Volume 236

Pim de Voogt *Editor*

Reviews of Environmental Contamination and Toxicology

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Foreword

International concern in scientific, industrial, and governmental communities over traces of xenobiotics in foods and in both abiotic and biotic environments has justified the present triumvirate of specialized publications in this field: comprehensive reviews, rapidly published research papers and progress reports, and archival documentations. These three international publications are integrated and scheduled to provide the coherency essential for nonduplicative and current progress in a field as dynamic and complex as environmental contamination and toxicology. This series is reserved exclusively for the diversified literature on "toxic" chemicals in our food, our feeds, our homes, recreational and working surroundings, our domestic animals, our wildlife, and ourselves. Tremendous efforts worldwide have been mobilized to evaluate the nature, presence, magnitude, fate, and toxicology of the chemicals loosed upon the Earth. Among the sequelae of this broad new emphasis is an undeniable need for an articulated set of authoritative publications, where one can find the latest important world literature produced by these emerging areas of science together with documentation of pertinent ancillary legislation.

Research directors and legislative or administrative advisers do not have the time to scan the escalating number of technical publications that may contain articles important to current responsibility. Rather, these individuals need the background provided by detailed reviews and the assurance that the latest information is made available to them, all with minimal literature searching. Similarly, the scientist assigned or attracted to a new problem is required to glean all literature pertinent to the task, to publish new developments or important new experimental details quickly, to inform others of findings that might alter their own efforts, and eventually to publish all his/her supporting data and conclusions for archival purposes.

In the fields of environmental contamination and toxicology, the sum of these concerns and responsibilities is decisively addressed by the uniform, encompassing, and timely publication format of the Springer triumvirate:

Reviews of Environmental Contamination and Toxicology [Vol. 1 through 97 (1962–1986) as Residue Reviews] for detailed review articles concerned with any aspects of chemical contaminants, including pesticides, in the total environment with toxicological considerations and consequences.

Bulletin of Environmental Contamination and Toxicology (Vol. 1 in 1966) for rapid publication of short reports of significant advances and discoveries in the fields of air, soil, water, and food contamination and pollution as well as methodology and other disciplines concerned with the introduction, presence, and effects of toxicants in the total environment.

Archives of Environmental Contamination and Toxicology (Vol. 1 in 1973) for important complete articles emphasizing and describing original experimental or theoretical research work pertaining to the scientific aspects of chemical contaminants in the environment.

The individual editors of these three publications comprise the joint Coordinating Board of Editors with referral within the board of manuscripts submitted to one publication but deemed by major emphasis or length more suitable for one of the others.

Coordinating Board of Editors

Preface

The role of *Reviews* is to publish detailed scientific review articles on all aspects of environmental contamination and associated (eco)toxicological consequences. Such articles facilitate the often complex task of accessing and interpreting cogent scientific data within the confines of one or more closely related research fields.

In the 50+ years since *Reviews of Environmental Contamination and Toxicology* (formerly *Residue Reviews*) was first published, the number, scope, and complexity of environmental pollution incidents have grown unabated. During this entire period, the emphasis has been on publishing articles that address the presence and toxicity of environmental contaminants. New research is published each year on a myriad of environmental pollution issues facing people worldwide. This fact, and the routine discovery and reporting of emerging contaminants and new environmental contamination cases, creates an increasingly important function for *Reviews*. The staggering volume of scientific literature demands remedy by which data can be synthesized and made available to readers in an abridged form. *Reviews* addresses this need and provides detailed reviews worldwide to key scientists and science or policy administrators, whether employed by government, universities, nongovernmental organizations, or the private sector.

There is a panoply of environmental issues and concerns on which many scientists have focused their research in past years. The scope of this list is quite broad, encompassing environmental events globally that affect marine and terrestrial ecosystems; biotic and abiotic environments; impacts on plants, humans, and wildlife; and pollutants, both chemical and radioactive; as well as the ravages of environmental disease in virtually all environmental media (soil, water, air). New or enhanced safety and environmental concerns have emerged in the last decade to be added to incidents covered by the media, studied by scientists, and addressed by governmental and private institutions. Among these are events so striking that they are creating a paradigm shift. Two in particular are at the center of ever increasing media as well as scientific attention: bioterrorism and global warming. Unfortunately, these very worrisome issues are now superimposed on the already extensive list of ongoing environmental challenges.

The ultimate role of publishing scientific environmental research is to enhance understanding of the environment in ways that allow the public to be better informed or, in other words, to enable the public to have access to sufficient information. Because the public gets most of its information on science and technology from internet, TV news, and reports, the role for scientists as interpreters and brokers of scientific information to the public will grow rather than diminish. Environmentalism is an important global political force, resulting in the emergence of multinational consortia to control pollution and the evolution of the environmental ethic. Will the new politics of the twenty-first century involve a consortium of technologists and environmentalists, or a progressive confrontation? These matters are of genuine concern to governmental agencies and legislative bodies around the world.

For those who make the decisions about how our planet is managed, there is an ongoing need for continual surveillance and intelligent controls to avoid endangering the environment, public health, and wildlife. Ensuring safety-in-use of the many chemicals involved in our highly industrialized culture is a dynamic challenge, because the old, established materials are continually being displaced by newly developed molecules more acceptable to federal and state regulatory agencies, public health officials, and environmentalists. New legislation that will deal in an appropriate manner with this challenge is currently in the making or has been implemented recently, such as the REACH legislation in Europe. These regulations demand scientifically sound and documented dossiers on new chemicals.

Reviews publishes synoptic articles designed to treat the presence, fate, and, if possible, the safety of xenobiotics in any segment of the environment. These reviews can be either general or specific, but properly lie in the domains of analytical chemistry and its methodology, biochemistry, human and animal medicine, legislation, pharmacology, physiology, (eco)toxicology, and regulation. Certain affairs in food technology concerned specifically with pesticide and other food-additive problems may also be appropriate.

Because manuscripts are published in the order in which they are received in final form, it may seem that some important aspects have been neglected at times. However, these apparent omissions are recognized, and pertinent manuscripts are likely in preparation or planned. The field is so very large and the interests in it are so varied that the editor and the editorial board earnestly solicit authors and suggestions of underrepresented topics to make this international book series yet more useful and worthwhile.

Justification for the preparation of any review for this book series is that it deals with some aspect of the many real problems arising from the presence of anthropogenic chemicals in our surroundings. Thus, manuscripts may encompass case studies from any country. Additionally, chemical contamination in any manner of air, water, soil, or plant or animal life is within these objectives and their scope.

Manuscripts are often contributed by invitation. However, nominations for new topics or topics in areas that are rapidly advancing are welcome. Preliminary communication with the Editor-in-Chief is recommended before volunteered review manuscripts are submitted. *Reviews* is registered in WebofScience™. Inclusion in the Science Citation Index serves to encourage scientists in academia to contribute to the series. The impact factor in recent years has increased from 2.5 in 2009 to almost 4 in 2013. The Editor-in-Chief and the Editorial Board strive for a further increase of the journal impact factor by actively inviting authors to submit manuscripts.

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In-Situ Remediation Approaches for the Management of Contaminated Sites: A Comprehensive Overview

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Abbreviations

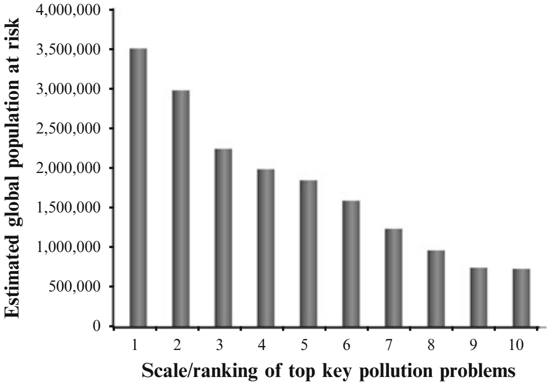
$	Dollar
<	Less than
>	Greater than
2,4-D	2,4-Dichlorophenoxyacetic acid
Ag	Silver
Al	Aluminium
AM	Arbuscular mycorrhiza
As	Arsenic
B	Boron
Be	Beryllium
BTEX	Benzene toluene, ethylbenzene and xylenes
C	Carbon
CCA	Chromated copper arsenate
Cd	Cadmium
CEC	Contaminants of emerging concern
CFU	Colony forming units
CN	Cyanide
Co	Cobalt
Cr	Chromium
Cs	Cesium
Cu	Copper
DC	Direct current
DCA	Dichloroaniline
DCE	Dichloroethane
DDT	Dichlorodiphenyltrichloroethane
DNA	Deoxyribonucleic acid
DNAPL	Dense non-aqueous phase liquid
DPE	Dual-phase extraction
DUS/HPO	Dynamic underground steam stripping with hydrous oxidation
EDTA	Ethylenediaminetetraacetic acid
EPH	Extractable petroleum hydrocarbons

EZVI	Emulsified zero-valent iron
FCC	Federal Communications Commission
Fe	Iron
Fe_2O_3	Iron oxide
FRTR	Federal Remediation Technologies Roundtable
g	Gram
GAC	Granular activated carbon
GHz	Gigahertz
h	Hour
HCB	Hexachlorobenzene
Hg	Mercury
HMW	High molecular weight
HPCD	Hydroxypropyl cyclodextrine
HTTD	High temperature thermal desorption
IAA	Indole-3-acetic acid
ISTD	In-situ thermal desorption
ISV	In-situ vitrification
J	Joule
K	Potassium
kg	Kilogram
kW	Kilo-watt
L	Litre
LNAPL	Light non-aqueous phase liquid
LTTD	Low temperature thermal desorption
m	Metre
M	Molar
MFCs	Microbial fuel cells
mg	Milligram
Mg	Megagram
MHz	Megahertz
min	Minute
Mn	Manganese
MPE	Multi-phase extraction
MTBE	Methyl tertiary-butyl ether
N	Nitrogen
n	Nano
NAD	Nicotinamide adenine dinucleotide
NAPL	Non-aqueous phase liquid
NH_3	Ammonia
Ni	Nickel
NO_3	Nitrate
P	Phosphorous
PAHs	Polycyclic aromatic hydrocarbons
Pb	Lead
PCBs	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo-*p*-dioxins
PCDF	Polychlorinated dibenzofurans

PCE	Perchloroethylene
PCP	Pentachlorophenol
PCPP	Pharmaceutical and personal care products
PFAS	Polyfluoroalkyl substances
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PFOSF	Perfluorooctanesulfonyl fluoride
PO_4	Phosphate
POPs	Persistent organic pollutants
PRB	Permeable reactive barrier
RDX	Royal demolition explosive
s	Second
Sb	Antimony
Sb_2O_3	Antimony trioxide
Se	Selenium
SO_4	Sulphate
Sr	Strontium
SVE	Soil vapor extraction
TCA	Trichloroethane
TCE	Trichloroethylene
TI	Thallium
TMB	Trimethylbenzene
TNT	Trinitrotoluene
TPH	Total petroleum hydrocarbons
U	Uranium
US EPA	United States Environmental Protection Agency
UV	Ultra-violet
V	Volt
VC	Vinyl chloride
VOC	Volatile organic compounds
W	Watts
WHO	World Health Organization
Zn	Zinc
ZVI	Zero-valent iron
µg	Microgram

1 Introduction

One of the major threats to the global environment addressed by the United States Environmental Protection Agency (US EPA) and World Health Organization (WHO) is ‘pollutants’. Pollutants are organic and inorganic man-made chemicals that contaminate the natural ecosystem. Due to industrialization and urbanization, the global chemical output grew from US$ of 171 billion in 1970 to 4.12 trillion by



In the figure, numerical from 1-10 signifies the scale/ranking of top ten key pollution problems with their respective source industry as detailed below:

1. Artisanal gold mining (Mercury pollution)
2. Industrial estates (Lead pollution)
3. Agricultural production (Pesticide pollution)
4. Lead smelting (Lead pollution)
5. Tannery operations (Chromium pollution)
6. Mining and ore processing (Mercury pollution)
7. Mining and ore processing (Lead pollution)
8. Lead-acid battery recycling (Lead pollution)
9. Naturally-occurring arsenic in groundwater (Arsenic pollution)
10. Pesticide manufacturing and storage (Pesticide pollution)

Fig. 1 Top ten toxic pollution problems and the estimated global population at risk. *Source*: Blacksmith Institute (2011)

2010 (Blacksmith Institute 2011). Mining activities, pesticides in agriculture, industrial manufacturing activities and accidents, vehicle emissions, and disposal of industrial effluents in natural waterbodies have been responsible for the outbreak of ten major toxic pollution problems in terms of number of people affected. These problems have subjected several million people at direct risk (see Fig. 1). The major source of toxic hot spots worldwide, viz., oil production along with its ancillary industries, does not appear in Fig. 1. It is because of the fact that sites that are contaminated by petrochemical industry tend to be neither abandoned nor defunct and are largely immune from regulatory control, and therefore this source has not been included in the list of world's top ten most toxic pollution problems by Blacksmith Institute (2011).

Over one thousand million pounds of toxic chemicals escape into groundwater and air annually. Currently, around two billion people worldwide drink contaminated water and breathe in high levels of toxic gases every day (GLIMUN 2009). These environmental pollutants can be broadly grouped into two kinds: firstly, priority (hazardous materials with a sufficient toxicological profile and regulated mitigation guidelines); and secondly, emerging (newly detected compounds that lack sufficient detection methods and regulated mitigation strategies) pollutants that include both organics and inorganics. The 21 POPs listed by Stockholm Convention (2010) include aldrin, chlordane, chlordecone, dieldrin, dichlorodiphenyltrichloroethane (DDT), endrin, heptachlor, hexachlorobenzene, α-hexachlorocyclohexane, β-hexachlorocyclohexane, hexabromobiphenyl, hexabromodiphenyl ether and heptabromodiphenyl ether, hexachlorobenzene (HCB), mirex, lindane (γ-hexachlorocyclohexane), toxaphene, pentachlorobenzene, tetrabromodiphenyl ether, pentabromodiphenyl ether, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (dioxins/PCDD), polychlorinated dibenzofurans (PCDF), perfluorooctanesulfonic acid (PFOS) and its salts, and perfluorooctanesulfonyl fluoride (PFOSF).

The priority inorganics listed by US EPA are metal(oid) and non-metals like cadmium (Cd), lead (Pb), antimony (Sb), arsenic (As), mercury (Hg), selenium (Se), silver (Ag), zinc (Zn), nickel (Ni), beryllium (Be), thallium (Ti), copper (Cu), nitrate (NO_3), ammonia (NH_3), sulphate (SO_4), phosphate (PO_4) and cyanide (CN). Chemicals that were not detected previously are being discovered in water and food. The most frequently conferred emerging pollutants include outsized classes of algal toxins, illegal drugs, nanoparticles, detergents, anti-fouling/foaming/corrosive chemicals, new pesticides, antimicrobials, disinfectants, antioxidants, flame retardants, chelating agents, artificial food preservatives, disruptive compounds, cosmetics, fuel additives, chemico-industrial by-products, man-made flourinated compounds, pharmaceutical and personal care products (PPCP), plasticizers and preservatives used to treat wood. Currently, the US EPA is investigating the contaminants of emerging concern (CECs) owing to the hazard they pose to health and ecology.

Toxic pesticides share the POPs listed in the elimination annexes under the Stockholm Convention. Though highly persistent, DDT is banned in many countries, but recent studies in South Africa continue to show up to 1930 ng DDT/g milk fat (Okonkwo et al. 2008). Limited use of banned chemicals like DDT in malaria vector control continues and remains controversial. In the US alone, about 34,000 Mg of PBDEs are exploited anually as flame retardants in automobiles, fabrics, furniture foams, construction materials, electronics and other appliances (McDonald 2005). PFAS like PFOS and PFOA persist in the environment (Buck et al. 2011) and bioaccumulate in human blood to a range of 30–44 µg/L causing bladder cancer and neurobehavioral alterations (Stockholm Convention 2005). According to the US EPA and European government agencies, from the 1990s onward much research costing billions of dollars was spent investigating the impact of carcinogenic POPs like PAHs and PCDD/Fs on people's health (Jones and De Voogt 1999).

About 100 different highly toxic PAHs originate from the incomplete burning of coal/petroleum/natural gas/waste, wood treatments, industrial liquefaction and gasification processes. Higher levels of contamination of about 300 g PAHs/g soil were been recorded as having cancerous effects (Megharaj et al. 2011). MTBE spilled from car accidents is an additional model of a compound that is now noticed in waterbodies at higher concentrations, thus posing a threat to human health (Klinger et al. 2002). The US EPA (2004) estimates that over 50 million m^3 soils (77 %) of the current superfund sites are contaminated with metals. Pb, Cd, Zn and As are highly hazardous heavy metals that persist at contaminated spots and can damage health and the environment. WHO (2003) set a guideline of 10 µg/L of As in drinking water. Phytotoxic effect and acute toxicity of Pb, Cd and Zn at high concentrations cause tumour cells in later stages of accumulation in aquatic receptors. Continuous exposure to non-metals like CN and SO_4 that are widely applied in medicine, mining, agriculture and food industries cause lung disease, heart problems and stomach ulcers in humans (Baselt and Cravey 2008).

Contaminants like phthalates and bisphenol A have been used in plasticizers as well as cosmetics for more than 50 years, and their production reached a recent peak of 3 million Mg (Deblonde et al. 2011). Many PPCPs like illicit drugs have been detected in the surface and groundwater systems associated with wastewater disposal

Table 1 Use of chemicals in the global industrial sector and its projections by 2016

Significant sector	Specific chemicals used	Global market projection		Leading nations in market	Reference
		Market value by 2011 (billion)	Anticipated increase (%) by 2016		
Electronics	Heavy metals, rare earth metals, solvents, polymers and flame retardants	30.7	15–20	China, USA, Japan and Germany	BCC Research (2011)
Textile	Oils, waxes, surfactants, flame retardants and water repellents	19	30	China, Asian countries, Middle east countries, Africa, Central and Eastern Europe	PR Newswire (2012)
Flame retardants	Brominated and chlorinated organics and inorganics	5.1	8–10	USA, Europe, Asia-Pacific China, North America and Asian countries	Industry Experts (2011)
Cement	Petroleum coke, coal, Hg, acid gases, VOCs, PAHs and dioxins/furans	200	14	China, India and USA	USGS (2011)

that can potentially lead to immunity deficit, endocrine disruption, nerve disorders and DNA repair (Johnson et al. 2008). For instance, the high rate of vulture mortality in India was by the direct oral exposure to veterinary diclofenac through feeding diclofenac-treated livestock (Oaks et al. 2004). The widespread use and sorption behavior of disinfectants, hormones and sterols in personal care products such as shampoos, soaps, cosmetics, deodorants, skin-care lotions, mouth rinses and tooth pastes contaminate the biosphere. Exposure of the human body to genotoxic nanoparticles (chemically-synthesized metal nanoparticles) is increasing daily due to advances in technology.

Daughton (2004) noted that out of 22,000 unregulated organic and inorganic chemical pollutants, nearly 6000 are commercially available and only fewer than 200 of them are addressed by the current regulations of US EPA and WHO. Moreover, the projected aim to increase the market values (up to 14–30 %) of specific industrial sectors that commercially use ample quantities of chemicals like heavy metals, flame retardants, dioxins/furans and PAHs in the leading nations by 2016 (Table 1), would elevate the level of environmental pollutants. They will pose a serious threat to living organisms by 2050 (BCC Research 2011; Industry Experts 2011; USGS 2011; PR Newswire 2012). Trillions of dollars are expected to be spent for the clean up of polluted sites in the USA alone (Kuiper et al. 2004). It is therefore important to restrain these priorities and emerging pollutants by developing newer and more appropriate cost-effective remedial tools that are rapid, realistic and adaptable in many physical settings.

For more than a decade, the primary focus of environmental experts is to adopt risk-based management approaches to clean up polluted sites. The need for the effective risk-based remediation led to the development of several physical, chemical, thermal and biological ex-situ and in-situ technologies that are currently widely used at contaminated sites (Sharma and Reddy 2004). *In*-situ is ‘in place’ remediation, where the soil is not unearthed but treated in the original place of contamination. In-situ remediation is a good option, since excavation involving higher transport costs is not an option when the treatment site is large and/or of greater depth in the soil. However, due to the soil heterogeneity, it is quite challenging to achieve uniform remediation throughout the treatment area (Carberry and Wik 2001).

In contrast, ex-situ approaches comprise the excavation of impacted media from the subsurface for on-site treatment or off-site disposal and subsequent re-deposition of the cleaned up soil. Ex-situ treatment time is generally shorter than in-situ and provides more treatment uniformity due to the possibility to screen, homogenize and monitor the contaminants. However, the cost of ex-situ treatment is high as excavation is involved and in most cases in-situ remediation is employed to treat contaminated sites, and research is more focused on developing in-situ remedial techniques than ex-situ (Jain et al. 2011). In-situ remedial approaches available for the clean up of polluted sites are many as described below, and can be broadly classified as technologies suitable for: (1) soil/sludge/sediment treatments like chemical extraction, flushing, fracturing, thermal desorption, vitrification, bioaugmentation, biostimulation, phytoremediation and electrokinetic separation; (2) groundwater/fresh water/leachate treatments such as subsurface steaming, dual-phase extraction, air sparging, bioslurping, natural attenuation and air stripping; (3) containments like physical barriers and reactive treatment walls; and (4) hazardous gas emission treatments, for example chemical oxidation, membrane bioreactors and biofiltration. Integrating physico-chemical and biological technologies is widely practiced for better clean up of polluted sites. Recently, for promising detoxification and destruction of contaminants, novel systems like mixed cell culture system, microbial fuel cells, metagenomic approaches and nanoremediation have been developed for treating various types of site-specific pollutants.

Though several in-situ treatment methods exist to remediate polluted sites, selecting an appropriate site-specific remediation technology is challenging, but is critical for successful clean up of polluted sites. Hence, a comprehensive overview of all the available remediation technologies to date is necessary to choose the right technology for an anticipated pollutant. In this review, we critically evaluate and discuss the following: (1) technological profile of existing in-situ remediation technologies for priority and emerging pollutants; (2) recent innovative technologies for on-site pollutant remediation; and (3) current challenges as well as future prospects for developing innovative approaches to enhance the efficacy of remediation at contaminated sites.

2 Selection and Suitability of Remedial Measures

The process of removing harmful chemicals from the contaminated air, soil and water (removal), or treating the contaminated site in order to change the harmful chemicals into less harmful ones (treatment), or leaving the contaminants in the ground and taking steps to prevent them from entering into soil, water and air, and to avert their spread to the people (containment) is stated as 'remediation'. The technological solutions that help to meet the site remediation goals within a reasonable period of time are collectively termed 'remediation technology'. In the last decade, the number of remedial techniques has increased considerably. Comprehensive information of specific remedial options suited for individual pollutants are summarized in many studies (Khan et al. 2004; Juwarkar et al. 2010; Megharaj et al. 2011). Due to the availability of various remediation technologies, selecting the right strategy has become a vital component in the risk-based management of contaminated sites.

Many factors need to be well considered in choosing a suitable remedial solution to a polluted land issue (Vik et al. 2001). These include: (a) the goals of the remediation work, for example, the aim to protect the environment and human health enabling the restoration of a formerly used land, and to limit the potential liabilities of a land, (b) risk management, (c) sustainable development, (d) stakeholders' views, (e) cost-benefit ratio, and (f) technological suitability and feasibility. Selection and suitability govern the promising outcomes of the process-based pollutant treatment. The factors that affect the suitability of remedial approaches are: (a) risk management applications (source reduction, pathway interruption and protection of receptors), (b) contaminants to be treated (type, concentration range, source, age and material handling characteristics), (c) remedial approach (removal, containment, rehabilitation, physical treatment, chemical treatment, biological treatment, solidification/stabilisation and thermal treatment), (d) process location (in-situ, ex-situ, on-site, off-site and in-vessel), (e) strategy (integrated approach, active or passive measures, long-term/low input, carrier-based measures and institutional measures), (f) implementation (process planning, site management, verification, monitoring, neighborhood impacts, aftercare and flexibility), and (g) outcome (recycling, destruction, removal, stabilisation and immobilization). Thus, considering the above factors, a right remediation technology can be selected for successful clean up of a problematic site. Available physical, chemical and biological technologies to remove pollutants in-place or in-situ are discussed below.

3 *In-Situ* Remediation Technologies for Soil and Groundwater

In-situ remediation technologies can be broadly classified as existing and emerging remedial options. Existing/established techniques include heating, soil flushing, fracturing, electrokinetic separation, physical barriers, soil vapor extraction, multi-phase extraction, air-sparging, natural attenuation, bioventing, bioaugmentation, biostimulation, and phytoremediation. Emerging techniques include microbial fuel cells, nanoremediation, genetic engineering, and photo-hetero microbial system. The following sections present a brief overview of the existing in-situ remedial options.

