-in) diameter injection wells, one screened 4.5 m (14.8 ft) into the saturated zone and the second screened just above the aquitard. An in-field pilot test will be used to establish design air flow rates and distribution. Air will be delivered to each sparge point at 560 L/min (20 cfm) using four 2,800 L/min (100 cfm) blowers. A series of manifolds will be used so that the air injection can be cycled between three injection points, such that air is sparged into each point 33% of the time. Each sparge point will contain a pressure gauge and flow totalizer so that air injection into each well can be accurately measured.

An SVE system will be required to collect vapors coming off of the treatment area. The SVE system will consist of nine extraction points spaced on 4.5 m (14.8 ft) centers, screened in the unsaturated zone. Vapors will be collected using three 2,800 L/min (100 cfm) blowers and treated by an aboveground system consisting of activated carbon. The aboveground system will be housed in a trailer. Labor costs for this remedy will include both system installation and start up and will require eight days for a two person crew; these costs also include setup of the carbon system by the vendor.

The O&M required for this system will involve weekly checks of system operation, with semiannual maintenance on injection wells, blowers, and the aboveground treatment system. Air monitoring of the off gas produced by the carbon treatment system will occur monthly while the system is in operation, with weekly sampling performed during the first month of operation. Quarterly monitoring will be performed for the first five years, followed by semiannual monitoring thereafter. The quarterly and semiannual sampling will include only VOCs.

20.3.3.4 In-Well Stripping

The in-well air stripping remedy will utilize a single row of three 15-cm (6-in) diameter stripping wells spaced on 25 m (82 ft) centers along the site boundary. The well spacing was determined by assuming that the effective radius of influence for each well will be 1.5 times the distance between the upper and lower screens, which in this case is the equivalent saturated thickness of the aquifer. A single well field pilot test will be used to determine the radius of influence prior to full scale implementation. A groundwater model also will be utilized in the design phase to verify well spacing and to ensure that flow will pass through the barrier. Air will be delivered to each well at 560 L/min (20 cfm) using a single 2,800 L/min (100 cfm) compressor. Each well will contain a pressure gauge and flow totalizer so that air injection into each well can be accurately measured. A pair of 2,800 L/min (100 cfm) blowers will be used to extract vapors from the top of the well. The vapors will be treated by an aboveground activated carbon system. The system will be housed in a trailer. Labor costs for this remedy will include both system installation and start up and will require six days for a two person crew; these costs include set up of the carbon system by the vendor.

The O&M required for this system will involve weekly checks of system operation, with semiannual maintenance on stripping wells, blowers, and the aboveground treatment system. Air monitoring of the off gas produced by the carbon treatment system will occur monthly while the system is in operation, with weekly sampling performed during the first month of operation. Quarterly monitoring will be performed for the first five years, followed by semiannual monitoring thereafter. The quarterly and semiannual sampling will include only VOCs.

20.3.3.5 Monitored Natural Attenuation

MNA relies on natural attenuation mechanisms (predominantly biodegradation) to reduce contaminants to acceptable levels over long periods of time. One year of monitoring data and the creation of a comprehensive groundwater fate and transport model for the site is incorporated into the design phase for this remedy. Other than the installation of additional monitoring wells, no other capital investment is required.

No O&M is required with this remedial option. Fourteen 5-cm (2-in) diameter monitoring wells will be installed. The higher number of wells than used in the other options is associated with more intensive monitoring typically required for MNA. Quarterly monitoring will be performed for the first five years, followed by semiannual monitoring thereafter. The quarterly and semiannual sampling will include both VOCs and traditional MNA parameters.

20.4 COST ANALYSES

20.4.1 Case 1: Residual Source Area

Detailed cost analyses for the three technologies considered in Case 1 are presented in Table 20.2. The NPV comparison is presented in Table 20.3. The NPV analysis indicates that EISB and ISCO are very close to the same NPV cost. This result is reasonable because the application approach in both cases is very similar; the primary difference is the amendment used. More extensive laboratory treatability work is required with EISB in the design phase, while the handling of potassium permanganate in the field requires more robust equipment and manual manipulation than does handling of EVO, resulting in marginally higher capital costs. In neither case does material cost (EVO or permanganate) constitute more than 15-20% of the total capital cost. The material costs would represent a greater fraction of the total costs if the source area contained a significant amount of dense nonaqueous phase liquid (DNAPL) or if the NOD demand was much higher than 2 g/kg soil. O&M costs in both cases are driven by amendment readdition requirements.

Air sparging has a NPV cost that is about 40% higher than either EISB or ISCO, due primarily to a combination of higher capital and O&M costs associated with the SVE system. Air sparging (with SVE) is more expensive than the other technologies even though the air sparging system was only operated for three years. Design costs for the air sparging system are marginally higher than for the other technologies because it is necessary to design both the subsurface components and the SVE and aboveground components and because in-field testing is generally required to verify air injection and distribution performance. Capital expenditures include purchase and installation of extraction wells and piping, as well as the aboveground carbon unit. Higher O&M costs are the result of electrical usage and the need to continually monitor the performance of the system, as well as the performance of routine maintenance. Monitoring costs for air sparging are somewhat higher than for the other remedies because air monitoring is required.

Table 20.2 Cost Comparison for Case 1

Cost Element	EISB	ISCO	Air Sparging
Design			
Predesign sampling & utility survey	$15,000	$15,000	$15,000
Laboratory studies	$20,000	$2,000	$0
Groundwater modeling	$20,000	$20,000	$20,000
In-field hydraulic testing	$2,000	$2,000	$15,000
Detailed design	$10,000	$10,000	$20,000
Permitting & reports	$10,000	$10,000	$15,000
Total design	***$77,000***	***$59,000***	***$85,000***
Capital			
Site Preparation	$2,000	$2,000	$2,000
Mobilization/demobilization of equipment	$0	$0	$0
Injection/monitoring well installation & development	$23,500	$23,500	$23,500
Process equipment	$9,000	$19,000	$16,500
Materials	$12,000	$12,000	$3,000
Labor	$13,000	$13,000	$20,000
Gas collection system (SVE)	$0	$0	$36,500
Aboveground treatment system & housing	$0	$0	$5,000
System start up costs	$0	$0	$2,000
Waste management & disposal	$1,000	$1,000	$1,000
Royalty/Licensing fees	$0	$0	$0
Reports	$5,000	$5,000	$5,000
Total capital	***$65,500***	***$75,500***	***$114,500***
Operation & Maintenance (Per Year or Event)			
Labor	$0	$0	$15,000
Utilities	$0	$0	$3,000
Amendment addition (per event)	$25,000	$19,000	$0
Replacement parts & materials	$0	$0	$1,500
Waste management & disposal	$0	$0	$10,000
Reports	$2,500	$2,500	$5,000
Average annual O&M *	***$5,500***	***$14,500***	***$34,500***
Monitoring Costs (Quarterly Sampling)			
Labor	$5,000	$5,000	$12,000
Analytical, groundwater	$7,000	$4,000	$4,000
Analytical, air	$0	$0	$4,000
Reports	$10,000	$10,000	$14,000
Total monitoring (per year)	***$22,000***	***$19,000***	***$34,000***

*Average annual O&M values appear solely for comparison purposes and were calculated by summing the O&M costs over the active life of the project and dividing by the number of years in the active phase. No discounting was applied to this calculation.

Table 20.3 Cost Comparison for Case 1

Cost Element	EISB	ISCO	Air Sparging
Total design costs	$77,000	$59,000	$85,000
Total capital costs	$65,500	$75,500	$114,500
Total O&M (30 yr NPV)	$25,500	$41,500	$98,000
Total monitoring (30 yr NPV)	$242,500	$227,500	$269,000
Overall total (30 yr NPV)	***$410,500***	***$403,500***	***$566,500***

Most of the difference in NPV cost between air sparging and EISB or ISCO would largely disappear if the SVE and aboveground treatment systems were removed. Some air sparging systems are operated without vapor collection and treatment, particularly where the contaminant of concern is a petroleum hydrocarbon and the addition of oxygen can stimulate EISB. This situation is not as common with chlorinated solvents. The need for an SVE system will be dictated by ambient air standards and region-specific air quality regulations, as well as the proximity of the system to nearby homes or businesses.

In all cases, monitoring costs constitute 50-60% of the total NPV cost for these remedies. This result reflects the need for long-term monitoring after source treatment is completed. Monitoring costs are somewhat higher for EISB than for the other technologies because of the larger number of analytes required, but this differential is minimal because the treatment times were fairly short and relatively comparable. This analysis suggests that more aggressive treatment (e.g., additional applications of either ISCO or EISB, or longer treatment via air sparging) could yield significant overall cost savings if it resulted in achieving maximum contaminant levels or at least in reducing the long-term monitoring requirements. However, the effectiveness of all three technologies depends on getting good amendment distribution and on the absence of low-permeability zones in the subsurface. The feasibility of achieving this outcome has yet to be demonstrated on a broad scale.

20.4.2 Case 2: Shallow Barrier

Detailed cost analyses for the three technologies considered in Case 2 are presented in Table 20.4. The NPV comparison is presented in Table 20.5. The NPV analysis indicates that MNA is the low-cost option in this case, with a NPV cost that is about 15% lower than the ZVI barrier, EISB and phytoremediation. Design costs for MNA include preimplementation monitoring and the development of a fate and transport groundwater model. However, the most significant cost driver for MNA is the monitoring costs. These costs are directly proportional to the number of wells to be monitored and the frequency of sampling.

While the ZVI barrier has the highest capital cost of any of the five remedies, its chief advantages are that it has low O&M costs once it is installed and its monitoring requirements are limited to VOCs. The significant capital costs associated with a ZVI barrier include equipment mobilization, trench installation, material cost and waste disposal, and royalty fees (15% of total capital). Material costs (primarily iron) constitute about 15% of the total. In this case, the shallow depth allows a continuous trenching method to be employed, which is cost effective relative to more conventional shoring methods (ITRC, 2000).

The EISB and phytoremediation remedies have NPV costs that are equivalent to the ZVI barrier. Whereas capital costs are relatively low for these remedies, O&M and monitoring costs are incrementally higher. In the case of the biobarrier, the higher O&M costs are due to the need

Table 20.4 Cost Comparison for Case 2

Cost Element	EISB	Air Sparging	Phyto	ZVI Barrier	MNA
Design					
Predesign sampling & utility survey	$15,000	$15,000	$20,000	$15,000	$32,000
Laboratory studies	$20,000	$0	$0	$0	$0
Groundwater modeling	$20,000	$20,000	$20,000	$20,000	$50,000
In-field hydraulic testing	$2,000	$15,000	$2,000	$0	$2,000
Detailed design	$10,000	$20,000	$20,000	$20,000	$10,000
Permitting & reports	$10,000	$15,000	$15,000	$12,000	$10,000
Total design	***$77,000***	***$85,000***	***$77,000***	***$67,000***	***$104,000***
Capital					
Site Preparation	$2,000	$2,000	$4,500	$10,000	$0
Mobilization/demobilization of equipment	$0	$0	$0	$50,000	$0
Injection/monitoring well installation & development	$23,500	$23,500	$6,000	$6,000	$12,000
Process equipment	$9,000	$16,500	$42,500	$0	$0
Utilities installation	$0	$0	$1,000	$0	$0
Trench installation	$0	$0	$0	$36,500	$0
Materials	$12,000	$500	$5,000	$28,500	$0
Labor	$13,000	$21,000	$8,500	$0	$0
Gas collection system (SVE)	$0	$35,000	$0	$0	$0
Aboveground treatment system & housing	$0	$20,000	$0	$0	$0
System start up costs	$0	$2,000	$0	$0	$0
Waste management & disposal	$1,000	$1,000	$2,000	$33,500	$0
Royalty/Licensing fees	$0	$0	$0	$25,500	$0
Reports	$5,000	$5,000	$5,000	$5,000	$5,000
Total capital	***$65,500***	***$126,500***	***$74,500***	***$195,000***	***$17,000***
Operation & Maintenance (Per Year or Event)					
Labor	$0	$15,000	$4,000	$0	$0
Utilities	$0	$4,000	$1,000	$0	$0
Amendment addition (per event)	$25,000	$0	$0	$0	$0
Replacement parts & materials	$0	$500	$500	$48,500	$0
Waste management & disposal	$0	$16,500	$0	$0	$0
Reports	$2,500	$5,000	$2,500	$5,000	$0
Average annual O&M *	***$9,000***	***$41,000***	***$5,000***	***$5,500***	***$0***
Monitoring Costs (Quarterly Sampling)					
Labor	$5,000	$12,000	$9,500	$5,000	$7,000
Analytical, groundwater	$7,000	$4,000	$4,000	$4,000	$14,500
Analytical, air	$0	$3,500	$0	$0	$0
Reports	$10,000	$14,000	$14,000	$10,000	$10,000
Total monitoring (per year)	***$22,000***	***$33,500***	***$27,500***	***$19,000***	***$31,500***

*Average annual O&M values appear solely for comparison purposes and were calculated by summing the O&M costs over the active life of the project and dividing by the number of years in the active phase. No discounting was applied to this calculation.

for amendment readditions every three years to provide a continuing supply of substrate for the dechlorinating bacteria. Subsequent amendment costs are evenly distributed between material costs (primarily EVO) and labor cost associated with the injection process. In the case of phytoremediation, the O&M costs include operation of an irrigation system for the first five years and general maintenance and upkeep of the grounds. Monitoring the health and activity of the trees also adds monitoring costs.

Table 20.5 Cost Comparison for Case 2

Cost Element	EISB	Air Sparging	Phyto	ZVI Barrier	MNA
Total design costs	$77,000	$85,000	$77,000	$67,000	$104,000
Total capital costs	$65,500	$126,500	$74,500	$195,000	$17,000
Total O&M (30 yr NPV)	$175,500	$797,000	$101,500	$92,000	$0
Total monitoring (30 yr NPV)	$267,000	$517,500	$333,500	$227,500	$384,500
Overall total (30 yr NPV)	***$585,000***	***$1,526,000***	***$586,500***	***$581,500***	***$505,500***

Air sparging has a NPV cost that is three times higher than all of the other options. The high cost of air sparging is due to the combination of higher capital and O&M costs associated with the SVE system. This effect is magnified in this case because the SVE system must operate for 30 years. Design costs for air sparging include design of the SVE system and aboveground components and the in-field testing required to verify air injection and distribution performance. Capital expenditures include purchase and installation of extraction wells and piping, as well as the aboveground carbon unit. The higher O&M costs for air sparging reflect the electricity use, the need to continually monitor the performance of the system, and the costs for routine maintenance. Monitoring costs are also higher than for the other remedies because air monitoring is required.

As previously stated, most of the difference in the NPV cost between air sparging and the other remedial options would diminish if the SVE and aboveground treatment system were removed. The need for an SVE system will be dictated by ambient air standards and region-specific air quality regulations, as well as by the proximity of the system to nearby homes or businesses.

In Case 2, monitoring costs constitute 33–75% of the total NPV cost for these remedies. Monitoring costs as a percent of total are highest for MNA and lowest for air sparging.

20.4.3 Case 3: Deep Barrier

Detailed cost analyses for the three technologies considered in Case 3 are presented in Table 20.6. The NPV comparison is presented in Table 20.7. The NPV value analysis indicates that MNA is the low cost option in this case. For Case 3, MNA is about 40% less expensive than the next closest remedy. The cost differential is much greater than existed between remedies for the shallow barrier because of the additional costs associated with implementing engineering solutions in deeper groundwater. Design costs for MNA include preimplementation monitoring and the development of a fate and transport groundwater model. Monitoring costs dominate for the remedy and are directly proportional to the number of wells requiring monitoring and to the frequency of sampling. In contrast to the shallow plume scenario, in this case, the biobarrier has a lower NPV cost than does the ZVI barrier. The higher cost of the ZVI barrier is primarily attributable to the capital costs associated with installing a ZVI barrier at depth. These costs are 4.5 times those required for the shallow barrier. The capital cost is driven by the need to install a deeper barrier combined with the need for a wider barrier to treat the higher contaminant flux. Significant capital costs for the ZVI barrier include mobilization, trench installation, material cost, and waste management, and a royalty fee (15% of total capital). In this case, material costs (primarily iron) account for 30% of the total capital cost. Although O&M requirements are similar for the two technologies and the monitoring requirement for the ZVI barrier is the lowest for any of the remedial options examined, this differential is not sufficient to overcome the higher capital cost.

Table 20.6 Cost Comparison for Case 3

Cost Element	EISB	Air Sparging	In-Well Stripping	ZVI Barrier	MNA
Design					
Predesign sampling & utility survey	$15,000	$15,000	$15,000	$15,000	$37,500
Laboratory studies	$20,000	$0	$0	$0	$0
Groundwater modeling	$20,000	$20,000	$20,000	$20,000	$50,000
In-field hydraulic testing	$2,000	$15,000	$25,500	$0	$2,000
Detailed design	$10,000	$20,000	$20,000	$20,000	$10,000
Permitting & reports	$10,000	$15,000	$15,000	$12,000	$10,000
Total design	***$77,000***	***$85,000***	***$95,500***	***$67,000***	***$109,500***
Capital					
Site Preparation	$2,000	$2,000	$2,000	$10,000	$0
Mobilization/demobilization of equipment	$0	$0	$2,000	$100,000	$0
Injection/monitoring well installation & development	$61,000	$61,000	$18,500	$11,000	$21,000
Process equipment	$9,000	$26,500	$40,000	$0	$0
Trench installation	$0	$0	$0	$194,000	$0
Materials	$35,000	$2,000	$2,000	$253,500	$0
Labor	$29,000	$21,500	$10,000	$0	$0
Gas collection system (SVE)	$0	$37,000	$0	$0	$0
Aboveground treatment system & housing	$0	$22,000	$16,000	$0	$0
System start up costs	$0	$2,000	$2,000	$0	$0
Waste management & disposal	$1,000	$1,000	$2,000	$187,500	$0
Royalty/Licensing fees	$0	$0	$0	$114,000	$0
Reports	$5,000	$5,000	$5,000	$5,000	$5,000
Total capital	***$142,000***	***$180,000***	***$99,500***	***$875,000***	***$26,000***
Operation & Maintenance (Per Year or Event)					
Labor	$0	$15,000	$12,000	$0	$0
Utilities	$0	$5,500	$2,500	$0	$0
Amendment addition (per event)	$64,000	$0	$0	$0	$0
Replacement parts & materials	$0	$1,000	$1,000	$219,000	$0
Waste management & disposal	$0	$17,000	$8,000	$0	$0
Reports	$2,500	$5,000	$5,000	$5,000	$0
Average annual O&M *	***$22,000***	***$43,500***	***$28,500***	***$22,500***	***$0***

(*continued*)

Table 20.6 (continued)

Cost Element	EISB	Air Sparging	In-Well Stripping	ZVI Barrier	MNA
Monitoring Costs (Quarterly Sampling)					
Labor	$5,000	$12,000	$12,000	$5,000	$7,000
Analytical, groundwater	$10,000	$5,500	$5,500	$5,500	$20,500
Analytical, air	$0	$3,500	$3,500	$0	$0
Reports	$10,000	$14,000	$14,000	$10,000	$10,000
Total monitoring (per year)	***$25,000***	***$35,000***	***$35,000***	***$20,500***	***$37,500***

*Average annual O&M values appear solely for comparison purposes and were calculated by summing the O&M costs over the active life of the project and dividing by the number of years in the active phase. No discounting was applied to this calculation.