3.1 Heating

The focus of in-situ heating technique is to increase temperature, decrease viscosity and adsorption, and increase solubility, facilitating the recovery of volatile and semi-volatile compounds (Khaitan et al. 2006). Heating is a promising approach to remediate NAPLs (non-aqueous phase liquids) and DNAPLs (dense non-aqueous phase liquids) (Table 2). Electrical resistance heating, injection of hot air and steam, thermal conductive heating, electromagnetic heating (radiofrequency/microwave technology) and vitrification-enhanced thermal decontamination are the five fully-developed, short- to medium-term thermal treatment techniques (Triplett Kingston et al. 2010). Heating does not remove contaminants but modifies their biological, chemical and physical properties, and that of soils and groundwater. This makes them more amenable to remediation efforts like soil vapor extraction, air sparging, bioremediation, etc. Overall, heating improves the performance of other technologies which ultimately reduce the remedial time frames and costs involved.

3.1.1 Injection: Steam/Hot Air

Injection of steam/hot air was developed to enhance the recovery of oil from petroleum reservoirs. Here, hot air/steam is injected downstream to the polluted land surface through injection wells. Injected steam/hot air heat the contaminated soil, vaporizes the contaminants and the vapors are stored in a condensation tank from where they are recovered either by physical displacement, co-distillation, vacuum extraction or enhanced desorption (US EPA 2006). Steam is injected in a cyclical manner whenever the soil reaches the steam temperature. Udell and McCarter (1998) found that cyclic steam injection enhances mass transfer and accelerates the clean up process. Schmidt et al. (2002) confirmed that injection of steam with air accelerated the rate of pollutant removal. Combination of steam injection with auger mixing system (steam is injected through augers of specific design) proved to be effective (Davis 1998). Laboratory studies and field demonstrations also confirmed this technology's ability to effectively recover up to 99 % volatile and semi-volatile organics (VOCs and SVOCs) such as diesel or jet fuels and some chlorinated solvents from the subsurface (Heron et al. 2005). Efficiency and effectiveness of this process depend on site characteristics which determine the contaminant distribution and preferred flow path of the injected steam.

Table 2 Field demonstrations of in-situ heating technologies at US EPA superfund sites

Remediated site	Contaminants of concern	Volume treated	Initial contaminant level	Target temperature (°C)	Target power (kW)	Duration (months)	% Remediated	Outcome	Reference	Lessons learnt
Electrical resistance heating (ERH)										
1. Installation restoration site 5, Alameda Point, Alameda, California	TCA, EDC, DCE	1104 m^3 soil	9600 mg/kg	22–92	421,000	6	86.5	+	Cacciatore et al. (2003)	Extracted contaminated vapors can be condensed and treated using granular activated carbon for better recovery
2. US DOE, Young-Rainey STAR center, Largo, Florida	TCE, DCE, Methylene chloride, Toluene, Petroleum hydrocarbons	9930 m^3 aquifer	2500 kg	84	>400	4.5	99.8	++	Heron et al. (2005)	Combination of steam-enhanced extraction and ERH is effective in heating the treatment zones
3. Charleston naval complex, South Carolina	DCE, VC, TCE Halogenated VOCs	3287 m^3 soil	9890 mg/kg	89	278	9	86.0	+	FRTR (2005b)	ERH performance can be rectified by using enhanced reductive dechlorination
4. ICN Pharmaceuticals site, Portland, Oregon	TCE, DCE, VC, Benzene, Toluene	39,000 Mg soil	544,000 mg/kg	NA	950	8	99.0	++	Sutter (2012)	Creation of 'hot floor' and heat up 'walls' prevent vertical as well as lateral migrations of steam and DNAPLs

(continued)

Table 2 (continued)

Remediated site	Contaminants of concern	Volume treated	Initial contaminant level	Target temperature (°C)	Target power (kW)	Duration (months)	% Remediated	Outcome	Reference	Lessons learnt
5. Air force plant 4, Fort Worth, Texas	TCE, Halogenated VOCs	3000 m^3 soil	2770 mg/kg	60	1300–2000	2.5	95.0	++	US EPA (2012)	Six phase ERH is highly suitable to remediate DNAPLs at field conditions
Steam injections										
1. Lawrence Livermore national lab gasoline spill site, Livermore, US	BTEX	76,455 m^3 soil	287,690 kg	80–90	NA	7	99.9	++	US EPA (2012)	Dynamic underground stripping is suited for BTEX removal at large-scale
2. Savannah river site 321-M solvent storage tank area, Aiken, South Carolina	PCP, TCA	39,757 m^3 aquifer	12,156 kg	87	NA	7	99.0	++	FRTR (2012)	Dynamic underground steam stripping coupled with hydrous oxidation is suggestive to remediate high concentrations of contaminants
3. Former hazardous waste disposal site, Muehlacker, Germany	TCE, BTEX, Halogenated VOCs, Nonhalogenated VOCs	3000 m^3 soil	2500 kg	NA	100	10.0	95.0	++	US EPA (2012)	Monitoring of gas and liquid flow rates as well as temperature is a vital factor that decides the success of a heating system

4. A.G. Communications systems site, Warrnambool, Australia	TCE, DCE, Xylene, Benzene	NA	15,875 kg	84–140	294	6–8	99.9	++	US EPA (2003)	Steam-enhanced extraction coupled with SVE is a viable technology to cleanup hydrocarbons
5. Cape Canaveral air force station, Cape Canaveral, Florida	TCE	1070 m^3 soil	1000 mg/kg	100	NA	12–14	99.9	+	Robert et al. (2004)	Zero-valent iron injection is an alternative to steam injections. Also, integration of thermal treatments with reductive dechlorination is an innovative technology that increases the mass removal of DNAPLs
Conductive heating/ In-situ *thermal desorption* (*ISTD*)										
1. Confidential chemical manufacturing facility, Portland	DCE, TCE, Halogenated VOCs	9940 m^3 soil	NA	250	NA	6	99	++	TerraTherm (2000)	Thermal desorption combined with vacuum extraction is a suitable technology to remove organic compounds from soils
2. Terminal site 1, Richmond, California	PCP, TCE, DCE, VC	5120 m^3 sediment	2867 mg/kg	100	NA	9.0	99.9	++	TerraTherm (2010)	ISTD with dual-phase extraction is a promising technology at field-scale

(continued)

Table 2 (continued)

Remediated site	Contaminants of concern	Volume treated	Initial contaminant level	Target temperature (°C)	Target power (kW)	Duration (months)	% Remediated	Outcome	Reference	Lessons learnt
3. Naval air warfare site, West Trenton, New Jersey	TCE, DCE, VC	565 m^3 aquifer	277 mg/kg	100	4,93,000	3.5	99.0	+	Carmen (2010)	Controlled or lower groundwater flow is essential to enhance the rate of subsurface heating in shorter lifespan with accelerated VOC removal
4. Former electrical equipment service facility, Jacksonville, Florida	TCE, DCE, VC	NA	NA	100	NA	8	97	++	Amy et al. (2010)	Thermal conductive heating coupled with multi-phase extraction system is a potential technique for removal of chlorinated solvents
In-situ *radiofrequency heating* (*ISRH*)										
1. Bedrock site, Fort Lewis, Washington	TCA	850 m^3 fractured bedrock	2,50,000 mg/kg	50–60	NA	3	99.9	+	US EPA (2012)	Radio-frequency heating is suited to remediate contaminated bedrocks

2. Former petrol station, UK	BTEX, Petroleum hydrocarbons	480 m^3 Soil	1100 kg	50	30	2.0	99.0	++	Huon et al. (2012)	A mean soil temperature of more than 50 °C in the remediation volume reduces total remediation time by more than 80 % when compared to conventional ISRFH with SVE
Microwave heating										
Studies are available only at laboratory-scale										
Vitrification										
1. Oak Ridge national lab, Tennessee	Sr, Cs	NA for sludge	500 g	1500	29	5 days	99.9	++	Spalding et al. (1992)	Use of fillings like dolomitic limestone and native soil could help in reaching the processing temperature

++, Successful (Achieved remedial goals with >90 % contaminant removal); +, Partially successful (Remedial goals were not achieved in stipulated time, but >85 % contaminant was remediated); NA, Not available

Advantages of steam/hot air injection include the fact that relatively more rapid remediation is possible; excavation operations are not needed and target compounds are not pumped into the subsurface. Steam stripping/hot air injection treatments are not suitable for shallow treatment areas, but are effective in fractured rock settings (Davis et al. 2005). Major risks associated with steam/hot air injection is the displacement of contaminants by the injected fluids to areas other than recovery points and the high initial capital cost for steam injection. The problem of vertical confinement of injected steam into the vadose zone was overcome by injecting cold air above the steam injector (Hodges and Falta 2008). This costs around 51 US$ to remediate per m^3 contaminated site via steam/hot air injection (US EPA 2004).

Implementation of steam injections for cleaning up chlorinated solvents and petroleum hydrocarbons is very successful (nearly 99 % remediation) at field-scale (FRTR 2012). Dynamic underground steam stripping with hydrous oxidation (DUS/HPO) is a patented technology that helps remediate chlorinated contaminated soils at field-scale (US EPA 2001). For example, in the Savannah River superfund site in South Carolina, 39,520 m^3 of aquifer, consisting of interbedded sands and clays overlying a clayey aquitard with a groundwater depth of 44 m, contaminated with 31,100 kg chlorinated solvents (PCP and TCA), the DUS/HPO system of remediation was implemented. Nine injection wells in three clusters, three vapor extraction wells on perimeters and a combination groundwater/vapor extraction well in the center, were laid down in the treatment zone. About 20,593,440 L of steam with a heat content of 4747×10^{10} J was injected for 134 days and the source zone was heated up to 87 °C. Air was also injected by air stripping at 8 m^3/h to support HPO. When the vapors were subjected to dual phase and soil vapor extractions, the cumulative contaminant mass removal was 1000 kg TCE and 30,000 kg PCE (99.9 % remediated) after 7-month system operation (FRTR 2012). This coupled DUS/HPO technology successfully remediated 95 % BTEX, halogenated and non-halogenated VOCs in 2983 m^3 soil over 10 months. It involved proper monitoring of the physico-chemical characteristics like temperature, gas and liquid flow rate which are the critical factors that decide the success of a heating technology at field-level (US EPA 2001).

Nilsson et al. (2011) proved that steam stripping coupled with steam distillation can remove volatile and non-volatile hydrocarbons (jet fuel) even from an unsaturated zone of low permeability soils at bench-scale. The principle behind the technology is that injecting steam in the unsaturated zone of low permeability soils leads to a steady rise in the water saturation level, drastically changes the soil pore structure, and creates small fractures of micron size that act as better routes for the steam flow. The injected steam brings in contaminant vaporization. Second, heating the treatment zone to a temperature less than 100 °C in the presence of steam distillation enhances vaporization of the semivolatile and non-volatile NAPL compounds which ensures increased remedial activity. An experiment was conducted in soil spiked with decane, dodecane, methylcyclohexane, TMB and NAPL in a rectangular tank. The dry soil was humidified to bring in saturation of about 14.2 %. Dry steam of approximately 140–150 °C was injected for 10 h after which approximately 73–91 % of the NAPLs were removed. While studying the effect of steam-enhanced extraction technique coupled with soil vapor extraction at an Illinois superfund site contaminated with TCE, DCE, xylene and benzene, about 99.9 % remediation was achieved by heating the soil to a temperature of 84–140 °C for 6–8 months (US EPA 2003).

The remedial clean up of contaminated sites is not always achieved through steam stripping. Only a few field-level remediation studies have been partially successful (Table 2), where the remedial goals were not achieved within the targeted period of remediation despite the considerable reduction in the contaminant's total mass. One such example is the employment of steam injections to remediate 1070 m^3 of TCA-contaminated field at the air force station, Cape Canaveral, Florida. The remedial objective was to achieve 99.9 % remediation within 9 months of treatment. Though the soil was heated up to 100 °C, only 80 % of the VOCs were remediated in the targeted time and mostly the contaminants were bioavailable, and it took nearly 14 months to achieve 99.9 % remediation. Prolonged degradation was assumed to be due to lateral movement of contaminant to the previously treated zones which could be rectified by setting up a proper monitoring system (Robert et al. 2004). Overall, uncertainties in implementing steam injection heating at full-scale can be overcome by developing new systems of steam injections with defined operational control systems, e.g. flameless thermal oxidizer and a liquid vapor knockout system. It is recommended that off-gas stream can be monitored by using flame ionization detectors combined with dry electrolytic conductivity detectors. Thus, the most promising steam injection heating of NAPLs and DNAPLs can be improved by better system rectifications as suggested above.

3.1.2 Electrical Resistance Heating

Electrical resistance heating (ERH), developed in the early 1990s, became a commercial stand-alone method in 1997. In ERH, an electrode placed directly in zones of low permeability creates resistance to the flow of electric current. Electrical resistance heats the soil and evaporates the semi-volatile and volatile toxins as steam. The steam is then condensed and extracted vapors of the volatile organics are then treated conventionally by means of granular activated carbon (GAC) or oxidation. This technology mainly involves volatilization and steam stripping that enhances the contaminant removal speed and efficiency (Beyke 2000). However, some fraction of VOCs will be degraded in-situ naturally by hydrolysis, biodegradation and reductive dehalogenation by nanoparticles (for instance, Fe^0). ERH is applied either as three- or six-phase heating systems. Since the 1990s many full-scale six- as well as three-phase ERHs were demonstrated (McGee 2003). Today, six-phase hexagonal array and three-phase triangular array are applied to treat irregularly-shaped polluted sites where soils are heated by a low-frequency electric charge delivered through three/six electrodes in globular array.

Most applications of ERH focus on remediating chlorinated solvents and petroleum hydrocarbons (Triplett Kingston et al. 2010). About 99 % of the contaminants of low boiling point such as PCE and TCE were remediated successfully by ERHs either alone (US DOE 2005), or in combination with steam injection extraction

(Heron et al. 2005) as detailed in Table 2. In ERH, uniform heating is achieved throughout the treatment area by maintaining the temperature control monitoring points. It also provides the feasible physical conditions required for the release of contaminants from tight soil tensions to an unsaturated region, from where they are extracted either by multiphase or vapor recovery system. Yet, high concentrations of heavy hydrocarbons and organic carbon content interfere and prevent the recovery of some organic contaminants. Fractured bedrocks can only be heated by ERHs and not nonporous rocks. However, integration of ERH outlimits the treatability of soil vapor extraction and multiphase solvent extraction techniques regardless of the permeability of soil or water saturation level, almost to any physical setting (Heron et al. 2005). Treatment time by ERH is typically less than a year.

Recently, ERH has been used to treat contaminated sedimentary bedrocks, and field trials were held in Maryland, New Jersey and Indiana (Kluger and Beykle 2010). In 2006, at Annaolis, Maryland, tetrachloroethylene (TCE) contamination was observed extensively in surface soils. The site (765 m^2) was heavily cemented with dense, fine silt and sand layers that extended to 12 m beneath the ground level. The remedial objective was to reduce the TCE concentration by 95 % in the contaminated site. Bedrocks were heated up to 90 °C for 7 weeks. After the operation time, when the samples were assayed the initial TCE concentration declined by 99.9 % which was more than the anticipated goal and the study proved the reliability of ERH even for bedrock treatments. Truex et al. (2011) evaluated the co-effect of zero-valent iron (ZVI) and ERH for in-situ TCE remediation in an aquifer at field-level, and observed 85 % reduction of TCE in 60 days of heating, confirming that the success of remediation was due to enhanced in-situ dechlorination and minimization of TCE volatilization when using combined techniques. The problem of lateral migration of injected steam and DNAPLs away from the contaminated to uncontaminated zone was prevented by the creation of hot floor and heat-up walls, wherein 99 % remediation was observed in an age-old chlorinated solvent (TCE, DCE, VC, benzene and toluene)-containing site within 8 months of ERH treatment (Sutter 2012).

Electrical resistance heating has been implemented to date at field-level in various superfund sites (US DOE, Young-Rainey STAR center, Florida; ICN Pharmaceuticals site, Oregon; Air force plant, Texas; Charleston Naval complex, South Carolina and Installation restoration site, California). Six-phase ERH (US EPA 2012) was highly successful in remediating chlorinated solvents, halogenated VOCs- and BTEX-contaminated soils, groundwater and DNAPLs from >95–99 % in 3–8 months when the treatment temperature ranged from 60 to 80 °C with a target power of >400–2000 kW in most cases at full-scale. In 2003, the US DOE completed a full-scale NAPL remediation at the Young-Rainey STAR center, Florida. Contaminated zone extended to nearly 10 m below the subsurface and was about 900 m^2 in area representing a total treatment volume of 9120 m^3. The site was contaminated with approximately 2500 kg NAPL constituents such as TCE, DCE, methylene chloride, toluene and petroleum hydrocarbons. A combination of electrical resistance heating and steam-enhanced extraction was used to remediate the contaminated site. Within 6 weeks, nearly 1000-fold mass of the contaminant was removed when the site was heated to a target temperature of 84 °C. In less than 5 months, all the contaminant concentrations reached well below the remedial goals (99.8 % removal).

ERH is most successful when integrated with other in-situ techniques (Heron et al. 2005). Only in some cases ERH failed to achieve the remedial goal of >95 % of immobilized contaminant level in the limited time frame at field-scale. According to the reports of FRTR (2005a), the highly saturated condition of the soil reduced its electrical resistance and consequently the total remedial efficiency was only 86 % over 9 months even when the soil was heated to 89 °C. In such a scenario, the integration of reductive dechlorination with ERH could enhance the remediation process. Integration of ERH with several remedial systems and adoption of novel recovery systems other than GAC-like material are to be explored in the near future to overcome the partial failure when implemented at full-scale. According to US EPA (2012), it costs an estimated 42 and 96 US$/m^3 at two full-scale ERH sites.

3.1.3 Electromagnetic Heating: Radio Frequency/Microwave

Radio frequency and microwave heating are in-situ processes that heat soil and enhance vapor extraction using electromagnetic energy. This technology had been used since the 1970s where bitumen was recovered from tar sand deposits. Radio frequency or microwave heating can be applied as identical to steam injection. The only difference is that antenna-like applicators are inserted into the exterior boreholes instead of steam. This technique can heat the soils over 300 °C. Generally, a set of frequencies (6.5, 13.5, 27.1 and 40.5 MHz for radio frequency, and 300 MHz to 300 GHz for microwave heating) assigned by the Federal Communications Commission (FCC) is used to remediate the volatile (PAHs and PCBs) as well as non-volatile (heavy metals) contaminants by electromagnetic heating (Appleton et al. 2005). Compared to conventional heating, radio frequency/microwave heating possesses the advantage of selective heating, shorter heating time, better process control and no direct contact with the heated material. It is also proved that microbial activity is not inhibited by electromagnetic fields (Jones et al. 2002). However, the technology is self-limiting because at one particular stage, the soil heats up and dries which stops the flow of current and limits the removal of the pollutant. Over the last decade, microwave technology has been integrated with UV illumination, pyrolysis and advanced oxidation processes for the conditioning and sanitation of sludge, regeneration of activated carbon and stabilization of heavy metals (Horikoshi et al. 2002; Klan and Vavrik 2006; Bo et al. 2006; Wu 2008).

Field-level application of electromagnetic heating is very limited. Especially, microwave heating is applied only at laboratory-level to clean up contaminated sites (Jones et al. 2002). Laboratory-scale trials using microwave energy to remediate contaminated soils focused mainly on the elimination of contaminants like PCBs, PAHs, HCB, chromium and heavy metals (Tai and Jou 1999; Abramovitch and Capracotta 2003; Liu and Yu 2006). Liu and Yu (2006) explored the role of GAC in microwave remediation of PCB-contaminated soil. More than 90 % PCB was remediated with 700 W microwave power after 15 min of irradiation when 200–500 °C temperature was maintained. Appleton et al. (2005) removed 99.8 % mercury, cyanides and PCBs in a very limited time span of 15 min to 3 h microwave treatment. To date, several studies proposed different microwave-incorporated remedial techniques only at lab-scale for various toxins in aqueous solutions, for example microwave irradiation in association with GAC (Bo et al. 2006), hydrogen peroxide (Klan and Vavrik 2006), UV/hydrogen peroxide (Han et al. 2004), titanium oxide nanotubes (Zhanqi et al. 2007), and UV/titanium mounted activated carbon (Liu et al. 2007). These were successful in removing 85–98 % toxins within 10–20 min microwave treatment. Thus, there is more potential to explore the performance of microwave heating in pilot- or field-scale in the near future.

On the other hand, radio frequency heating is applied at full/pilot-scale to remediate VOCs even in fractured bedrocks. Not many field-scale remediation studies are available for radio frequency heating compared to steam injection/electrical resistance heating. Huon et al. (2012) studied the effect of radiowave supported degradation of BTEX and petroleum hydrocarbons in a former petrol station site in the UK. The 99 % remediation achieved with a target temperature of 50 °C in 2 months indicated that when the target temperature is increased up to 50 °C, it attains the maximum degradation of VOCs at field-scale in a shorter period than usual. Recently, dielectric heating using radiofrequency energy is emerging as a novel choice for energy transfer applicable in quite a few remediation technologies, such as adsorptive-catalytic off-gas treatment, biodegradation, decontamination and/or drying of brickworks and thermal regeneration of drying agents in natural gas/biogas treatment (Huon et al. 2012). Overall, many possibilities exist to utilize the principle behind electromagnetic heating and employ its prime advantage of successful remediation in a short time at large-scale by designing new remedial systems. It costs about 150–250 US$ per Mg for small-scale electromagnetic heating clean up.

3.1.4 Thermal Conductive Heating/Thermal Desorption

After 12 years of improvement and full-scale demonstrations, thermal conduction heating, also known as thermal desorption, is currently a technically mature, cost-effective soil and groundwater remediation method with vacuum extraction (Heron 2008). In thermal conduction, vacuum and heat are simultaneously applied to subsurface land (to about 1 m), either with vacuum wells or surface heater blankets or with a group of vertical heaters operated at very high temperature (>500–900 °C). In this method, transport of radiant heat dominates near the heaters and most of the heating at greater soil depths is accounted by thermal conduction. As the source area gets heated up, pollutants in the soil are vaporized or destroyed either by boiling, evaporation, oxidation, pyrolysis or steam distillation (Baker and Heron 2004). Though thermal conduction heating is not designed to degrade organic pollutants, thermal desorbers can still be used to partially or completely remove the organic compounds depending upon the type of organics present and the temperature of the desorbers. Generally, the extracted hydrocarbons are discharged into the atmosphere after treating in an afterburner, carbon adsorption unit, condenser or catalytic oxidation chamber. Oxidizers and afterburners decompose the organic compounds. Carbon adsorption units and condensers trap the organics for disposal or for subsequent treatment.

A thermal remedial approach based on zone combustion method for the remediation of dioxin-contaminated zone was proposed by Kasai et al. (2000) and Harjanto et al. (2002). Stable thermal remediation of coke particles in the packed soil bed was employed in this method. In a laboratory-scale experiment, 90 % dioxin was removed from the soil, and the removal rate was improved with the pretreatment (addition of limestone, pre-granulation and drying) of the contaminated soil. Thermal blankets and thermal wells proved to be greatly efficient in removing a diverse range of contaminants such as hydrocarbons, pesticides, PCBs, inorganics (Hg, As and Cd), DNAPLs, gasoline, combination of radionuclides, chlorinated solvents, carcinogens, etc. (Conley et al. 2000; TerraTherm 2010).

Generally, there are two types of thermal desorption systems based on the temperature employed: high temperature (HTTD: 315–537 °C) and low temperature (LTTD: 93–315 °C) thermal desorption systems. LTTD/hot gas decontamination is applicable for VOCs and fuels, wherein HTTD is useful to remove SVOCs, PAHs, PCBs and pesticides. Hot gas decontamination/LTTD removed 99.9 % explosives at the US Army Environmental Center, and is widely used to decontaminate the equipment and structures polluted with explosive residues using a temperature of 250 °C created by hot air (US EPA 2012). Time taken to clean up 20,000 Mg contaminated material was only 4 months with the LTTD system (FRTR 2005b). Another advantage is that the system's effectiveness is not affected by the subsurface heterogeneities compared to other methods. With reference to conductive heating, the distance between the wells is taken into account because the closer the wells are, the faster the desired temperature obtained with increased remedial efficiency (Bierschenk et al. 2004). Conductive heating operates best in unsaturated soil. In case of soils with low hydraulic conductivity, dewatering and combination of piping activities promote the pollutant degradability (US EPA 2004).

Compared to steam injection, vertical and horizontal sweep is very uniform in conductive heating/thermal desorption system. Also, ISTD is adaptable to many types of *ex*-situ processes. Since flow paths are created even in tight silt and clay layers, escape and capture of the vaporized waste product is relatively higher in this operation. Furthermore, improved transport of vaporized contaminants prevents the soil's drying and shrinking. In this system of heating, however, recovery of toxin depends on the toxin type. Also contaminant recovery is essential where metals are not subject to decomposition reactions like mercury. Other concerns include the need to control water recharge for the polluted regions located below the water table, site accessibility for better installation, and the high cost of material handling requirements. However, the combined effectiveness of both vapor and heat flow leaves no area untreated, yielding a sweep efficiency of nearly 100 %.

Conductive heating/in-situ thermal desorption is a successful, heating technique that could be exploited for field-scale remediation of NAPL-contaminated zone, much like steam/hot air injections and ERHs. Field studies conducted so far confirm the potential of conductive heating to remediate >95 % VOCs and SVOCs (TerraTherm 2000; Carmen 2010; TerraTherm 2010; Amy et al. 2010). *In*-situ thermal desorption with dual phase extraction is a promising technology at field-scale as it remediated 99.9 % PCP, TCE, DCE and VC from a sediment of 3915 m^3 volume in 9 months by employing heat of 100 °C (TerraTherm 2010). Amy et al. (2010) explained the positive effect (97 %) of combined application of multi-phase extraction and thermal conductive heating at field-scale over an 8-month period in a site contaminated with chlorinated solvents. TerraTherm (2000) recommended thermal desorption combined with vacuum extraction for removing volatile organics from soil at field-scale. Success of conductive heating depends on the controlled groundwater flow as it is essential to enhance the rate of subsurface heating in a shorter lifespan with accelerated VOC removal. Such controlled groundwater flow was successful in remediating 99 % TCE, DCE and VC in 566 m^3 contaminated aquifer within 3.5 months (Carmen 2010). Therefore, in the case of conductive heating to enhance its efficiency, special control systems must be designed in the near future. FRTR (2005b) estimated that the cost ranges from 35 to 250 US$ to treat per m^3 contaminated site by thermal conduction/desorption heating systems.

3.1.5 Vitrification

In-situ vitrification (ISV) has been employed since the late 1990s. It uses an extensive electrical heat of very high temperature (1600–2000 °C) so that most contaminants are volatilized (organics), while the remainder (heavy metals and radionuclides) are converted into chemically-inert, obsidian glass-like products (Dermatas and Meng 2003). Vitrification can be grouped into three processes on the basis of energy source: (a) electrical processes (electrical energy through graphite electrodes), (b) thermal processes (external heat and typical reactor), and (c) plasma processes (high energy received via electrical discharges) (Acar and Alshawabkeh 1993; Wait and Thomas 2003). Specifically, vitrification converts leachable sludge into an immobile solid so that wastes are prevented from contaminating the soil, groundwater and surface water.

In-situ vitrification is particularly suited to treat high-level radiowastes (US EPA 1997a) as it is a non-contact technology (workers are not exposed to any waste) with effective contaminant destruction and immobilization capacity (FRTR 2006). In this system, redisposal is not required after treatment and it is a best option when a site is difficult to clean or standards of clean up are high. The other advantages of vitrification are: a vitrified product may be usable; as it is an inert, impermeable solid, it reduces leaching for a greater time period; an extensive array of organic and inorganic pollutants can be treated; and both in-situ and *ex*-situ options are available. However, ISV has some limitations. Energy requirement and cost to treat contaminants at deeper depths are very high, and it requires special application methods (Thompson 2002). To ensure that the contaminants are completely immobilized, long-term monitoring is often required. *In*-situ vitrification is not applicable when contaminated soil is <2–7 m below ground level. To overcome the limitation of melt ejection event, Planar ISV was developed with some modification of conventional vitrification (replacement of the horizontal array of started path material by vertical planes), and successfully demonstrated at the Los Alamos national laboratory park in the late 1990s (Coel-Roback et al. 2003). ISV is applicable to sites with high clay content. To treat the materials in permeable aquifers, dewatering is required. At the same time dynamic compaction is required to treat sites with large voids (US EPA 1997b). The overall cost for in-situ vitrification ranges from 80 to 300 US\$/m^3 (Khan et al. 2004).

Dellisanti et al. (2009) presented an in-field joule heating vitrification method that completely melted tons of zinc- and lead-rich ceramic waste by progressive heating up to 1850 °C. Field studies related to in-situ vitrification application were carried out only in the late 1990s, and field-scale remediation studies of this specific technology are not available in recent years. Spalding et al. (1992) achieved 99.9 % remediation of strontium- and cesium-contaminated site in Tennessee within 5 days when the treatment zone was raised to a temperature of 1500 °C. Using filling materials helped to achieve the targeted treatment temperature in short time. In order to reduce the treatment cost involved in excavation in *ex*-situ vitrification mechanisms, in-situ vitrification could be an option (US EPA 1997a). The reason for the scarce applicability of this technology in recent years might be due its high treatment cost. If a suitable alternative to reduce the treatment cost is found, this means that vitrification can completely clean up even a very high contaminated site in a year. The scope of vitrification technology has increased to immobilizing high level nuclear waste so that it is easy to recycle nuclear fuel and reuse it. Thus, vitrification is a promising technology for managing nuclear waste and more system models are expected to be developed in the long-run (Vienna 2010).

Overall, among the in-situ thermal treatment technologies, electrical resistance heating, steam stripping and thermal conductive heating are the most widely exploited and successful ones at field-scale. In contrast, electromagnetic heating and vitrification technologies must be improved to overcome the existing limitations for a wider application.

3.2 Soil Flushing

Soil flushing is a developing technology that has been used successfully in the full-scale removal of organics. The US EPA completed the construction of a mobile soil flushing system during the early 1990s for use at spills and uncontrolled hazardous waste sites (FRTR 1999). In in-situ soil flushing, an aqueous solution or water is flooded into or sprayed over the contaminated surface, the pollutant bearing fluid is then collected by strategically placed wells or trenches and brought to the surface for removal or on-site treatment, recirculation and reinjection (Logsdon et al. 2002; Di Palma et al. 2003). Extracted fluids are always subjected to required treatments to meet the appropriate discharge standards before being released in the locality (Otterpohl 2002; Son et al. 2003). Flushing solutions may be water, acidic aqueous solutions, basic solutions, chelating or complexing agents, co-solvents or surfactants (US EPA 1990). Water will extract water-soluble constituents, while acidic solutions aid in removing metals such as Zn, Pb and some phenols. Chelating, reducing and complexing agents are useful to recover metals. Surfactants assist in the removal of hydrophobic organics (Logsdon et al. 2002; Alter et al. 2003). Generally, surfactants and co-solvent flooding technology are widely practiced for removing fuels and chlorinated solvents. Using a two-phase co-solvent flushing fungal biosorption process, in-situ remediation of DDT-contaminated soil was achieved by Juhasz et al. (2003).

Soil flushing is considered to be a mature technology due to its oil field applications. In relatively uniform and permeable soils, flushing is most efficient. However, high per cent soil, silt/clay content, surfactant adherence to soil, and reactions of flushing fluids with soil limit the efficiency of the flushing process (Reddy and Saichek 2003). The achievable treatment level varies depending on the soil hydraulic conductivity and contact as well as appropriateness of the flushing solution with the contaminant. Soil flushing is successful in treating pollutants that do not tend to sorb onto the soil and the ones that are fairly soluble in the extracting fluid. Acidity and alkalinity of the soil, and precipitation resulting from interaction between flushing fluid and soil interferes with the system's efficiency (Khan et al. 2004). It generally takes longer time to achieve clean up standards by soil flushing. However, the main key advantages of this remediation technique are that the recovered fluids are reusable and the process does not involve excavation as well as redisposal problems. This negates the cost and risks associated with the pollutant removal. Also, it is relatively very simple to design and operate (Reddy and Saichek 2003).

Of the uses of water, cyclodextrins, chelants and surfactants as flushing liquids, surfactant-enhanced remediation was widely employed to remediate sites contaminated with heavy metals and hydrocarbons at field-scale (Lee et al. 2005), pilot-scale (Svab et al. 2009), and laboratory-scale (Wang and Mulligan 2009). Soil flushing was able to achieve more than 90 % remediation at pilot-scale and more than 88 % remediation at field-scale when combined with a suitable cationic surfactant. When anionic surfactants were used for PCBs, it could achieve only 56 % remediation in 12 months. Thus, the type of surfactant used determines the success of soil flushing. Svab et al. (2009) studied the flushing process of a real PCB-contaminated site in which an aqueous solution of anionic surfactant (Spolapon AOS 146 solution of 40 g/L) was passed through 1.7 m^3 of polluted sandy soil. In 2.5 months, a decontamination efficiency of 56 % was achieved, but it could have been 90 % or above if duration of flushing was extended for another 6 months. Soil flushing with surfactant solution was reported to be a serious competitor to expensive thermal methods that are used to treat soils of low contamination levels as it is cost-effective and suited for both in-situ and *ex*-situ types.

Lee et al. (2005) found that 88 % TPH could be removed by flushing 2 % surfactant solution over the diesel-contaminated soil with a hydraulic conductivity of 2×10^{-4} cm/s for 44 days. Jawitz et al. (1998) confirmed that even complex NAPLs having more than 200 constituents could be remediated by flushing 5.5 % solution composed of surfactant (polyoxyethylene oleyl ether) and alcohol (pentanol) mixture.

Schnarr et al. (1998) proved the efficiency of in-situ chemical flushing using potassium permanganate at field-scale. Within 120 days, around 62 % of the initial source concentration of chlorinated solvents was reduced by flushing 10 g/L of potassium permanganate at total flow rates up to 100 L/day. Jawitz et al. (2000) reported the enhanced solubilization and extraction of DNAPLs at a former dry cleaning site in Jacksonville, Florida by in-situ alcohol flushing (95 % ethanol and 5 % water mixture over a period of 5 days). At a former manufactured gas plant site, Reddy et al. (2010) evaluated the enhanced remediation of soil contaminated with PAHs and heavy metals using different flushing agents, which included deionized water, chelant (0.2 M EDTA), cyclodextrin (10 % hydroxypropyl-β-cyclodextrin/HPCD) and surfactant (5 % Igepal CA-720). The effect of each flushing solution was tested in distinct column at a constant hydraulic gradient (1.2×10^{-4} cm/s).

The effects of rate limited solubilization or desorption of PAHs were also investigated by additional column tests using HPCD and Igepal at a lower hydraulic gradient (0.2×10^{-4} cm/s). EDTA (about 0.2 M) removed a maximum of 25–75 % of the toxic heavy metals from the soil under different hydraulic gradient conditions compared to other flushing agents. Also, the removal of PAHs depended on the micelle formation in surfactant-enhanced systems, whereas in the HPCD-enhanced system, it relied on the stereo-selective diffusion of hydrocarbons to the non-polar cavity of HPCD. Overall, the study showed that selectivity towards the target contaminant, flushing solution affinity and the existing hydraulic gradient condition determine the efficacy of contaminant removal in soil flushing systems. Lestan et al. (2008) also proved the efficiency of chelating agents like EDTA in remediating 60 % metals. Udovic et al. (2007) reported that EDTA could immobilize Pb by 83 % and that immobilization of Pb was enhanced (>6.5 times) by the use of earthworm, *Eisenia foetida*.

Cyclodextrin-enhanced vertical flushing (Blanford et al. 2001) and citric acid-enhanced flushing (Kantar and Honeyman 2012) methods successfully remediated uranium (98 %) and TCE (99 %) at field-scale. Kim et al. (2008) found that Co and Cs removal efficiency by electrokinetic flushing for 5 days was 6.8–7.7 times better than electrokinetic remediation alone. The field studies that were successful in remediating contaminants by flushing techniques, surface flushing in particular, are many as detailed in Table 3. Integration of electrokinetic remediation has gained momentum in recent years. Tsai et al. (2009) adopted a three-stage treatment train system that started with a preliminary biodegradable surfactant application followed by Fenton-like oxidation flushing and ended with enhanced bioremediation approach. They reported a TPH removal of 80 % from oil-contaminated soil. To attain 99 % remedial efficiency, which is currently around 60–80 %, much more integrated methods can be designed to enhance the efficacy of bioremediation by soil flushing. Also, exploring more avenues to reuse the recovered flushing solution with groundwater and separation of reusable surfactants from the flushing fluids, these strategies may improve the operational efficiency of the soil flushing system. Also, better monitoring systems for air emissions of volatile toxins from recovered flushing fluids should be established. The flushing cost depends on concentration and type of extraction fluid used. Roughly, 20–200 US$ was spent to treat a Mg of contaminated soil (US EPA 2012).

Table 3 Performance of notable in-situ soil flushing studies

Site	Key contaminant	Remediation (%)	Associated technology	Specific feature	Outcome	Type
1. Military vehicle repair shop site, Pusan, Korea	Petroleum hydrocarbons, Kerosene, Lubricating oils	88	Surfactant-enhanced remediation and steam injections	• Circulation of 2 % sorbitan monooleate surfactant solution in contaminated site • Chemically-enhanced treatment system with dissolved air floatation • Significant than flushing with water alone	√√	F
2. Oxidized mine tailing sandy soil sample, Bathurst, Canada	As, Pb, Cu, Zn	93	Surfactant-enhanced subsurface remediation	• Use of 70 pore column flushing • 0.1 % Biosurfactant (Rhamnolipids from *Pseudomonas aeruginosa* JBR425) in alkaline solution was flushed	√√	BS
3. OU1 site, Hill AFB, Layton, USA	TCA, Naphthalene, TCE, TMB, Decane	90	Cyclodextrin-enhanced vertical flushing	• 10 % Cyclodextrin was flushed for 10 days at the rate of 4.54 L/min	√√	F
4. Quartz soil, Mersin, Turkey	U	98	Citric acid-enhanced remediation	• Increasing concentration of citric acid increased the contaminant removal efficiency • Maintenance of slightly acidic to alkaline condition was required for better performance	√√	BS
5. Real PCB-contaminated soil, Czech Republic	PCB	56	Surfactant-enhanced remediation	• Use of anionic surfactant (Spolapon AOS 146) • Contaminant treatment time was 1 year which could be prolonged for attaining success	X	P
6. TCE-contaminated aquifer, Tucson, Arizona	TCE	99	Cyclodextrin-enhanced vertical flushing	• Use of self-controlled air strippers that reduced monitoring related factors • One pass cyclodextrin flush was cost-effective	√√	PS

7. Former manufactured gas plant site, New York, USA	PAHs, Heavy metals	50–75	Surfactant-enhanced remediation	• Performance of water, chelant (EDTA), surfactant (5 % Igepal), and cyclodextrin (10 % HPCD) was compared at a time • Surfactant-enhanced degradation was significantly efficient	√	P
8. US coast guard, Elizabeth, North Carolina	Jet fuel	98	Biodegradation	• Rate of biodegradation could be accelerated by injecting oxygen through injection pumps	√√	P
9. CFB Borden research site, Canada	PCE, TCE	62	*In*-situ oxidation	• Potassium permanganate was flushed at a rate of 100 L/day for 290 days • Effectiveness depends on the distribution and dissolution of DNAPLs on the subsurface	√	F
10. Winton's food and fuel, Palmer, USA	MTBE	>95	Multiphase extraction	• Remediation system installed was SVE and passive aquifer oxygenation system • Almost all MTBE was removed in 2 months	√√	F
11. Hill AFB, OU1 site, Florida	Jet fuel	99	Solvent-enhanced remediation and SVE	• A mixture of 70 % ethanol and 12 % pentanol in water was flushed	√√	F
12. Hill AFB OU2 site, Texas	TCE	99	Surfactant-enhanced remediation	• 8 % Surfactant, 4 % isopropanol, and 4 % NaCl were used for flushing	√√	F
13. Dover air force base test cell, USA	PCE	64	Solvent-enhanced remediation and SVE	• Co-solvent flushing was implemented • 70 % Ethanol was flushed	√	F
14. Hill air force base OU1 site, USA	Jet fuel, Chlorinated solvents	85	Solvent-enhanced remediation and SVE	• Co-solvent flushing was employed • 70 % Ethanol and 12 % pentanol was flushed	√√	F
15. Former dry cleaner site, Jacksonville, Florida	PCE	63	Solvent-enhanced remediation	• 95 % Ethanol was flushed in 3 days	√	F
16. Hill air force base, Utah	n-Decane, TMB, Naphthalene, DCB, Xylene	90–95	Surfactant- and solvent-enhanced remediation	• Microemulsion flushing was employed • 10 % Surfactant (polyoxyethylene), and 5.5 % pentanol was flushed in 18 days	√√	F

√√, Successful; √, Partially successful; X, Not successful; P, Pilot-scale; F, Field-scale; BS, Bench-scale

3.3 Fracturing: Pneumatic/Blast-Enhanced/Lasagna™/Hydro

Low-permeable and fine-grained soils that are a major challenge for in-situ pollutant removal by conventional techniques like soil vapor extraction and bioremediation can be treated by fracturing (Gafar et al. 2008). Fracturing techniques are categorised into pneumatic fracturing, blast-enhanced fracturing, Lasagna™ process for treating contaminated soils, and hydrofracturing for remediating contaminated waterbodies (FRTR 2012). Of all the available methods, hydrofracturing and pneumatic fracturing are the most widely used ones at full- or pilot-scale. These methods enhance the mass transfer of the pollutant in dense soils by creating new fractures and by making the existing fractures larger. Creating fractures helps to enhance the permeability and alter the path of liquid flow, thereby assisting in increasing the efficiency and cost-effectiveness of conventional in-situ treatment technologies. Fracturing also helps to reduce the number of extraction wells, labor and material costs required for treating the contaminated site. In the case of blast-enhanced fracturing, new fractures are created when the drilled boreholes are filled with explosives and detonated. It is applicable in sites with fractured bedrock formations (Miller 1996). Hydrofracturing is a pilot-scale technology where relatively high pressure fluid, especially water, is injected at modest rates into the source area that is to be fissured which initially creates a circular notch beneath the borehole. Later when biodegradable gel and slurry of sand is forced at high pressure, individual fractures are created.

Eventually, fractures become highly permeable as the gel degrades (Cipolla et al. 2008). To enhance the contaminant recovery, soil vapor extraction technology can be used in conjunction with the hydraulic fracturing process (Nilsson et al. 2011). Lasagna™ is an integrated technology that combines the principle of electroosmosis with fracturing, wherein fractures are created by hydraulic fracturing (Roulier et al. 2000). In pneumatic fracturing, existing fissures are enlarged and new fractures or channels are created by injecting highly pressurized air or other gases, and contaminant removal is accelerated by in-situ electrokinetics, enhanced in-situ biodegradation, soil vapor extraction and bioventing (Bhandari et al. 2007). This type of fracturing by gases is employed only when fractures are left to remain open without support for a longer period of time.

With no particular target group, fracturing is applicable to treat a diverse array of contaminants. It is used chiefly to fracture limestone, clay, silt, bedrocks and shale. However, fracturing does not work well in areas of high seismic activity and clay content. Usually, fractures are installed at 2–18 m below the subsurface. Even shallow fractures roughly between 2 and 8 m could be established. By itself, fracturing is not a remediation technology. To facilitate the reduction of concentration and mass of the contaminant, it has to be combined with other techniques. One of the noted advantages of fracturing is that it could extend the applicability of several other in-situ remedial approaches. For example, fracturing enhances fluid flow rate in the fissured zones in in-situ electrokinetics, enhances the delivery of nutrients and oxygen into inaccessible locations in case of in-situ biodegradation, creates fractured pathways to collect the injected air laden with contaminants in in-situ air sparging, and creates heating zones by injecting graphite into the fractures in in-situ vitrification. However, fracturing has some limitations: (1) final location of newly created fractures is uncontrollable; (2) fracturing near existing wells could damage the well casings and seals; (3) it creates new routes for unnecessary spread of contaminants; (4) prior investigations of the possible structures of trapped free product and underground utilities are always required; and (5) this technique is not appropriate for fill materials or disturbed soils (Nilsson et al. 2011).

Regarding hydraulic fracturing, relatively large volumes of solid materials are delivered to the subsurface as fillings for fractures that could slowly release nutrients and oxygen to improve in-situ aerobic degradation of toxins by microbes (Davies et al. 2012). Even an electrically conductive material like graphite is filled in the fractures to enhance electroosmosis and perhaps electrical heating for in-situ vitrification. Also, metal fractures like elemental iron are filled in the created fractures to degrade an extensive range of chlorinated compounds favoring reductive dechlorination (Comba et al. 2011). More successful field studies employing nanoparticles in fractures created either by pneumatic or hydraulic means are documented by Forman et al. (2010). At field fracturing, the medium allows the creation of pathways for distribution of nano-ZVI particles into clay as well as sandy soils (Saleh et al. 2008).

Several pilot-scale studies (Table 4) confirm that, when fracturing techniques are integrated with other in-situ treatment technologies, they could help to achieve the remedial goal (Nilsson et al. 2011). The first documented field study targeting chloroform and ZVI usage in remediating a VOC-contaminated site by pneumatic fracturing was at Hunters Point Shipyard, San Francisco, California by Forman et al. (2010). They reported that groundwater contaminated by TCE over 100 μg/L and PCE above 15 μg/L could be effectively treated by integrating ZVI with pneumatic fracturing. Another full-scale pilot demonstration of integrating pneumatic fracturing with bioremediation in a gasoline-contaminated site in-situ was done by Venkatraman et al. (1998). In an in-situ bioremediation zone set up, soil amendment delivery directly to the indigenous microbial populations, transport rates and subsurface air flow were enhanced by pneumatic fracturing system. The system operated for 50 weeks and it comprised periodic pumping of nitrate, ammonium and phosphate salts. Formation of a series of aerobic methanogenic and denitrifying bacterial degradation zones were indicated by off-gas data and 79 % of soil-phase benzene, toluene and xylenes were removed using the integrated approach. Accounting for all physical losses, mass balance calculations showed that biodegradation removed nearly 85 % of the total mass of BTEX. Nilsson et al. (2011) conducted a steam injection pilot-scale test in the unsaturated zone of a strongly heterogeneous fractured soil polluted by jet fuel. Formerly, sub-horizontal and sand-filled hydraulic fractures were created at three depths to stimulate the soil. Through one hydraulic fracture, steam was injected and from the remaining fractures, NAPL vapors were extracted by applying vacuum-enhanced extraction. Hydraulic fractures prevented the escape of injected steam and extracted gas/liquid. Concentration of total hydrocarbons was reduced by 70 % over the entire zone (1.5–5.5 m depth) and by 40 % in the upper target zone (1.5–3.9 m depth). A similar study using hydraulic fracturing with steam injection was reported by Tzovolou et al. (2010) in a field-scale.