Table 20.7 Cost Comparison for Case 3

Cost Element	EISB	Air Sparging	In-Well Stripping	ZVI Barrier	MNA
Total design costs	$77,000	$85,000	$95,500	$67,000	$109,500
Total capital costs	$142,000	$180,000	$99,500	$875,000	$26,000
Total O&M (30 yr NPV)	$421,500	$849,500	$562,000	$382,500	$0
Total monitoring (30 yr NPV)	$302,500	$536,500	$536,500	$246,500	$455,000
Overall total (30 yr NPV)	***$943,000***	***$1,651,000***	***$1,293,500***	***$1,571,000***	***$590,500***

Capital costs associated with the deep biobarrier are 2.2 times higher than those for the shallow biobarrier. Using aquifer matrix sorption to dictate the EVO loading results in significantly overdosing the barrier relative to stoichiometric donor demand, so that the amount of donor added is insensitive to contaminant flux in the groundwater. The residence time in the biobarrier is also sufficient in both cases. O&M costs for the biobarrier take the form of amendment addition every three years. Monitoring includes both VOCs and parameters used to assess the availability of donor in the barrier.

In-well air stripping is the third most expensive option in this analysis, having a NPV cost that is 40% higher than bioremediation. The higher cost for this technology is associated with its relatively high O&M and monitoring requirements. O&M costs are the result of electrical usage and the need to continually monitor the performance of the system, as well as the costs for routine maintenance. Monitoring costs are higher because of the air monitoring requirements.

In-well air stripping has a lower NPV than air sparging because both the capital and O&M costs are lower. The capital cost for in-well air stripping is lower because fewer wells are required and an SVE system is not needed. The capital cost differential is a strong function of the radii of influence achievable by the in-well air stripping wells. If the specified radii of influence cannot be achieved, the cost advantage will be lost. Although the aboveground treatment is the same for both systems, O&M requirements are higher for air sparging due to the need to maintain the SVE system. As previously stated, most of the difference in NPV cost between these remedies and the other treatment options would diminish if the SVE and aboveground treatment system were removed. The need for these systems will be dictated by ambient air standards and region-specific air quality regulations, as well as the proximity of the system to nearby homes or businesses. Monitoring costs are the same for both remedies.

In this case, monitoring costs constitute 15–80% of the total NPV cost for these remedies. Monitoring costs as a percent of total are highest for MNA and lowest for the ZVI barrier.

20.4.4 Comparison of *In Situ* Remedies with Pump-and-Treat

For many years, it was customary to use pump-and-treat as the basis for comparison for all other groundwater remedies. While pump-and-treat has gradually fallen out of favor with many regulators and practitioners, a cost estimate is included here for thoroughness and because it emphasizes the economic benefits of *in situ* remediation. This comparison will be done only for Cases 2 and 3 because pump-and-treat is not typically applied to a source area. For each case, the pump-and-treat remedy will utilize a single row of three 15-cm (6-in) diameter extraction wells spaced on 25 m (82 ft) centers along the site boundary. The actual well spacing will be determined by field hydraulic testing in combination with groundwater modeling. Groundwater will be extracted at up to 18.9 L/min (5 gpm) in Case 2 and 189 L/min (50 gpm) in Case 3. Upon extraction, the groundwater will pass through a low profile air stripper equipped with a 2,800 L/min (100 cfm) compressor to deliver air to the stripping tower (USACE, 2001). The vapors will be treated by an aboveground activated carbon system (USEPA, 2006; Prakash et al., 1994). The clean effluent will be discharged into storm sewers on the site (USEPA, 2007). The system will be housed in a trailer. Labor costs for this remedy include both system installation and start up and will require 10 days for a two person crew; setup of the carbon system will be by the vendor.

The O&M required for this system will involve weekly checks of system operation, as well as semiannual maintenance on extraction wells, pumps, and the aboveground treatment system. Effluent water sampling and air monitoring of the off gas produced by the carbon treatment system will occur monthly while the system is in operation; weekly sampling will be performed during the first month of operation. Quarterly groundwater monitoring will be performed for the first five years, followed by semiannual monitoring thereafter. The quarterly and semiannual groundwater sampling will include only VOCs.

Detailed cost analysis for pump-and-treat for Cases 2 and 3 are presented in Table 20.8. The NPV comparison is presented in Table 20.9. For Case 2, pump-and-treat has a comparable cost to air sparging but is significantly more expensive than any of the other remedial options evaluated. The additional expense is the result of higher O&M and monitoring costs associated with both air sparging and pump-and-treat. For Case 3, pump-and-treat is the most costly remedy, about 25% more expensive than air sparging and the ZVI barrier.

Table 20.8 Costs for Pump-and-Treat System–Case 2 and Case 3

Cost Element	Case 2	Case 3
Design		
Predesign sampling & utility survey	$15,000	$15,000
Laboratory studies	$0	$0
Groundwater modeling	$20,000	$20,000
In-field hydraulic testing	$10,000	$10,000
Detailed design	$20,000	$20,000
Permitting & reports	$20,000	$20,000
Total design	***$85,000***	***$85,000***

(*continued*)

Table 20.8 (continued)

Cost Element	Case 2	Case 3
Capital		
Site Preparation	$10,000	$10,000
Mobilization/demobilization of equipment	$0	$0
Extraction/monitoring well installation & development	$12,000	$22,000
Process equipment	$0	$0
Materials	$500	$2,000
Labor	$20,000	$20,500
Gas collection system (SVE)	$0	$0
Aboveground treatment system & housing	$57,000	$67,000
System start up costs	$3,500	$3,500
Waste management & disposal	$1,000	$1,000
Royalty/Licensing fees	$0	$0
Reports	$5,000	$5,000
Total capital	***$109,000***	***$131,000***
Operation & Maintenance (Per Year or Event)		
Labor	$18,500	$18,500
Utilities	$2,000	$3,500
Amendment addition (per event)	$0	$0
Replacement parts & materials	$5,000	$28,500
Waste management & disposal	$500	$500
Reports	$5,000	$5,000
Average annual O&M *	***$31,000***	***$56,000***
Monitoring Costs (Quarterly Sampling)		
Labor	$15,500	$15,500
Analytical, groundwater	$9,000	$10,500
Analytical, air	$3,500	$3,500
Reports	$14,000	$14,000
Total monitoring (per year)	***$42,000***	***$43,500***

*Average annual O&M values appear solely for comparison purposes and were calculated by summing the O&M costs over the active life of the project and dividing by the number of years in the active phase. No discounting was applied to this calculation.

Table 20.9 Cost Comparison for Pump-and-Treat for Cases 2 and 3

Cost Element	Case 2	Case 3
Total design costs	$85,000	$85,000
Total capital costs	$109,000	$131,000
Total O&M (30 yr NPV)	$599,000	$1,102,500
Total monitoring (30 yr NPV)	$682,000	$701,500
Overall total (30 yr NPV)	***$1,475,000***	***$2,020,000***

20.4.5 Effect of Discount Rate on Cost Calculations

All economic comparisons in this chapter have been made using a discount rate of 3% for annual costs. This real discount rate is appropriate for government entities, while a higher discount rate may be more appropriate for the private sector. Using a higher discount rate will diminish the importance of future costs relative to present costs.

For example, the calculations used to create the cost comparison for Case 3 were redone using a real discount rate of 7% and are shown in Table 20.10. The impact of the discount rate change is evident when Table 20.7 and Table 20.10 are compared. In this context, the higher discount rate diminishes the importance of O&M and monitoring costs relative to design and capital costs. There is a significant impact on the NPV cost for MNA, EISB, air sparging and in-well air stripping, but far less of an impact for the ZVI barrier, reflecting the fact that the primary costs for the ZVI remedy were capital costs. The relative ranking of the technologies is also affected. While MNA, EISB and in-well air stripping are still 1-3 in the ranking, air sparging now has a lower NPV cost than the ZVI barrier.

Table 20.10 Cost Comparison for Case 3 at 7% Discount Rate

Cost Element	EISB	Air Sparging	In-well Stripping	ZVI Barrier	MNA
Total design costs	$77,000	$85,000	$95,500	$67,000	$109,500
Total capital costs	$142,000	$180,000	$99,500	$875,000	$26,000
Total O&M (30 yr NPV)	$256,500	$538,000	$356,000	$201,000	$0
Total monitoring (30 yr NPV)	$206,500	$352,000	$352,000	$168,500	$310,500
Overall total (30 yr NPV)	***$682,000***	***$1,155,000***	***$903,000***	***$1,311,500***	***$446,000***

20.5 SUMMARY

This chapter presents a basic methodology for performing cost analyses for a number of remedial options typically applied to chlorinated solvent source areas and plumes. The methodology employs a NPV calculation to compare the total cost of various remedial options and to identify significant cost drivers within each option. In this analysis, a template site is used to demonstrate the approach for both source treatment and plume containment. In the cases presented here, remedial technologies that destroy contaminants *in situ* are generally more cost effective than technologies that transfer the contaminants to the surface for treatment, primarily because of the lower O&M costs associated with *in situ* treatment.

These *in situ* remedies include MNA, EISB, ISCO, phytoremediation and in some cases ZVI barriers. ZVI barriers are the exception here because the capital cost is very sensitive to the emplacement method, which is dictated by the barrier depth. Monitoring costs accumulate over the 30-year life of these projects and can make up a significant portion of the total cost in many instances. This is especially true for MNA; while MNA still represents the low cost alternative for deeper plumes, other remedial options may be comparable in cost for shallow plumes. Additionally, there can be economic benefit to treating sources if early site closure can be achieved. However, the feasibility of achieving this outcome has yet to be demonstrated on a broad scale. Finally, the discount rate employed in the NPV analysis impacts the importance of present versus future costs. Specifically, using a higher discount rate will diminish the importance of future O&M and monitoring costs relative to present capital costs.

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CHAPTER 21

FUTURE DIRECTIONS AND RESEARCH NEEDS FOR CHLORINATED SOLVENT PLUMES

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21.1 INTRODUCTION

Remediation of chlorinated solvent plumes has improved tremendously over the past 25 years. Several treatment and containment technologies have been developed and successfully deployed. These technologies have allowed management of plumes for far less cost than the earlier presumptive remedy of pump-and-treat. The ability to restore contaminated sites has increased as well, reducing health and environmental risks and often allowing for higher value uses of redeveloped lands.

Nonetheless several challenges remain, and continued research and development will be needed. Subsurface remediation is an inherently uncertain endeavor, a fact that is often overlooked, and this uncertainty is the source of many of the remaining challenges. There are clearly opportunities to improve remediation success, further reduce costs and better manage the uncertainties involved in site characterization and cleanup. However, it must be recognized that some of the obstacles limiting the ability to remediate contaminated plumes may not be solvable.

The remaining challenges continue to make plume remediation a costly and difficult process at many sites. Many large and complex contamination sites have been known for 20 to 40 years or more, and they probably will continue to be problems for decades to come. In addition, new problems have arisen, and more will certainly surface in the future. This chapter will address how better progress can be made on these challenges. It focuses on the developments needed in the next 5 to 10 years, both because it is difficult to look much further ahead and because many responsible parties, notably the Department of Defense (DoD), plan to make rapid progress on site remediation during the next decade and will need a focused research agenda.

The chapter begins with a discussion of the reasons why further research and development is needed. What are the major unknowns and what are the likely changes in society and the regulatory environment that will drive future research and development? After briefly discussing the remaining uncertainties and the present technological and societal trends, the remainder of the chapter provides greater detail on the major research needs. The emphasis of this chapter is on the potential practical impacts of the research on future technology development. These needs have been organized into broad topic areas, and several different research objectives may be incorporated into any one topic area. Furthermore, in many cases, these issues are interrelated, so some overlap is inevitable in the discussions. The authors of this chapter gratefully acknowledge the discussion, advice, counsel and recommendations of the remediation researchers and practitioners who met during the Strategic Environmental Research and Development Program (SERDP)/Environmental Security Technology Certification Program (ESTCP) Partners in Environmental Technology Technical Symposium and Workshop in

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Washington, D.C., in December 2008.[1] This chapter reflects the discussions the authors had with these experts.

21.2 WHY IS MORE RESEARCH AND DEVELOPMENT NEEDED?

Despite all of the progress that has been made, remediation of chlorinated solvent sites remains complex, contentious, expensive and time consuming. Chlorinated solvents are still the most prevalent groundwater contaminants, and there are still many large and challenging plumes requiring remediation. Clearly, there is room for improvement. In addition, applied research will be needed to respond to changes in society and in the regulatory environment. There are three broad reasons for needing continued research and development:

- Uncertainties remain, and these uncertainties cost time and money.
- There has been a renewed emphasis on plume characterization and remediation.
- Societal trends will require changes in remediation decisions and practices.

21.2.1 Remaining Uncertainties

Subsurface remediation involves an inherently high level of uncertainty, and this uncertainty has been particularly troublesome for chlorinated solvent sites. The subsurface is heterogeneous, and generally costly and difficult to access. Like other dense nonaqueous phase liquids (DNAPLs), chlorinated solvents can have residual source zones that are difficult to find and treat, and the DNAPL constituents can spread over large distances. It is hard to predict the distribution and fate of contaminants, and unpleasant surprises are common. As a result, the characterization phase of most projects can take an extremely long time and require several phases of investigation because the information from each phase frequently raises new questions. Ultimately, despite the time and money spent on characterization, there is still considerable uncertainty in most cases when remediation decisions need to be made.

These remediation decisions also can take a long time, often triggering legal actions and further studies. Again, these delays and added costs are largely a result of the uncertainty involved. Better knowledge of the current site conditions and greater certainty in predictions of remediation performance should make future decisions faster and easier.

In most cases, the greatest technical challenge with subsurface remediation is the effective delivery of reagents. This topic is the focus of another volume in this series (Kitanidis and McCarty, 2010), but it will be covered briefly in this chapter. Given favorable environmental conditions, reagents such as chemical oxidants or reductants, electron donors and microorganisms generally can be relied upon to destroy contaminants, if they come into contact with them. However, it is very challenging to adequately and cost effectively distribute reagents to ensure good contact. The subsurface is highly heterogeneous, and often most of the flow of reactants occurs in a small fraction of the total volume treated. Therefore, maximizing the delivery of

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[1] Personal Communication with Linda Abriola, Tufts University; Mike Annable, University of Florida; Bob Borden, North Carolina State University; Ron Falta, Clemson University; Bruce Henry, Parsons; Paul Johnson, Arizona State University; Rick Johnson, Oregon Health and Science University; Andrea Leeson, DoD SERDP/ESTCP; Dave Major, Geosyntec Consultants; Perry McCarty, Stanford University; Jim Mercer, GeoTrans, Inc.; Chuck Newell, GSI Environmental, Inc.; Jack Parker, University of Tennessee; Tom Sale, Colorado State University; Tom Simpkin, CH2M HILL; John Vogan, EnviroMetal Technologies, Inc. (2008).

soluble or gaseous reagents to poorly soluble contaminants that have migrated into lower flow areas is one of the primary concerns of remediation practitioners. Improvements that would allow better distribution of injected materials would significantly lower the costs and improve the performance of plume (and source) remediation technologies.

The performance of remediation systems is often unclear, difficult to predict and disappointing. Assessing performance is no trivial task given the scales and variability involved, and it is particularly difficult to diagnose and optimize performance quickly. Even with seemingly optimal treatment conditions, it has proven extremely difficult to remediate many sites to typical cleanup criteria given the current technological and resource limitations. Responsible parties may be left with continuing costs for managing contaminated sites long after active remediation efforts are completed. In fact, post-treatment monitoring is rapidly becoming the largest cost item for responsible parties, as many sites have transitioned to long term monitoring and natural attenuation.

As mentioned earlier, many of the most technically challenging sites still require active treatment. In particular, there are many large and/or deep plumes that will require remediation. There are also several chlorinated solvent plumes located in fractured rock environments, and these plumes are extremely difficult to remediate. The estimates of the remediation costs for these sites are daunting, so technical improvements could reduce the overall remediation costs significantly, as well as allow cleanup to move forward more quickly with greater confidence in the outcome.

21.2.2 Renewed Focus on Plumes

Remediation of chlorinated solvents has gone through a few shifts in emphasis over the years. Initially, the focus was on using pump-and-treat systems to contain plumes and ensure that potential exposures were controlled. As this volume demonstrates, research and practice have focused for several years on developing and deploying *in situ* technologies that are more cost effective than pump-and-treat remedies. The emphasis then shifted to source remediation, starting in the late 1990s, as site managers made progress containing the plumes and began to consider future steps towards site closure. Research responded to the shift in focus from improving plume containment to improving source treatment (e.g., SERDP, 2001; SERDP, 2006). Now, as the limitations of source depletion are increasingly recognized, a future shift back to plume remediation seems likely.

The focus is shifting back to plumes for several reasons. First, practitioners have recognized that the boundaries between “plume” and “source” are not clear at contaminated sites, especially for chlorinated solvents that have been present for 30 or more years. Over time, the DNAPL constituents migrate and may accumulate in less permeable zones within the plume. As dissolution and diffusion continue, these accumulations may come to represent a significant fraction of the total residual mass (Chapman and Parker, 2005). The back diffusion from these secondary sources can sustain plumes for long periods of time, even after the source zone is removed or contained (Sale et al., 2008).

Second, it has become obvious that total source removal will not be achieved at most chlorinated solvent sites, at least given current technologies (Stroo et al., 2003; NRC, 2005). Because it is difficult to locate, access and effectively treat all of the source material, some contamination often remains after active remediation is completed (Sale et al., 2008). Source treatment can be very expensive, but it can yield impressive reductions in concentrations within and downgradient of the source zone. Hence, the benefits of partial source depletion are often hotly debated (Kavanaugh et al., 2003). One of the most important questions in these debates is the effect of source depletion on plume longevity. It is therefore critically important to better understand and predict plume responses to treatment over time (SERDP, 2005). There are limited long term data on plumes downgradient of treated source zones, leaving little choice but to use computer models to predict these responses, and those models need further development and validation.

A third and related reason for the renewed interest in plumes is the increasing awareness that plume characteristics can largely determine the potential benefits of source treatment. In particular, the mass storage in the plume and the later release of those contaminants into more transmissive zones could be a key factor in deciding whether and how to remediate source zones. If the mass stored in the plumes can sustain the plume at similar concentrations and for similar durations, whether or not the source is partially depleted, then extensive source remediation may yield relatively little risk and cost reduction. Additionally, the natural attenuation capacity of the plume may be a critical factor. With minimal natural attenuation capacity, the lifecycle costs for site management may not be greatly affected by source removal. However, if the remaining flux of contaminants from untreated primary and secondary sources can be naturally attenuated over an acceptable distance, then source treatment may greatly reduce the plume longevity and the costs for site management. Improved abilities to assess these key plume characteristics should lead to improved source management decisions.

Of course, recognition that contaminant mass stored in plumes can result in continued risks and costs may be yet another reason to shift the research focus back to plumes. If source treatment will not achieve regulatory criteria downgradient in a reasonable timeframe, one response may be to require further plume remediation. Treatment of the entire plume, or even partial treatment of the secondary sources of contaminants that have diffused into less permeable zones, could be extremely expensive and difficult. Therefore, it may be necessary to develop and evaluate technologies that can treat large volumes of the subsurface cost effectively or at least treat the contaminants that are stored within the less transmissive areas of the plume.

21.2.3 Societal Trends

Society is also changing, and these changes will affect remediation practices and drive future research and development. Among the key drivers of change will be climate change, population growth and the increasing scarcity of clean water. Climate change will necessitate energy efficiency and reduced carbon emissions in treatment approaches. Population growth will increase the pressures on water and land resources, as well as the need for cleanups and site redevelopment. The need for clean water will lead to even greater pressures to remediate impacted aquifers in ways that do not impair water quality downgradient. All three of these issues are separate aspects of an overall need to develop a more sustainable society, a society that "meets the needs of the present without compromising the ability of future generations to meet their own needs" (Brundtland, 1987).