Table 4 Performance of selected in-situ remediation studies at field- and pilot-scale

Site	Contaminants	Highlights/comments	Result	Scale	Reference
Soil fracturing					
1. Robert Gray army airfield, Ford Hood, Texas	Jet fuel	• Hydraulic fracturing combined with steam injection and electroheating of unsaturated zone of tight clay soils was employed • Pollutant removal efficiency was 77–86 %	√	P	US EPA (2012)
2. Petroleum-contaminated site, Saskatchewan, Canada	LNAPL, Petroleum hydrocarbons, Benzene, Toluene	• Dual-phase vacuum extraction with pneumatic fracturing enhancement system was suggested to be supportive for groundwater remediation • Bioslurping with enhancement of pneumatic fracturing achieved complete remediation at sites contaminated with very high concentration of hydrocarbons	√√	F	Zhang et al. (2009)
3. Gasoline-contaminated site, New Jersey	Benzene, Toluene, Xylene	• Integration of pneumatic fracturing with in-situ bioremediation was established • In in-situ bioremediation, for a period of 50 weeks, phosphate, nitrate, and ammonium salts were injected periodically which helped to remove 85 % BTX	√√	F	Venkatraman et al. (1998)
4. Hunters point shipyard, San Francisco, California	TCE, Chloroform	• Pneumatic injected micro-scale zero-valent iron was used to treat the chlorinated compounds • This technology was employed in target hotspot area where concentration of PCE and TCE exceeded 15 and 110 mg/kg, respectively	√√	F	Forman et al. (2010)
5. Military airport, Poland	Jet fuel	• Combination of steam injection with hydraulic fracturing was implemented • Average concentration of total hydrocarbon was reduced by 72 %	√	P	Nilsson et al. (2011)
Air sparging					
1. Contaminated site, Kansas	TCE, DCE	• *In*-situ ozone sparging was used • TCE concentration was reduced from 94 to 100 %	√√	F	Nelson et al. (1994)
2. Five points superette, Johnsonville, USA	MTBE	• About 98 % remediation of MTBE was achieved in 2 years of air sparging	√√	F	Wilson (2001)

3. Contaminated aquifer, Kalkaska, Michigan	BTEX	• Pulsed air injection was the technology used (combination of volatilization and biodegradation mechanism to enhance contaminant removal efficiency) • Increased average removal rate of hydrocarbons by a factor 3 compared to conventional air stripping system	√√	F	Yang et al. (2005)
4. Coastal plain sediments, New Jersey	TCA, TCE	• Air sparging combined with SVE was the best alternative to conventional pump-and-treat technology at field level	√√	F	Gordon (1998)
5. Petroleum hydrocarbon spilled site, Kaohsiung, Taiwan	BTEX	• More than 70 % BTEX was removed through biosparging in 10 month remedial period	√	F	Kao et al. (2008)
Physical barriers					
1. Nortel network site, Northern Ireland	TCE	• Zero-valent iron permeable reactive barrier was installed in groundwater • Additive remediation effect was achieved by reductive dechlorination due to zero-valent iron • Ten years performance evaluation of the established barrier system in different sites. Finally, 98 % remediation was achieved per site in 2 years	√√	F	Phillips et al. (2010)
Multi-phase extraction					
1. Sparks solvents/fuel site, Sparks, Nevada, USA	MTBE, PCE, TCE, Petroleum hydrocarbons	• Remediation system consisted of granular activated carbon/fluidized bed reactor • 99 % Remediation was achieved after 2 years	√√	F	US EPA (2012)
2. BP at south of the border, South Carolina, USA	MTBE	• Air sparging with multi-phase extraction was implemented • Totally, 1350 m^2 area was treated • 88 % MTBE was removed, and the total remediation cost was US$ 2,14,000	√√	F	US EPA (2012)
3. Site at Texaco, Healdsburg, USA	Benzene, Ethylbenzene, MTBE, Butyl alcohol, Toluene	• Multi-phase extraction was combined with pump-and-treat technology • 97 % Remediation was achieved	√√	F	FRTR (2012)

(continued)

Table 4 (continued)

Site	Contaminants	Highlights/comments	Result	Scale	Reference
4. Greek petroleum refinery, Greece	LNAPLs	• Bioslurping technology was operated for 4 years • Significant groundwater contamination was not minimized by free-phase recovery (bioslurping), hence integration of air sparging was suggested	√	F	Gidarakos and Aivalioti (2007)
5. Confidential So., California, USA	Chlorinated volatile organics, DCA	• SVE system combined with thermal conductive heating along with high vacuum single pump extraction system employed • Around 3538 kg of DCA and CVOCs (99 %) were removed in 400 days • Costed about 58 US$/m^3	√√	P	US EPA (2012)
6. Sand pit, CFB, Borden, Canada	Hexane, Pentane	• Multi-phase extraction system was used • LNAPLs were recovered using a patented technology—'Supersaturated Water Injection' where nucleating CO_2 bubbles could volatilize LNAPLs • 50–70 % LNAPLs were removed which was comparatively higher than air sparging even when smaller volume of gas was injected	√√	P	FRTR (2012)
Electrokinetic remediation					
1. Chromated copper arsenate-treated waste wood, Denmark	As, Cr, Cu	• Electrodialytic remediation (combination of electrokinetics with low level direct current as cleaning agents) was established using electrodes of 60 V set up at increased distance (between 60 and 150 cm) than usual • 0.5 M Phosphoric acid and 5 % oxalic acid were used as additives to facilitate desorption of CCA compounds • Within 21 days, 82 % Cr, 88 % Cu, and 96 % As were removed	√√	P	Pedersen et al. (2005)
2. Red soil, Yingtan, Jiangxi Province	Cu	• 700 kg Cu-contaminated red soil was remediated using 80 V energy • 76 % Cu was removed in 140 days with the consumption of 224 kW h/m^3 energy	√√	P	Zhou et al. (2006)

3. 20-Year old chemical plant, China	Hexachlorobenzene, Zn	• 0.5 m^3 Sediment was treated under a constant voltage in a polyvinyl chloride reactor • 563 kW h/m^3 Energy was consumed in 6 months • Consumption of energy was subsequently increased periodically • Remedial per cent was <50 • Long-term ageing of sediment and co-occurrence of HCB and Zn was the reason behind low contaminant removal efficiency	X	P	Li et al. (2009a)
4. Military small arms training facility site, Boston	Pb	• Amendment of organic acid at the cathode-reduced voltage and energy requirement by 70 % and enhanced Pb extraction • Concentration of Pb was reduced by 85 % after 112 days of processing • Cost of treatment was between 14 and 18 US$/m^3/month	√√	P	US EPA (2012)
Bioventing					
1. Diesel oil contaminated site, Copenhagen, Denmark	Diesel	• About 96 % of 2000 mg/kg diesel oil was removed in 112 days of treatment using the coupled effect of bioventing, nutrient addition and oil-degrading bacteria	√√	F	Moller et al. (1996)
2. Transformer oil contaminated soils, Budapest, Ullatosu	EPH	• *In*-situ cyclodextrin-enhanced bioventing coupled with *ex*-situ nutrient addition was the technology employed • 99 % Remediation was achieved in 46 weeks	√√	P	Molnar et al. (2005)
3. Former petroleum refinery, West central region, USA	BTEX, Diesel, Gasoline	• Wind-assisted air injection technique removed 88–95 % pollutants • Long-term passive bioventing was highly successful as well as cost-effective, full-scale technology at remote locations with high, sustained wind speeds and permeability	√√	P	Zenker et al. (2005)
4. Flat Hill top site at a weather station, USA	TPH, BTEX	• Successful wind-driven bioventing stimulated remediation with no power requirement and minimal operation and maintenance • Monitoring indicated a 20 % oxygen delivery by wind-driven energy and greater than 90 % reduction in VOC concentrations in 2 months	√√	P	Dominguez et al. (2012)

(continued)

Table 4 (continued)

Site	Contaminants	Highlights/comments	Result	Scale	Reference
Natural attenuation					
1. Gasoline spill site, Garysburg, North Carolina	BTEX	• About 99 % BTEX was removed by natural attenuation along with iron-reducing biodegradation process in 2 years • Natural attenuation was the remedial option at the gasoline spill site to remediate the contaminated groundwater	√√	F	Kao and Wang (2001)
2. Canadian forces base, Borden	PAHs, Biphenyl, Carbazole	• After 14 years of treatment, only 3 of 11 contaminants were reduced significantly and the remaining were not remediated due to increasing mass flux and limited degradation potential • Greatest mass loss was associated with the compounds that have high solubility and low partitioning co-efficient	X	F	Fraser et al. (2008)
3. Low farmland, Andalusia, Spain	Diesel	• Stimulated natural attenuation was the best remedial measure for hydrocarbon degradation • Soil remediation by natural attenuation was enhanced by the practice of tilling or adding water which could enhance the contaminant evaporation	√	F	Serrano et al. (2008)
4. MGP site, New York	PAHs	• In a 14-year old groundwater natural attenuation process, 99 % contaminant was remediated • Monitored natural attenuation was a viable remedial strategy for groundwater sites impacted by PAHs	√√	F	Neuhauser et al. (2009)
5. Slag heaps, Temascaltepec, Mexico	Cd	• Role of plants and arbuscular mycorrhizal (AM) fungi with natural attenuation was substantiated • Glomalin protein of AM fungi was reported to sequester 0.028 mg/g Cd	√	F	Gonzalez-Chavez et al. (2009)
6. Campine region, Belgium, Netherland	Pb, Cd, Zn	• Phytoattenuation was used • Risk reduction and generation of an alternative income for agriculture as well as gradual reduction of the pollution levels were the main goals • Metal removal was low for Cd and Pb compared to Zn • Removal efficiency was enhanced by the introduction of winter crops for bioenergy purposes in crop rotation	√	F	Meers et al. (2010)

7. Military facility site, Korea	BTEX	• BTEX attenuation rate was 8.69×10^{-4}/day and the remediation time was 17.5 years • Rate of biodegradation and natural attenuation was very less and integration with other supportive remedial measures were suggested	X	F	Choi and Lee (2011)
Phytoremediation					
1. Metal-contaminated site, Dornach, Switzerland	Cu, Zn, Cd	• Only 10–30 % remediation was achieved by *Alyssum murale* and *Thlaspi caerulescens* • Limitations in phytoavailability of metals was due to the high soil pH	X	F	Kayser et al. (2000)
2. Houston site, USA	MTBE	• Phytohydraulic containment of MTBE was successfully achieved • About 36.5–67.0 % MTBE was removed after 1 year from the groundwater plume using poplar plants	√	F	Hong et al. (2001)
3. Dredged sediment disposal site, Belgium	Cd, Cu, Pb, Zn	• About 57 % of the heavy metals were significantly removed by implementing capping of willow trees for 1.5 years	√	F	Vervaeke et al. (2003)
4. Paint factory site, Czech Republic	PCB	• Austrian pine, black locust, ash and willow trees were tested • Austrian pine and black locust significantly increased the number of PCB degrading bacteria in the rhizosphere and helped to achieve >60 % remediation	√	F	Leigh et al. (2006)
5. Indian Harbor canal, USA	PAHs	• After 1 year of planting, nearly 70 % PAHs reduction was observed in the sediment samples raised with *Carex stricta*, *Tripsacum dactyloides* and *Panicum virgatum* compared to *Salix exigua*, *Populus* spp. and *Tripsacum dactyloides*	√	F	Euliss et al. (2008)
6. Agricultural soil, Witzwil, Switzerland	Cd, Cu, Zn	• Efficient remediation was achieved by the extraction of Cd using tobacco plants • Phytoextraction was aided by the application of 4.28 Mg sulphur/10,000 m^2/year	√	F	Fassler et al. (2012)

(continued)

Table 4 (continued)

Site	Contaminants	Highlights/comments	Result	Scale	Reference
7. Agricultural soil, Zhejiang, China	Phthalic acid esters	• Phytoremediation of phthalic acid esters by intercropping *Medicago sativa*, *Lolium perenne* and *Festuca arundinacea* • *M. sativa* in monoculture removed over 90 % of the contaminant • Intercrop of all the three plant species contained the highest shoot concentration of total phthalic acid esters of about 4.7 mg/kg dry wt.	√√	F	Ma et al. (2012)
Bioaugmentation					
1. Dover's air force base, DE	TCE	• Mixed enrichment culture capable of dechlorinating TCE to ethene was inoculated into the contaminated aquifer at 2×10^{11} cells/L • Groundwater was fed with lactate after bioaugmentation on day 1 • Within 90 days, VC and ethene disappeared in monitoring wells • After 509 days, TCE and DCE were fully dechlorinated to ethene	√√	F	Ellis et al. (2000)
2. USN hydrocarbon national environmental test site, Port Hueneme, California	MTBE	• A microbial consortium, MC-100, capable of degrading MTBE was inoculated • With 30 days of bioaugmentation and oxygen injection, MTBE was degraded to non-detectable level after 261 days	√√	F	Salanitro et al. (2000)
3. Bachman road residential wells site, San Diego, California	PCE	• *Desulfuromonas* sp. and *Dehalococcoides* sp. were bioaugmented in the contaminated groundwater • Complete dechlorination of PCE to ethene was observed in less than 50 days	√√	F	Lendvay et al. (2003)
4. Metal- and organic-contaminated soil, Tucson, Arizona	Cd, 2,4-D	• Dual bioaugmentation strategy with metal-detoxifying and organic-degrading microbial populations was adopted • Cd-resistant *Pseudomonas* sp. enhanced degradation of 2,4-D in reactors inoculated with *Ralstonia eutropha* • Dual bioaugmentation was effective at co-contaminant remediation	√√	P	Roane et al. (2001)

5. Kelly air force base, Texas, USA	PCE	• Bioaugmentation was carried out with a mixed culture containing *Dehalococcoides ethenogenes* to a density of 10^9 cells/L • Methanol and acetate were added as electron donors • Complete dechlorination was achieved after 142 days	√√	F	US EPA (2012)
6. Ho Chung mangrove swamp, Hong Kong, China	PAHs	• At the end of 2 weeks, natural attenuation based on the presence of indigenous microbes degraded more than 99 % PAHs, while biostimulation along with the addition of mineral salt medium degraded only 9 % PAHs	√	P	Yu et al. (2005)
7. Vegetable garden site soil, Pietermaritzburg	PAHs	• Combined application of biostimulation with ammonium phosphate and hydrogen peroxide enhanced PAH degradation by 100 % compared to biostimulation alone (90 %)	√	P	Atagana (2006)
8. MAG-1 area, Fort Dix, Burlington	Chlorinated ethenes	• *Dehalococcoides* sp. was bioaugmented into the contaminated aquifer • A density of 3.9×10^{13} cells/L showed significantly higher degradation with less remedial time compared to 3.9×10^{11} and 3.9×10^{12} cells/L	√√	F	Schaefer et al. (2010)
Biostimulation					
1. Site at Kururi, Japan	TCE	• Methane was used as the stimulator • Injection of methane, oxygen, nitrate and phosphate into the contaminated groundwater gradually stimulated the methane oxidizers in the aquifer, and about 10–20 % TCE was removed in a week	√√	F	Eguchi et al. (2001)
2. Old Rifle site, USA	U	• Acetate was used as the stimulator • Uranium was completely immobilized after 109 days by sulphur-reducing bacteria	√√	F	Yabusaki et al. (2007)
3. Polar desert site, Tanquary fiord, High Arctic	Petroleum hydrocarbons	• Diammonium phosphate along with surfactants was the best biostimulator for the degradation of petroleum hydrocarbons at extreme climatic conditions	√√	F	Sanscartier et al. (2009)
4. Oily sludge contaminated site, China	TPH, PAH	• Manure was used as a nutrient-rich biostimulator for hydrocarbon degradation	√√	F	Liu et al. (2010)

√√, Successful; √, Partially successful; X, Not successful; P, Pilot-scale; F, Field-scale

Table 5 Performance of electrokinetic remediation in combination with other technologies for the removal of organics

Contaminant	Combined technology					Remediation (%)	Reference
	F	B	S	U	L		
Hydrocarbons							
1. PAH	+	+	+	+	–	70–80	Park et al. (2005); Yang et al. (2005); Pham et al. (2009); Gomez et al. (2010)
2. Petroleum hydrocarbons	+	–	–	–	–	97	Tsai et al. (2009)
3. Diesel	–	+	–	–	–	64	Kim et al. (2010)
4. Phenol	–	+	–	–	+	80–95	Luo et al. (2006)
Chlorinated solvents							
1. TCE	+	–	–	–	+	75–90	Yang and Liu (2001); Harbottle et al. (2009)
2. VC	–	+	–	–	–	90	Tiehm et al. (2009)
Pesticides							
1. HCB	–	–	+	+	–	75–80	Oonnittan et al. (2009); Pham et al. (2009)
2. DDT	–	+	–	–	–	13	Karagunduz et al. (2007)

+, Technology implemented; –, Technology not implemented; F, Fenton's process; B, Bioremediation; S, Surfactant-enhanced remediation; U, Ultrasonic technology; L, Lasagna technology

However, more research is warranted to explore the fillings like nanoparticles or nutrient releasing solids for fractures that could aid the systems' efficiency. Ho et al. (1999) reported that Lasagna™ technology could successfully remediate phenol and TCE by 90 % when combined with electrokinetic remediation (Table 5). Performance studies of many more integrated remedial approaches like dual-phase extraction, bioslurping with fracturing as reported in US EPA (2012) can also be tested in field-scale to accelerate the current remedial percentages of 75–99.9 achieved in other conventional in-situ treatments. The approximate cost for pneumatic fracturing ranges from 8 to12 US$ per Mg. Based on creating 4–6 fractures per day, the cost of establishing hydrofractures is estimated to be 1000–1500 US$. In Lasagna™, cost is estimated to be 160–180 US$ per Mg for remediation in a year, 100–20 US$ per Mg if 3-year period is allowed for remediation (FRTR 2012).

3.4 Physical Barriers: Treatment Walls/Permeable Reactive Barriers

Barriers are the critical components such as designed covers/caps, slurry/permeable walls, landfills and grout curtains that are commonly used to restrict or control the movement of contaminant plumes in groundwater. Such physical barriers are generally well constructed with a multi-component system of highly impermeable material for long-term performance in order to eliminate the movement of the contaminant plume into aquifers and surface waterbodies (Inyang and de Brito Galvao 2004). This technology has been effective for a series of chemicals such as halogenated organics, chlorinated solvents, hydrocarbons, radionuclides and metals (US EPA 2012). Conditions that determine the efficiency of the physical barrier systems are properties of the barrier materials, component dimensions and system configurations. One of the widely implemented, viable, cost-effective subsurface barrier technologies is permeable reactive barriers (PRBs) (Scherer et al. 2000). In PRBs the flow of contaminated groundwater is not restricted, wherein they are allowed to pass over the barrier materials (reactive fluid) for the passive degradation or immobilization of contaminants. This treatment system can permanently restrict the contaminant migration to uncontaminated region and relatively decrease the volume of toxic contaminant residues by subsequent treatments (Testa and Winegardner 1990).

Generally, usage of physical barriers has the following advantages: minimized contaminant leaching; stabilization of contaminants by transforming the waste into a physical form that reduces the release potential of the contaminant; no need for excavation; passive remediation (no requirement for any energy input); potential for transfer of contaminants to other aquifers is minimal; and surface structures are not required except monitoring wells. Physical barrier systems also have their disadvantages: limited application to shallow plumes (<15 m); the risk that concentrated metals will be discharged into the groundwater if the reactive fluid is not removed in time; contaminated site should be well delineated and characterized before implementing the system; field data on the longevity of the reactive fluid and loss of permeability is scarce; site-specific constraints such as pH adjustment, subsurface utilities, inaccessibility, etc. may exist; and biological activity may limit the effectiveness of the reactive wall.

Many types of installation designs are currently available for PRBs like excavation and backfill (use of removable sheet piling and biodegradable polymer slurry), overlapping caissons (use of steel caissons), soil mixing (injecting and mixing reactive fluid with augers), high pressure jetting (injecting grouts to make impermeable walls), and vertical hydraulic fracturing (pumping gel containing reactive media into fractures created in permeable sands). All these techniques are utilized for establishing several barrier designs (Benner et al. 2001). Funnel-and-gate (vertical impermeable sheet pilings or slurry walls) and continuous trench (trench excavated and refilled with reactive material) design of PRBs are being implemented at field-scale by the US EPA (Strigel et al. 2001). Of the two, funnel-and-gate is more cost-effective for large or deeper contaminated plumes because voluminous reactive material is required for continuous trench design. In funnel-and-gate design, slurry walls, sheet pipes and other materials used to form the funnel are often easier and more economical to install than reactive walls. Plumes with mixed contaminants can be funnelled through a gate with multiple reactive walls in a series for achieving better remediation (Anderson and Mesa 2006).

A wide range of materials like ZVI, calcite/limestone, zeolite, metal oxides, microorganisms, polymers and organics (straw, hay, peat, wood, leaf mulch, mushroom compost and municipal solid waste), have been exploited as reactive materials to remediate contaminated groundwater. US EPA (2012) listed several sites where PRBs successfully remediated organics and inorganics (Table 6).

Table 6 Successful PRB reactive materials at field-scale in superfund sites

Site	Contaminants	Successful reactive materials	Construction	Reliability
1. Aircraft maintenance facility, Southern Oregon, USA	TCE	Zero-valent iron (ZVI) pellets	Funnel-and-gate	++
2. Watervliet arsenal superfund site, Watervliet, New York	Halogenated VOCs	Mixtures of ZVI, sand and concrete	Continuous trench	++
3. FE warren air force base, Cheyenne, Wyoming	TCE, DCE, VC	ZVI particle and sand	Trench box	++
4. Former industrial site, Belfast, Northern Ireland	TCE, DCE	ZVI particle	Slurry wall funnel as well as in-situ reactive vessel	++
5. Nickel rim mine site, Sudbury, Ontario, Canada	Pb, Co, Cd, Cu, Ni, Zn, NO_3, SO_4	Leaf compost, peat, sewage sludge, manure, sawdust, wood waste, composted leaf mulch, pine mulch, pine bark and microbes (*Geobacter metallireducens* and *Alteromonas putrefaciens*)	Cut and fill	++
6. Tonolli superfund site, Nesquehoing, Pennsylvania	Pb, Cu, Cd, As, Zn	Limestone	Continuous trench	–
7. Former mill site, Monticello, Utah	U, As, Mn, Se	ZVI particle	Funnel-and-gate	++
8. Former industrial site, Brunnam Gebirge, Austria	PAH, BTE, TCE, DCE	Activated carbon	Adsorptive reaction with hydraulic barrier	++
9. Solar pods plume, Golden, Colorado	NO_3, U	ZVI particle and wood chips	Reaction vessels	++
10. Chalk river lab, Ontario, Canada	Sr	Zeolite	Funnel-and-gate	+
11. Y-12 Oak ridge national lab, Tennessee	U, HNO_3	Iron oxides	Funnel-and-gate as well as Continuous trench	++

++, Successful technology; +, Partially successful technology; –, Unsuccessful technology

Gilbert et al. (2003) concluded that municipal compost is not an appropriate carbon source to support continuous activity of sulphate-reducing bacteria under high flow rates when a mixture of ZVI, limestone and compost was used as an additive in PRB laid to remove metal in acid-mine drainage. Funnel-and-gate design of PRB successfully remediated the sites contaminated with TCE, U, As, Mn and strontium so far in the US EPA superfund sites at Oregon, Utah, and in Canada using reactive materials like ZVI and zeolite. Also, 75–90 % removal of Pb, Cu, Cd, As, Zn, U and nitrate was observed in the superfund sites of New York, Pennsylvania and Tennessee using mixtures of sand and concrete, ZVI and iron oxides as reactive materials in continuous trench PRB system. A successful PRB installation in Ontario employed municipal compost, leaf compost and wood chips to remove nickel from an acid-mine drainage contaminated aquifer (US EPA 2012). There are many positive results for using anoxic limestone drains as a barrier material for decontaminating Pb and acid groundwater (Maynard 2005).

The majority of installed PRBs use ZVI as a reactive medium at field-level. Wilkin et al. (2006) noted that a ZVI permeable reactive barrier is effective in reducing the concentration of Cr from 1500 μg/L to <1 μg/L in 8 years at the US coast guard support centre near Elizabeth City, North Carolina. A recent field study at a network site in Northern Ireland indicated that 98 % remediation was achieved by using ZVI permeable reactive barrier in 2 years at a long-term high TCE-contaminated site (Phillips et al. 2010). Benner (2000) observed 90 % reduction in sulphate concentration in the organic carbon barrier at Nickel Rim, Ontario. Bayer et al. (2004) suggested that the problem of not achieving full aquifer restoration within a reasonable time frame using pump-and-treat technology can be rectified by integrating it with the barrier system. This is because vertical, physical hydraulic barriers such as sheet piles or slurry walls in the field could potentially minimize the pumping required to gain a thorough capture of a given polluted zone. Also, Waybrant et al. (2002) found that PRBs can potentially enhance bacterial sulphate reduction and metal sulphide precipitation which will help to prevent the associated release of dissolved metals and acid-mine drainage in a contaminated aquifer.

Of all these studies, the use of PRBs in association with microbes to promote biodegradation of contaminants is increasing rapidly. For the PRBs to be more effective in the future, cheap, widely available reactive fluid materials can be tested, and optimised barrier systems could be framed to overcome the constraints of heterogeneous sites, and the technology might be more economical and promising for wide range of pollutants. In other words, value-added or innovative materials can be evaluated as additives for barriers to enhance the containment system performance.

3.5 Soil Vapor Extraction

One of the most widely accepted, cost-effective soil remedial approaches for treating SVOCs and VOCs is soil vapor extraction (SVE). It is also known as vacuum extraction, soil venting as well as in-situ enhanced volatilization (Zhan and Park 2002).

In this method, through horizontal/vertical wells, vacuum is applied to create a concentration/pressure gradient that induces the removal of gas phase volatiles from soil. Vapors of volatile constituents are drawn towards the extraction wells and then treated with the carbon absorption technique before being emitted into the atmosphere or reinjected to the subsurface. This method is also used in air stripping and groundwater pumping for treating contaminated groundwater. In areas of higher groundwater levels, water table depression pumps are often used to offset the effect of upwelling induced by high pressure vacuum. SVE is more effective in treating more volatile and lighter petroleum compounds like gasoline (Zhan and Park 2002). It only promotes the in-situ degradation of low volatile organics and not their complete removal as the process involves continuous air flow through the soil. Generally, almost all petroleum products can be remediated by integrating SVE with bioventing, steam injections, radio frequency heating techniques, because volatility of the heavier contaminant will be accelerated by hot air injections (Qin et al. 2009). However, the energy requirement for volatility enhancement should be considered to reduce the capital cost. Using this method, naphthalene, perchloroethylene, benzene, toluene, xylene, biphenyl, TCE, TCA and gasoline have all been successfully removed from the zone of contamination.

SVE could treat large volumes of soil at reasonable cost in a short time (a few months to 2 years) with minimal soil disturbance (Barnes et al. 2002). It is also advantageous due to its proven performance at field- and pilot-scale, readily available equipment and easy installation, minimal site disturbance, compatibility with other technologies and applicability at sites with free products. However, the applicability of this method is limited to sites with a low water table (>1 m below ground level) and volatile compounds. Also, soil characteristics like structure, stratification, permeability and moisture content greatly affect the performance of the system as the ease and rate of vapor movement through the soil is impacted by these soil factors (RAAG 2000). Usually, low permeability, high moisture content and preferential flow behaviors by layering/fractures can extend remedial times by limiting the air flow through the soil pores. Other restrictions of this method include the need for air emission permits, requirement for expensive treatment of atmospheric release of extracted vapors, treatment of only unsaturated soil zone and need for integration with other technologies to reduce the contaminant concentration to more than 90 %. Recently, different types of subsurface covers have been established to avoid surface water infiltration that could limit the air flow rates, subsequently reducing the fugitive vapor emissions (Boudouch et al. 2009).