However, ensuring sustainability while maintaining economic growth and development is challenging. Businesses and governments have responded to this challenge by promoting sustainable development (Barbier, 1987; Schmandt and Ward, 2000). The principles of sustainable development will apply to all aspects of an organization's activities, particularly its environmental practices. There is an evolving effort to promote "sustainable remediation" (Gill and Mahutova, 2004; U.S. Sustainable Remediation Forum, 2009; AFCEE, 2009) or remediation approaches that meet the risk reduction objectives for a site while minimizing collateral environmental damages. The U.S. Environmental Protection Agency (2008a) has advanced a related concept, "green remediation," defined as "the practice of considering all environmental effects of remedy implementation and incorporating options to maximize the net environmental benefit of cleanup actions" (see Figure 21.1).

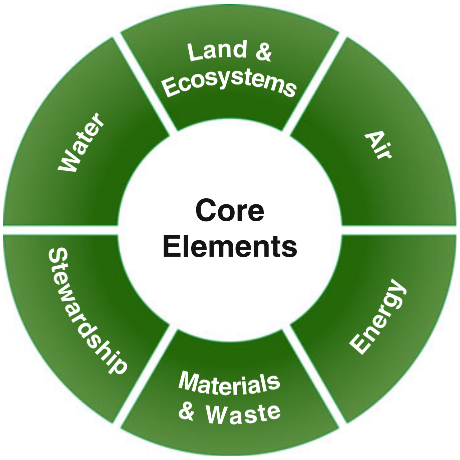

Figure 21.1. Core elements of green remediation. Green remediation seeks the optimal balance of these core elements. From USEPA, 2008a.

But how will sustainability be incorporated into remediation decisions and operations? It is often difficult to balance the benefits and the negative effects of remediation activities, especially when there is a wide range of environmental, economic and social factors to consider (Efroymson et al., 2003). Considering the net environmental benefits of remediation alternatives may result in unexpected outcomes. For example, the short term use of technologies that use large amounts of energy and water and/or cause relatively high greenhouse gas emissions may be preferable to more passive technologies that will require ongoing energy inputs over a long time and long term loss of the groundwater resource. While at present there is no clear method for measuring and evaluating net environmental benefits, many companies and government agencies have committed to sustainable practices throughout their operations, and efforts to develop and apply sustainability metrics to compare remediation systems have been started (Dixon et al., 2007).

There are other societal trends that will impact remediation practices and may drive future research and development. Notably, regulatory priorities will continue to change over time. Advances in toxicology and analytical chemistry may change risk based cleanup levels, or the emphasis on common cocontaminants may increase. For example, the concern over N-nitrosodimethylamine (NDMA) has increased in recent years, causing a reevaluation of the remediation approach for some chlorinated solvent plumes (Mitch et al., 2003). 1,4-dioxane is another common cocontaminant at chlorinated solvent sites that can affect management decisions (USEPA, 2008b).

One important example of regulatory changes affecting plume management has been the increased emphasis on vapor intrusion risks. Within the last decade, vapor migration and intrusion into buildings has been of increasing regulatory concern (e.g., USEPA, 2002; ITRC, 2007). Vapor intrusion often may represent the greatest potential risk at a site, particularly when groundwater is not used as a drinking water source. Assessing the risks of vapor intrusion can be technically challenging and very expensive, and the potential for vapor intrusion into nearby residences often raises the level of public concern at a site. Hence, there is a continuing need for better methods and protocols to measure vapor intrusion and evaluate the migration of vapors in the subsurface.

A final important societal trend to consider is the changing motivations of responsible parties. The concerns of responsible parties will change depending on economic and political circumstances, but there also will be natural progression over time as long term remediation efforts continue. While risk assessment and characterization technologies were emphasized initially, many sites have now made significant progress towards cleanup. In the DoD, for example, a large fraction of the total of over 31,000 sites have reached the stage of Remedy-In-Place (RIP), and military leaders are making rapid progress towards their stated goal of achieving final RIP status at virtually all DoD sites within the next 5 to 10 years (DoD, 2008). However, future economic conditions may change the willingness of some responsible parties to proceed with costly remedial actions.

The push to remediate sites will impact research needs. Research on source zone technologies may become less important as the identifiable sources are addressed using existing technologies. Research on relatively low cost technologies to "polish" the residual contamination likely will become more important. Polishing may involve treating remaining source materials, enhancing attenuation within the plume, or treating mass stored in lower permeability regions of the plume. Decision support systems to help managers select and implement appropriate technologies faster and easier will be of great value. In the long term, cost effective post-treatment monitoring may be the most important need as a wave of remediation efforts result in more passive site management at the vast majority of sites.

21.3 WHAT SPECIFIC RESEARCH AND DEVELOPMENT IS NEEDED?

The following sections discuss research and development needs for different stages of the remediation process. A few needs of a more global nature are identified first (applying systems analysis to remediation problems and quantifying uncertainty). The discussion then focuses on the research needed to improve predictive models and the fundamental understanding of the underlying fate-and-transport processes. The final portions of this section deal with the needs for improvements to existing treatment technologies, better tools to diagnose performance during treatment, and more cost effective monitoring during and after remediation.

21.3.1 Apply Systems Analysis and Engineering

The historic approach to contaminated groundwaters often has been piecemeal, dealing with various aspects of the problem as they are recognized. The design and operation of complex remediation projects should be analyzed from a systems perspective, in which the various components of the system are viewed holistically (Theis et al., 2003). In such a systems analysis (and its implementation through systems engineering), specific objectives and associated constraints are clearly articulated, and the available information and knowledge are organized to assist managers in operating the systems that are needed to accomplish those objectives (NRC, 1998).

Cost effective and reliable management of chlorinated solvent sites, particularly the large and complex sites, will require high level and integrated systems analysis. Systems engineering approaches are intended to integrate environmental remediation and waste management efforts across entire sites. Such site wide integration is necessary to handle soil and groundwater contamination underlying several operating areas, contaminants being retrieved from a particular area that will be disposed of elsewhere on the site, and the impacts that remediation of one area or facility may have on other areas. This type of approach requires accurate and cost effective measurements and robust models to understand the system.

21.3.2 Quantify and Minimize Uncertainty

Given the complexity of the contaminated subsurface and the difficulties in obtaining representative samples, uncertainty is inevitable. However, the uncertainty is rarely quantified or addressed in making decisions (Copty and Findikakis, 2000). Computer models and conceptual site models should explicitly estimate these uncertainties, as well as the costs that would be required to reduce the uncertainty to manageable levels (e.g., Wang and McTernan, 2002).

The uncertainty is largely due to the spatial variability and the limited amount of spatial information that is available. Consider that all of the water entering a series of 5-centimeter (cm) (2-inch [in]) wells at 1.5 meter (m) (5-foot) spacing across the entire width and depth of a plume represents only roughly 3% of the total water in the plume (5 cm out of 1.5 m [or 2 inches out of every 60 inches] if there is no convergence or divergence around the wells). Most sampling, though, is performed at a much lower spatial density, and even such a relatively high sampling density may not be sufficient. For example, Li et al. (2007) estimated that 6–7% of the groundwater may need to be sampled in order to accurately measure the impact of source zone treatments on the contaminant mass discharge. They concluded that "most field applications to date may not have been based upon a sample size sufficient to accurately quantify the uncertainty of mass discharge, and the estimated mass discharge may have large errors."

The temporal variability in concentrations, flow rates and flow directions adds even greater uncertainty. Groundwater elevations and directions often change seasonally or between years, so trends in concentrations or mass flux can be difficult to identify and quantify against a backdrop of such natural variability. On a smaller timescale, groundwater and contaminant fluxes can vary significantly over as little as a few days or weeks, so any sample represents only a snapshot in time and many samples may be needed to understand the natural variations.

Even though there are numerous sources of uncertainty in estimates of plume characteristics, the uncertainty is rarely quantified explicitly. The implications of the uncertainty in making estimates are often ignored, but ignoring the background uncertainty can make it difficult to develop measurable objectives for a remedial action or to decide on the need for any active remediation. If the uncertainty involved is appreciated, it should not be surprising that smaller sources often are missed during characterization efforts or that relatively large safety factors often must be used for *in situ* remedial designs (e.g., AFCEE, 2004).

Methods will be needed to directly quantify uncertainty and to incorporate uncertainty into models and management strategies. Improvements in measurements and data analysis to minimize the level of uncertainty also would improve conceptual site models and the level of confidence in predictions and decisions.

21.3.3 Improve Predictive Models

Models are critical to making decisions regarding site management, such as whether to allow monitored natural attenuation (MNA) or to implement costly hydraulic containment of a plume. However, the models are only as good as the underlying science. There are several key data gaps in the scientific understanding of dissolved chlorinated solvent sites. Source zone processes are not well understood, and the fundamental physical, chemical and biological processes are not fully understood. Further, the data limitations of hydrogeology make it essential to develop models designed to address the inherently high degree of uncertainty. As suggested in the preceding section, managing uncertainty in hydrogeological modeling is a critical research need.

In these cases and others, the limitations in fundamental knowledge make mechanistic modeling very difficult, and models tend to rely heavily on fitting parameters and coefficients.

Although these may calibrate well to prior data, they may still have unreliable predictive ability. Several very good models are available that have proven valuable for chlorinated solvent site management, but the scientific basis remains incomplete. Furthermore, the advances in computer hardware and software have made it possible to develop increasingly powerful numerical models that can simulate the complex interacting processes controlling contaminant fate and transport. Use of such models to optimize treatment and monitoring systems is expanding and has the potential to greatly reduce costs and uncertainty (e.g., Zhang et al., 2005).

Modeling needs for different objectives are described briefly below. Several of the research needs reflect the incomplete scientific underpinning of current predictive modeling for sites with contaminated groundwater.

21.3.3.1 Plume Responses

The response of a plume to upgradient treatment is a slow process with a great deal of spatial heterogeneity. New equilibrium conditions can take years to become established. Measuring the response is difficult against a backdrop of high uncertainty and limited data. Residual effects of treatment, such as enhanced abiotic or biological reduction of solvents, may persist for years and complicate assessments of the long term response. While modeling is essential to decision making, it may be difficult to confirm the predictions and site managers may not be sure how well remediation has performed.

In recent years, researchers have made significant progress in understanding the impact of source treatment on plumes (Basu et al., 2007) and in developing models that are complex and faster yet more user friendly (e.g., Widdowson et al., 2005; Falta, 2008). There has been a rapid increase in experience with source treatment technologies, and there are considerably more data available on the effects of source depletion on plumes than there was even 5–10 years ago (e.g., Sale et al., 2008). However, back diffusion from secondary sources and natural attenuation processes within the plume, notably abiotic and biological degradation, can have a large impact on the plume response, and there is still a lot of uncertainty associated with these processes.

Accurately predicting and monitoring plume responses to treatment is critical to site management since reducing downgradient risk is such a common objective for remedial actions. Given its importance, improving plume response models and strengthening the underlying scientific basis for these models were key recommendations of a recent workshop on research priorities for DNAPL sites (SERDP, 2006).

21.3.3.2 Plume Longevity

The longevity of chlorinated solvent plumes is a critical factor in the management strategy for most sites. The rationale and goals for active remediation often are based on model predictions of the plume's longevity under different scenarios. Plume longevity also largely controls the life cycle cost analyses and liability estimates for large chlorinated solvent sites because of the cumulative costs for long term monitoring. There is obviously very little long term information on plume responses to treatment, so managers must rely to a large extent on model predictions.

But the longevity of a given plume is difficult to predict. In many cases, chlorinated solvent plumes can last for centuries without active treatment (Sale et al., 2008), and it is likely that they still may last for decades, if not centuries, even after effective source depletion or containment (Newell and Adamson, 2005). Conversely, in aquifers with ongoing natural biodegradation, plumes may contract rapidly following source remediation, and the longevity and life cycle costs may be greatly reduced by treatment (e.g., Chapelle et al., 2004).

Greater accuracy of models will be important going forward, but that accuracy is limited by understanding of the factors controlling longevity. In particular, the storage and later release of mass from less permeable regions within the plume may be a critical factor in longevity assessments (Chapman and Parker, 2005). A better fundamental understanding will be important and should lead to predictive models that can be used with greater confidence.

21.3.3.3 Vapor Migration

Volatile chemicals in groundwater can migrate as vapors through the vadose zone and into buildings (Fitzpatrick and Fitzgerald, 2002). Vapor migration and attenuation within the vadose zone largely determine the potential risks (Figure 21.2). Understanding vapor migration also is important when designing and evaluating remediation through injection and/or extraction of vapors, and it can be a key issue in modeling the fate of volatile organic compounds (VOCs) or evaluating the attenuation of sources and plumes (Weidemeier et al., 1999).

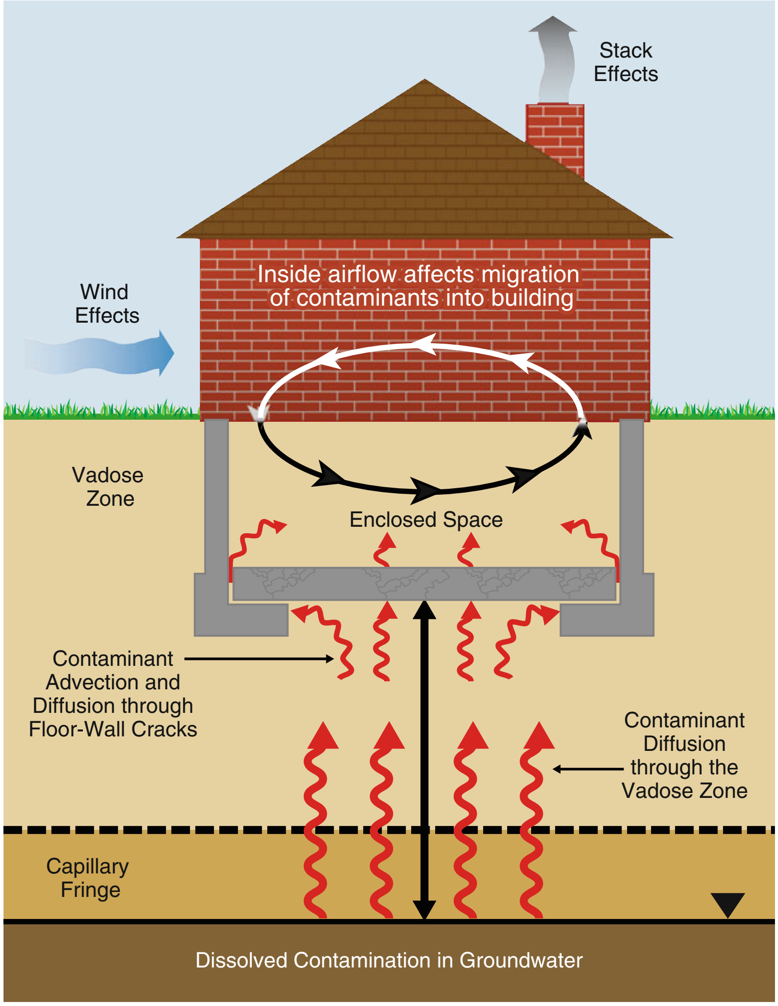

Figure 21.2. Conceptual model of vapor migration from contaminated groundwater to indoor air (from ITRC, 2007).

The ability to model and predict vapor migration is limited. Useful models are available (e.g., Jury et al., 1990; Johnson and Ettinger, 1991; Rathfelder et al., 2000; Abreu and Johnson, 2005), but the complexities of vapor transport and degradation are difficult to simulate. Further refinement of vapor migration models is needed. These models should estimate the uncertainty in the input parameters and provide a range of outputs to reflect the level of uncertainty. Such features would allow users to gain confidence in model predictions and to focus future sampling efforts to reduce model uncertainty.

21.3.3.4 Source Zone Processes

Although the focus of this monograph is on dissolved plumes, the uncertainties regarding source zone processes are important as well. As mentioned earlier, the responses of plumes to source depletion or isolation are not well understood, so the benefits of source treatment are difficult to predict. Similarly, modeling the behavior of sources over time has proven to be very difficult, and more deterministic models would be valuable. Although progress has been made, source behavior remains a source of considerable uncertainty (e.g., Falta et al., 2005; Christ et al., 2006).

As pointed out in Chapter 6, there is need for improved models that will allow for the use of site characterization data to develop useful quantitative descriptions of DNAPL source zone architecture and the resulting source function. More robust and accurate source function modeling would allow more certain predictions of treatment effects and better informed decisions regarding the selection, design and operation of remedial technologies.

21.3.4 Improve Fundamental Process Understanding

There is still much to be learned about the physical, chemical and biological processes that occur during remediation and how these processes respond after remediation (e.g., Costanza and Pennell, 2007). Despite two decades of research and the practical success achieved in remediating chlorinated solvents *in situ*, the fate of these contaminants and their byproducts in subsurface environments is not fully understood. Presumably, better fundamental understanding will continue to lead to more effective and efficient characterization, remediation and monitoring.

21.3.4.1 Biodegradation

Biodegradation is a key process affecting chlorinated solvents, and it has become the basis for a large fraction of the *in situ* plume treatments to date. However, chlorinated solvent biodegradation still is not fully understood, and improvements in remediation are likely as a result of research on the basic biology and ecology of the key organisms involved. A better understanding of the *cis*-1,2-dichloroethene (*cis*-DCE) and vinyl chloride (VC) biodegradation processes in particular could expand the range of environmental conditions in which MNA or active biological remediation could be employed.

Stalling at *cis*-DCE or VC during natural or enhanced biodegradation is a common concern, and the mass balances based on concentrations of the known metabolites are often unsatisfactory. Biodegradation of ethene and ethane probably occurs, but little is known about the process(es) involved. Further, there are other potential degradation pathways for *cis*-DCE and VC that are not well understood, particularly oxidation and abiotic reactions.

For anaerobic processes, the only strains known to completely biodegrade perchloroethene (PCE) and trichloroethene (TCE) are from one species, *Dehalococcoides ethenogenes*

(Maymó-Gatell et al., 2001). Still, surprisingly little is known about these unique and valuable organisms. A clearer and more mechanistic understanding of these important microorganisms should lead to better predictive models, and thus more confidence in remedial decisions such as MNA. Better understanding could also lead to improved bioaugmentation cultures and methods that could enhance *in situ* bioremediation. For example, *Dehalococcoides* spp. seem to be very sensitive to pH, and fermentation of organic compounds added to the subsurface often can acidify the groundwater and inhibit complete dechlorination. More acid tolerant bioaugmentation cultures could allow bioremediation without the need to add alkaline materials or pH buffering agents.

Cometabolic aerobic biodegradation of TCE has been known to occur for over 20 years, but this process has been used only rarely for *in situ* bioremediation. However, it may be valuable for MNA of some larger aerobic plumes (Sorenson et al., 2000). Even slow attenuation can be a significant factor when deciding how to remediate these large plumes, but slow attenuation processes can be difficult, time consuming and expensive to demonstrate and measure. Techniques such as probes specific for the enzymes responsible for TCE cometabolism (M. Lee et al., 2008) could allow faster, more accurate and less costly assessments of these attenuation processes, thereby improving the ability of the responsible parties to manage and monitor these large plumes.