Almost in all the in-situ techniques at field-scale, SVE is the principal recovery system (Table 7). Cho et al. (1997) used SVE in combination with biodegradation to successfully remediate 98 % jet-fuel at the US coast guard facility, Elizabeth City, North Carolina. Hoier et al. (2007) successfully remediated 77 % TCE using the pneumatic SVE technique. The operational cost varied from 20 to 50 US$ per Mg of contaminated soil. A pilot SVE system installed at a small landfill at the Savannah River site was successful to address TCE contamination present in the layered vadose zone (Switzer and Kosson 2007). In the study by Noonkester et al. (2005), sets of 2–3 extraction wells laid in the vadose zone of high chlorinated

Table 7 Status of in-situ soil vapor extraction studies

Site	Key contaminant	Remediation (%)	Associated technology	Specific feature	Outcome	Nature	Reference
1. Canadian forces base, Borden, Ontario	PCE	60	None	• 60 % PCE was removed after 250 days • Heterogeneity of the system (changing well configuration, pulsed pumping, and use of short screen drive points to localize the flow) is the reason for the decreased mass removal	X	F	Fountain (1998)
2. Winton's food and fuel, Palmer, USA	MTBE	>95	Multi-phase extraction	• Remediation system installed was SVE and passive aquifer oxygenation • Almost all MTBE was removed in 2 months	√√	F	US EPA (2012)
3. US coast guard, North Carolina	Jet fuel	98	Biodegradation	• Rate of biodegradation could be accelerated by injecting oxygen through injection pumps	√√	P	Cho et al. (1997)
4. TCE-contaminated soil, Denmark	TCE	>77	Pneumatic SVE	• Enforcing large pressure drops on the system to enhance recovery from low-permeable areas was achieved by pneumatic SVE • Pneumatic venting increased removal rates of the contaminant by 77 %	√	BS	Hoier et al. (2007)

(continued)

Table 7 (continued)

Site	Key contaminant	Remediation (%)	Associated technology	Specific feature	Outcome	Nature	Reference
5. Former Kelly air force base, San Antonia, Texas	TCE	97	Electrical resistance Heating	• Over 544 kg chlorinated solvents were treated in an area over 14 × 10^5 m^2 • Soil was heated up to 90 °C • In 14 months, contaminant was successfully removed	√√	F	US EPA (2012)
6. Beach soil, Porto, Portugal	Benzene	85–94	Bioremediation	• Soil with higher organic matter content was more populated by indigenous microorganisms that enhanced the contaminant degradation • Organic matter content had opposite effects on the remediation of soils through the combination of SVE and bioremediation • Higher natural organic matter hindered SVE but enhanced bioremediation	√	F	Soares et al. (2010)

√√, Successful; √, Partially successful; X, Not successful; P, Pilot-scale; F, Field-scale; BS, Bench-scale solvent-contaminated site were treated using SVE at 1 month intervals. Up to 3 months, it allowed continuous operation of the SVE system to individual wells for rebound of the contaminants between treatments. The process of operation intended to maximize contaminant recovery from individual wells and reduced the overall capital investment and the SVE system's operating cost. Kirtland and Aelion (2000) reported that continuous air sparging/SVE is effective in removing 87 % petroleum hydrocarbons from low permeability soil in 44 days. SVE with electrical resistance heating was able to remediate 97 % of a TCE-contaminated superfund site in a month by heating the contaminated zone to about 90 °C (US EPA 2012). Soares et al. (2010) studied the effect of bioremediation with the SVE system in a benzene-contaminated site. They found that high organic matter in soil could hinder the SVE system's operation though it was able to elevate the indigenous microbial population. Although there have been several SVE success stories, the system's performance depends on soil heterogeneity which is a crucial factor for successful remediation.

3.6 Electrokinetic Remediation

Electrokinetic (EK) remediation has emerged as a highly explored remediation technology at pilot-scale in the twenty-first century. EK remediation is also known as electrochemical decontamination, electrokinetic soil processing or electromigration. It makes use of electric current to treat slurries and soils contaminated with heavy metals, radionuclides and mixed inorganic species or certain organic compounds. When an electric current is applied in the contaminated soil, an acid is produced in the anode compartment that is transported across the soil and desorbs the pollutants from the soil surface (Cameselle et al. 2013). It also initiates electromigration of contaminants existing in the pore fluids and those present at the electrodes and form an electric potential difference which may lead to electroosmosis generated flushing of different contaminant classes (Bonilla et al. 2000; Virkutyte et al. 2002). In general, EK remediation is a controlled co-application of electroosmosis and electrical migration with electrolysis at the electrodes.

Generally, EK separation works well for low permeable soils composed of clays or silt clay mixtures. For efficient performance the presence of a pore fluid in the soil pores both to transport the contaminants injected into or extracted from the soil mass and also to conduct the electrical field is required. It may be likely to saturate certain partially saturated soils by electromagnetic advection of the analyte; however, it is required under such circumstances to engineer the process (Reddy and Chinthamreddy 2003). Many reports depict the success of electrokinetics in combination with other technologies such as Fenton's process, Lasagna treatment, ultrasonic extraction techniques and bioremediation to remediate sites contaminated with heavy metals like Pb, Cr, Zn, Hg, Fe, Mg and Cd (Zhou et al. 2005; Li et al. 1998); radionuclides like thorium, radium and uranyl; polar organic compounds such as acetic acid and phenol; and nonpolar compounds like benzene, toluene, ethylene and xylene (Gomes et al. 2012) as depicted in Table 5. This technique is mainly utilized to inject nutrients, electron acceptors and other additives into the contaminated zones so that the in-situ biodegradation process could be achieved for better contaminant degradation of more than 85 % (Pedersen et al. 2005). Generally the construction of conventional subsurface barriers like slurry walls, sheet-pile cut-off walls and grout curtains used in EK remediation is expensive and may require heavy machinery. In such cases, portability and ease of installation of electrodes surrounding the contaminated zone makes EK barriers a better alternative to conventional methods. In addition, the EK method provides early responses which helps to minimize the spread of the contaminant in time. Generally, the formation of undesirable products by the oxidation/reduction process and interference by buried metallic constituents/high moisture content of the soil limit the system's efficiency.

EK remediation is proposed more in conjunction with other in-situ remedial techniques especially for injection of surfactants (Oonnittan et al. 2009; Wan et al. 2011) that enhance the solubility and transport of the contaminant; for contaminant extraction using penetrating probes for toxin precipitation in migrating plumes; for injection of grouts for waste containment and soil stabilization; for leak detection systems in containment barriers and repair of failing containment barriers; and for pore fluid and soil characterization. Also, investigations on injecting chemical conditioners at the cathode and anode that would modify the chemical reaction at the electrode thereby enhancing the system efficiency are currently increasing day-by-day (Li et al. 2009a). So far, chemical conditioners like acetic acid, thorium ions and chelating agents such as EDTA, ammonium ions, etc. have been explored to enhance the performance of EK remediation (Lestan et al. 2008). Zhou et al. (2006) remediated 76 % of Cu using 80 V power in 140 days. Alshawabkeh et al. (2005) found that when organic acid was amended at the cathode region of the EK remedial system, it reduced the energy requirement by 70 % and enhanced the degradation of Pb by 85 % in 112 days of treatment. Pedersen et al. (2005) evaluated the effect of phosphoric acid and oxalic acid as additives to facilitate the efficient removal of Cr, Cu and As in the waste wood field site in Denmark by EK remediation. By passing an electric current of 60 V for 21 days, removal of the heavy metals was 82–96 %.

Electrochemically-enhanced oxidation is an emerging and promising approach for treating contaminated groundwater systems. Presently, EK remediation is used to remediate widespread organics like that of heavy metals in conjunction with other techniques (Alshawabkeh et al. 2005). EK remediation with Fenton's process was successful in removing 99.7 % phenol, 80 % PAH and 75 % TCE (Yang and Liu 2001). With surfactant and cosolvent-enhanced remediation, EK remediation was successful in remediating 75–80 % PAHs and chlorinated solvents using SDS, Igepal, Butylamine, Tween 89, HPCD, etc. (Saichek and Reddy 2005). Bioremediation, ultrasonic technology and Lasagna technologies were also integrated with EK remediation to remove 75–95 % organic pollutants (Ho et al. 1995; Luo et al. 2006; Huang et al. 2012).

Overall, this technology is quite tempting for field implementation since it constitutes a solution to cost-prohibitive remedial sites. The only concern is to achieve the complete clean up by reducing the energy and power requirement by using various natural energy resources which can be explored by further research. Yuan et al. (2009)

conducted a preliminary study to consider the use of a solar cell to generate an electric field for EK remediation of Cd-contaminated soil instead of direct current (DC) power supply. The EK remediation mediated by solar cell was found to drive the electromigration of Cd in contaminated soil and achieved comparatively higher removal efficiency by the high output potential generated, and was influenced by weather conditions. Moreover, the greater life time (20 years) and low running cost by the use of solar cells relatively reduced energy expenditure when compared with the traditional DC power supply. Wan et al. (2010) and Yang and Chang (2011) reported that an integrated strategy of electrokinetics coupled with nanotechnology/permeable reactive barriers along with the use of surfactants could help to achieve the remedial goals in short periods. Full-scale cost estimate of this system is about 117 US$ per m^3 soil. On the whole the scope for field remediation using electrokinetics is more promising.

3.7 Multi 3-Phase/Dual-Phase/Vacuum-Enhanced Extraction/Bioslurping

One of the best available technologies for treating saturated levels of VOCs that reached the groundwater table is multi-phase extraction (MPE). MPE is also termed bioslurping or vacuum-enhanced extraction or dual-phase extraction (DPE). In MPE, pumps of very high vacuum are used to remove various combinations of contaminated groundwater, hydrocarbon vapor and separate phase petroleum products from the subsurface. Extracted fluids and vapors are then re-injected or disposed into the subsurface (US EPA 2012). MPE typically maximizes the pollutant extraction rates especially in layered and fine grained soils. Increasing air phase permeability and by lowering the water table helps to maximize the effectiveness of SVE in the vadose zone. MPE could clean up different phases of contaminants (dissolved, vapor, residual and non-aqueous) in both saturated and vadose zones compared to the conventional pumping systems that address only two phases (Abriola and Pinder 1985). Complete removal of the contaminant is established by dissolution, volatilization and advective transport. In general, MPE can act as an ideal alternative to potentially applicable techniques like SVE and pump-and-treat.

The applicability of MPE is governed mainly by soil characteristics and to a lesser extent contaminant properties like hydraulic conductivity of the soil, and volatility/vapor pressure of the contaminant. MPE is most applicable to VOCs like petroleum hydrocarbons (BTEX), degreasing agents (TCE) and chlorinated as well as non-chlorinated solvents. Studies also tend to state that MPE is rarely applicable to treat non-volatile contaminants, provided airflow is kept higher by subsequent introduction of oxygen that could stimulate biodegradation (Rahbeh and Mohtar 2007).

MPE is effective even on moderate to low permeable soils. Even in low permeability settings when other in-situ remedial techniques are applied, where excavation is the major need, MPE could remove the contaminant source without excavation, and reduce the duration and cost of remediation (Hassanizadeh and Gray 1979).

It also reduces the number of recovery wells and is effective for capillary zone removal. Besides, it increases the total fluid recovery, maximizes aquifer transmissivity at the wellhead and minimizes the free product dispersal. On the other hand, requirement of vacuum pump or blower and more potential treatments, initial startup, adjustment periods, depth limitations and higher capital costs compared to conventional pumping approaches are disadvantages of the MPE system. Generally, when the target contaminants include long-chained hydrocarbons, the MPE of contaminants such as liquids and vapors is combined with bioventing, air sparging, or bioremediation. Use of DPE with these technologies shortens the clean up time at a site contaminated with VOCs and fuels. To recover groundwater in higher yielding aquifers, this technique can be used with the pump-and-treat method (Kram 1993). However, site geology and contaminant distribution limit the effectiveness of the system.

MPE can be designed and implemented in three main forms: single pump, dual pump, and bioslurping. In the single pump system, contaminants are extracted in both liquid and vapor phase by employing one vacuum pump which may be a liquid-ring pump/a jet pump/a blower. Single pump MPE, also termed 'vacuum groundwater extraction', is limited to 9 m depth below groundwater though it is best suited to treating low permeable soils. Bioslurping is the same as the single pump MPE scheme; however, the drop tube in a bioslurping application is generally set below the liquid-air interface and is very effective for free-product recovery. Due to increased airflow, in-situ aerobic biodegradation is enhanced in bioslurping. Yen et al. (2003) assessed the recovery of petroleum hydrocarbons in contaminated unconfined aquifer by bioslurping. Gidarakos and Aivalioti (2007) studied the long-term and large-scale application of bioslurping of a Greek petroleum refinery site. They found that 4-year application of bioslurping over a 1,000,000 m^2 contaminated site can potentially remove LNAPLs, but appropriate groundwater remediation techniques like air stripping were recommended to directly treat the groundwater. Dual-phase system uses a surface blower to extract vapors and two pumps to extract liquids from the well. Dual-pump systems, just a combination of groundwater recovery systems and SVE, are generally easier with short treatment time (6 months to 2 years), and applicable over a wide range of site conditions compared to single-pump systems although the equipment costs are higher (US EPA 2012). Three-pump systems are also available.

Studies indicated that continuous temporary DPE treatment is more promising than pulsed/intermittent permanent DPE systems because pulsed DPE hinders enhanced biodegradation and the product recovery. Furthermore, in almost all of the in-situ groundwater remediation studies using other conventional techniques (SVP/thermal conduction heating), MPE systems are widely implemented which assures complete remediation of VOCs as suggested by Nelson et al. (2009). Bierschenk et al. (2004) also reported that 99 % DCA and CVOCs was recovered by high vacuum pump extraction system when the contaminated site was subjected to thermal conductive heating for 400 days. Nelson et al. (2009) made use of a patented technology named 'supersaturated water injection (SWI) system' where nucleating gas bubbles could volatilize LNAPLs. In this study, an LNAPL composed of 103 kg of volatile pentane, 30 kg of non-volatile soltrol and hexane was emplaced at residual saturation below the water table. The SWI technology removed 50 % less volatile hexane and 78 % pentane. The mass removed was comparatively higher to that expected by air sparging. Rahbeh and Mohtar (2007) studied the positive effect of multi-phase transport models to full-scale treatment by air sparging and SVE of BTEX-contaminated site. A similar field study envisaging the success of air sparging with MPE was done by Jang and Aral (2009).

Likewise, there are more prospects to integrate MPE system with other conventional remedial technologies to enhance their efficiency. However, the technology could be improved by implementing an automated operational system to reduce labor costs and improve safety, minimizing size of treatment to access more limited space, integrating with pneumatic or hydraulic fracturing in extremely low permeability formations, etc. The technology requires approximately 30–75 US$ per m^3 for its operation (FRTR 2012).

3.8 Air Sparging

Air sparging, also known as 'in-situ volatilization' and 'in-situ air stripping', involves the injection of gas (usually air/oxygen) under pressure into the subsurface saturated zone in order to volatilize the contaminants sorbed onto the soil surface as well as dissolved in the groundwater by increasing the subsurface oxygen concentrations (US EPA 2012). The injected air flows through the saturated and vadose zones, volatilizes the contaminants and migrate them upwards to the vadose zone, from where they are either subjected to bioremediation or removed by SVE system. Air sparging is one of the best stimulators for biodegradation of pollutants as it is always documented to be a supporter of microflora in the contaminated sites, especially for aerobic soils (Brennerova et al. 2009). Since 1980, in-situ air sparging had been used to remediate a broad range of VOCs and SVOCs (Khan et al. 2004) including diesel, jet fuel, oils, greases, gasoline, chlorinated solvents and fuels. This technique is less applicable for treating fuels like diesel and kerosene, and more applicable to remediate sites contaminated with BTEX as they are readily transferable from the dissolved phase to the gaseous phase. Air sparging performs better only when it is combined with other remediation techniques like SVE and pump-and-treat.

This technology has a few merits: minimal disturbance of treatment zone by implementation; easily installable and readily available equipment; very low treatment time usually shorter than 1–3 years when the conditions are optimized; less costly (20–50 US$/Mg) compared to other in-situ treatment systems; and no post-treatment requirements/recovered product disposal related issues. Air sparging is unsuccessful for non-biodegradable and non-strippable contaminants, silt/clay sediment sites, and when the vertical pathways of air becomes hampered (Kirtland and Aelion 2000; Benner et al. 2002). Neither is this technique suited for treating stratified soils and confined aquifers, and when air is sparged into the contaminated zone, this risks contaminants migrating into the uncontaminated zones. Besides, field-level implementation of air sparging requires a comprehensive pilot study beforehand to ensure the contaminant migration and vapor control limit which consumes additional time and cost (Tomlinson et al. 2003; Adams and Ready 2003).

An in-situ air sparging system with multiple injection wells performed better than a single injection well in-situ air sparging system and was effective in capturing and remediating the detoured contaminant plume (Jang and Aral 2009). At field-scale, Kao et al. (2008) showed >70 % BTEX removal within 20 months at an average groundwater temperature of 18 °C through the biosparging system. They explained that biosparging operation caused the shifting of anaerobic to aerobic conditions inside the BTEX plume which increased the population of heterotrophs that aided in BTEX biodegradation. Aivalioti and Gidarakos (2008) reported 99 % removal of BTEX at the aquifer (600 m^2) of a Greek petroleum refinery site in 5 months by biosparging. At bench-scale, a surfactant (sodiumdodecylbenzene sulfonate)-enhanced air sparging system that involved nitrogen gas at a steady flow rate of 0.12 L/min removed about 78 % PCE from a contaminated aquifer (Kim et al. 2009). The use of biosurfactants along with air sparging for removing volatile contaminants was recommended by Abdel-Moghny et al. (2012).

Available literature (Table 4) indicates that air sparging when combined with other conventional techniques like SVE or volatilization/biodegradation mechanisms is cost-effective and efficient in treating petroleum contaminants at large-scale (Kao et al. 2008). Jennifer (2008) proved that an air sparging system that ran for 3 days in a BTEX-contaminated groundwater could remove 21 % residue by volatilization, 22 % by biodegradation, and 0.1 % by leakage—the three usual processes that occur in every biosparging mechanism. Liang and Chen (2010) evaluated the complete destruction of BTEX in a contaminated site using iron-activated persulfate chemical oxidation coupled with a wet scrubbing system. Complete BTEX removal was achieved by the use of a citric acid chelated iron activator. Hence, there are more prospects to enhance the efficacy of air sparging-related remedial systems by developing continuous systems (e.g., pulsed air injection) integrated with eco-friendly remedial technologies that are more economical.

3.9 Bioventing

Bioventing stimulates the in-situ aerobic biodegradation of fuels, non-halogenated VOCs, SVOCs, herbicides and pesticides by the delivery of oxygen to the contaminated plume. Unlike biosparging where nutrients and or air pumped into the saturated zone, this system injects or extracts air through an unsaturated zone. In contrast to SVE, bioventing uses low air flow rates that are necessary to maintain microbial activity. Optimal flow rates maximize the biodegradation process and minimize contaminant volatilization as vapors pass gradually through biologically active soil (Lee et al. 2001). Since low air volume is required for the process, it could even degrade semi-volatile organic compounds in low permeability soils.

Conventional bioventing systems use an electric blower to deliver oxygen to the subsurface wells. Natural air-exchange is used in the passive bioventing systems to deliver oxygen via bioventing wells to the subsurface with a one-way valve that helps to maintain a controlled air flow relative to the drop in atmospheric pressure (Kao et al. 2001). This technology is most applicable for mid-weight petroleum products like diesel compared to heavier compounds which generally take longer to biodegrade; lighter compounds tend to volatilize quickly and can be treated better along with the SVE system. Halogenated organics are also treatable by this technique, but this is less effective. A cometabolite is required to biodegrade chlorinated compounds using this system (Sui et al. 2006). Where sites are contaminated with high concentrations of organic compounds or heavy metals, this technology is not applicable because the higher contaminant concentrations hinder microbial growth. It is ineffective in treating areas with very high water tables as well as soils with low moisture content which affects soil aeration, and in turn, the microbial survivality (Dupont 1993).

All that bioventing requires is the presence of indigenous microbes that are able to degrade the pollutant of concern along with oxygen and nutrients required for microbial growth. Bioavailability of the contaminant also matters a lot. Bioventing is a very simple, inexpensive and publicly accepted technology, where the used equipment requires only low maintenance and can be left unattended for longer periods of time. It needs only a short treatment period between 6 months to 2 years and generally does not require off-gas treatments. Yet, this technology cannot always reach low clean up limits. Mostly, saturated soils are difficult to aerate and saturated soil zones of low air permeability are created by the fluctuating water tables which constrain the system (Barnette et al. 2005).

At pilot-scale, bioventing was highly successful (Molnar et al. 2005; Dominguez et al. 2012). Cometabolic bioventing effectively degraded 95 % TCE in unsaturated soil zone when methane was used as the growth substrate (Sui et al. 2006). Moller et al. (1996) studied the effects of inoculation of oil-degrading bacterium, nutrient addition and bioventing on bioremediation of diesel in unsaturated soils. With 112 days of monitoring, about 96 % degradation was achieved. The influence of cyclodextrin-enhanced bioventing in soils, contaminated with transformer oil, was reported by Molnar et al. (2005). The average transformer oil concentration in 50 m^3 of contaminated soil was about 20,000 mg/kg and 1.0 mg/L in groundwater. *Ex*-situ physico-chemical treatment of groundwater was also combined along with in-situ bioventing of the unsaturated zone. Application of nutrients together with 50 % randomly methylated-beta-cyclodextrins (RAMEB) three times during a 46-week experimental period caused a significant reduction in the soil TPH concentration by 99 %.

Hvidberg (2007) conducted a novel treatment train consisting of an enclosure, in-situ alkaline hydrolysis, pump-and-treat and bioventing, and remediated 95 % of a large pesticide-contaminated site located on Denmark's north-western coast. Using small-scale respirometers containing soil contaminated with gasoline, the effects of forms and concentration of nitrogen as well as soil water content along with microbes on biodegradation rate of gasoline were determined (US EPA 2012).

Results indicated that soil water content of 18 % and C:N ratio of 10:1 are highly suited to bring about effective gasoline degradation. Also, bacteria were the dominant organisms involved in gasoline degradation. Magalhaes et al. (2009) combined an air-injection bioventing system and a biotrickling filter for the treatment of toluene-contaminated soil over a short period of time, and observed about 99 % removal of toluene in just 5 days.

Recently, sustainable wind-driven bioventing technology was proposed by Dominguez et al. (2012) at pilot-scale to decontaminate petroleum hydrocarbons. Because of the diurnal and seasonal wind drifts of the site, natural air pulsing occurred and bioventing was able to reduce 90 % VOCs in 2 months though the total treatment time without adding an energy source was 15 months; by doing so, energy equivalent to 20,000 kW/h/year was saved. Naturally, the drop in the amount of energy reduced the extent of greenhouse gases produced (an equivalent of approximately 12 Mg of CO_2/year). They also reported that the wind-driven method is highly cost-effective as it can maximize available resources by using existing groundwater wells and minimize water consumption as well as waste generation resulting from the installation of new wells. Zenker et al. (2005) suggested that long-term passive bioventing by using wind-driven energy is a cost-effective, full-scale, in-situ remediation technology to treat VOCs at remote locations with high, sustained wind speeds and permeable vadose zones. Thus, there are more prospects to explore the degradability of bioventing, especially the passive system, as that of the wind-driven systems for varied mixed contaminants in large-scale. Typically, bioventing costs about 20 US$ to treat per m^3 soil (Juwarkar et al. 2010).

3.10 Natural Attenuation

Natural attenuation/in-situ bioremediation/bioattenuation/passive remediation/intrinsic remediation was not an acceptable technology until 1994. Only by 1998, US EPA recognized bioattenuation as a viable technique to remediate groundwater and soil in its superfund sites, and it has now been accepted as a valid method for treating petroleum-contaminated sites by several state underground storage tank programs (US EPA 2012). So far, many projects have been successfully completed in the superfund sites as presented in Table 8. To date, several studies are being reported with this technology at full-scale. This technique employs the use of natural processes to reduce the concentration of contaminants at polluted sites and restrict the spread of pollutants from chemical spills. In case of natural attenuation, pollutants are simply left in place and the naturally-occurring processes like dispersion, volatilization, dilution, radioactive decay, biodegradation and sorption of the toxins onto the soil clay/organic matter help to clean up the site. Biological degradation reduces contaminant mass; simple dilution or dispersion reduces the contaminant concentrations; and adsorption helps to bind the contaminants to soil particles and prevent the contaminant migration. In this way, the environmental contaminants are left undisturbed (Khan et al. 2004).