21.3.4.2 Chemical Oxidation and Reduction

Although oxidation is rarely used for plume remediation, there are some important questions regarding the underlying process that certainly are applicable to source remediation and may have applications for plume treatment as well. Improving delivery of oxidants, or reductants, is a continuing issue. Several oxidants are available, and there has been rapid progress in their use, although there is still much to be learned (e.g., Teel and Watts, 2002; Liang and Lai, 2008; Siegrist et al., 2008). The most widely used oxidant to date for chlorinated solvents has been permanganate, which can be rapidly reduced by natural organic compounds. Permanganate also tends to form a “rind” of manganese oxides around residual contamination that can restrict further oxidation (West et al., 2007). Reducing the precipitation of these oxides could improve the total contaminant destruction achievable (Crimi and Ko, 2009). Methods to modify formulations to increase the efficacy and effective longevity of oxidants in the subsurface could improve the efficacy and cost effectiveness of the technology (e.g., Kakarla et al., 2002; Smith et al., 2008).

There is also some potential to modify the formulations or operating conditions so that chemical oxidants could be more cost competitive for plume remediation. For example, use of controlled release permanganate has been proposed for plume treatment (E. Lee et al., 2008). It also may be possible to effectively add slow release permanganate by injecting concentrated solutions that will sink and remain largely separate from the groundwater because of the density difference between hypersaline solutions and fresh water (Schwartz, 2008).

Chemical reduction of chlorinated solvents is used more commonly for plume remediation than chemical oxidation (Brown and Mueller, 2008). Chemical reduction happens naturally, particularly with iron minerals that can be common in the subsurface, and may be a significant natural attenuation process (Ferrey et al., 2004). It also may be enhanced by addition of zero-valent iron, for example, or by addition of hydrogen in the presence of a catalyst such as palladium (Davie et al., 2008).

The mechanisms of chemical reduction of chlorinated solvents, however, are not entirely clear. In natural systems, it seems that much of the abiotic degradation that occurs actually involves a complex interaction of biological and nonbiological processes. The term “*in situ* biogeochemical transformation" has been used to describe these interrelated effects (AFCEE et al., 2008). Several processes may be involved, but all are characterized by a complex interaction between the activities of microorganisms and geochemical processes that can result in the reduction of chlorinated solvents (Figure 21.3). The current understanding is that active mineral phases are formed under certain geochemical and microbiological conditions (e.g., iron- or sulfate-reducing conditions, within a certain pH range, etc.). However, the optimal geochemistry conducive to producing the most reactive mineral species is unknown. Further, the microbial community structure and activity that is most favorable for active mineral formation is not well understood. In addition, it is not known which parameters are the key indicators of active *in situ* biogeochemical transformation. Even the best procedures for collecting and handling samples derived from matrices other than groundwater are not well established or demonstrated.

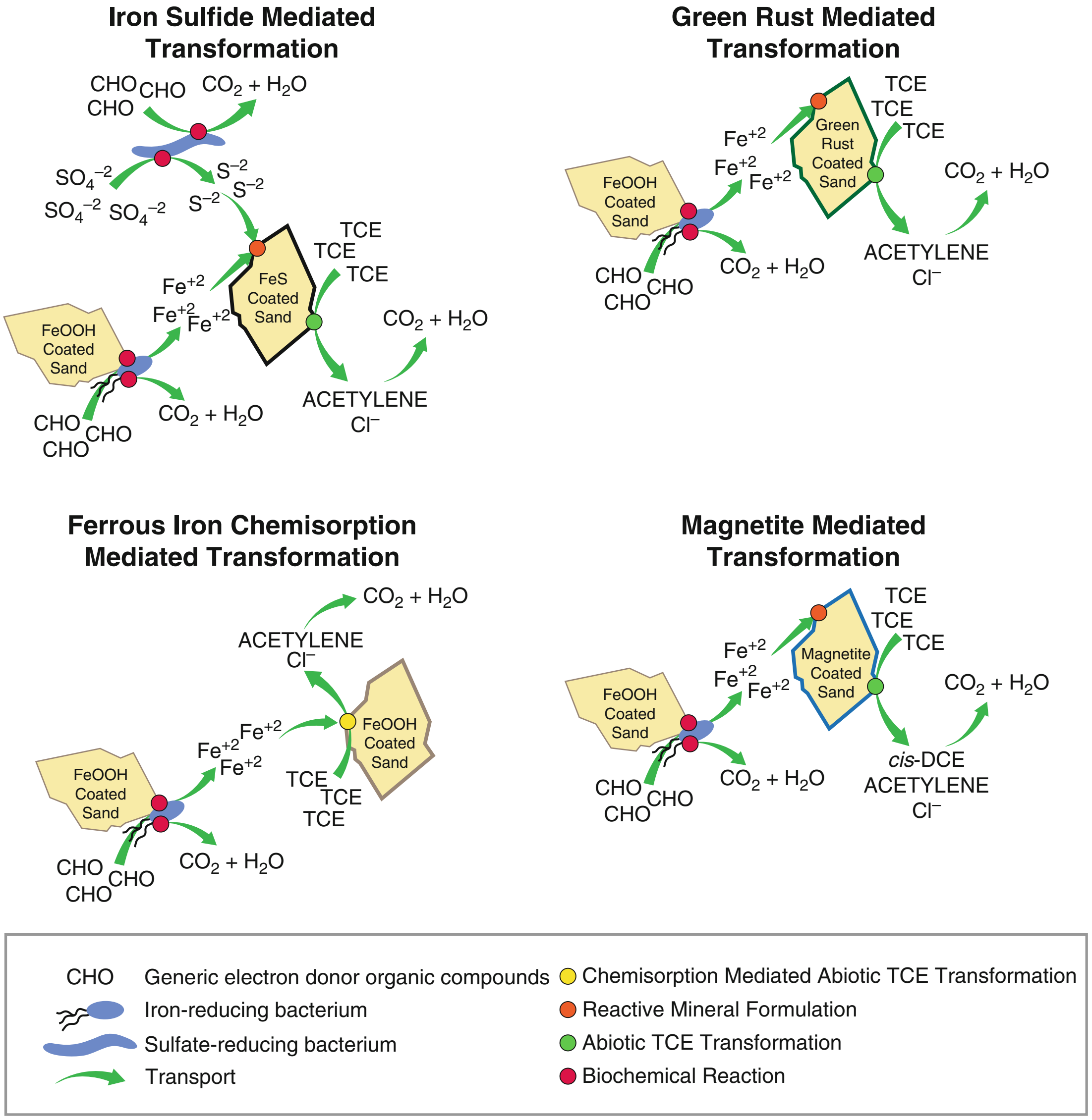

Figure 21.3. Complex interaction between the activities of microorganisms and geochemical processes (from AFCEE et al., 2008).

In addition, it would be helpful to determine the best amendments to promote biogeochemical reduction, and to perform carefully monitored demonstrations to provide guidance on the likely costs and performance of the technology under field conditions. Expanded geochemical models are needed because existing models are typically equilibrium based models that do not take biological processes into account, although geochemical models based on kinetics are being developed. However, because of the difficulty in measuring and monitoring active biogeochemical phases, practitioners need geochemical models to predict the formation and fate of all active phases. The models ideally would integrate aspects of equilibrium and kinetic geochemical models, microbiological processes, and both groundwater and solid phase chemistry.

21.3.5 Improve Remediation Technologies

Although plume remediation technologies have improved considerably, the need for further improvements remains. Chlorinated solvent sites can pose particularly difficult technical challenges because these compounds tend to sink through aquifers in a complex and largely unpredictable fashion, disperse over large volumes, become trapped in inaccessible areas and diffuse into low permeability zones.

The following discussion focuses not on individual technologies but on the remaining challenges that pose problems for most, if not all, of the technology options available. Certainly there will be improvements in each of the physical, chemical and biological technology alternatives. There also will be improvements as potential synergies between technologies are exploited, but this discussion will focus on the practical problems that will pose challenges for any remediation technology.

21.3.5.1 Treatment of Large Dilute Plumes

Although the contaminant plumes at most solvent contaminated sites are contained over relatively short distances (impacting less than 10 acres), there are many sites with plumes that extend long distances (in some cases, several miles downgradient from the source). Over most of the impacted area, the contaminant concentrations are generally relatively low (< 100 micrograms per liter). In addition, the plumes may be too deep for existing cost effective containment technologies (such as permeable reactive barriers).

These large, dilute plumes present difficult challenges and are very expensive to contain and remediate. A disproportionate share of the resources and attention often goes to relatively few sites because of the costs and technical difficulties involved in treating large volumes of water dispersed over large areas. Because the contaminant concentrations over a large area may be relatively low, active remediation may be cost inefficient (on a cost-per-unit-mass basis). Yet, because the concentrations exceed drinking water standards and are likely to continue exceeding standards for a long time, there is pressure to actively remediate these plumes.

Often, these plumes are present in permeable aquifers and generally have low organic carbon content, so there is little retardation. In addition, the aquifers are often aerobic, with relatively high influxes of electron acceptors, so it is difficult to establish and maintain reducing conditions. Another difficulty is that attenuation processes in aerobic plumes often are difficult to measure and are relatively slow (e.g., biodegradation half lives greater than 1 to 2 years).

Understanding the long term risks associated with these plumes is critical when assessing the benefits of active remediation. In addition, better understanding of the natural attenuation processes affecting these plumes would be valuable, because even slow attenuation processes can have a positive impact on large plumes. However, measuring these slow attenuation processes can be technically difficult and time consuming. It also will be important to develop more cost effective technologies for sites where remediation is necessary. Addition of inexpensive, long lived electron donors is one approach worth developing and testing, and methods to stimulate abiotic reduction of contaminants could be particularly valuable for such situations.

Currently, most plumes of this type are being hydraulically contained at high costs and require costly monitoring programs involving relatively large numbers of wells that are often monitored for decades. Reducing the costs to manage these large plumes could dramatically reduce the current and future liability of responsible parties with such sites.

21.3.5.2 Delivery of Reagents to Low Permeability Zones

Low permeability zones within chlorinated solvent plumes pose particularly difficult challenges. Continuing dispersal of solvents over time can result in a significant fraction of the remaining mass occurring in low permeability areas located within the original “plume.” As contaminants move downgradient and then diffuse into lower permeability materials, they essentially form secondary sources. The back diffusion from these secondary sources can continue to sustain plumes at levels well above typical health based criteria for long periods of time (Chapman and Parker, 2005). Advective transport of reagents to contaminants in such areas is limited, making effective treatment difficult (Dekker and Abriola, 2000; Saenton et al., 2001).

There have been efforts to improve delivery either via intermittent or long term recirculation through a target zone or via coinjection of chemicals, such as surfactants designed to improve distribution of reductants in the subsurface (Oostrom et al., 2007). One option is to use polymers that are compatible with chemical oxidants to increase the sweep efficiency during injections, thereby contacting more of the subsurface contamination (Figure 21.4). Use of partitioning electron donors or similar technologies may allow delivery of reagents more effectively to the separate DNAPL phase (Roberts, 2008). However, these approaches are often costly and may not be sufficiently effective, particularly if the contaminants are sequestered within a low permeability matrix.

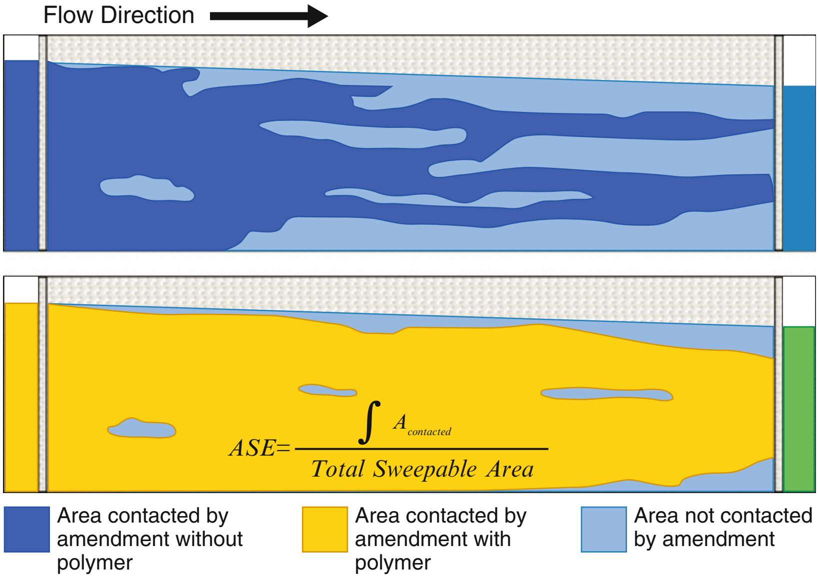

Figure 21.4. Illustration of the potential increase in sweep efficiency (ASE) as a result of amendment with chemical oxidant and a compatible surfactant (from Silva et al., 2007, courtesy John McCray, Colorado School of Mines, Golden, CO, USA).

Reynolds et al. (2008) proposed delivery directly to low permeability zones by using electrokinetics to target delivery of oxidants. Treatment of such zones may represent an attractive opportunity for such technology combinations or the deliberate use of two technologies simultaneously or in series to improve treatment. Numerous combinations have been proposed, and it seems likely that combining technologies into "treatment trains" will allow more effective and/or efficient remediation in the future (NAVFAC, 2007; Sale et al., 2008).

21.3.5.3 Treatment in Fractured Environments

Sites with fractured clay or rock matrices long have been considered one of the greatest technical challenges for remediation. The complex geology and the difficulties in measuring the movement of contaminants and fluids in fracture networks and rock matrices present difficult challenges. The diffusion of contaminants into rock matrices makes it difficult to deliver reagents to the contaminants or to control the long term back diffusion that may sustain plumes for long periods of time (Parker et al., 1994). In a review of the state of the practice, Steimle (2002) stressed the need to develop improved methods for characterizing and treating fractured rock sites but noted that there had been rapid progress in developing remediation strategies for these sites.

There has been continued improvement in characterization and remediation of contaminants in fractured systems in the last few years. Several characterization and remediation technologies are currently being used both at pilot- and full-scale levels to treat these sites, and some results have been promising (e.g., Werner and Helmke, 2003; Beyke and Fleming, 2005). Although natural attenuation may be difficult to demonstrate at a fractured rock site, it may be very important to the management of these sites and there have been some successful demonstrations (Lenczewski et al., 2002).

Remediation of fractured aquifers will continue to be difficult and costly, and cleanup to standard treatment goals may be technically impracticable in some instances. Furthermore, remediation timeframes may well be excessive due to reverse diffusion rates in fractured settings. Given the costs and technical challenges involved, improved treatment of fractured rock sites is urgent. For example, a preliminary review by the Army Environmental Center of cleanup efforts indicated that of 34 installations where aquifer restoration may be technically impractical, 26 are underlain by karst or fractured rock aquifers. The projected cleanup costs for these 34 installations represent approximately 50% of the Army's total projected environmental restoration costs (SERDP, 2006).

21.3.5.4 Green Remediation

As pointed out earlier, sustainable or green remediation will be an increasingly important driver in decisions. Protocols and metrics for evaluating the sustainability of differing remedial alternatives will need to be developed. In addition, it is likely that technologies will evolve to improve their performance relative to sustainability metrics. Finally, techniques to measure key sustainability parameters will be needed.

Clearly, the pressure to address sustainability will continue, and it will have a profound effect on future research and practice. Technological and operational changes to improve energy efficiency and/or reduce greenhouse gas emissions will be important for many reasons. A greater emphasis on remote monitoring and control seems likely to reduce the need for site visits. Changes designed to reduce excess methane or carbon dioxide generation may be important. Modifications to reduce secondary water quality impacts resulting from remediation also seem likely, as the need for clean, fresh water increases.

21.3.6 Improve Diagnostic Tools

Diagnosing performance is an underappreciated aspect of remediation projects. Knowing how well remediation is working in near real time allows managers to optimize the treatment operations and identify other contaminated areas. Good diagnosis also can lead to a more efficient transition to other technologies so that costly technologies are not turned off too soon or operated after objectives have been met. In the case of long term remedies, such as biowalls or zero-valent iron barriers, better diagnostic methods could help identify potential failures for less cost than the use of long term monitoring or could potentially extend their useful life before replacement or recharge.

However, useful diagnosis can require a lot of data. Often it requires rapid analysis of the data as well. In some cases, such as during *in situ* air sparging, the data needed for diagnosis may not be collected or used in conventional characterization or performance monitoring programs (Johnson et al., 2001). The following sections describe some of the tools that have the potential to improve remediation system diagnosis.

21.3.6.1 Mass Flux and Attenuation Capacity

Mass flux describes the local rate of contaminant migration in mass per unit time per unit cross sectional area of an aquifer (Figure 21.5). The mass flux can be difficult to quantify because it varies significantly within most dissolved plumes, given the typical spatial and temporal variability in both contaminant concentrations and groundwater flow (e.g., Guilbeault et al., 2005). Recent developments have made mass flux measurements more useful and cost effective (Schwarz et al., 1998; Hatfield et al., 2004). However, as mentioned earlier, it may require a dense array of monitoring points with frequent sampling to have reasonable certainty in the resulting flux estimates.

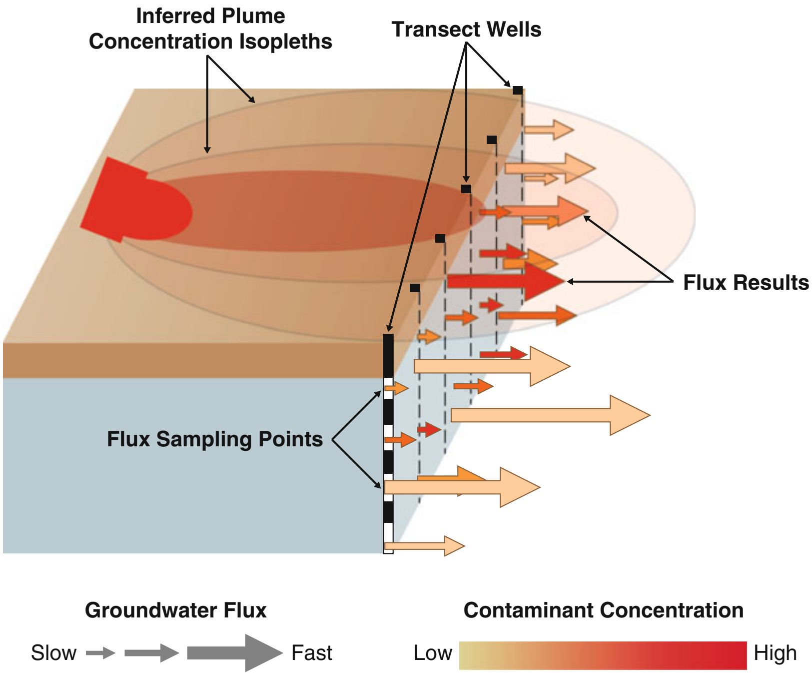

Figure 21.5. Measuring mass flux using wells along a transect. Results illustrate spatial variations in mass flux across a contaminant plume.

Often, mass flux (or more properly, mass discharge - the total mass flux across an entire plume, expressed as mass per unit time) can be a more useful metric than point concentrations or mass removal because it is more directly related to risk and site care requirements (ITRC, 2010). It can provide a technically sound basis for selecting, designing and monitoring the performance of remediation (Soga et al., 2004) and can also help managers decide when to transition between technologies (ITRC, 2008). Understanding the overall mass balance and the attenuation capacity of the aquifer, and its sustainability, allows credible performance and economic comparisons of approaches. It also provides a basis for estimating the impacts of treatment on the time required to complete site remediation, which is often a critical regulatory concern at chlorinated solvent sites.

Mass flux and attenuation capacity often are not quantified or explicitly considered partly because of the uncertainty regarding these estimates and partly because of the regulatory focus on point concentrations. Greater use of mass flux for decision making (and possibly for establishing cleanup goals) will require research to validate mass flux measurement techniques (particularly in difficult environments, such as bedrock), to understand the strengths and limitations of different methods that have been tried, and to develop and test better methods to measure attenuation capacity. Guidance is needed on the methods to estimate mass flux and on the use and interpretation of mass flux data.