Table 8 Recent application of natural attenuation at US superfund sites (US EPA 2012)

Site	Contaminant
^{G} Altus Air Force Base, Altus, Oklahoma	TCE
^{S} Wyckoff/Eagle Harbor, Puget Sound, Washington	Hg
^{G} Naval Surface Warfare Center, Indian Head, Maryland	Perchlorate
^{S} Louisiana Pipeline Terminals, Gulf Coast, Louisiana	PAHs
^{S} Ketchikan Pulp Company Site, Ketchikan, Alaska	NH_3, Sulfides, Methylphenol
^{S} Bremerton Naval Complex, Bremerton, Washington	PCBs, Hg

^{G} Groundwater; ^{S} Sediment

Natural attenuation processes can be categorised as destructive (where contaminants are destroyed) and non-destructive (where the concentration of the contaminant is reduced) (Gelman and Binstock 2008). This remediation technology is a proactive approach that is mostly mislabelled as the 'walk away' or 'do nothing' technique to site clean up that focuses on the authentication and monitoring of natural clean up methods other than relying completely on engineered systems (Khan and Husain 2002). Bioattenuation is mainly employed for removing herbicides, non-halogenated VOCs and SVOCs, fuels and pesticides from aquifer or soil particularly hydrophobic organics of high molecular weight like PAHs (Clement et al. 2000; Hejazi 2002; Nobre and Nobre 2004). This process could be applied for halogenated VOCs and SVOCs, but it may require longer treatment times. Surface geology, microbiology and hydrology decide the success of the bioattenuation processes. Before a site is processed by natural attenuation, it is necessary to assess the efficacy of natural processes that are occurring to reduce the contaminant levels over time. The treatment zone should be situated in a region remote from the potential receptors with less risk to ecology or public health. Bioattenuation is highly applicable for low to high permeable soils because high permeability speeds up the contaminant migration. Low permeability prevents the air, water and nutrients from dispersing throughout the soil and slows down the contaminant breakdown.

Several packages are offered for predictive modelling of bioattenuation. For instance, BIOSCREEN to stimulate bioattenuation from petroleum fuel discharges and BTEX, BIOCHLOR for chlorinated solvents, Bioredox-MT3DMS for chlorinated solvents and petroleum hydrocarbons, and BIOSLURP for NAPLs (Mulligan and Yong 2004). Natural attenuation is quite simple compared to other techniques where it is possible to be carried out with little/no site disturbance. This method could be used with other methods as pre- or post-treatment options at contaminated sites. However, this technique often needs a longer clean up period to achieve the remediation objectives compared to other conventional techniques and is generally very slow, where long-term monitoring is required. Performance of natural attenuation systems is often unpredictable. Generally, the by-products are ecologically more risky than the parent compounds. For instance, VC, the degradation product of TCE, is more toxic than TCE itself. Also, resolubilization and desorption of pollutants could occur and the modelling data need to be evaluated with caution as it is subjected to significant uncertainty. Cost of natural attenuation treatment is variable and no specific cost estimate is available (Khan et al. 2004).

Gonzalez-Chavez et al. (2009) carried out a field-scale natural attenuation study with the help of Arbuscular Mycorrhizal (AM) fungi and plants in a slag heap polluted with highly available Cd. The experimental results confirmed that glomalin protein produced by AM fungi could cause Cd stabilization, and use of plants and AM fungi aid the natural attenuation process. Bento et al. (2005) compared the biological degradation of TPH-polluted soil collected from the USA and China with natural attenuation, and concluded that natural attenuation increased (fourfold) the microbial activity and TPH degradation activity. Johnson et al. (2003) reviewed the potential of benzene degradation under a range of anaerobic groundwater conditions by natural attenuation. Many studies on the biodegradation of PAHs have been done but our knowledge of biodegradation behavior in the field compared to BTEX or chlorinated solvents is limited (Juhasz and Naidu 2000; Rogers et al. 2002).

Margesin and Schinner (2001) reported that natural attenuation is an eco-friendly technology that could significantly remove diesel oil even under unfavorable conditions, for instance, those present at about 3000 m above sea level in an alpine glacier. Using the mass flux method of detection, Kao and Wang (2001) reported 99 % BTEX degradation by natural attenuation at field-scale. Asta et al. (2010) observed that even very high concentrations (up to 4 mg/L) of As(III) and As(V) acidic discharge of the abandoned Tinto Santa Rosa mine in the Iberian pyritic belt, Spain, could be bioattenuated by sorption using iron oxyhydroxysulphate and iron oxyhydroxide as stream bed precipitates. Serrano et al. (2008) concluded that after a diesel spill in agricultural soil, most of the aliphatic hydrocarbons persist in the subsurface (up to 0.1 m) and volatilization was the main cause for the decline in aliphatic hydrocarbon concentration. Also, natural attenuation was the main source of aliphatic hydrocarbon degradation in soil when pH, moisture and temperature of the soil were optimized in the order of increasing microbial enzyme activity. A significant decrease (99 %) in dissolved mono and polycyclic hydrocarbon concentration was observed in a 14 year-old manufactured gas plant site subjected to monitored natural attenuation (Neuhauser et al. 2009).

Meers et al. (2010) introduced an analogy of phytoattenuation where the concept of natural attenuation and phytoremediation was integrated with a risk-based approach. They conducted a field experiment using energy crop (maize) that could result in the production of 33,000–46,000 kW h/10,000 m^2 of renewable electrical and thermal energy annually which by exchange of fossil energy would imply a decline of about 21×10^7 kg/m^2/year CO_2 if used to substitute a coal-fed power plant. They also detected a significant yearly decline of 0–5 mg/kg Zn in the subsurface though not Cd and Pb. A long-term natural attenuation study was conducted by Fraser et al. (2008) at a site that was contaminated by naphthalene, phenol, xylene, methyl naphthalene, acenaphthene, biphenyl, anthracene, dibenzofuran, fluorene, phenanthrene and carbazole. More than 90 % of naphthalene, biphenyl and carbazole entering the plume were completely removed after a 14-year attenuation process. Concentration of the remaining pollutants, however, was observed to be expanding due to limited degradation potential and increased mass flux.

Biotransformation emerged as the major process that controls the natural attenuation mechanism. Cozzarelli et al. (2011) conceptualized natural attenuation processes in landfill leachate plumes. He et al. (2010) found that enhanced reductive dechlorination could mobilize As at field-scale. Choi and Lee (2011) suggested the integration of some active remedial measures with biodegradation and natural attenuation to achieve the anticipated remedial goal in short time. Macias et al. (2012) conducted the natural pre-treatment and passive remediation of highly contaminated acid-mine drainage. Their results confirmed that coupled application of natural Fe-oxidising lagoon pretreatments and limestone-DAS (reactive substrate) passive treatments is a viable and potential approach to remediate acid-mine drainages contaminated with high concentrations of heavy metals. All these studies dictate that although natural attenuation is an eco-friendly technique, it takes a couple of years to achieve the anticipated remedial goal. Hence, integrating suitable remedial techniques that could support the attenuation processes are required to reduce the remedial time in the near future.

3.11 Phytoremediation

Phytoremediation involves the use of vegetation (grasses/plants/trees), its associated microorganisms and enzymes to remove, destroy, immobilize or contain pollutants from contaminated media. Some plants have the potential to accumulate large amounts of heavy metals that are not exploited in their function, and are generally known as‘hyperaccumulators’ (Susarla et al. 2002). Plants with the ability to take up and process or degrade even organics for their physiological needs are also referred to as hyperaccumulators (Vouillamoz and Mike 2001). Compared to other technologies although phytoremediation is time-consuming, it is the most cost-effective of the other remedial approaches as very large volumes of contaminated soil can be treated in-situ where excavation is not required (Mench et al. 2010). Most information related to phytoremediation is associated to its application in soil at field and laboratory level, and its utility in groundwater remediation is increasing interest (Juwarkar et al. 2010).

Phytoremediation is of five types: (1) phytotransformation (appropriate to treat both water and soil where pollutant remediation occurs by means of plant metabolism), (2) rhizofiltration (a water remediation method where pollutants are accumulated by the plant roots), (3) phytostimulation (microbial degradation is stimulated by plant activity in the root zone), (4) phytoextraction (contaminant uptake from the soil), and (5) phytostabilization (reducing the contaminant migration using plants) (Barcelo and Poschenrieder 2003; Gosh and Singh 2005). Phytoremediation is used to treat PAHs, PCBs, petroleum hydrocarbons, heavy metals, radionuclides, non-aromatic chlorinated solvents, organophosphate insecticides, explosives, BTEX, surplus mineral and nitrotoluene ammunition wastes (Nedunuri et al. 2000; Barac et al. 2004; Sheng and Gong 2006; Leigh et al. 2006; Al-Qurainy and Abdel-Megeed 2009; Ahmadpour et al. 2012). Phytoremediation is also applied in landfill covers, buffer regions for agricultural run-off, industrial wastewater, and drinking water treatments (Mench et al. 2010).

The use of phytoremediation is, generally its application has several limitations before it can be implemented at a site. First of all, it is vital that the polluted site to be remediated should be able to suitably support the plant growth followed by the availability of feasible growth conditions (weather, soil properties like nutrient availability, texture, pH and moisture). The second limitation is that phytoremediation is applicable only at shallow depths (upper 0.2–0.25 m of the soil horizon). Only in some cases can deeper depths be remediated when it is integrated with other technologies or some hybrid trees (for example, poplar trees that could grow to a depth of 5 m). Third, since it takes time for the establishment of plants in the remedial sites it is not suitable for rapid treatments. Phytoremediation is also restricted by the rate of root growth as denser root mass is ideal to contact more pollutants and slower growth rates increase the treatment time (Yang 2008; Gerhardt et al. 2009). Even winter could shut down the system completely as plants become dormant. Clean up generally takes more than one growing season.

Another problem is the risk of bioaccumulating the contaminant in the food chain as there is a potential for plant-eating animals to be exposed to the contaminants when they eat the phytoaccumulators. To avoid such circumstances, 'phytomining' is practised where plants are harvested and disposed or destroyed after the extraction of reusable metals (Chaney et al. 2007). Even overhead nettings and perimeter fencing are mounted to prevent animals grazing on contaminated plant materials. Phytoremediation is suited only to lower contaminant concentrations as very high contaminant levels could restrict the establishment of phytoremediators (Vishnoi and Srivastava 2008). Finally, it is recommended to confirm that transpiration and unwanted volatilization of the toxins to the atmosphere through plant uptake does not occur. On the whole, to assess the fate of the contaminants, sites undergoing phytoremediation must be continuously monitored.

Comparable advantages are evident in the phytoremediation system. Phytoremediation is an aesthetically-pleasing, passive and solar energy-driven technique that is able to treat outsized contaminants with minimal site disturbance along with minimal generation of secondary wastes where the end products are only CO_2 and H_2O, but not any hazardous toxins. This technique is low cost for treating large-scale contaminated sites with low contaminant concentrations (Mench et al. 2010). Usually, the unused top soil could be used for agriculture. About 5–18 US$ is expended to clean up an m^2 contaminated site by plants. So far, numerous plant species were tested for their ability to remediate organic and inorganic contaminants like pesticides, PAHs, chlorinated solvents, diesel, phenol, BTEX, Cr, Cd, Zn, Ni, Cu, As, Hg, Mn, Co, Pb, Se, U, N and P at field-scale as summarized in Table 9. Over the last 10 years, the potential use of trees as a suitable vegetation cover for polluted sites has also received increasing attention (US EPA 2012).

James (2001) and Pulford et al. (2002) proposed that deep rooting plants could reduce highly toxic Cr(VI) to Cr(III) since organic products of root metabolism could act as reducing agents. Research on the application of phytoremediating plant with inorganic, organic and bio-amendments revealed promising results (Green and Hoffnagle 2004). Banuelos et al. (2005) reported that Indian mustard can be genetically modified to produce more biomass in the polluted soil and hyperaccumulate

Table 9 Plants used in phytoremediation for the removal of selected organic and inorganic pollutants

Contaminant	Plant used
Pesticides	*Artemisia annua*, *Kochia sieversiana*, *Kochia scoparia*, *Xanthium strumarium*, *Oryza sativa* cv. Nipponbare, *Lemna minor*, *Elodea canadensis*, *Cabomba aquatic*, *Pisum sativum*, *Cucurbita pepo*, *Eichhornia crassipes*, *Corbicula fluminea*, *Pistia stratiotes*, *Lemna minor*
PAHs	*Lolium multiflorum*, *Lolium perenne*, *Betula pendula*, *Galega orientalis*, *Brassica campestris*, *Cordia subcordata*, *Festuca arundinacea*, *Melilotus officinalis*, *Panicum virgatum*, *Astragalus membranaceus*, *Aeschynomene indica*, *Avena sativa*, *Capsicum annum*, *Pinus strobus*, *Salix viminalis*
Chlorinated solvents	*Arabidopsis thaliana*, *Festuca arundinacea*, *Panicum virgatum*, *Cucurbita pepo*, *Populus* sp., *Salix* sp., *Brassica napus*, *Hydroponic Leucaena*, *Elodea canadensis*
Diesel	*Pinus sylvestris*, *Pinus sativum*, *Festuca rubra*, *Lolium perenne*, *Trifolium repens*, *Jatropha curcas*, *Cyprus rotundus*, *Salix alba*
Phenol	*Vetiveria zizanoides*, *Astragalus chrysopteru*, *Hordeum vulgare*, *Typha angustifolia*
BTEX	*Paspalum vaginatum*, *Zoysia tenuifolia*, *Galega orientalis*, *Populus deltoides*
Cr	*Trigonella foenum-graecum* L., *Spinacia oleracea* L., *Brassica campestris* L., *Helianthus annuus*, *Eichhornia crassipes*, *Callitriche cophocarpa*, *Polianthes tuberosa*, *Genipa Americana*
Cd	*Thlaspi caerulescens*, *Lolium perenne* cv. *Elka*, *Solanum nigrum*, *Trifolium repens*, *Brassica napus*, *Populus canadensis*, *Populus deltoides*, *Juncus subsecundus*, *Ricinus communis*, *Alyssum* sp., *Typha domingensis*
Zn	*Tithonia diversifolia*, *Helianthus annuus*, *Paulownia tomentosa*, *Arabidopsis halleri*, *Thlaspi caerulescens*, *Salix caprea*, *Anthyllis vulneraria*, *Lupinus albus*, *Azolla caroliniana*, *Picris divaricata*
Ni	*Alyssum corsicum*, *Alyssum murale*, *Alyssum lesbiacum*, *Thlaspi goesingense*, *Sebertia acuminata*, *Lycopersicon esculentum*, *Solanum nigrum*, *Amaranthus* sp., *Populus alba*, *Spirodela polyrhiza*
Cu	*Zea mays*, *Aeolanthus biformifolius*, *Commelina communis*, *Elsholtzia splendens*, *Brassica juncea*, *Baccharis sarothroides*, *Aldama dentata*, *Lemna gibba*, *Onobrychis viciifolia*, *Dyera costulata*, *Lemna minor*
As	*Arundo donax*, *Tagetes erecta*, *Tagetes patula*; *Pteris vittata*, *Pityrogramma calomelanos*, *Helianthus annuus*, *Agrostis tenuis*, *Chrysopogon zizanioides*, *Cynara cardunculus*
Hg	*Eichhornia crassipes*, *Pistia stratiotes*, *Scirpus tabernaemontani*, *Colocasia esculenta*, *Silene vulgaris*, *Elodea nuttallii*, *Brassica juncea*, *Azolla pinnata*
Mn	*Eichhornia crassipes*, *Phytolacca americana*, *Phytolacca acinosa*, *Vigna unguiculata*, *Alyssum* sp., *Typha angustifolia*, *Phragmites* sp.
Co	*Glycine max*, *Pistia stratiotes*, *Ambrosia artemisiifolia*, *Pleurotus pulmonarius*
Pb	*Vetiveria zizanioides*, *Thlaspi praecox*, *Mimosa pudica*, *Brassica juncea*, *Ambrosia artemisiifolia*, *Apocynum cannabinum*, *Bidens triplinervia*, *Zea mays*, *Typha latifolia*, *Salix* sp., *Lemna minor*
Se	*Brassica napus*, *Festuca arundinacea*, *Spartina patens*, *Arabidopsis thaliana*, *Pteris vittata*, *Stanleya pinnata*
U	*Helianthus annuus*, *Phragmites* sp., *Lagonychium farctum*, *Vetiveria zizanioides*
B	*Lemna gibba*, *Salvinia natans*, *Populus* sp., *Vetiveria zizanioides*
N and P	*Thalia geniculata*, *Onenathe javanica*, *Phyla lanceolata*, *Eichhornia crassipes*, *Ipomoea aquatica*, *Pistia stratiotes*, *Populus deltoides*, *Chlorella vulgaris*

Se in a short time. Ma et al. (2001) demonstrated that Chinese brake fern (*Pteris vittata*) could hyperaccumulate 22,000 mg/kg As in their shoots. Gumaelius et al. (2004) also indicated that *P. vittata* could accumulate 200-fold higher As than any other vegetation. Raskin and Ensley (2000) showed that sunflower had greater ability to remove Pb from leaf compared to corn, spinach, Indian mustard, tobacco and rye.

Plants like sunflower, corn, spinach, Indian mustard, tobacco and rye have been tested for their potential to accumulate Pb from effluent, wherein sunflower showed the highest potential to remove Pb (Raskin and Ensley 2000). A field experiment by Zhuang et al. (2007) revealed that *Rumex crispus* is an ideal candidate for phytoextraction of Zn and Cd from soil. Another field trial conducted by Shu et al. (2004) compared the growth and metal accumulation ability of four grasses (*Imparata cylindrica* var. *major*, *Paspalum notatum*, *Vetiveria zizanioides* and *Cynodon dactylon*) supplemented with and without complex fertilizer (NPK) and domestic refuse. The results showed that among the grass species selected for phytostabilization and phytoextraction of metal-contaminated soils, *V. zizanioides* was the best choice. About 70 % loss of total petroleum hydrocarbons was recorded after one year's growth of *Carox exigua*, *Panicum virgatum*, *Tripsacum dactyloides* and *Vicia faba* (Euliss et al. 2008). Diab (2008) observed 47 % degradation of total petroleum hydrocarbons in 60 days by *V. faba*.

Komarek et al. (2008) explored the influence of chelant-enhanced phytoextraction of heavy metals. They confirmed that adding EDTA significantly increased the translocation rate of Pb content in poplar plants. A similar field study by Zhuang et al. (2005) indicated the great potential of *Viola baoshaensis* for removing Pb, Cd and Zn in the presence of ammonium additives/EDTA. Otto et al. (2008) indicated that narrow plant filter strips could commendably decrease herbicide run-off from agricultural soils because of the plants' ability to promote infiltration, delay surface runoff and adsorb herbicides. Root zone effects in a constructed wetland system were noticed using plant growth-promoting rhizobactera like *Rhizobium leguminosarum* and *Pseudomonas aeruginosa* by Radwan et al. (2007). Mendelssohn et al. (1995) conducted a multidisciplinary experimental program to evaluate the use of bioremediation products such as microbial seeding, inorganic fertilizer and soil oxidant, as a means of oil biodegradation enhancers in coastal salt marshes with *Sagittaria alterniflora*. Their experimental results showed that fertilizer application enhanced the rate of phytoremediation at wetlands, and degradation of oil was greater in the drained condition than in the flooded condition.

An AM fungus colonized the phytoremediators that were raised in a metal(loid) remediating site and aided in the nutrient acquisition for their host plants (Meharg 2001). Manceau et al. (2008) reported that two common wetland plants, *Iris pseudacorus* and *Phragmites australis*, transformed Cu into metallic nano-sized particles near and in root zones colonized by AM fungi. The role of potential amendments like gravel sludge, biosolids, oxides of Fe, Mn, Al and Ti, coal fly ashes, ZVI grit and alkaline materials in phytostabilization was reviewed in the literature (Friesl et al. 2006; Kumpiene et al. 2008; Mench et al. 2009; Vangronsveld et al. 2009). Mench et al. (2007) reported that a long-lasting phytostabilization effect was obtained for ZVI grit product and biosolids. According to McGrath et al. (2006), in a 3-year cropping season, *Thlaspi caerulescens* crop extracted up to 0.4 % Zn and 3 % Cd, and the maximum annual removal was 0.4 g Zn, and 0.07 g Cd m^{-2}. Vervaeke et al. (2003) conducted a field trial implementing green capping using willow trees in sediment contaminated with Cd, Cu, Pb and Zn. It was found that after 1.5 years nearly 57 % mineral oil was significantly reduced in the sediment with a pronounced 79 % decrease in the root zone. Euliss et al. (2008) conducted a field study and discovered that about 70 % PAHs from the contaminated sediment could be remediated by planting *C. stricta*, *T. dactyloides* and *P. virgatum* over a 1 year period. Hong et al. (2001) achieved phytohydraulic containment and 36.5–67.0 % methyl tert-butyl ether (MTBE) removal from a groundwater plume using poplar plants. Hultgren et al. (2009) observed 100 % phenanthrene and 80 % pyrene degradation efficiency in the presence of *Salix viminalis*, but merely 63 and 68 % PAH degradation was achieved without plants. Fassler et al. (2012) indicated that application of elemental sulphur helps to enhance the phytoextraction of metals at real contaminated sites.

Phytoremediation of phthalic acid esters by intercropping *Medicago sativa*, *Lolium perenne* and *Festuca arundinacea* was demonstrated by Ma et al. (2012) in the largest e-waste recycling site in China. Over 80 % of the phthalic acid esters were removed by effective monocropping of *Medicago sativa* and intercropping of all the three crops. Galazka et al. (2012) studied the effect of *Festuca pratensis* with and without the inoculation by diazotrophic bacteria (*Azospirillum* spp. and *Pseudomonas stutzeri*) on the degradation of a mixture of PAHs and diesel fuel. It was observed that inoculation of diazotrophs with phytoremediators helped to achieve more than 70 % remediation. Under aerobic conditions, surfactant solution (Tween 80) was effective in the rhizodegradation of oil with added benefit on the indigenous soil microbes (Memarian and Ramamurthy 2012). These days, transgenic/genetically modified plants are emerging as a promising technology which is discussed in the later part of this review under emerging techniques. In most field studies, only 50–70 % remediation was achieved at least with 1 year of treatment time. Solutions to achieve >90 % remediation in most cases by reducing the treatment time should be worked out in future by integrating the plants with supportive physico-bio-chemical elements.

3.12 Bioaugmentation

Biostimulation and bioaugmentation possess the ultimate goal of decontamination through biotransformation (Brar et al. 2006). Bioaugmentation and biostimulation can be either an in-situ or *ex*-situ treatment process. A handful of successful field-scale studies have confirmed the performance of biostimulation and bioaugmentation as stand-alone and integrated systems (Table 10). Rather than nutrient load, specialization and selectivity of inoculated microbes determine the bioremediation potential (Hamdi et al. 2007). In bioaugmentation, metabolic activity of indigenous

Table 10 Bioaugmentation and biostimulation: successful case studies at field-/pilot-scale

Research group	Year	Contaminant	Technology		Stimulants		
			BS	BA	Fertilizer	Surfactant	Others
[f] Sanscartier et al.	2009	TPH and PAHs	♣	–	♣	♣	♣ (1)
[f] Tsutsumi et al.	2000	Crude oil	–	♣	–	♣	–
[f] Duke et al.	2000	Crude oil and fuel oil	♣	–	♣	–	♣ (2)
[f] Lendvay et al.	2003	PCE, DCE	♣	♣	♣	–	–
[f] Delille et al.	2002	Crude oil	♣	–	♣	–	♣ (3)
[f] US EPA	2012	PCE, DCE	♣	♣	–	–	♣ (4)
[p] Straube et al.	2003	PAHs	♣	♣	♣	–	–
[p] Yu et al.	2005	PAHs	–	♣	–	–	–
[p] Atagana	2006	PAHs	♣	♣	♣	–	♣ (4)
[f] Maes et al.	2006	DCA	♣	♣	–	–	♣ (4)
[f] Jimenez et al.	2006	PAHs	♣	–	♣	–	–
[p] Malina and Zawierucha	2007	TPH and PAHs	♣	♣	–	–	♣ (4)
[f] Garcia-Blanco et al.	2007	Crude oil	♣	–	♣	–	–
[p] Jacques et al.	2008	PAHs	♣	–	–	–	–
[f] Kauppi et al.	2011	TPH and PAHs	♣	♣	♣	–	–

[f] Field-scale study; [p] Pilot-scale study; BS, Biostimulation; BA, Bioaugmentation; '♣', Implemented/used specific technology/stimulant; '–', Technology/stimulant was not implemented/used; 'Others' include: (1) Moisture and temperature amendments, (2) Forced aeration, (3) Fish compost, and (4) Electron donors/acceptors like acetate, methanol, ethanol, hydrogen peroxide, etc.

soil microbes is further enhanced by inoculating consortia or single cells of microbes containing genes for biodegradation so that these genes are transferred to indigenous and rhizospheric microbes (Gentry et al. 2004). Genetically modified organisms or indigenous or allochthonous wild types are the specialized organisms that are included in bioaugmentation. According to Dejonghe et al. (2001), bioaugmentation corresponds to an increase in the genetic diversity or gene pool of the targeted site.