21.3.6.2 Molecular Biological Tools

Molecular biological tools (MBTs) are techniques that target specific biomarkers (e.g., specific nucleic acid sequences, peptides, proteins or lipids) to provide information about organisms and processes relevant to assessment and/or remediation of contaminants (Koenigsberg et al., 2005; Stroo et al., 2006). In the context of bioremediation, MBTs also include any other modern technology that measures microbial activity *in situ*. Such tools include enzyme probes, deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) probes, microarrays and compound specific isotope analyses (CSIA). Figure 21.6 illustrates three promising techniques (DNA microarrays, fluorescence *in situ* hybridization [FISH] and quantitative polymerase chain reaction [PCR] analysis). CSIA also has proven to be a promising tool for discriminating between processes impacting chlorinated solvents and monitoring remediation progress (e.g., Sherwood-Lollar et al., 2001).

These technologies have the potential to improve the design, implementation, performance and monitoring of remediation technologies (Lovley, 2003). Knowing which genes are present and/or active or which proteins are being expressed could help determine if bioremediation is a feasible alternative, if bioaugmentation is needed, and possibly estimate the rates of natural or enhanced biodegradation (e.g., Cupples, 2008). However, there are several barriers to the widespread use of MBTs in site remediation, including:

- Difficulties in obtaining representative samples of the subsurface,
- Lack of knowledge regarding key biomarkers,
- Difficulties in developing rate information from the use of MBTs, and
- Insufficient confidence among practitioners and regulators in the results of MBT analyses (SERDP, 2005).

Practical guidance is needed on how to best sample for biomarkers, how to use the results and how to alter the design, implementation, operation and monitoring of enhanced bioremediation systems based on the results of these analyses.

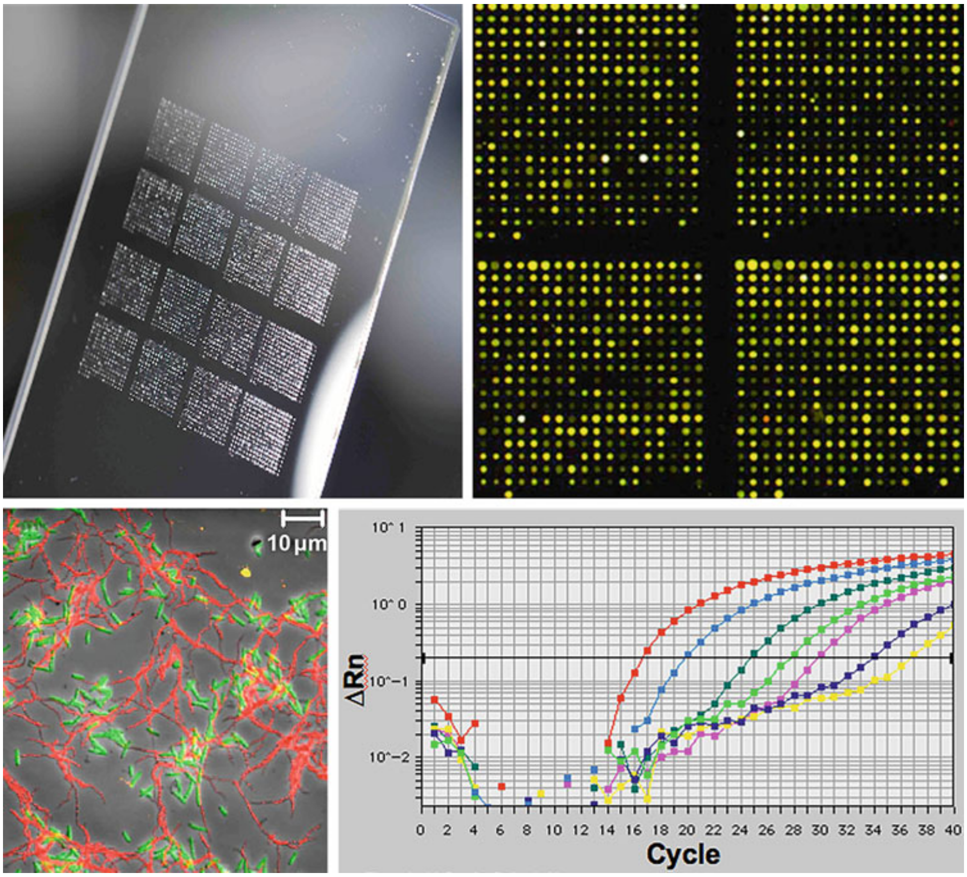

Figure 21.6. Molecular biological techniques. Microarray slides capable of detecting thousands of genes from a sample by the reactions to different probe sequences (upper panels), a photomicrograph from a flourescent *in situ* hybridization (FISH) analysis that is capable of visualizing cells that contain specific target genes (lower left) and polymerase chain reaction (PCR) results used to quantify target genes in an environmental sample based on the fluorescence resulting from hybridization of the gene to a specific DNA sequence after a given number of cycles of polymerization (lower right). Courtesy of Frank Löffler, Georgia Institute of Technology, Atlanta, GA, USA.

21.3.6.3 Geophysical Tools

Geophysical tools include several surface and borehole technologies that can be used to measure subsurface physical properties. Methods include measurements of magnetic, electric, thermal, seismic, radioactive and electromagnetic properties. Geophysics has been widely used to map geologic features, to find water or petroleum resources and to detect saltwater intrusion.

Geophysics also has been used for several years for contaminated site investigations, to characterize subsurface physical properties, to map groundwater flow paths or to find buried drums or separate phase contamination. The most common methods used for contaminated site investigations are ground penetrating radar, electrical resistance tomography, seismic reflection, cross well radar, borehole flowmeters and electromagnetic induction techniques. Geophysical methods are attractive because they are noninvasive and can provide continuous information between boreholes. There has been a rapid development of geophysical technologies for use in subsurface analysis (Meju, 2000).

Geophysical tools can be particularly useful for measuring changes in subsurface properties. For example, injection of fluids may cause changes in the electrical properties of the groundwater that can be measured with sensors placed in boreholes. Hence, geophysics may provide valuable diagnostic tools capable of measuring the progress of remediation or the movement of injected materials. Examples of the use of geophysical tools for monitoring the performance of remediation systems include measurements of the migration of bioremediation reagents (Lane et al., 2006), injected steam (Grégoire et al., 2007) and the progress of air sparging and *in situ* thermal treatment (LaBrecque et al., 1996). The most effective approach may be to use several methods in combination (see Figure 21.7).

More research is needed to adapt the technologies and data analysis methods of geophysics for use in remediation. It may be difficult to obtain the necessary resolution at reasonable cost, but having a three dimensional picture of the movement of injected materials from relatively few boreholes could greatly improve the performance of *in situ* remediation technologies.

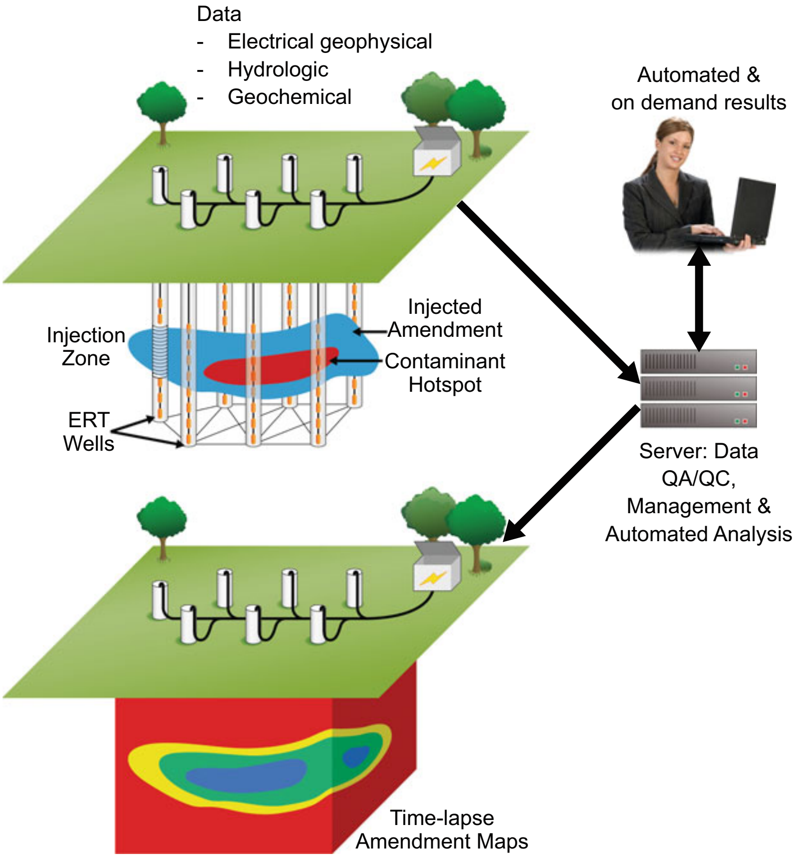

Figure 21.7. Use of geophysical tools to develop three-dimensional maps of amendment distribution over time. Electrical resistance tomography (ERT) wells are installed around injection points to monitor changes in resistivity and transmit data to remote locations. Courtesy Fred Day-Lewis, USGS.

21.3.7 Improve Monitoring

Monitoring is one of the most critical cost items for chlorinated solvent sites, largely because the costs can continue for so long. Further, there remains too much uncertainty regarding monitoring results and often the natural spatial and temporal variability is not acknowledged. Geoprobe and passive sampling systems have greatly reduced the costs for obtaining samples, but most sites still rely on permanent wells, relatively frequent sampling and expensive chemical analyses.

Reducing monitoring costs and increasing confidence in the results represent perhaps the greatest opportunities for reducing the life cycle costs of managing contaminated sites. Monitoring could be greatly improved if reliable, low cost, real time sensors were available for the major contaminants of concern. In many cases, current analytical methods were developed for site characterization and involve time consuming and costly sample preparation and laboratory analysis. Some efforts to develop such sensors are underway, and more are likely. However, the discussion in this section focuses on two particularly important near term needs for improved monitoring tools and methods.

21.3.7.1 Long Term Groundwater Monitoring

The number of sites adopting long term management strategies such as MNA for residual contamination continues to increase. As a result, the monitoring costs and the proportion of the total site management costs that are dedicated to monitoring continue to escalate. For example, the Air Force has estimated its annual groundwater monitoring costs could exceed $30 million (AFCEE, 2006), and the U.S. Department of Energy (USDOE) has estimated its monitoring costs at up to $100 million per year (USDOE, 2001). Since this contamination may persist for decades or even longer, long term monitoring represents a huge ongoing financial burden. Because much of the monitoring relies on labor intensive sampling of wells that were originally intended for site characterization and not long term monitoring, it is often inefficient and overly costly.

Responsible parties, such as the DoD, have started to optimize the monitoring plans for their sites, often relying on algorithms developed to identify the most efficient use of existing wells and to eliminate redundant sampling points or wells providing little useful information (e.g., Ling et al., 2004; Li and Hilton, 2005). The use of such optimization programs is expanding rapidly, and the long term monitoring costs could be reduced by 20-40% through the use of optimization techniques (AFCEE, 2006). However, the sampling and analytical methods generally remain labor intensive, time consuming and relatively costly. More efficient sampling and analysis methods could yield enormous savings over time.

One promising approach has been the development of passive samplers, which are capable of reducing the labor costs for sampling monitoring wells (Vrana et al., 2005). Passive sampling devices are being rapidly adopted, and new devices are being developed (e.g., De Jonge and Rothenberg, 2005). These devices can not only reduce sampling costs, but they also allow continuous sampling over relatively long sampling times (days to weeks), reducing the variability due to temporal variations. Although passive sampling devices are not suitable for all conditions, field validation testing has shown that they can provide results comparable to those obtained using conventional methods at many sites (e.g., Harte, 2002).

Despite these advances, the costs remain high, largely because of the labor involved in sampling and the large numbers of wells involved. Further, turnaround times for off-site chemical analyses limit the ability to adjust sampling plans or operations in the field. The evolution of *in situ* real time sensors and remote monitoring methods should allow significantly more cost effective long term monitoring techniques and rapid adjustments. For example, “Lab-on-a-Chip” sensors have been developed that are capable of monitoring chlorinated solvent and explosives concentrations for far less than conventional methods (e.g., Ramsey and Collins, 2005). Such sensors need further development and field demonstration, and practitioners need guidance for their use and limitations.

21.3.7.2 Vapor Migration and Intrusion

The issue of vapor migration—in particular, the potential for vapor intrusion into buildings—has been an important and poorly understood area for a long time. At present, the limitations of our understanding and tools often result in oversimplifying the problems. Most regulators and practitioners understand that risk assessments using existing models often understate or overstate the risks. However, a more site specific risk assessment often becomes very expensive and may be contentious (ITRC, 2007). Expensive indoor air sampling is usually needed, and other indoor (and outdoor) sources of solvents are common. Temporal variations in indoor air vapor concentrations can be extreme. Further, vapor migration through the subsurface can be highly heterogeneous, with most flow occurring through a small fraction of the volume, and subsurface vapor concentrations can fluctuate rapidly over a wide range.

Even though there has been a lot of concern about vapor intrusion in recent years, it is not yet clear that it is a widespread problem (Tillman and Weaver, 2005). It is difficult to evaluate whether vapor intrusion is occurring because of the temporal and spatial variability in soil gas and subslab measurements, the unknown other sources that commonly confound indoor air sampling, or the lack of information on the accuracy of models (ITRC, 2007).

Improved methods and procedures for sampling indoor air concentrations of solvents could reduce the uncertainties and the costs. Knowing the total mass in the indoor air over reasonable exposure periods is difficult when the concentrations can vary dramatically over time. In addition to knowing the total potential exposure, it is also important to determine the relative contributions of different sources. There are several possible indoor and outdoor sources of chlorinated solvents, and these can greatly complicate any assessment of vapor intrusion risks.

Measuring vapor migration in the subsurface is also difficult. The key parameters controlling migration rates, such as soil moisture and organic carbon content, vary greatly in space and time. The distribution of VOCs in both the saturated and unsaturated zones also can be very difficult to determine (Silka, 1998). The movement of moisture beneath buildings is particularly problematic.

Further research will be needed to respond to the increasing regulatory emphasis on vapor intrusion risks. Continued research and development should reduce the uncertainties regarding these risks. For example, if a national database of vapor intrusion sites were available, it could help quantify the extent of the problem. Improvements in indoor air sampling techniques and data interpretation could reduce the costs and concerns involved in assessing the vapor intrusion pathway, and research on the critical parameters affecting subsurface vapor transport would help guide future site assessments.

21.4 SUMMARY

Groundwater remediation remains too often contentious, complex and costly. The subsurface is highly heterogeneous and dynamic—the variations in both space and time virtually ensure a high level of uncertainty in all of the remediation phases, yet the uncertainty is rarely quantified or even acknowledged. Part of the uncertainty results from an incomplete understanding of the underlying chemical and biological processes. More effective and cost effective tools to characterize, diagnose and monitor sites with contaminated groundwater would be helpful.

Practitioners have no choice but to rely on model predictions in making decisions regarding plume management, but these models depend on a solid scientific understanding that is not always available. Furthermore, the available models often require a great deal of site specific data, which is rarely available. Better predictions of the impacts of remediation on plume extent and longevity could improve decision making and reduce the costs for compliance and performance monitoring.

It is interesting that the focus of remediation for chlorinated solvent sites has moved from plume to source and is now focusing again on the plume. In many cases, practitioners have found that they need to understand the plume better in order to make the best source management decisions. In addition, cost effective ways to clean up large plumes are needed, or at least to treat the mass stored in the less permeable regions of the plume. Increased concern over vapor intrusion has also refocused attention on the plumes. Future research will have to focus more on the plume characteristics and on the responses of plumes after treatment.

Finally, remediation will have to change in response to societal changes. In particular, the ever increasing emphasis on sustainability will affect remediation in many ways, and research will be needed to address the many issues related to sustainability. Other changes that will drive research include the increased focus by regulators and the public on the risks of vapor intrusion, the increasing financial burden associated with long term monitoring and the increased concern over common cocontaminants.

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LIST OF ACRONYMS AND ABBREVIATIONS

°C	degrees Celsius
°F	degrees Fahrenheit
°K	degrees Kelvin
µg/kg	microgram(s) per kilogram
µg/L	microgram(s) per liter
µm	micrometer
µM	micromolar
µmoles	micromoles
1,1-DCA	1,1-dichloroethane
1,1-DCE	1,1-dichloroethene
1,2-DCA	1,2-dichloroethane
2,4-DCP	2,4-dichlorophenol
1,1,1-TCA	1,1,1-trichloroethane
1,1,2-TCA	1,1,2-trichloroethane
1,1,1,2-TeCA	1,1,1,2-tetrachloroethane
1,1,2,2-TeCA	1,1,2,2-tetrachloroethane
A/m^2	amps per square meter
AATDF	Advanced Applied (Environmental) Technology Development Facility
ac	acre
ACL	Alternative Cleanup Level
ACS	American Chemical Society
ADE	advection dispersion equation
AFB	Air Force Base
AFCEE	Air Force Center for Environmental Excellence (renamed the Air Force Center for Engineering and the Environment)
AGU	American Geophysical Union
AMIBA	Aqueous and Mineralogical Intrinsic Bioremediation Assessment
API	American Petroleum Institute
AQDS	anthroquinone disulfonic acid
ART	Accelerated Remediation Technologies
ASTM	American Society for Testing and Materials
ASU	Arizona State University
atm	atmosphere
atm/M	atmosphere/mole fraction
ATSDR	Agency for Toxic Substances and Disease Registry
ATV	acoustic televiewer
AVO	amplitude versus offset
AVS	acid volatile sulfides
BCI	Bioremediation Consulting Inc.
BDL	below detection limit
BET	Brunauer-Emmett-Teller
bgs	below ground surface
BiRD	Biogeochemical Reductive Dechlorination
BTEX	benzene, toluene, ethylbenzene and xylene(s)
CA	chloroethane
CAA	Clean Air Act
CAH	chlorinated aliphatic hydrocarbon
CCAFS	Cape Canaveral Air Force Station
cDNA	complementary DNA
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CES	chromium extractable sulfide
CF	chloroform
CFB	Canadian Forces Base
CFC	chlorofluorocarbon
cfm	cubic feet per minute
CFR	Code of Federal Regulations
CHP	catalyzed hydrogen peroxide (H_2O_2) propagations
cis-DCE	*cis*-1,2-dichloroethene
cm	centimeter
CM	chloromethane (also termed methyl chloride)
cm/sec	centimeter(s) per second
CMT	continuous multi-channel tube
COC	Contaminant of Concern
COD	chemical oxygen demand
CPT	cone penetrometer testing
CRD	catalytic reductive dehalogenation
CSIA	compound-specific isotope analysis
CSM	Conceptual Site Model
CSMoS	Center for Subsurface Modeling Support
CT	carbon tetrachloride
CVOC	chlorinated volatile organic compound

-D	dimensional
DC	direct current
DCA	dichloroethane
DCAA	dichloroacetic acid
DCE	dichloroethene
DCM	dichloromethane
DCT	drainable core technique
DDC	density-driven convection
DDT	dichlorodiphenyltrichloroethane
DERP	Defense Environmental Restoration Program
DGGE	denaturing gradient gel electrophoresis
DHC	*Dehalococcoides*
DHE	Department of Health and Environment
DIRB	dissimilatory iron-reducing bacteria
DNA	deoxyribonucleic acid
DNAPL	dense nonaqueous phase liquid
DNT	dinitrotoluene
DO	dissolved oxygen
DOC	dissolved organic carbon
DoD	U.S. Department of Defense
DOS	Distance of Stabilization
DP	direct push
DT	dithionite
DVI	dual-valent iron
E_{LUMO}	lowest unoccupied molecular orbital energy
Ea	activation energy
EA	electron acceptor
EC	electrical conductivity
ECD	electron capture detector
ED	electron donor
EDB	ethylene dibromide
EDTA	ethylenediaminetetraacetic acid
EE/CA	Engineering Evaluation/Cost Analysis
Eh	redox potential
EISB	enhanced *in situ* bioremediation
EM	electromagnetic
EOS®	Edible Oil Substrate
ER	electrical resistivity
ER	extraction and reinjection
ERD	enhanced reductive dechlorination
ERH	electrical resistive heating
ERT	electrical resistance tomography

ESTCP	Environmental Security Technology Certification Program
ETH	ethene
ETI	EnviroMetal Technologies, Inc.
EVO	emulsified vegetable oil
EZVI	emulsified zero-valent iron
FDR	False Discovery Rate
FFD	fuel fluorescence detector
FID	flame ionization detector
FISH	flourescent *in situ* hybridization
f_{OC}	fraction of organic carbon
FRTR	Federal Remediation Technology Roundtable
ft	feet
FTA2	Fire Training Area 2
FTIR	fourier transform infrared
g	gram
GAC	granular activated carbon
gal	gallon
GAO	Government Accountability Office
GC	gas chromatography
GCW	groundwater circulation well
GHG	greenhouse gas
GIS	geographic information system
gpm	gallon(s) per minute
GPR	ground penetrating radar
GUI	graphical user interface
GWERD	Ground Water and Ecosystem Restoration Division
ha	hectare
HCA	hexachloroethane
HCFC	hydrochlorofluorocarbon
HDPE	high-density polyethylene
HFCS	high fructose corn syrup
HPLC	high performance liquid chromatography
hr	hour
HRC®	Hydrogen Release Compound
HRT	hydraulic retention time
HSRC	Hazardous Substance Research Center
IAS	*in situ* air sparging
ID	inner diameter
IDW	investigation-derived waste
in	inch
IP	ionization potential
ISCO	*in situ* chemical oxidation
ISCR	*in situ* chemical reduction

ITRC	Interstate Technology & Regulatory Council
IUPAC	International Union of Pure and Applied Chemistry
K_H	Henry's Law constant (H_i also used)
K_{oc}	soil organic carbon/water partition coefficient
K_{ow}	octanol-water partition coefficient
kg	kilogram
KGB	Koaxiale Grundwasserbeluftung
kJ/mole	kilojoules per mole
km	kilometer
kPa	kilopascal
L	liter
L/min	liter(s) per minute
lb	pound
LEL	lower explosive limit
LF3	Landfill Number 3
LHG	Lower Hawthorn Group
LIF	laser-induced fluorescence
LLNL	Lawrence Livermore National Laboratory
LNAPL	light nonaqueous phase liquid
LTM	long-term monitoring
LUST	leaking underground storage tank
m	meter
M	molar/molarity
MBT	molecular biological tool
MC	methylene chloride
MCL	maximum contaminant level
MDL	minimum detection limit
mg	milligram
mg/kg	milligram(s) per kilogram
mg/L	milligram(s) per liter
mi	mile
MIBK	methyl isobutyl ketone
min	minute
MIP	Membrane Interface Probe
mL	milliliter
mM	millimolar
mm	millimeter
mmol	millimole
MNA	monitored natural attenuation
mol	mole
MPCA	Minnesota Pollution Control Agency
mRNA	messenger ribonucleic acid
MS	mass spectrometry
MTBE	methyl tertiary butyl ether
mV	millivolt
NAPL	nonaqueous phase liquid
NAS	Natural Attenuation Software
NAS	Naval Air Station
NAS-JEB	Naval Air Station–Joint Reserve Base
NASA	U.S. National Aeronautics and Space Administration
NATO	North Atlantic Treaty Organization
NAVFAC	Naval Facilities Engineering Command
NDMA	nitrosodimethylamine
NFA	No Further Action
NFESC	Naval Facilities Engineering Service Center
NGWA	National Ground Water Association
nM	nanomolar
nmol	nanomole
NOD	natural oxidant demand
NOM	natural organic matter
NPL	National Priorities List
NPV	Net Present Value
NRC	National Research Council
NWIRP	Naval Weapons Industrial Reserve Plant
O&M	operations and maintenance
OC	organic carbon
OD	outer diameter
OHSU	Oregon Health & Science University
OM&M	operations, monitoring and maintenance
op-LFER	one parameter linear free energy relationship
OPS	operating properly and successfully
ORP	oxidation-reduction potential
OSHA	Occupational Safety and Health Administration
OSWER	Office of Solid Waste and Emergency Response
OTV	optical televiewer
OU	Operable Unit
OVA	organic vapor analyzer
PAH	polycyclic aromatic hydrocarbon
PCA	pentachloroethane

PCB	polychlorinated biphenyl
PCE	perchloroethene (also termed tetrachloroethene)
PCR	polymerase chain reaction
PDB	Pee Dee Belemnite (Vienna Standard)
PDB	polyethylene diffusion bag
PEL	permissible exposure limit
PETN	pentaerythritol tetranitrate
PFM	passive flux meter
PHS	U.S. Public Health Service
PI	principal investigator
PID	photoionization detector
PITT	Partitioning Interwell Tracer Test
PLFA	phospholipid fatty acid analysis
PNNL	Pacific Northwest National Laboratory
pp-LFER	polyparameter linear free energy relationship
ppb	part(s) per billion
PPE	personal protective equipment
ppm	part(s) per million
ppmv	part(s) per million by volume
PRB	permeable reactive barrier
PSA	pressure swing adsorption
psi	pounds per square inch
psig	pounds per square inch gauge
PTA	pilot test area
PVC	polyvinyl chloride
PVDF	polyvinylidene fluoride
QA/QC	quality assurance/quality control
qPCR	quantitative polymerase chain reaction
QSAR	quantitative structure activity relationship
RABITT	Reductive Anaerobic Biological *In Situ* Treatment Technology
RAO	Remedial Action Objective
RBCA	risk-based corrective action
RCF	root concentration factor
RCRA	Resource Conservation and Recovery Act
RDX	cyclotrimethlyenetrinitramine (also Royal Demolition eXplosive)
RETEC	Remediation Technologies, Inc.
RFT	refractive flow and treatment
RIP	Remedy-In-Place
RNA	ribonucleic acid
ROD	Record of Decision
ROI	radius of influence
ROS	reactive oxygen species
rRNA	recombinant RNA
RSK	Risk Based Standards for Kansas
RT	room temperature
RT-PCR	real-time polymerase chain reaction
RT3D	Reactive Transport in Three Dimensions
RTDF	Remediation Technologies Development Forum
RTF	remediation timeframe
SC	soil conductivity
SCAPS	Site Characterization and Analysis Penetrometer System
SEAR	surfactant-enhanced aquifer remediation
sec	second
SEM	scanning electron microscopy (micrograph)
SER	steam-enhanced remediation
SERDP	Strategic Environmental Research and Development Program
SITE	Superfund Innovative Technology Evaluation
SMOC	Standard Mean Ocean Chloride (Standard)
SOD	soil oxidant demand
SOM	soil organic matter
SP	spontaneous potential
SRB	sulfate-reducing bacteria
SRSNE	Solvents Recovery Service of New England
SRT	Sustainable Remediation Tool
SS	spill site
STOMP	Subsurface Transport over Multiple Phases
SuRF	Sustainable Remediation Forum
SVE	soil vapor extraction
SVOC	semivolatile organic compound
T-RFLP	terminal restriction fragment length polymorphism
TBA	tertiary butyl alcohol
TCA	trichloroethane
TCAA	trichloroacetic acid

TCAAP	Twin Cities Army Ammunition Plant
TCE	trichloroethene
TCEth	trichloroethanol
TCH	thermal conductive heating
TDEM	time domain electromagentic
TDP	thermal dissipation probe
TDS	total dissolved solids
TEAP	terminal electron accepting process
TeCA	tetrachloroethane
TER	Technology Evaluation Report
TI	Technical Impracticability
Ti-mmo	titanium-mixed metal oxide
TIO	Technology Innovation Office
TMDL	total maximum daily load
TNT	2,4,6-trinitrotoluene
TOC	total organic carbon
TOR	Time of Remediation
TOS	Time of Stabilization
TPH	total petroleum hydrocarbons
trans-DCE	*trans*-1,2-dichloroethene
TSCF	transpiration stream concentration factor
UEL	upper explosive limit
UF	Upper Floridian
UHG	Upper Hawthorn Group
UIC	underground injection control
USACOE	U.S. Army Corps of Engineers
USCG	U.S. Coast Guard
USDOE	U.S. Department of Energy
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UST	underground storage tank(s)
UV	ultraviolet
UVB	Unterdruck-Verdampfer-Brunnen
UXO	unexploded ordnance
V	volt(s)
VC	vinyl chloride
VFA	volatile fatty acid
VFC	vertical flux chamber
VOA	volatile organic analysis
VOC	volatile organic compound
VLF	very low frequency
W/m^2	watts per square meter
WERC	Waste Management Education & Research Consortium
yr	year
ZVI	zero-valent iron

UNIT CONVERSION TABLE

MULTIPLY	BY	TO OBTAIN
acres	0.405	hectares
acres	1.56 E-3	square miles (statute)
centimeters	0.394	inches
cubic feet	0.028	cubic meters
cubic feet	7.48	gallons (U.S. liquid)
cubic feet	28.3	liters
cubic meters	35.3	cubic feet
cubic yards	0.76	cubic meters
feet	0.305	meters
feet per year	9.66 E-7	centimeters per second
gallons (U.S. liquid)	3.79	liters
hectares	2.47	acres
inches	2.54	centimeters
kilograms	2.20	pounds (avoir)
kilograms	35.3	ounces (avoir)
kilometers	0.62	miles (statue)
liters	0.035	cubic feet
liters	0.26	gallons (U.S. liquid)
meters	3.28	feet
miles (statue)	1.61	kilometers
ounces (avoir)	0.028	kilograms
ounces (fluid)	29.6	milliliters
pounds (avoir)	0.45	kilograms
square feet	0.093	square meters
square miles	640	acres

LIST OF FIGURES

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GLOSSARY[1,2]

Abiotic Occurring without the direct involvement of organisms.

Absorption The uptake of water, other fluids, or dissolved chemicals by a cell or an organism (as tree roots absorb dissolved nutrients in soil).

Acclimation Time required for physiological adjustment by an organism to environmental change.

Acetogen A bacterium that generates acetate as a product of anaerobic respiration.

Activated carbon A highly adsorbent form of carbon used to remove odors and/or toxic substances from liquid or gaseous emissions.

Active treatment *In situ* bioremediation approach in which water-soluble amendments are added to the subsurface intermittently, frequently, or even continuously, by pumping liquid solutions into injection wells. Also includes other treatment technologies including but not limited to *in situ* chemical oxidation and reduction, air sparging and phytoremediation.

Adsorption A process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (the adsorbate).

Advection Transport of molecules dissolved in water along the groundwater flow path at an average expected velocity.

Aerobic Environmental conditions where oxygen is present.

Aerobic respiration Process whereby microorganisms use oxygen as an electron acceptor to generate energy.

Air sparging Technology in which air or oxygen is injected into an aquifer to volatilize or biodegrade contaminants.

Aliphatic compounds Any chemical compound belonging to the organic class in which the atoms are not linked together to form a ring.

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[1] This glossary is a compilation of definitions of terms synthesized by the volume editors and chapter authors. Select definitions are reprinted from *In Situ Bioremediation: When does it work?* (National Research Council, 1993) with permission from the National Academies Press, Copyright 1993, National Academy of Sciences.

[2] The editors of this volume gratefully acknowledge the exceptional assistance of Sarah Hunt, Cara M. Patton, and Deanne E. Rider in compiling this glossary.

Allotrope A structurally different form of an element.

Alluvial Relating to or involving sand deposited by flowing water.

Analytical model A mathematical model that has a closed form solution (the solution to the equations used to describe changes in a system can be expressed as a mathematical analytic function). Analytical solutions can be more exact and aesthetically pleasing than numerical models, but analytical solutions to equations describing complex systems can often become very difficult.

Anaerobic "Without air". Generally refers to occurring or living without oxygen present. Thus, in an anaerobic groundwater system, the chemistry is characterized by reductive conditions. Sometimes anaerobic is used (e.g., in wastewater treatment) to indicate a lack of any electron acceptors (including nitrate and sulfate). In groundwater, a dissolved oxygen concentration below 1.0 milligrams per liter (mg/L) is generally considered anaerobic.

Anaerobic respiration Process whereby microorganisms use an electron donor such as hydrogen and a chemical other than oxygen as an electron acceptor. Common substitutes for oxygen are nitrate, sulfate, iron, carbon dioxide, and other organic compounds (fermentation).

Anisotropy In hydrogeology, the conditions under which one or more hydraulic properties of an aquifer vary from a reference point.

Annular well space The space between the wall of the well and the native material. The annular well space is typically filled with sand or a sealant, depending on the location.

Anode An electrode through which an electric charge flows into a polarized electrical device.

Anoxic "Without oxygen". For example, anoxic groundwater is groundwater that contains no dissolved oxygen.

Aquifer An underground geological formation that stores groundwater. A confined aquifer lies beneath a confining unit of lower hydraulic conductivity. An unconfined aquifer does not have a confining unit and is defined by the water table.

Aquitard An underground geological formation of low permeability that does not readily transmit groundwater.

Assimilative capacity The capacity of a natural body of water to receive and degrade wastewaters or toxic materials, ideally without occurrence of a contaminated plume.

Attenuation Reduction of contaminant concentrations over space or time. Includes both destructive (e.g., biodegradation, hydrolysis) and non-destructive (e.g., volatilization, sorption) removal processes.

Attenuation Rate The rate of contaminant concentration reduction over time. Typical units are milligrams per liter per year (mg/L/yr).

Autotrophic Self-sustaining or self-nourishing. Organisms that have the ability to synthesize their own food from inorganic materials, e.g., carbon dioxide and ammonium.

Bacterium A single-celled organism of microscopic size (generally 0.3 to 2.0 micrometers [µm] in diameter). As opposed to fungi and higher plants and animals (*eukaryotes*), bacteria are *prokaryotes* (characterized by the absence of a distinct, membrane-bound nucleus or membrane-bound organelles and by DNA that is not organized into chromosomes).

Bedrock The solid or fractured rock underlying surface solids and other unconsolidated material or overburden.

Bentonite A colloidal clay, expansible when moist, formed by chemical alteration of volcanic ash.

Bioaugmentation Addition of microbes to the subsurface to improve the biodegradation of target contaminants. Microbes may be "seeded" from populations already present at a site or from specially cultivated strains of bacteria.

Bioavailability The degree or ability to be absorbed and ready to interact in an organism.

Biobarrier A remediation technology designed to intercept and biologically treat a contaminant plume as it passes through a permeable subsurface barrier. Biobarriers are created by installing wells or trenches across the width of a plume to deliver substrate to the microorganisms in the aquifer as groundwater flows through the barrier.

Biochemical Produced by or involving chemical reactions of living organisms.

Biodegradation Biologically mediated conversion of one compound to another.

Biofouling Impairment of the functioning of wells or other equipment as a result of the growth or activity of microorganisms.

Biomarker A biochemical within an organism that has a particular molecular feature that makes it useful for identifying a specific biological activity.

Biomass Total mass of microorganisms present in a given amount of water or soil.

Bioremediation Use of microorganisms to control and destroy contaminants.

Biotransformation Biologically catalyzed transformation of a chemical to some other product.

Biowall A form of passive *in situ* bioremediation, in which the contaminant plume is intercepted and treated as it passes through an emplaced porous barrier (e.g., trenches filled with sand-mulch mixtures). Microorganisms growing on the wall materials remove contaminants through biodegradation processes as groundwater passes through the barrier.

Capture zone The three-dimensional region that contributes the groundwater extracted by one or more wells or drains.

Catalyst A substance that promotes a chemical reaction but does not itself enter into the reaction.

Chlorinated solvent A hydrocarbon in which chlorine atoms substitute for one or more hydrogen atoms in the compound's structure. Chlorinated solvents commonly are used for grease removal in manufacturing, dry cleaning and other operations. Examples include trichloroethene, perchloroethene and trichloroethane.

Cometabolism The simultaneous metabolism of two compounds, in which the degradation of the second compound (the secondary substrate) depends on the presence of the first compound (the primary substrate). For example, in the process of degrading methane, some bacteria can degrade hazardous chlorinated solvents that they would otherwise be unable to attack.

Conceptual site model A hypothesis about how contaminant releases occurred at a site, the current state of the contaminant source, an idealized geochemical site type, and the current plume characteristics (plume stability).

Dechlorination A type of dehalogenation reaction involving replacement of one or more chlorine atoms with hydrogen.

Degradation The transformation of a compound through biological or abiotic reactions.

Dehalogenation Replacement of one or more halogens (e.g., chlorine, fluorine or bromine) with hydrogen atoms.

Dehalorespiration Energy-yielding respiratory metabolism that encompasses the reductive metabolism of halogenated compounds, such as chlorinated and brominated ethenes.

Dense nonaqueous phase liquid (DNAPL) A liquid that is denser than water and does not dissolve or mix easily in water (it is immiscible). In the presence of water, it forms a separate phase from the water. Many chlorinated solvents, such as trichloroethene, are DNAPLs.

Desorption Opposite of sorption; the release of chemicals from solid surfaces.

Diffusion Dispersive process resulting from the movement of molecules along a concentration gradient. Molecules move from areas of high concentration to areas of low concentration.

Dilution The combined processes of advection and dispersion resulting in a net dilution of the molecules in the groundwater.

Dispersion The spreading of molecules along and away from the expected groundwater flow path during advection as a result of mixing of groundwater in individual pores and channels.

Dispersivity An empirical factor that quantifies how much contaminants stray away from the path of the groundwater carrying them. Some of the contaminants will be "behind" or "ahead" the mean groundwater path, giving rise to a longitudinal dispersivity. Some will be "to the sides of" the pure advective groundwater flow, leading to a transverse dispersivity. There may also be vertical dispersivity, generally to a lesser degree than the others.

Dissimilatory A biochemical process in which an inorganic compound is used for an energy source but is not assimilated into the organism (as occurs in perchlorate reduction to chloride, the metabolites are all inorganic compounds).

Electron A negatively charged subatomic particle that may be transferred between chemical species in chemical reactions. Every chemical molecule contains electrons and protons (positively charged particles).

Electron acceptor Compound that receives electrons (and therefore is reduced) in the oxidation-reduction reactions that are essential for the growth of microorganisms and for bioremediation. Common electron acceptors in the subsurface are oxygen, nitrate, sulfate, iron and carbon dioxide. Chlorinated solvents (e.g., trichloroethene) can serve as electron acceptors under anaerobic conditions.

Electron donor Compound that donates electrons (and therefore is oxidized) in the oxidation-reduction reactions that are essential for the growth of microorganisms and bioremediation. Organic compounds (e.g., lactate) generally serve as an electron donor during anaerobic bioremediation. Less chlorinated solvents (e.g., vinyl chloride) can also serve as electron donors. Hydrogen generated in fermentation reactions also can serve as an electron donor.