Rhizoremediation, suggested by Kuiper et al. (2004), is indeed one form of bioaugmentation. Mrozik and Piotrowska-Seget (2010), El Fantroussi and Agathos (2005), and Iwamoto and Nasu (2001) stated that bioaugmentation is applicable only when biostimulation and bioattenuation fails. The major factors affecting bioaugmentation are: (1) environmental (temperature, pH, moisture content, electrical conductivity, availability of electron acceptors, availability of nutrients and toxic molecules); (2) microbial (horizontal gene transfer of wild type strains and genetically modified organisms, microbial interactions and mutation, microbial diversity, toxic metabolites produced from degradation compounds, metabolic activity or enzyme induction and activity); (3) physico-chemical bioavailability of contaminants (solubility in water, complexation, stability, toxicity of pollutants, mass transfer limitations and irreversible sorption); (4) growth substrates (bioavailability and concentrations of contaminants and substrates, limiting factors like NPK and preference of other substrates other than the contaminants); and (5) aerobic or anaerobic process (electron acceptor/donor availability and reduction/oxidant potential).

Generally, microbes that express catabolically superior toxin-degrading enzymes and are highly resistant to environmental stresses should be selected for bioaugmentation (Singer et al. 2005). According to Belotte et al. (2003), the best bioaugmentation approach is to preselect the microorganisms from their own physical setting. Experiments conducted so far in bioaugmentation used fungi belonging to the genera, *Verticillium*, *Penicillium*, *Mucor*, *Aspergillus* and *Absidia*, and gram-negative bacteria like *Sphingomonas*, *Pseudomonas*, *Flavobacterium*, *Alcaligenes* and *Achromobacter* (Mrozik and Piotrowska-Seget 2010). Mostly, all types of pollutants are subjected to bioaugmentation, and there is no specific category of target pollutant to treat. For pollutants of less water solubility (PCBs and PAHs), it is essential to use the surfactant-producing strains so that the contaminants are made more bioavailable (Dua et al. 2002; Johnsen et al. 2005; Mrozik and Piotrowska-Seget 2010). It will be more favorable to make use of a strain that could produce a surfactant and degrade the targeted pollutant. In many cases a single strain was shown to be less effective than consortia (Kuiper et al. 2004), because the toxic intermediate of the degradative pathway of one strain in a consortium may be further degraded by other strains possessing suitable catabolic pathways.

Bioaugmentation has five general sustainability criteria which add to its merits. They are: its ability to harness or mimic a natural process, elimination of energy or natural resource consumption, reduction or no release of toxic gases into the atmosphere, permanent contaminant-destroying ability, and reusability or recycling ability of inactive lands or discarded materials. However, the main disadvantage is the requirement of voluminous microbes for large-scale treatment of sites contaminated with high concentrations of pollutants where cost might be high and the variability and uncertainty exist with regard to the acclimated microbes. The major disadvantage is that it takes a long time (up to several years) to achieve the remedial goal since the system is slow. So far, no accurate cost estimation is available for this technology as it is highly variable.

The ability of the native soil microbes to degrade PAHs in a long-term polluted soil was reported by Li et al. (2009b). They also found that after supplementing a microbial consortium comprising three bacteria belonging to the genera *Zoogloea*, *Flavobacterium* and *Bacillus*, and five different fungi, *Aspergillus niger*, *Penicillium chrysogenum*, *Alternaria alternata*, *Phanerochaete chrysosporium* and *Cuuninghamella* sp., the degradation rate of PAHs significantly increased to 41.3 %. Alisi et al. (2009) studied the degradation of phenanthrene and diesel oil using microbial consortium of selected native strains and observed a removal of 75 % total hydrocarbon and 60 % isoprenoid in 42 days. A group of bacteria isolated from a gasoline-polluted soil was encapsulated as enriched consortia in gellan gum microbeads by Moslemy et al. (2002). The encapsulated cells exhibited a higher gasoline degradation rate with a shorter lag phase compared to their free cell counterparts at the corresponding microbial concentrations. Monard et al. (2008) found a significant increase in atrazine mineralization by earthworm digestion in soils bioaugmented by *Chelatobacter heintzii* and *Pseudomonas* sp. Olaniran et al. (2006)

reported that EDC was remediated completely by a synthetic consortium made of *Klebsiella* sp., *Bacillus cereus*, *B. subtilis*, *Achromobacter xylosoxidans*, *Acinetobacter* sp., *Pseudomonas aeruginosa* and *Acinetobacter haemolyticus*, where the microbes' survival was enhanced by supplying NPK in the ratio of 3:1:6.

Until now, only on-sites like pristine places and hot springs were given attention for strain selection. Verstraete et al. (2007) suggested that deep sea/underground should also be explored. Gentry et al. (2004) observed chlorobenzoate degradation by activated soils. Van der Gast et al. (2004) reported 85 % degradation of processing waste metal fluids by a consortium of four indigenous bacterial strains assembled on the basis of their degradation abilities and tolerance to fluctuating chemistry of the treated fluid. Plangklang and Reungsang (2009) studied the importance of 'formulation' of an inoculum which is a crucial factor that affects the viability of pollutant-degrading microbes, and noticed that immobilized *Burkholderia cepacia* on corn corb involved in carbofuran degradation could survive for 30 days compared to the free cells. Recently, few commercial inocula have only been tested in bioaugmentation systems at laboratory level, but not in field-scale. KB-1™ and Bio-Dechlor INOCULUM™, composed of consortia of multiple *Dehalococcoides* sp. with other bacterial types (PCE-cis-DCE dechlorinators, fermenters and acetogens) were used for remediation of groundwater (Loffler and Edwards 2006).

Enzyveba—a patented, stable and complex consortium of eukaryotic and prokaryotic organisms, used by Marcopolo Engineering SpA, Italy—was tested and proved to be: firstly, a bioactivator of landfills/composting facilities/wastewater treatment plants; and secondly, a commercial degrader of diesel fuels (Di Toro et al. 2008). Van Dillewijin et al. (2007) showed that axenic plants inoculated with a plant growth-promoting bacterium (*Pseudomonas putida*) could remove 80–88 % trinitrotoluene. Lebeau et al. (2008) reported that bioaugmentation increased the accumulation of metals by plant shoots to a factor of 5.0 without any obvious difference between the degrading microbe types (either bacteria or fungi). Using 10^{12} CFU/kg inoculum, 80 % degradation of dichlorodibenzo-*p*-dioxin was achieved compared to 10^{10} CFU/kg inoculum where only 46 % degradation was achieved (Hong et al. 2007).

At field-scale, the effect of soil bioaugmentation was confirmed for trinitrotoluene (Van Dillewijin et al. 2007) and atrazine (Strong et al. 2000). Truu et al. (2003) and Juhanson et al. (2009) demonstrated the combined effect of phytoremediation and bioaugmentation in full-scale. Zhang et al. (2008) treated the largest soil surface of 7000 m^2 by bioaugmentation (*Cunninghamella echinulata* and *Enterobacter cloacae* as a consortium) for salt- and petroleum-contaminated soil in which wheat straw enhanced petroleum degradation with subsequent salt leaching. Diplock et al. (2009) reported that it generally takes three times longer for conducting field trials by bioaugmentation compared to laboratory studies. Length of treatment at field-scale has been reported to extend from a few weeks to nearly 3 years (Hesselsoe et al. 2008; Juhanson et al. 2009). Further research should formulate a commercial inoculum for diverse contaminant types and make the bioaugmentation approach more mechanized so that inoculated organisms' role is better understood when removing pollutants. Also, strategies to reduce the remedial time and integration with other biological tools to increase the remedial effects could be used along with further implementation of comparable field studies using other technologies.

As in most cases, bioaugmentation fails at field-scale which is assumed to be due to unfavorable soil physico-chemical factors and antibiotics produced by the native microbes that harm the artificially-inoculated microbes. A new approach of using an enzyme-based, cell-free product was proposed by Scott et al. (2008) to remediate atrazine-contaminated fluids. The cell-free approach is limited in that is applicable only to efficient and viable enzymes that do not rely on diffusible cofactors like NAD, etc. However, enzyme immobilization on carriers would make them highly stable and resistant to changes caused by substrate concentrations, pH, temperature, etc. Hence, it is important to select a cost-effective carrier material for the enzyme product as well as study different mechanisms for the efficient delivery of enzymes into the natural ecosystem.

3.13 Biostimulation

Biostimulation refers to the addition of specialized growth-limiting nutrients such as carbon, nitrogen and phosphorous in contaminated sites so that naturally-occurring microbes are present in sufficient numbers and types to degrade the waste effectively (Trindade et al. 2005). As such, biodegradation is enhanced by the amendment of water-based solutions such as electron acceptors, nutrients and other additives (Juwarkar et al. 2010). Acetate, sulphate, nitrate, ethanol and electrodes are the electron donors that are used in biostimulation of contaminated sites. Herbicides, pesticides, fuels, non-halogenated SVOCs, VOCs, heavy metals and radionuclides like U were successfully removed via biostimulation at field-scale (Eguchi et al. 2001; Brar et al. 2006). While it is applicable, it is less effective to degrade halogenated organics. This approach requires the presence of indigenous microbes that are potent to degrade a target pollutant. Likewise, it is problematic that the toxins are bioavailable and not tightly sorbed to the soil particles. Although the cost of biostimulation technologies tends to change depending on the site, it is considered one of the cheapest remedial alternatives applicable for both soil and groundwater. This technology is not suited for sites contaminated with high concentrations of pollutants as it would hinder the microbial growth. Tight, impermeable subsurface lithology makes it difficult to spread the water-based solution throughout the treatment zone. Fractures create preferential pathways in the subsurface, from where the nutrient solution could preferentially flow and aid the microbial activity.

The extensive use of biostimulation as a promising remedial approach has several limitations, most of these being concerned with soil heterogeneity. Every site has its own unique soil chemistry, hydrology and geology affecting the native microbial populations available for degradation. For instance, iron-rich soils support bigger populations of strains like *Geobacter* sp. that utilize iron as its electron acceptor that could concurrently reduce heavy metals like U (Bopp et al. 2010). However, iron-poor soils do not support the survival of such bacterial strains and are harder to remediate. Co-contamination additionally creates some problems as one contaminant could be toxic to the microbes stimulated to degrade the other contaminant (Atagana 2006). A co-contaminant may also increase the mobility of the contaminant.

For example, use of gasoline additives always increases the migration of BTEX in groundwater (Da Silva et al. 2005). Non-target microbial consumption or loss of stimulant due to diffusion away from the treatment zone can inhibit the ideal growth of decontaminating bacteria. For example, during U reduction, anaerobic environments with low nitrate levels prevent the electron donors from being consumed by bacteria that use nitrate or oxygen as terminal electron acceptors (Yabusaki et al. 2007). Further, long-term monitoring is required to validate the effectiveness of the biostimulation system particularly with regard to heavy metal contamination. Hence, the above limitations must be rectified if biostimulation is to become a more reliable technology.

Almost in all cases, biostimulation is applied in conjunction with bioaugmentation (Table 10). In a study to determine the efficiency of biostimulation in restoring oil-contaminated coastal marsh dominated by *Spartina alterniflora* through the addition of phosphorous and nitrogen under temperate condition, Garcia-Blanco et al. (2007) reported that >80–90 % oil disappeared after 20 weeks. Biostimulation of a petroleum spilled site was successful in Bellingham, Washington when the activity and population of sulphur-reducing bacteria such as *Desulfobacter* sp. that could degrade petroleum was stimulated by the addition of growth limiting nutrient (sulphate) (Bhowmik et al. 2009). By the injection of hydrogen peroxide into ground wells, aerobic conditions favorable for PAHs degradation were established by Menendez-Vega et al. (2007). Adding an electron donor such as lactate increased the degradation rate of PECs to VC (Hirschorn et al. 2007). After 2 years of ethanol (electron donor) amendment, U(VI) was reduced to 1.0 μM from 5 μM in a radionuclides-contaminated site at Oak Ridge, Tennessee as ethanol stimulated the activity of sulphur-reducing bacteria (Wu et al. 2006a).

Yabusaki et al. (2007) conducted a field experiment at the Old Rifle site in Western Colorado and observed complete immobilization of U(VI) in groundwater by iron-reducing *Geobacter* sp. whose activity was stimulated by acetate amendment. Eguchi et al. (2001) reported that removal of 10–20 % TCE in a week was achieved by methane oxidizers due to the stimulation of growth by the supply of growth-limiting nutrients such as methane, oxygen, nitrate and phosphate. Hamdi et al. (2007) observed degradation of pyrene (63 %) and benzo(a)pyrene (21 %) within a few weeks when the activity of the PAH degraders was stimulated by the addition of biostimulants like decaying rice straw and sludge compost. Similarly, Wu et al. (2008) demonstrated the ability of ground corn cob to stimulate PAH degradability of *Monilinia* sp. About 82–95 % TCE was dechlorinated to ethene when the dechlorinated culture (*Dehalococcoides* strain KB-1) was supplied with enough growth-limiting elements like methanol, ethanol, acetate and lactate as mixtures (Hood et al. 2008). Increase in PAH degradation by *Pseudomonas aeruginosa* strain 64 using biostimulators (ground rice hulls and dried bloods) was reported by Straube et al. (2003).

Enhanced bioremediation of petroleum hydrocarbons (up to 96 %) was achieved by Sarkar et al. (2005) by the amendment of inorganic fertilizers and biosolids. A similar study was conducted by Delille et al. (2009) using a commercial fertilizer to remediate diesel oil in Antarctica's coastal sea. While studying the effect of fertilizer as a stimulating agent to aid biological degradation of synthetic diesel oil at extreme temperature, Horel and Schiewer (2009) reported that fertilizer applications could stimulate the contaminant degradation up to three and eight times higher at 20 and 6 °C, respectively, compared to nutrient deficient conditions. The optimal CNP ratio (range of 100:9:2/199:10:1/250:10:3) required to commence any in-situ BTEX remedial measure was reported by Wolicka et al. (2009).

Use of biosurfactants to aid biodegradation of pollutants along with biostimulants was also demonstrated (Ron and Rosenberg 2002; Bordoloi and Konwar 2009; Hazra et al. 2012). In recent years, numerous organisms that could produce biosurfactants were identified and used in conjunction with bioaugmentation and biostimulation. Lipopeptides produced by *Rhodococcus* sp., *Bacillus subtilis* and *Nocardiopsis alba* (Abdel-Mawgoud et al. 2009; Haddad et al. 2009; Gandhimathi et al. 2009), glycolipid from *Pseudozyma hubeiensis* and *Nocardiopsis lucentensis* (Fukuoka et al. 2008; Kiran et al. 2010), glucolipid and trehalose lipid from *Rhodococcus erythropolis* (Peng et al. 2007), rhamnolipid produced by *Pseudomonas aeruginosa* and *Burkholderia plantari* (Chen et al. 2007; Abdel-Mawgoud et al. 2009; Hormann et al. 2010) are the biosurfactants used so far for the bioremediation of affected areas. Apparently, the combined application of biostimulation and bioaugmentation with biosurfactant is a promising approach to speed up the remedial mechanism (Baek et al. 2007; Tyagi et al. 2011). Though biostimulation has proved to be effective with organic and inorganic contaminants, additional field experiments should be conducted to develop good models for the widespread use of biostimulation systems. Also, by confirming that biostimulation decreases toxin levels within a shorter time frame and by improving the ease of implementation, biostimulation could be demonstrated as an ideal strategy for degrading environmental contaminants at large-scale.

3.14 Biosorption

Additionally, an effective biological technique that is just as good as bioaccumulation or biostimulation is biosorption where either natural resources or microorganisms are used. Biosorption is gaining importance owing to its inherent advantages (low cost by use of industrial, agricultural and waste biomass; process operation under ranging pH and temperature as the biosorbent is active; easy storage or use; ability of the binding sites to accommodate a variety of ions; higher degree of rapid toxicant uptake; high possibility of biosorbent regeneration and reuse with possible toxicant recovery) over bioaccumulation processes (Vijayaraghavan and Yun 2008). Biosorption is generally used for the removal of pollutants from water, especially those that are not easily biodegradable such as metals and dyes. A variety of biomaterials, including industrial and agricultural wastes, bacteria, fungi and algae are known for their biosorption potentials. Juwarkar et al. (2010), Vijayaraghavan and Yun (2008), Volesky (2006), and Loukidou et al. (2004) vividly discussed the biosorption process in their reviews. Melo and D'Souza (2004), Tunali et al. (2005), and Aravindhan et al. (2004) demonstrated Cr biosorption by seaweed and fungal biomass. Successful sorption was reported for Cd by red alga (Sari and Tuzen 2008), rice polish agricultural waste (Kumar and Bandyopadhyay 2006), wheat bran (Singh et al. 2006), and black gram husk (Saeed and Iqbal 2003). Sorption of Cu by lichen biomass immobilized in grape stalks (Ekmekyapar et al. 2006), spent grains (Lu and Gibb 2008), marine alga (Da Silva et al. 2002), green alga (Deng et al. 2007), activated carbon (Esmaeili et al. 2008), and polysulfone matrices (Beolchini et al. 2003); Ni sorption by cone biomass (Malkoc 2006); biosorption of Pb with the use of polymerized banana stem (Noeline et al. 2005); and sorption of Zn by orange peel cellulose with fungal cells immobilized in Ca-alginate beads (Lai et al. 2008), mature jamun (King et al. 2008) and neem tree barks/leaves (Arshad et al. 2008) have been reported. Bhattacharyya and Sharma (2004) suggested neem leaf powder as a suitable sorbent of dyes. New remedial approach such as the use of bioreactive organoclays which result in accelerated sorption and biodegradation/transformation of noxious pollutants of concern like Cr was reported by Sarkar et al. (2011). Using seaweed-based treatment technology as a biosorbent for remediating complex metals in wastewaters is a recently advanced option available for site clean up (Ahmady-Asbchin et al. 2009).

Thus, remedial in-situ technologies are quite promising for a wide range of pollutants and are becoming more sophisticated. Of all the available in-situ remedial techniques, bioaugmentation with biostimulation, biosorption, rhizoremediation, surfactant-enhanced remediation and EK remediation are considered to be promising for rapid degradation of contaminants because they are ecofriendly and cost-effective.

4 Emerging Technologies

Of the conventional technologies that are discussed above, physico-chemical methods such as heating, flushing, etc. are generally costly and the remedial approach is often incomplete due to the conversion of parent compounds into transformation products which are more recalcitrant and equally hazardous to non-target organisms. On the other hand, biological remediation processes like phytoremediation, bioaugmentation, etc. offer an environmentally friendly and economically feasible option to remove hazardous toxins from the environment. Since the natural ability of plants and microbes for decontamination is exploited and the organic pollutants in theory could be completely mineralized to water and CO_2 without any residual effects, along with the intended reduction in bioavailability of the target contaminant with cost-effectiveness, currently bioremediation is mainly focused on further developments such as integrating a few promising physico-chemical technologies (Megharaj et al. 2011; Rayu et al. 2012). In this context, the use of microbial fuel cells, nanoparticles, transgenic plants and microbes, and photo-hetero microbial consortia approaches has entered a new phase and leading to improvements in how well existing risk-based environmental remedial systems perform. These emerging technologies are mostly biological and expected to give rise to the birth of an ‘era of green biotechnology' in the near future. The massive exploitation of these recently advancing novel remediation approaches will bring about a rapid + reliable + low cost + risk-based contaminant clean up strategy.

4.1 Microbial Fuel Cells

A microbial fuel cell (MFC), also known as 'green power generation system' is a bioelectrochemical device that converts chemical energy into electrical energy by the catalytic reaction of microorganisms on organic compounds or metals (Aelterman et al. 2009). Generally, microbial metabolism is harnessed through fuel cells to convert organic materials or wastewaters into hydrogen, electricity and industrially useful chemicals while remediating the polluted environmental sites (Erable et al. 2012). In the last few years, MFC-related investigations have been intensified due to the promise of sustainable energy production from organic wastes. MFCs are highly adaptable and have greater potential to deliver energy in a sustainable fashion; however, their widespread application is feasible only after major improvements have been made. There are different types of MFCs as can be seen in Fig. 2 (Kim et al. 2002; Rabaey and Verstraete 2005; Logan et al. 2006; Liang et al. 2007). Mediator-less MFC includes plant-MFC (microbes aerobically breakdown and release electrons from small mass carbohydrates that are exuded from plant roots as a result of photosynthesis), metal-reducing MFC (use of microbes that possess the ability to reduce Fe(III) to Fe(II) during the oxidation of the carbonaceous

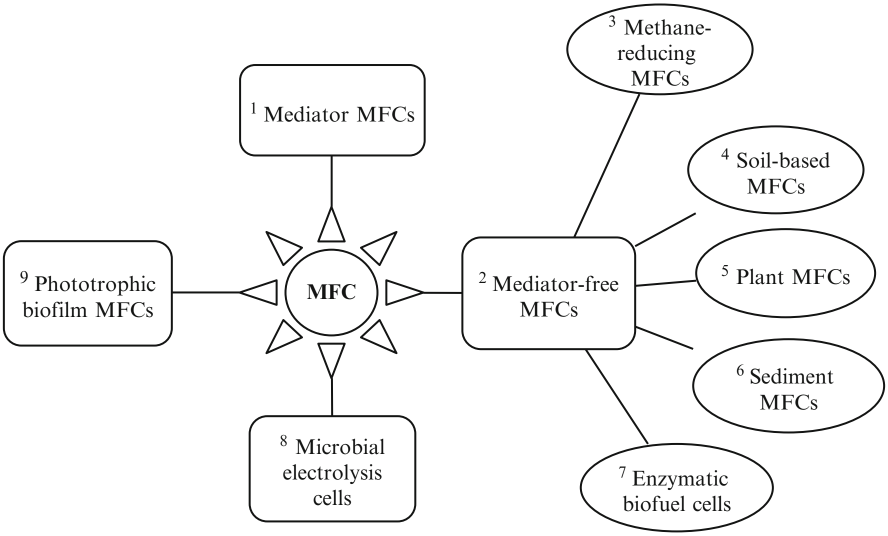


Fig. 2 Microbial fuel cell (MFC) types. Superscript indicates the reference for each technology: [1] Logan et al. (2006); [2] Nwokocha et al. (2012); [3] Lee et al. (2008); [4] Ringelberg et al. (2011); [5] Strik et al. (2008); [6] Donovan et al. (2011); [7] Huang et al. (2011); [8] Jeremiasse et al. (2010); [9] Strik et al. (2008)

substrate to CO_2), enzymatic biofuel cells (enzymatic biocathodes), and sediment MFC types (anode placed in nutrient-rich marine sediments and cathode placed in seawater above the sediment and the resulting voltage gradient generates power in marine environments) (Nwokocha et al. 2012). Generated electrons and protons (by means of a proton-exchange membrane) flow through a load to the cathode and subsequent reduction of oxygen ions by protons produces water. To produce a sufficient rate of oxygen reduction, catalysts like platinum and iron-tetra methoxy phenyl porphyrin were used (Logan 2010). Water thus produced is pure and thereby this process is highly suited for its application in remediation and water purification while generating electricity (Scott and Murano 2007). The power output by this system is generally low and variable; however, up to 90 % columbic efficiency could be achieved (Clauwert et al. 2008; Lee et al. 2008).

The function and efficiency of MFCs depend on the nature of the carbon source used, design and configuration of the fuel cell, nature and type of the electrons and proton-exchange membrane in usage, nature of inoculum and presence of electron acceptors as mediators. Different feedstocks including organic acids, alcohols, acetate, proteins, amino acids, inorganic sulphides, industrial effluents such as paper recycling sludge, brewery effluent, and food processing effluents were applied for the production of electricity using MFCs (Lee et al. 2008). MFC is a very efficient and clean method for energy production because when plant-MFCs are globally implemented, the production of dangerous greenhouse gases by the plants in natural ecosystem will be reduced while generating electricity. Also, MFC can be operated indoors or within communities and can be used as a private source of power for houses. It utilizes a very low temperature of 18–35 °C for energy production. Furthermore, MFCs are considered to be renewable and sustainable energy sources since energy is tapped from already existing feedstocks such as organic waste and wastewaters. Plant-MFCs can capture solar energy which is renewable as well as available for approximately 5.5 billion years (Rozendal et al. 2008). Moreover, production of energy from industrial wastewater and effluents represents energy savings which can be invested into cost-effective, ever-green energy production at large-scale as this system is neither expensive nor time-consuming.

Drastic reduction in the proton transfer, ohmic losses caused by electrical resistance to the electrode, electrode and proton-exchange chamber, activation losses or leaching to voltage loss, and electron quenching reactions (competing reactions such as fermentation, methanogenesis, respiration result in electron loss) limit electricity generation in MFCs (Clauwert et al. 2008). In spite of these limitations, MFC technology is a viable option in the race to obtain green energy from natural wastes. Overall, MFC can be used to clean up all contaminant types as well as radioactive elements from the ground. No clear cut details are available on the total cost involved in contaminated site clean up when using this technology.