Electron shuttle A chemical compound that stimulates the degradation of contaminants by facilitating the transfer of electrons to and from bacteria, or between contaminants and inorganic compounds. An electron shuttle compound, like a quinone, can be either reduced or oxidized, and thus can shuttle electrons between the ultimate electron donor (e.g., organic carbon) and the ultimate electron acceptor (e.g., ferric iron).

Emulsified edible oil A formulation in which an edible oil (such as soybean oil) is dispersed into water (e.g., through stirring or use of homogenizers) to form a mixture of oil droplets in water. Emulsifying the oil greatly improves the distribution of the oil in the subsurface.

Enzyme A protein created by living organisms to use in transforming a specific compound. The protein serves as a catalyst in the compound's biochemical transformation.

Ex situ Latin term referring to the removal of a substance from its natural or original position, e.g., treatment of contaminated groundwater aboveground.

Fenton's Reagent A solution consisting of hydrogen peroxide and an iron catalyst used to oxidize contaminants.

Fermentation Oxidation of organic compounds occurring in the absence of any external electron acceptor.

Fluvial Of, relating to, or happening in a river.

Geochemical Produced by or involving non-biochemical reactions of the subsurface.

Glaciofluvial Pertaining to streams fed by melting glaciers or to the deposits and landforms produced by such streams.

Growth substrate An organic compound upon which bacteria can grow, usually as a sole carbon and energy source.

Hydraulic conductivity A measure of the rate at which water moves through a unit area of the subsurface under a unit hydraulic gradient.

Hydraulic fracturing Method used to create fractures that extend from a borehole into rock and clay formations. Fractures are typically maintained by a proppant, a material such as grains of sand or other material that prevent the fractures from closing. Used to increase or restore the ability to transmit fluids.

Hydraulic gradient Change in head (water pressure) per unit distance in a given direction, typically in the principal flow direction.

Hydraulic head Elevation of a water body above a particular datum level. Specifically, the energy possessed by a unit weight of water at any particular point; measured by the level of water in a manometer at the laboratory scale or by water level in a well, borehole, or piezometer in the field. Water invariably flows from points of larger hydraulic head to points of lower head.

Hydraulic residence time The average time water spends within a specified region of space, such as a reactor or a treatment zone within the subsurface.

Hydrocarbons Chemical compounds that consist entirely of carbon and hydrogen.

Hydrogen bonding Attractive force between the hydrogen attached to an electronegative atom of one molecule and an electronegative atom of a different molecule. Usually the electronegative atom is oxygen, nitrogen or fluorine, which have partial negative charges, and the hydrogen then has a partial positive charge.

Hydrogenolysis Chemical reaction in which a carbon-carbon or carbon-heteroatom single bond is cleaved (or "lysed") by hydrogen. The heteroatom may vary, but it often is O, N or S. Usually conducted catalytically using hydrogen gas.

Hydrolysis The decomposition of organic compounds by interaction with water.

Hydrophilic Having a strong affinity for water. Hydrophilic compounds tend to be found in the aqueous phase.

Hydrophobic "Water-fearing". Hydrophobic compounds, such as oils and chlorinated solvents, have low solubilities in water and tend to form a separate nonaqueous phase.

Hypoxic A condition of "low" or "deficient" oxygen content.

Hysteresis A retardation of an effect when the forces acting upon a body are changed. For example, the relationship between moisture content and water potential generally differs depending on whether a soil is being wetted or dried. Similarly, sorption and desorption of a compound may occur at different rates.

Immiscibility The inability of two or more substances or liquids to readily dissolve into one another, such as oil and water.

Impermeable Not easily penetrated. The property of a material or soil that does not allow, or allows only with great difficulty, the movement or passage of water.

In situ Latin term meaning "in place"—in the natural or original position, e.g., treatment of groundwater in the subsurface.

In situ air stripping Treatment system that removes or "strips" volatile organic compounds from contaminated ground or surface water by forcing an airstream through the water, causing the compounds to evaporate.

In situ anaerobic bioremediation *In situ* (in place) bioremediation is an innovative remedial technology that eliminates the need for aboveground treatment by using biological processes to destroy or transform contaminants in groundwater or soil while they are underground. Anaerobic bioremediation requires an absence of oxygen.

In situ bioremediation The use of microorganisms to degrade contaminants in place with the goal of obtaining harmless chemicals as end products. Generally, *in situ* bioremediation is applied to the degradation of contaminants in saturated soils and groundwater, although bioremediation in the unsaturated zone can occur.

In situ chemical oxidation (ISCO) Technology that oxidizes contaminants in place by adding strong oxidants such as permanganate or peroxide, resulting in detoxification or immobilization of the contaminants.

In situ chemical reduction (ISCR) Technology that reduces contaminants in place by addition of chemical reductants such as zero-valent iron, resulting in detoxification or immobilization of the contaminants.

In situ thermal treatment Treatment system that generates high temperatures to remove and destroy contaminants in place. In practice, three types of technologies have been used—steam injection, electrical resistance heating (generating heat by applying an electrical current) and thermal conductive heating (using electrical subsurface heaters to radiate heat outwards through the solid matrix).

Influent Water, wastewater or other liquid flowing into a reservoir, basin or *in situ* target treatment zone.

Inoculum 1. Bacteria or fungi injected into compost to start biological action. 2. A medium containing organisms, usually bacteria or a virus, that is introduced into living organisms or environmental media.

Inorganic compound A chemical that is not based on covalent carbon bonds. Perchlorate is an inorganic compound, as are metals, nutrients such as nitrogen and phosphorus, minerals and carbon dioxide.

Insertion reactions An insertion reaction is a chemical reaction where one chemical entity interposes itself into an existing bond of typically a second chemical entity.

Interfacial tension The force at the interface between two immiscible liquids (such as a chlorinated solvent NAPL and water) that results from the attractive forces between the molecules in the different fluids. Generally, the interfacial tension of a given liquid surface is measured by finding the force across any line on the surface divided by the length of the line segment (so that interfacial tension is expressed as force per unit length, equivalent to energy per unit surface area).

Intrinsic bioremediation A type of *in situ* bioremediation that uses the innate capabilities of naturally occurring microbes to degrade contaminants without requiring engineering steps to enhance the process.

Intrinsic remediation *In situ* remediation that uses naturally occurring processes to degrade or remove contaminants without using engineering steps to enhance these processes.

Investigation-derived waste (IDW) Waste generated in the process of investigating or examining an actual or potentially contaminated site; includes solid and hazardous waste, media (including groundwater, surface water, soils and sediments) and debris.

Ionization The physical process of converting an atom or molecule into an ion by adding or removing charged particles, such as electrons or other ions.

Ionization potential Work required to remove (to infinity) the topmost electron in an atom or molecule when the gas atom or molecule is isolated in free space and is in its ground electronic state.

Isoconcentration More than one sample point exhibiting the same concentration.

Isotope Any of two or more species of an element in the periodic table with the same number of protons. Isotopes have nearly identical chemical properties but different atomic masses and physical properties. For example, the isotopes carbon 13 (^{13}C) and carbon 12 (^{12}C) both have 6 protons, but ^{13}C has one extra neutron and thus a greater mass.

Isotope fractionation Selective degradation of one isotopic form of a compound over another isotopic form. For example, microorganisms degrade the ^{12}C isotopes of perchloroethene more rapidly than the ^{13}C isotopes.

Karst Geologic formation of irregular limestone deposits with sinks, underground streams, and caverns.

Kinetics The rate at which a reaction occurs.

Lactate A salt or ester of lactic acid.

Leachate Solution formed when water percolates through a permeable medium. When passing through contaminated media, the leachate may contain contaminants in solution or in suspension.

Leaking Underground Storage Tank (LUST) Congress created the Leaking Underground Storage Tank (LUST) Trust Fund in 1986 by amending Subtitle I of the Resource Conservation and Recovery Act (RCRA). The LUST Trust Fund has two purposes. First, it provides money for overseeing and enforcing corrective action taken by a responsible party, who is the owner or operator of the leaking underground storage tank (UST). Second, the Trust Fund provides money for cleanups at LUST sites where the owner or operator is unknown, unwilling, or unable to respond, or which require emergency action.

Leaving group Atom (or group of atoms) that is displaced as a stable species, taking with it the bonding electrons. Typically, the leaving group is an anion (e.g., Cl^-) or a neutral molecule (e.g., H_2O). A "good" leaving group refers to one that is relatively easy to displace.

Life cycle cost The overall estimated cost for a particular remedial alternative over the time period corresponding to the life of the program including direct and indirect initial costs plus any periodic or continuing costs of operation and maintenance.

Light non-aqueous phase liquid (LNAPL) A non-aqueous phase liquid with a specific gravity less than 1.0. Because the specific gravity of water is 1.0, most LNAPLs float on top of the water table. Most common petroleum hydrocarbon fuels and lubricating oils are LNAPLs.

Lipid Amphiphilic molecule, possessing the ability to separate two different phases or layers (such as separating water and oil). Often refers to a cell's outer membrane. An amphiphile possesses both a polar-charged region, which attracts water molecules, and a non-charged and non-polar area, which attracts non-polar oils and fats.

Liquid chromatography A chemical separation technique in which the mobile phase (a liquid) passes over or through a stationary phase.

Log K_{ow} Logarithimic expression of the octanol-water partition coefficient (K_{ow}), a measure of the equilibrium concentration of a compound between octanol and water.

London-van der Waals forces Weak, transient electrical forces (attractive or repulsive) between two molecules that arise from the movement of their intermolecular electrons.

Long-term monitoring (LTM) Monitoring conducted after a remedial measure achieves its objectives, to ensure continued protection and performance.

Mackinawite An iron nickel sulfide mineral capable of abiotic degradation of chlorinated ethenes ([Fe, Ni]1+xS, where x=0 to 0.11). Occurs in serpentinized peridotites as a hydrothermal alteration product, and in the reducing environment of fine-grained river muds. May be produced by the action of magnetotactic and sulfate-reducing bacteria.

Macroscopic Large enough to be seen by the unaided eye.

Magnetite Common mineral of black iron oxide (Fe_2+Fe_3+$2O_4$), strongly attracted to magnetic fields. Important iron ore. Capable of reducing chlorinated solvents in groundwater.

Mass balance An accounting of the total inputs and outputs to a system. For dissolved plumes, it refers to a quantitative estimation of the mass loading to a dissolved plume and the mass attenuation capacity within the affected subsurface environment.

Mass discharge The rate of mass flow across an entire plume at a given location. Also referred to as "total mass flux" or "integrated mass flux." Expressed in units of mass per time (e.g., grams per day [g/day]), mass discharge essentially integrates several individual mass flux measurements (expressed as mass/area/time, e.g., grams per square meter per day [g/m^2/day]).

Mass flux The rate of mass flow across a unit area (typically measured in g/m^2/day). Typically calculated by measuring groundwater contaminant concentrations and groundwater velocity at individual sampling points across a transect. Often incorrectly used interchangeably with mass discharge or mass loading (expressed in g/day) to describe the mass emanating from a source zone or the mass passing a given transect across the plume.

Mass spectrometer Instrument used to identify the chemical structure of a compound. Usually, the chemicals in the compound are separated beforehand by chromatography.

Mass transfer The general term for the physical processes involving molecular and convective transport of atoms and molecules within physical systems. In this context, the term refers to the transport of solute mass from the nonaqueous phase (e.g., nonaqueous phase liquid [NAPL]) into the aqueous phase. The rate of mass transfer is controlled by the differences in concentrations between the phases, as well as the interfacial tension at the NAPL:water interface.

Matrix diffusion Diffusion of compounds in groundwater into, and back out from, the surrounding solid materials in the subsurface. Important in matrices such as low-permeability clays and rock matrices in which diffusion is the rate-controlling process for contaminant movement. Can result in initial attenuation of plumes and eventual long-term releases of contaminants back into the groundwater.

Matrix storage Storage of compounds in the surrounding solid materials in the subsurface. Significant fractions of the total contaminant mass may be stored in the low-permeability or inaccessible areas, greatly complicating subsurface remediation.

Maximum contaminant level (MCL) Standards set by the U.S. Environmental Protection Agency (USEPA) for drinking water quality that provides for a legal threshold limit on the amount of a hazardous substance that is allowed in drinking water under the Safe Drinking Water Act. The limit is usually expressed as a concentration in milligrams or micrograms per liter of water.

Media Specific environments (air, water, soil) that are the subject of regulatory concern and activities.

Membrane Interface Probes (MIPs) Probe with a permeable membrane on its side that is heated at desired intervals to volatize nearby organic compounds. The volatile organic compounds (VOCs) permeate the membrane and are delivered to the surface for analysis using one or more detectors, such as a photo ionization detector (PID), flame ionization detector (FID) or an electron capture detector (ECD). Useful as a semi-quantitative tool to locate VOC contamination.

Messenger RNA (mRNA) A molecule of RNA that serves as a template for protein synthesis. mRNA is transcribed from a gene and then translated by ribosomes in order to manufacture a protein. The sequence of a strand of mRNA is based on the sequence of a complementary strand of DNA.

Metabolic intermediate A chemical produced by one step in a multistep biotransformation (e.g., vinyl chloride produced during stepwise reduction of perchloroethene to ethene).

Metabolism The chemical reactions in living cells that convert food sources to energy and new cell mass.

Metabolite The intermediates and products of metabolism.

Metal chelators Chemicals that form multiple bonds with a single metal ion to produce soluble, complexed metal-chelant molecules. Used to enhance solubility and uptake of metals or to inhibit production of precipitates or scale.

Methane monooxygenase Enzyme capable of oxidizing the C-H bond in methane, as well as other alkanes. Found in both soluble (sMMO) and particulate forms (pMMO) in methanotrophs (bacteria capable of growth on methane). Also capable of TCE degradation.

Methanogen (methanogenic bacteria) A microorganism that exists in anaerobic environments and produces methane as the end product of its metabolism. Methanogens use carbon dioxide, or simple carbon compounds such as methanol, as an electron acceptor.

Methanogenesis Process of producing methane gas during biological metabolism.

Methanotroph (methanotrophic bacteria) A microorganism able to metabolize methane as its only source of carbon and energy. Methanotrophs can grow aerobically or anaerobically and require single-carbon compounds.

Micelle An aggregate of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic "head" regions in contact with surrounding solvent, sequestering the hydrophobic single-tail regions in the micelle center.

Microcosm A laboratory vessel established to resemble the conditions of a natural environment.

Microemulsion Clear, stable, isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a cosurfactant. The aqueous phase may contain salt(s) or other ingredients; the "oil" may actually be a complex mixture of different hydrocarbons and olefins. Microemulsions form upon simple mixing of the components and do not require the high shear conditions generally used in the formation of ordinary emulsions. The two basic types of microemulsions are direct (oil dispersed in water) and reversed (water dispersed in oil).

Microorganism (microbe) An organism of microscopic or submicroscopic size. Bacteria are microorganisms.

Mineral A naturally occurring solid formed through geological processes that has a characteristic chemical composition, a highly ordered atomic structure, and specific physical properties. A rock, by comparison, is an aggregate of minerals and/or mineraloids, and need not have a specific chemical composition.

Mineralization The complete degradation of an organic chemical or organism to carbon dioxide, water, and possibly other inorganic compounds or elements.

Miscible Two or more liquids that can be mixed and will remain mixed under normal conditions.

Mitigation Measures taken to reduce adverse impacts on the environment.

Modified Fenton's reagent Hydrogen peroxide modified by addition of ferrous (II) or ferric (III) iron to dramatically increase its oxidative strength. This increase is attributed to the production of hydroxyl radicals (OH●), and initiation of a chain reaction, involving formation of new radicals. The reaction of iron catalyzed peroxide oxidation at pH 3-5 is called a "Fenton's Chemistry" after its discoverer H.J.H. Fenton.

Moiety One of the portions or subdivisions into which something is divided.

Mole fraction The number of moles of a component of a solution divided by the total number of moles of all components.

Molecular biological tool (MBT) Laboratory tests that can measure the presence and activity of microbes at a site. They can be used to assess the potential for and performance of monitored natural attenuation and bioremediation strategies for remediation of environmental contaminants.

Molecular diffusion Also known as "simple diffusion," it is the inactive, spontaneous transport of a substance from a region of high concentration to a region of low concentration by means of random molecular motion.

Monitored natural attenuation (MNA) Refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a timeframe that is reasonable compared to that offered by other more active methods.

Monod kinetics Equation based on the Michaelis-Menten equation for enzyme kinetics that relates a bacterial culture's specific growth rate (μ) to the substrate concentration (s). Requires empirically derived parameters for the maximum growth rate (μ_{max}) with excess substrate available, and the half-maximal saturation constant (Ks)—the substrate concentration at which the growth rate is half of μ_{max}. The fundamental equation is $\mu = \mu_{max}$ (s/[Ks+s]).

Monte Carlo simulation A problem-solving technique used to approximate the probability of certain outcomes by running multiple trial runs, called simulations, using random variables. Monte Carlo methods allow evaluation of complex situations involving random behavior, such as games of chance, and can reduce uncertainty in estimating future outcomes in areas such as risk assessment or actuarial analyses.

Montreal Protocol Treaty signed in 1987 that governs stratospheric ozone protection and research and the production and use of ozone-depleting substances. It provides for the end of production of ozone-depleting substances such as chlorofluorocarbons (CFCs), continued assessment of the ozone layer, and assistance to developing nations to promote the transition to ozone-safe technologies.

Mudstones A fine grained sedimentary rock whose original constituents were clays or muds—hardened mud; a mix of silt and clay-sized particles.

Nanoscale Generally deals with structures of the size 100 nanometers or smaller. For example, reactive iron produced in this size range is referred to as nanoscale iron.

Natural attenuation Reduction in the mass, toxicity, mobility, volume or concentration of contaminants in soil and/or groundwater caused by natural processes that act without human intervention. These *in situ* processes include biodegradation, dispersion, dilution, sorption, volatilization, radioactive decay, and chemical or biological stabilization, transformation, or destruction of contaminants.

Natural organic matter (NOM) A form of naturally occurring organic matter (originating from organisms) that has been broken down to some base-level compounds (such as cellulose, chitin, protein, lipids, etc.). NOM provides nutrients to insects, bacteria, fungi, fish and other organisms at the base of the food chain.

Nonaqueous phase liquid (NAPL) An organic liquid that is maintained as a separate phase from water.

Non-wetting DNAPL Wettability is a measure of a liquid's relative affinity for a solid. Where two liquid phases are present, the "wetting" fluid will preferentially spread over the solid surface at the expense of the "non-wetting" fluid. Wettability is depicted by the concept of a Contact Angle. Since wettability conventionally refers to the non-aqueous phase, the angle is measured through the aqueous phase. A majority of DNAPL contaminants are non-wetting (water occupies the smaller pore spaces and preferentially spreads across solid surfaces while the DNAPLs are restricted to the larger openings).

Numerical model A mathematical model that uses a numerical time-stepping procedure to estimate behavior of a system over time (as opposed to an analytical model). The mathematical solution is represented by a generated table and/or graph. Numerical models require greater computing power, but they can allow more realistic simulations of complex systems.

Octanol-water partition coefficient (K_{ow}) Ratio of the concentrations of a chemical in octanol and in water, at equilibrium and at a specified temperature. Octanol is an organic solvent used as a surrogate for natural organic matter. This parameter is used in many environmental studies to help determine the fate of chemicals in the environment. Inversely related to aqueous solubility (a high K_{ow} indicates a compound will preferentially partition into an organic phase rather than into water).

Oligotrophic 1. Any environment, ecosystem, or area that is low in nutrients and/or primary production. 2. Organisms adapted to low-carbon environments.

Organic 1. Referring to or derived from living organisms. 2. In chemistry, any compound containing carbon.

Oxic Containing oxygen or oxygenated. Often used to describe an environment, a condition or a habitat in which oxygen is present.

Oxidant A chemical that oxidizes (or removes electrons) from another. A collective term for some of the primary constituents of photochemical smog.

Oxidation Transfer (loss) of electrons from a compound, such as an organic contaminant. Results in an increase in the valence of elements, such as conversion of ferrous (Fe(II)) to ferric (Fe(III)) iron. The oxidation can supply energy that microorganisms can use for growth and reproduction. Often (but not always), oxidation results in the addition of an oxygen atom and/or the loss of a hydrogen atom.

Oxidation-reduction potential (ORP) The tendency of a solution to either gain or lose electrons when it is subject to change by introduction of a new species. A solution with a higher (more positive) reduction potential than the new species will have a tendency to gain electrons from the new species (to be reduced by oxidizing the new species); a solution with a lower (more negative) reduction potential will have a tendency to lose electrons to the new species (to be oxidized by reducing the new species). A positive ORP indicates the solution is aerobic, while a negative ORP indicates reducing conditions are dominant.

Oxygenase An enzyme that introduces oxygen into an organic molecule.

Partition coefficient (K_d) Ratio of the concentrations in a liquid phase in contact with a solid phase. Measure of the sorption potential, whereby a contaminant is divided between the soil and water phase.

Partitioning interwell tracer testing (PITT) Method to quantify the volume of nonaqueous phase liquid (NAPL) in a contaminated aquifer by injecting and recovering a tracer that will partition into the NAPL phase. PITT provides information about the NAPL volume distribution in a relatively large-scale area.

Passivation Process of making a material "passive" in relation to another material. Often used to refer to the formation of a hard non-reactive surface film on many reactive or corrosive materials (such as aluminum, iron, zinc, magnesium, copper, stainless steel, titanium and silicon) that inhibits further reactivity.

Passive injection (passive treatment) Remediation approach involving additions of amendments to the subsurface on a one-time or very infrequent basis.

Passive treatment *In situ* bioremediation approach in which amendments are added to the subsurface on a one-time or infrequent basis. Passive treatment relies on the use of slow-release electron donors, which can be injected into the subsurface or placed in trenches or wells.

Pathogen Microorganisms (e.g., bacteria, viruses or parasites) that can cause disease in humans, animals and plants.

Percarbonate Any of a family of perhydrates of carbonate compounds, such as sodium percarbonate ($2Na_2CO_3{\cdot}3H_2O$). Strong oxidant.

Perchlorate An anion consisting of one chlorine atom and four oxygen atoms, with the chlorine atom present at an oxidation state of +7. Perchlorate occurs naturally; because it is a potent oxidizer, it also has been manufactured and used for solid rocket propellants and explosives.

Perchlorethene (PCE, perchloroethylene, tetrachloroethene, tetrachloroethylene) A colorless, nonflammable organic solvent, $Cl_2C{:}CCl_2$, used in dry-cleaning solutions and as an industrial solvent.

Percolation 1. Movement of water downward and radially through subsurface soil layers, usually continuing downward to groundwater; can also involve upward movement of water. 2. Slow seepage of water through a filter.

Permanganate General name for a chemical compound containing the manganate (VII) ion, (MnO_4^-). Because manganese is in the +7 oxidation state, the manganate (VII) ion is a strong oxidizing agent.

Permeability The rate at which liquids pass through soil or other materials in a specified direction.

Permeable reactive barrier (PRB) A permeable zone containing or creating a reactive treatment area oriented to intercepting and remediating a contaminant plume.

Persulfate Ions or compounds with more oxygen than normal sulfates, such as potassium persulfate ($KHSO_5$). Strong oxidants.

pH An expression of the intensity of the basic or acid condition of a liquid. Represents the logarithm of the reciprocal of the hydrogen ion concentration (thus, pH $7 = 10^7$ H^+ grams/liter). pH may range from 0 to 14, where 0 is the most acid and 7 is neutral. Natural waters usually have a pH between 6.5 and 8.5.

Phospholipid fatty acid analysis (PLFA) Analysis of the phospholipids, which are major components of all cell membranes. PLFA can provide a broad description of the entire microbial community with information obtained about viable biomass concentrations, community composition, and metabolic status.

Photolysis The splitting of molecules by means of light energy.

Phytoaccumulation Plant uptake and retention of a compound within plant tissues.

Phytodegradation Degradation of a contaminant within a plant; also called phytotransformation

Phytoextraction Extraction of contaminants from soil or water by plants.

Phytophotolysis Photolysis of contaminants within plants.

Phytoremediation The use of plants and in some cases the associated rhizosphere (root zone) microorganisms for *in situ* remediation of contaminants.

Phytostabilization Use of vegetation to hold soil and sediments in place, and to immobilize toxic contaminants in soil or stabilize dissolved phase plumes, in order to mitigate their impact on the environment.

Phytotransformation Metabolism of organic pollutants inside plant tissues; also called phytodegradation.

Phytovolatilization Transmission of contaminants to the atmosphere after plant uptake and translocation.

Piezometer A non-pumping well, generally of small diameter, for measuring the elevation of a water table.

Plume A zone of dissolved contaminants. A plume usually originates from a contaminant source zone and extends for some distance in the direction of groundwater flow.

Pneumatic fracturing Injection of gas into the subsurface at pressures exceeding the natural *in situ* pressures and at flow volumes exceeding the natural permeability of the subsurface. Creates a network of artificial fractures in a geologic formation that can facilitate removal of contaminants out of the geologic formation; may be used to introduce remedial agents.

Polymerase chain reaction (PCR) Technique to amplify a single or few copies of a specific DNA sequence by several orders of magnitude. Allows detection of a target gene or parts of a gene, even when present at low concentrations in soils or groundwaters for example. PCR relies on thermal cycling, consisting of cycles of repeated heating and cooling of the reaction for DNA melting and enzymatic replication.

Polychlorinated biphenyls A group of toxic, persistent chemicals used in electrical transformers and capacitors for insulating purposes, and in gas pipeline systems as lubricant. The sale and new use of these chemicals, also known as PCBs, were banned by law in 1979.

Polyvinyl chloride (PVC) A tough, environmentally indestructible plastic that releases hydrochloric acid when burned.

Porosity The fraction of the subsurface volume filled with pores or cavities through which water or air can move.

Potentiometric surface map A contour map that represents the top of the groundwater surface in an aquifer.

Precipitate A substance separated from a solution or suspension by chemical or physical change.

Pressure transducer A sensor device that converts pressure into an analog electrical signal, allowing measurement.

Primary substrates The electron donor and electron acceptor that are essential to ensure the growth of microorganisms. These compounds can be viewed as analogous to the food and oxygen that are required for human growth and reproduction.

Protein Complex nitrogenous organic compounds of high molecular weight made of amino acids. Essential for growth and tissue repair. Many, but not all, proteins are enzymes.

Proteomics The large-scale study of proteins, particularly their structures and functions. The proteome (combination of "protein" and "genome") is the entire complement of proteins produced by an organism or system. Proteomics can allow identification and quantification of the proteome to indicate the biochemical capabilities in a sample.

Pyrite An iron sulfide mineral with the formula FeS_2. The most common of the sulfide minerals. Also called fool's gold.

Radius of influence (ROI) The radial distance from the center of an injection point or well to the point where there is no significant impact from the injected material.

Raoult's Law Relates the vapor pressure of components to the composition of the solution. If the components are sufficiently similar, the vapor pressure of the solution will depend on the vapor pressure of each chemical component and the mole fraction of the component present in the solution. Used to predict the soluble concentrations of each compound in a mixture of similar compounds (e.g., benzene, toluene, ethyl benzene and xylenes [BTEX] in gasoline) that is in equilibrium with the aqueous phase, based on the mole fraction of each compound in the mixture.

Recharge Process by which water is added to a zone of saturation, usually by percolation from the soil surface (e.g., the recharge of an aquifer via precipitation and infiltration).

Record(s) of Decision A public document that explains which cleanup alternative(s) will be used at National Priorities List sites where, under Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Trust Funds pay for the cleanup.

Redox (redox potential) Reduction/oxidation reactions—those in which atoms have their oxidation number changed. For example, carbon may be oxidized by oxygen to yield carbon dioxide or reduced by hydrogen to yield methane. The redox potential (ORP) reflects the tendency of a chemical species to acquire electrons and thereby be reduced. In a redox reaction, one chemical species—the reductant or reducing agent—loses electrons and is oxidized, and the other—the oxidant or oxidizing agent—gains electrons and is reduced.

Reducing Environmental conditions that favor a decrease in the oxidation state of reactive chemical species (e.g., reduction of sulfates to sulfides).

Reductase An enzyme catalyzing a reducing reaction.

Reduction Transfer of electrons to a compound such as oxygen; occurs when another compound is oxidized.

Reductive dechlorination (hydrogenolysis) Reaction involving removal of one or more chlorine atoms from an organic compound and their replacement with hydrogen atoms. A subset of reductive dehalogenation. Key reaction for anaerobic degradation of chlorinated solvents.

Reductive dehalogenation The process by which a halogen atom (e.g., chlorine or bromine) is replaced on an organic compound with a hydrogen atom. The reactions result in the net addition of two electrons to the organic compound.

Remediation Cleanup or other methods used to remove or contain contamination.

Retardation Slowing of the movement of compounds in an aquifer relative to the groundwater velocity. For example, a contaminant plume exhibiting a retardation factor of 5 expands one-fifth as fast as the water itself or a nonreactive tracer such as chloride, which has a retardation factor near 1.0.

Reverse osmosis A treatment process used in water systems by adding pressure to force water through a semi-permeable membrane. Reverse osmosis removes most drinking-water contaminants. Also used in wastewater treatment. Large-scale reverse osmosis plants are being developed.

Rhizodegradation Degradation of compounds by organisms living on or near plant roots.

Rhizofiltration A form of bioremediation that involves filtering water through a mass of roots to remove toxic substances or excess nutrients.

Rhizosphere The soil on and near the roots of plants. This soil zone, directly influenced by root secretions, is teeming with microorganisms that feed on sloughed-off plant cells and the compounds released by roots.

Salinity Salt content of water.

Saturated zone Part of the subsurface that is beneath the water table and in which the pores are filled with water.

Sediments Soil, sand and minerals carried from land into water bodies.

Seepage velocity The average pore water velocity. Since groundwater flow actually occurs only through interconnected pores and not through the entire subsurface volume—as assumed in calculating the Darcy velocity (V)—the seepage velocity (Vs) is equal to the Darcy velocity divided by the porosity (n), or Vs=V/n.

Semi-passive treatment *In situ* bioremediation approach in which amendments are added to the subsurface intermittently (at intervals of a few weeks to a few months). Generally, water-soluble compounds serve as the electron donor. The accumulation of biomass can also serve as a longer-term source of electron donors.

Slug test A particular type of aquifer test where water is quickly added to or removed from a groundwater well, and the change in hydraulic head is monitored through time, to determine the near-well aquifer characteristics. It is a method used by hydrogeologists and civil engineers to determine the transmissivity and storativity of the subsurface material surrounding the well.

Soil organic matter (SOM) Organic constituents in the soil, including undecayed plant and animal tissues, their partial decomposition products, and the soil biomass. SOM includes high–molecular-weight organic materials (such as polysaccharides and proteins), simpler substances (such as sugars, amino acids and other small molecules), and humic substances.

Soil vapor extraction (SVE, soil venting) An established technology for the *in situ* remediation of VOCs in soils. The process removes soil vapor contaminated with VOCs and enhances the mass transfer of VOCs from the soil pores to the vapor phase by applying a vacuum to extract soil contaminants and gases.

Solubility Ability of a substance to dissolve (or solubilize). The solubility of a specific solute is its maximum concentration in a given solvent at a reference temperature.

Solvent A substance, usually a liquid, capable of dissolving another substance.

Sorb To take up and hold by either adsorption or absorption.

Sorption Collection of a substance on the surface of a solid by physical or chemical attraction. Can refer to either absorption (in which one substance permeates another) or adsorption (surface retention of solid, liquid, or gas molecules, atoms or ions).

Sorption isotherm Describes the sorption of a material at a surface at constant temperature. Determined by comparing the sorbed concentration of a compound to its concentration in solution. Describes the ability of a dissolved contaminant to adsorb or absorb onto the solid particles (soil or particulates).

Source strength The mass discharge from a source zone. Represents the mass loading to the plume per unit time (e.g., grams trichloroethene released per day).

Source zone A subsurface zone that serves as a reservoir of contaminants to sustain a dissolved plume. The source includes the material that is or has been in contact with the separate phase (DNAPLs for chlorinated solvents); the source zone mass includes the sorbed and aqueous phase contaminants, as well as any residual NAPL.

Sparge To inject air below the water table to strip dissolved VOCs and/or oxygenate groundwater to facilitate aerobic biodegradation of organic compounds.

Specific conductance (electrical conductivity) Rapid method of estimating the dissolved solid content (total dissolved solids) of a water supply by testing its capacity to carry an electrical current.

Stabilization/solidification Remediation technique in which contaminants are physically bound or enclosed within a stabilized mass (solidification), or their mobility is reduced due to chemical reactions induced between a stabilizing agent and the contaminants (stabilization).

Stakeholder A person (other than regulators, owners or technical personnel) who has a legitimate interest in a contaminated site.

Steady-state A condition of a physical system or device that does not change over time or in which any one change is continually balanced by another, such as the stable condition of a system in equilibrium.

Steam enhanced remediation (SER) An *in situ* thermal treatment technology involving steam injection and aggressive vapor and liquid extraction system to mobilize and remove organic contaminants from a source zone.

Steric effects The influence of the spatial configuration of reacting substances upon the rate, nature and extent of reaction.

Sterilization The removal or destruction of all microorganisms, including pathogenic and other bacteria, vegetative forms and spores.

Stoichiometry The calculation of quantitative (measurable) relationships of the reactants and products in a balanced chemical reaction.

Storativity The volume of water an aquifer releases from or takes into storage per unit surface area of the aquifer per unit change in head. It is equal to the product of specific storage and aquifer thickness. In an unconfined aquifer, the storativity is equivalent to the specific yield. Also called storage coefficient.

Stratum (strata) A layer of rock or soil with internally consistent characteristics that distinguishes it from contiguous layers. Each layer is generally one of a number of parallel layers that lie one upon another, laid down by natural forces. Typically seen as bands of different colored or differently structured material exposed in cliffs, road cuts, quarries and river banks.

Substrate A compound that microorganisms can use in the chemical reactions catalyzed by their enzymes.

Sulfate reducing bacteria (SRB, sulfate reducer) Bacteria that convert sulfate to hydrogen sulfide. Sulfate-reducing bacteria often play important roles in the oxygen-limited subsurface.

Superoxide radical anion Superoxide is an anion with the chemical formula O_2^-. It is important as the product of the one-electron reduction of dioxygen O_2, which occurs widely in nature. With one unpaired electron, the superoxide ion is a free radical and, like dioxygen, is paramagnetic. Superoxide is biologically quite toxic and is deployed by the immune system to kill invading microorganisms. Because superoxide is toxic, nearly all organisms living in the presence of oxygen contain isoforms of the superoxide scavenging enzyme, superoxide dismutase, which is an extremely efficient enzyme; it catalyzes the neutralization of superoxide nearly as fast as the two can diffuse together spontaneously in solution.

Surfactant A material that can greatly reduce the surface tension of water when used in very low concentrations. Primary ingredient of many soaps and detergents.

Surfactant flushing (Surfactant enhanced aquifer remediation, SEAR) Remediation technology involving injection of a solution of surfactants into a subsurface containing NAPLs. Surfactants increase the effective aqueous solubility of the NAPL constituents, greatly enhancing NAPL removal during flushing.

Syntrophic (syntrophism) A biological relationship in which organisms of two different species or strains are mutually dependent upon one another for nutritional requirements.

Thermodynamic The study of the conversion of energy into work and heat and its relation to macroscopic variables, such as temperature and pressure.

Tortuosity The actual length of a groundwater flow path, which is sinuous in form, divided by the straight-line distance between the ends of the flow path.

Total dissolved solids (TDS) Combined content of all inorganic and organic substances in a liquid that are present in a molecular, ionized or micro-granular (colloidal) suspended form.

Total organic carbon (TOC) Mass of carbon bound in organic compounds in soils, sediments, and water. Often used as a nonspecific indicator of water quality.

Toxicity The degree to which a substance or mixture of substances can cause harm to organisms. Acute toxicity involves harmful effects in an organism through a single or short-term exposure. Chronic toxicity is the ability of a substance or mixture of substances to cause harmful effects over an extended period.

Tracer test Used to "trace" the path of flowing water. Tracer tests are conducted by dissolving a tracer chemical into groundwater at concentrations that do not significantly change the aqueous density. Tracer chemicals must behave conservatively, meaning that no mass is lost through reaction or partitioning into differing phases. Typical tracer chemicals are chloride or bromide.

Transcription Transfer of information in DNA sequences to produce complementary messenger RNA sequences, which are then translated into functional polypeptides and proteins.

Translation The decoding of messenger RNA to produce specific polypeptides. It occurs after transcription.

Transmissivity Rate at which water of a prevailing density and viscosity is transmitted through a unit width of an aquifer or confining bed under a unit hydraulic gradient (units of area/time, e.g., ft^2/day). It is a function of properties of the liquid, the porous media and the thickness of the porous media. Equal to hydraulic conductivity (K) times aquifer thickness.

Trichloroethane (TCA) An industrial solvent (CH_3CCl_3). Other names for it include methyl chloroform and chlorothane. Occurs in two isomers: 1,1,1-TCA and 1,1,2-TCA.

Trichloroethene (TCE) A stable, low–boiling-point colorless liquid (CH_3Cl:$CHCl_2$). Used as a solvent or metal-degreasing agent, and in other industrial applications. Toxic if inhaled, and a suspected carcinogen. Also called trichloroethylene.

Unsaturated zone The area above the water table where soil pores are not fully saturated, although some water may be present. Also called the vadose zone.

Vadose zone Subsurface solids above the water table, where pores are partially or largely filled with air. Also called the unsaturated zone.

Vapor intrusion Migration of volatile chemicals from the subsurface into overlying buildings.

Vapor pressure A measure of a substance's propensity to evaporate. The force per unit area exerted by vapor in an equilibrium state with surroundings at a given pressure. It increases exponentially with an increase in temperature. A relative measure of chemical volatility, vapor pressure is used to calculate water partition coefficients and volatilization rate constants.

Vaporization Conversion of a substance from the liquid or solid phase to the gaseous (vapor) phase. There are two types of vaporization: evaporation and boiling.

Vinyl chloride (VC) A chemical compound (CH_2:CHCl) that is highly toxic and believed to be oncogenic. A colorless compound and an important industrial chemical chiefly used to produce the polymer polyvinyl chloride (PVC).

Viscosity The molecular friction within a fluid that produces flow resistance.

Volatile Evaporating readily at normal temperatures and pressures.

Volatile organic compound (VOC) Any organic compound that has a high enough vapor pressure under normal conditions to significantly vaporize and enter the atmosphere.

Volatilization Transfer of a chemical from the liquid to the gas phase (as in evaporation).

Water solubility The maximum possible concentration of a chemical compound dissolved in water. If a substance is water-soluble, it can very readily disperse through the environment.

Water table The top of an unconfined aquifer. Indicates the level below which subsurface solids and rock are saturated with water.

Wellhead The assembly of fittings, valves, and controls located at the surface and connected to the flow lines, tubing, and casing of the well so as to control the flow from the reservoir.

Wettability The relative degree to which a fluid will spread into or coat a solid surface in the presence of other immiscible fluids.

Xenobiotic A substance that is not normally found in organisms.

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