Rhoads et al. (2005) and Clauwaert et al. (2007) observed the reduction and successive reoxidation of Mn(II) coupled with oxygenation reduction in enzymatic (biocathode) fuel cells. Pure culture of *Geobacter metallireducens* is able to oxidize toluene, benzoate and petroleum hydrocarbons using an electrode as the terminal electron acceptor (Bond et al. 2002; Lin et al. 2005; Zhang et al. 2010a). Also, an electron transfer system was reported with *Geobacter* sp. or consortia using nitrate, tetrachloroethene, U(VI), Cr (VI) as electron acceptors (Strycharz et al. 2008; Cao et al. 2009; Tandukar et al. 2009). Huang et al. (2010) reported an enhancement in Cr(VI) reduction (2.4 mg/g VSS/h) and energy generation (2.4 W/m^3) from biocathode MFCs using native bacteria isolated from Cr(VI)-contaminated zone. A higher power output along with biodegradation of toluene, benzene and naphthalene (36–94 %) of organic-rich sediment was obtained by Yuan et al. (2010a) in a novel tubular air-cathode MFC with a cloth cathode assembly loaded with an external resistance of 30 Ω in 6 months. Catal et al. (2009) observed simultaneous electricity generation and Se removal in single chamber MFC with glucose and acetate as carbon sources. In 72 h, 99 % of 200 mg/L Se was removed with an increased columbic efficiency of 38 %.

Zhang et al. (2009) investigated the feasibility of pyridine biodegradation in a two-chamber MFC with an electrical resistance of 100 Ω. With complete pyridine degradation in 12 h, maximal voltage of 623 mV and a maximal power density of 1.7 W/m^3 were obtained in 90 days when glucose was supplemented at a concentration of 500 mg/L. Huang et al. (2011) observed 27 % of Cr(VI) reduction and 61 % of power generation below 22 °C at a pH of 5.0 in a biocatalytic graphite fiber cathode MFC. Jang et al. (2006) observed over 85 % nitriloacetic acid was removed under anaerobic conditions using oligotrophic and copiotrophic MFCs when nitriloacetic acid was supplied as a sole source of carbon. Aulenta et al. (2009) recommended the use of conductive materials to manipulate and control a range of microbial bioprocesses, and also suggested the implications of novel biosensors for MFCs. Yuan et al. (2010b) reported a novel bioelectrochemical method to successfully degrade nitrophenol using power derived from a MFC when acetate was used as a potential substrate. A higher power density was obtained with a reduction rate constant of 0.41/h when the MFC had a higher output voltage of 0.5 V. Devasahayam and Masih (2012) recorded a maximum voltage of 779 mV when a resistance of 100 Ω was applied along with the use of 0.4 % sucrose as substrate using *E. coli*. Scott-Emuakpor et al. (2012) successfully demonstrated the use of a tungsten trioxide-based photoelectrocatalytic fuel cell system for water treatment of dichlorophenols which is a new technology for mineralization of organic contaminants.

Luo et al. (2011) studied the combined effect of MFCs with Fenton-like technique to degrade refractory pollutants and generate electricity in both cathode and anode chambers. At a pH of 3.0, maximum power density of 15.9 W/m^3 was achieved with 100 % furfural removal. Luo et al. (2009) achieved 95 % phenol degradation within 60 h with a maximum power density of 28.3 W/m^3 by using graphite packed MFC with a ferricyanide cathode. Thus, studies relating to MFC in remediation are numerous at bench-scale as listed in Table 11. This potential for energy production linked to contaminant clean up is expected to be improved further for full-scale implementation as MFCs have been used at field-scale only by a few research bodies like Queensland University in Australia. There are challenges in obtaining genetically modified strains of exoelectrogenous anaerobic microbes to improve energy production and survival in MFC, designing novel MFCs to overcome existing shortfalls, and use of novel catalysts to aid the system efficiency. These are being researched currently and are expected to lead to further innovations in remedial research.

Table 11 Recent MFC remedial studies carried out at bench-scale

Contaminant	Substrate	Contaminant reduction (%)	Duration (days)	Reference
1. Uranium	–	87	40	US EPA (2012)
2. Nitrate	Acetate	95	45	Lefebvre et al. (2008)
3. Phenol	–	95	2.5	Luo et al. (2009)
4. Pyridine	Glucose	100	90	Zhang et al. (2009)
5. Toluene, Benzene, Naphthalene	–	36–94	185	Yuan et al. (2010a)
6. Nitrophenol	Acetate	26.9	60	Yuan et al. (2010b)
7. Chromium	–	80	20	Huang et al. (2011)
8. PAHs	–	75.54	18	Mohan and Chandrasekhar (2011)
9. Furfural	–	100	0.5	Luo et al. (2011)
10. Phenol	–	100	10	Huang et al. (2011)

4.2 Nanoremediation

Of late, nanoremediation has become one of the main foci of research and development with great potential for contaminated site clean up and protecting the environment from pollution. Nanoremediation involves the application of reactive materials (1.0–100 nm size) which initiate both catalysis and chemical reduction of the contaminants of concern and result in detoxification and transformation of pollutants. The small size and novel surface coatings of the nanoparticles enable them to be more widely distributed in comparison to larger-sized particles, and this unique property makes them best suited for in-situ applications (Tratnyek and Johnson 2006). The maximum surface area-to-weight ratio of nanoparticles maximizes the adsorptive surfaces onto which the contaminants like As get bound and immobilized (Karn et al. 2009). Nano-sized particles provide a solution for faster and more cost-effective site remediation as their reaction is much more effective than other materials.

So far, nano-scale zeolites, metal oxides, carbon nanotubes, noble metals and titanium dioxide have been evaluated for use in nanoremediation (Karn et al. 2009). Of these, currently nano-scale zero-valent iron (nZVI) is widely used in groundwater remediation (Rajan 2011). Nanotechnology has also been attributed towards reducing the NAPLs from underground oil tanks by in-situ use of a material utilizing nano-sized oxides (Jiemvarangkul et al. 2011). Generally, this reactive nanoremediation strategy focuses mainly on the organic pollutants, and seems to work well for chlorinated solvents such as PCBs (tested by US Air Force). When injected as slurry, nanoparticles drift along with the flow of groundwater, effectively creating an ‘anti-pollution plume’. Also, it enables remediation in deeper soils that are not accessed even by pump-and-treat methods. It is compatible even with other technologies like phytoremediation and aid as an expanding tool for contaminant clean up. But, particle-particle aggregation because of their small size limits its mobility in the natural environment (Phenrat et al. 2008). In such a case, polymer coating is suggested to improve their mobility. Even they could be unexpectedly carried away to longer distances in the environment depending upon the groundwater composition and hydrological conditions (Novikov et al. 2006). In addition, self-aggregation property of the nanomaterials with suspended solids or sediments increases their possibility to enter into food chain or drinking water source that lead to their entry into humans and other living organisms causing oxidative stress response, pulmonary toxicity, mutagenesis and cell death (Wiesner et al. 2006). Removing the nanoparticles form the environment may also represent a significant problem due to their small size.

Copper, iron and silver nanoparticles have been shown to cause ecotoxicological effects on micro- and macro-flora/fauna (Boxall et al. 2007). The environmental risks of nanoparticles remain unanswered beyond their positive effects in removing the contaminants. More understanding as well as quantification of toxicity, possible hazards, mobility, stability, bioavailability, and recalcitrance of manufactured nanoparticles are needed (Zhu et al. 2012) since US EPA has suspected the likelihood of biomagnification of nanoparticles. Thus, to expand the applicability of nanoremediation to full-scale, there is a need to improve engineering applications using nanotechnology for in-situ applications, increase research to assess the effects of nanoparticles on ecological and public health, and develop analytical tools to quantify and monitor the manufactured nanoparticles in the bionetwork.

In a pilot test, Henn and Waddill (2006) found that ZVI could decrease the concentration of TCE in about 6–9 months. Cao et al. (2005) also found the ability of ZVI to completely reduce perchlorate to chloride without producing any intermediates. About 99 % As removal was shown using 12 nm dia ferrous oxide nanoparticles at bench-scale (Rickerby and Morrison 2007). In other field test conducted in Europe and North America, nZVI was effective in reducing Cr(VI) and chlorinated solvents (Mace et al. 2006). Ability of nZVI to migrate even to a depth of 6 m was proved in a field study conducted at Naval Air Station, Jacksonville that helped to reduce 99 % TCE concentrations (Gavaskar et al. 2005). Also, ZVI was effective in the removal of different metals like Cr(VI), U(VI) and Co(II) (Uzum et al. 2008). Ability of gold nanoparticles supported on alumina to remove Hg from drinking water and reduction of Cr(VI) through sorption by cerium oxide nanoparticles was reported by Lisha and Pradeep (2009) and Recillas et al. (2010). Shipley et al. (2011) used nZVI impregnated with clays to adsorb and degrade heavy metals like Zn and Cu from wastewater. By adopting this practice of advanced adsorption, limitations of conventional adsorption technology (low efficiency and high operational cost) could be overcome as the use of nanoparticles is cost-effective in the remediation of various pollutants in aqueous solution including heavy metals, PCBs and nitrocompounds (Li et al. 2006).

Skubal et al. (2002) modified the surface of titanium dioxide nanoparticles with thiolactic acid (a bi-dental chelating agent) and used it for removing Cd from wastewaters. Zaera (2012) reported the use of nanotechnology for the manufacture of better-defined catalysts that aid the environmental remediation. Zhang et al. (2010b) proved the ability of iron nanoparticles (core size of 15 nm) coated with ferromagnetic carbon to effectively reduce >95 % of Cr(VI) in wastewater by means of carbon shell physical adsorption which was much higher than the remediation by commercially available iron nanoparticles. ZVI nanoparticles with a dia of <90 nm and specific surface area of 25 m^2/g removed up to 96 % of atrazine (100 mg/L) within 72 h under anoxic conditions (Bezbaruah et al. 2009a). At lab-scale, in a batch and column experiment reductive immobilization of chromate in soil and water using stabilized iron particles was shown by Xu and Zhao (2007). Tungittiplakorn et al. (2004) demonstrated the ability of engineered nanoparticles (amphiphilic polyurethane nanoparticle of 17–97 nm dia) for soil remediation of PAHs (80 %). Ghauch et al. (2009) reported the removal of antibiotics from water using iron nanoparticles.

Xiao et al. (2010) recommended the use of multivalent carbon nanotube-reinforced polyacrylic acid/polyvinyl alcohol nanofibrous mats for generating other functionalized nanofiber-based complex materials with enhanced mechanical properties for applications in environmental remediation, catalysis, sensing and biochemical sciences. Palladium nanoparticles bioprecipitated on *Shewanella oneidensis* and encapsulated in polyurethane removed 98 % TCE in 22 h (Hennebel et al. 2009). He et al. (2007) stabilized Fe-Pd nanoparticle with sodium carboxymethyl cellulose which resulted in successful dechlorination of TCE in groundwater and soil. Crane et al. (2011) studied the combined effect of ZVI particle and nano-Fe_3O_4 for U removal (>98 % within 2 h) from carbonate-rich water sample collected from Lisava valley, Banat, Romania. Decabrominated diphenyl ether (a class of the emerging pollutant) and polybrominated diphenyl ether were removed up to 90 % within 40 min by treating with ZVI nanoparticles (Shih and Tai 2010). Nano-ZVI particles of 10–90 nm encapsulated in biodegradable calcium alginate beads were capable of degrading 89–91 % TCE in 2 h (Bezbaruah et al. 2011). About 96–99 % As and Cr along with phosphate were removed by mixed magnetite-maghemite nanoparticles at a pH 2.0 (Chowdhury and Yanful 2010). Singhal et al. (2012) observed 98 % malathion remediation by using ZVI at a pH of 8.2 in 12 h.

Calcium peroxide nanoparticles have been used as an innovative agent for in-situ chemical oxidation by Olyaie et al. (2012). Noubactep and Care (2010) recommended the use of Fe-Pb nanoparticles for reductive dechlorination of lindane. Li et al. (2010) proposed foam delivery of nanoparticles for vadose-zone remediation. There are much more advanced laboratory studies in the emerging field of nanoremediation involving the application of bimetallic, stabilized, engineered, polymeric nanoparticles for the remediation of organics and inorganics as listed in Table 12. Thus, nanoparticles are highly promising to remediate more than 95 % contaminants in few hours at bench-scale. However, at pilot-scale when tested in the superfund sites by US EPA, nanoparticles removed 60 % contaminant in few weeks (Table 13). Field-scale implementations of chemical/synthetic nanoparticles, available in large number, are expected in the near future. But, full-scale use of nanoparticles obtained from green synthesis is yet in the bench-scale level, and requires more attention in future research.

Amaladhas et al. (2012) synthesized silver nanoparticles from leaf extract of *Cassia angustifolia* that have antibacterial effect against *E. coli* and *Salmonella* sp.

Table 12 Nanoremediation studies and their success

Nanoparticles	Contaminant	Remediation (%)	Reference
1. Amphiphilic polyurethane nanoparticle ^{b}	PAHs	80	Tungittiplakorn et al. (2004)
2. Starch-stabilized Fe-Pd ^{b}	PCB	80	He and Zhao (2005)
3. ZVI ^{f}	TCE	99	Henn and Waddill (2006)
4. ZVI ^{b}	Cr(VI)	90	Xu and Zhao (2007)
5. ZVI ^{b}	Atrazine	96	Bezbaruah et al. (2009b)
6. Carboxymethyl cellulose and polyacrylic acid stabilized ZVI ^{b}	RDX	98.3	Naja et al. (2008)
7. ZVI entrapped in biopolymer, calcium alginate beads ^{b}	NO_3	50–73	Bezbaruah et al. (2009a)
8. Electrochemically-stabilized maghemite nanoparticle ^{b}	As(V)	99	Park et al. (2009)
9. ZVI ^{f}	TCE	99	Gavaskar et al. (2005)
10. Biopalladium polyurethane nano cubes ^{b}	TCE	98	Hennebel et al. (2009)
11. Carboxymethyl cellulose-stabilized iron ^{b}	Hg	99	Xiong et al. (2009)
12. Multivalent carbon nanotube-reinforced polyacrylic acid/ polyvinyl alcohol nanofibrous mat ^{b}	TCE	93	Xiao et al. (2010)
13. ZVI ^{b}	DBDE	90	(Shih and Yai 2010)
14. Ferromagnetic carbon coated iron nanoparticle ^{b}	Cr(VI)	95	Zhang et al. (2010b)
15. Magnetite and maghemite ^{b}	As, Cr, PO_4	96–99	Chowdhury and Yanful (2010)
16. Carboxymethyl cellulose-stabilized iron ^{b}	Cr(VI)	100	Wan et al. (2010)
17. Iron oxide ^{b}	As(V)	>90	Shipley et al. (2011)
18. Iron nanoparticle in alginate biopolymer ^{b}	TCE	89–91	Bezbaruah et al. (2011)
19. Magnetite and ZVI ^{b}	U	98	Crane et al. (2011)
20. Fe-Ni ^{b}	Cr(VI)	75	Kadu et al. (2011)
21. ZVI ^{b}	Malathion	98	Singhal et al. (2012)

^{b} Bench-scale; ^{f} Field-scale

along with pollutant-degrading capabilities. Saha et al. (2009) reported green phytochemical synthesis of calcium alginate stabilized Au and Ag nanoparticles (solid-phase biopolymer-based catalyst) for nitrophenol reduction. Virkutyte and Varma (2011) recommended the green synthesis of metal nanoparticles which could be used as enzymes and biodegradable polymers in surface functionalization and stabilization applications. Smuleac et al. (2011) discussed about membranes containing reactive Fe/Pd and Fe nanoparticles embedded in polymer film which was

Table 13 Nanoremedial full-scale studies conducted at superfund sites by US EPA (2012)

Site	Technology	Duration of operation (months)	Contaminant reduction	Outcome	Objective met??
1. Alabama soil, Northern Alabama	Nano-scale ZVI	1	40–61 % TCE, PCE, PCBs	• Confirmed the effectiveness, mobility, and ability of nZVI to degrade contaminants	Yes
2. Dry cleaning facility site 45, Parris island, South Carolina	Emulsified ZVI and nano-scale iron	32	86 % DNAPL	• Achieved 75 % DNAPL mass removal	Yes
3. Hanford site 100, Washington	Nano ZVI	12	70 % Cr(VI)	• Reduction of Cr(VI) under the influence of iron injection • No adverse groundwater quality effects by nZVI injection that would impact human or environmental receptors • No significant loss of permeability in the aquifer	Yes
4. Space launch complex 34, Cape Canaveral, Florida	Emulsified ZVI	8	60 % TCE	• 50 % TCE removal • No change in aquifer quality due to EZVI treatment • No environmental impact due to EZVI injection	Yes
5. Parris island, Port Royal, South Carolina	Emulsified ZVI	30	65 % TCE, DCE, VC	• Evaluated long-term performance of nano-scale EZVI injected into the saturated zone to enhance in-situ dehalogenation of DNAPLs containing TCE	Yes
6. Penn-Michigan manufacturing site, West Lafayette, Ohio	Ohio-swellable organo-silica-nanoparticle	9	40 % TCE	• Achieved less than 5 μg/L TCE	No
7. Pharmaceutical facility, Research triangle park, North Carolina	Bi-metallic nanoparticles	3	90 % TCE, DCE, VC	• Achieved considerable source mass reduction	Yes
8. Picatinny arsenal, rockaway township, New Jersey	Nano-scale ZVI	12	54 μg/L TCE, 180 μg/L CCl_4	• Achieved a final concentration of 2 μg/L CCl_4, and 1 μg/L TCE	No

prepared by using a non-toxic, biodegradable green tea extract instead of the most commonly used sodium borohydride. Gold nanoparticles termed as ‘green gold’ were prepared using leaf extract of *Terminalia catappa* by Ankamwar (2010). A rapid and reliable process for green synthesis of nano-sized materials using microwave irradiation and supernatant of *Bacillus subtilis* culture was reported by Saifuddin et al. (2009). Baruwati and Varma (2009) synthesized metal nanoparticle form the grape pomace extract which is almost like achieving a high value product from waste. Table 14 presents the biological sources for the green synthesis of different nanoparticles that may have potential in their use in bioremediation. Overall, combination of green nanoparticle synthesis and biological remedial processes with nanotechnology are the emerging, remarkable and innovative remedial approaches.

4.3 Transgenic Plants and Microbes

Advances in protein and genetic engineering techniques opened up new avenues for the development of genetically modified microorganisms (GMOs) and plants to function as ‘exclusive biocatalysts’ in which certain desirable enzymes or degradation pathways from diverse organism are brought together in a single host with the aim to perform specific reactions (Van Aken 2009; Demain and Vaishnav 2009). In genetic engineering, catabolic genes associated with insertion sequences are rapidly disseminated or DNA is shuffled among the microbial groups to expand the novel degradative pathway (Maestri and Marmiroli 2011). Engineering of catabolic enzymes enhances the degradative rates or broadens the substrate specificity. When a single strain is constructed by genetic engineering to perform a number of related or unrelated metabolic activities, the predictability and efficiency of the process gets significantly enhanced and the recombinant organism is able to degrade a wide range of recalcitrant pollutant rapidly within a shorter time period. Even the use of genes that encode the biosynthetic pathway of biosurfactant could improve the rate of biological degradation by increasing the pollutant bioavailability in the natural ecosystem. Also, the genes conferring resistance to critical stress factors enhance both the survival and performance of the designed catalyst (Dua et al. 2002).

Metabolic engineering approaches also involve deletion strategies for removing competitive reactive pathways (Kind et al. 2011). Mixtures of inorganic and organic chemicals that are even at high concentrations could be possibly treated at a time by GMOs (Singh et al. 2011). New evidences on the metabolic pathways and bottlenecks of degradation are still accumulating, resulting in the need to accentuate the use of available molecular approaches (Megharaj et al. 2011). However, there is a problem with the introduction of GMOs into the environment because of the legal restrictions on their release into the natural ecosystem, additional energy needs imposed by the existence of engineered genetic materials in the bacterial cells, and the low survival of the foreign strains that have been introduced into the real problematic lands (Maiti and Maiti 2011). In such a case, the survival rate of the foreign microbial strains could be enhanced by the use of species reinforced by root

Table 14 Nanomaterials synthesized from biological sources

Nanoparticle	Biological source
Ag	1. *Capsicum annuum* L. extract 2. Coffee (*Coffea arabica*) and tea (*Camellia sinensis*) extracts 3. Leaf broth of *Magnolia kobus* 4. In-vitro cultures of *Brassica juncea* 5. Culture filtrate of *Phoma glomerata* 6. *Opuntia ficus-indica* mediated synthesis 7. *Cassia fistula* leaf broth 8. *Cacumen platycladi* extract 9. Electrochemically active biofilm (bacteria) 10. Culture filtrate of *Trichoderma harzianum* 11. Culture filtrate of *Aspergillus niger*
Au	1. Leaf extract of *Tamarindus indica* 2. Extracts of *Cymbopogon flexuosus* 3. *Rhodopseudomonas capsulata* 4. Cell mass of *Stenotrophomonas maltophilia* 5. Leaf extract of *Terminalia catappa* 6. Leaf extract of *Coleus amboinicus* 7. Leaves of zero-calorie *Stevia rebaudiana* 8. Dried flower extract of *Carthamus tinctorius*
Fe	1. *Camellia sinensis* extract
Metallic	1. Sweet desert willow (*Chilopsis linearis*) 2. *Vitis vinifera* extract
Oxide	1. *Fusarium oxysporum* with precursor salt (barium acetate and potassium hexafluorotitanate) 2. Extract of *Physalis alkekengi*
Ag protein	1. Leaf extract of *Piper betle*
Magnetic Fe_2O_3	1. Regenerated cellulose films
Sb_2S_3	1. Microbial synthesis by *Serratia marcescens*
PLA	1. Leaf extracts of medicinally important plants (*Syzygium cumini*, *Bauhinia variegata*, *Cedrus deodara*, *Lonicera japonica* and *Elaeocarpus sphaericus*)
Fe, Fe/Pd	1. *Camellia sinensis* extract
Au, Ag, Zn, Magnetic Fe_2O_3	1. Biomass of *Medicago sativa*
Au, Ag	1. Fruit extract of *Emblica officinalis* 2. *Cinnamomum camphora* extract 3. Leaf extract of *Camellia sinensis* 4. Biomass of *Cinnamomum camphora* leaf 5. *Sorghum bicolor* powder 6. *Hibiscus rosa sinensis* leaf extract 7. Leaf extract of *Zingiber officinale*
Au–Ag–Cu alloy	1. In-vivo *Brassica juncea* plant

colonizers (plants) that would have a selective advantage over other factors. Thus, judicial blocks can be overcome with the use of plants rather than microorganisms as ‘engineered environmental biosystems’. For remediation purpose, it is, therefore, a potential approach to use plants, and selectively support the metabolism of pollutant-degrading rhizosphere organisms. By improving symbiotic microorganisms, the potential of degrading bacteria (engineered endophytes) to colonize the roots can be manipulated (Weyens et al. 2009; Abhilash et al. 2012). Further, the engineered endophytic strains increase the phytoremediation of water-soluble VOCs (Barac et al. 2004). GM plants could be developed as they significantly help to reduce the need for agrochemicals required for crop growth thereby reducing the environmental pollution.

On the other hand, plants containing transgenes are either responsible for metabolism of organic compound or result in better uptake of inorganic mixtures so that the pollutant accumulated plants could be removed and destroyed which ultimately prevent the pollutant migration to zones where they pose a threat to the public health (Seth 2012). Either the use of GMOs as such or engineered endophytes or transgenic plants are being called for large-scale implementations to remove contaminants more effectively from the environment (Cherian and Oliveira 2005). However, the possibility of imbalanced food chain, unintended gene transfer through cross pollination leading to unknown effects on other plants/organisms and allergic properties by the unintended change in the genetic make-up of the livings in the biosphere by GMOs with great potential to harm human health limits the use of GM materials widely at full-scale in the natural ecosystem by the regulatory bodies. Whatever it is, this situation would change in the long-run. After 10–20 years from now, GMOs would find a promising remedial phase in the real contaminated site clean up approaches. Classes of contaminant to be treated, nature of recipient plants, target genes, source of transgenes, final result of transformation and patents for the transgenic plants or microbes are the critical components of a GM system. Success of a GM system mainly relies on choosing a promoter sequence among constitutive promoters with high levels of expression (Halpin 2005). Both organic and inorganic pollutants such as chlorinated solvents, halogenated/petroleum hydrocarbons and heavy metals could be treated by transgenic plants and microbes. There is no data on the cost details pertaining to GMO-related remedial practices.

A transgenic system for soil As removal was tested by Dhankher et al. (2002) in *Arabidopsis thaliana* by introducing two genes, glutamylcysteine synthetase (GCS) and arsenate reductase C (*arsC*) from *E. coli*. The transgenic plant accumulated 2–3 times more As/g. Similarly, transgenic *Arabidopsis thlaspi* showed plant tolerance towards Ni and Cd due to antioxidative defense mechanism (Boominathan and Doran 2003; Freeman et al. 2004). Transgenic *Arabidopsis* and tobacco plants that carried bacterial organo-mercury reductase (*merA*) and mercury lyase (*merB*) genes were able to absorb methyl mercury and elemental Hg(II) from soil, releasing volatile Hg(0) from foliage into air (Rugh et al. 2000). LeDuc et al. (2004) reported increased uptake and volatilization of Se by Indian mustard and *Arabidopsis* when a gene encoding the selenocysteine methyltransferase was cloned from *Astragalus bisulcatus* (Se-hyperaccumulator) to the two test plants. Transgenic plants with improved potential for TNT removal was reported by Gullner et al. (2001) and Hannink et al. (2001). Zhou et al. (2013) recently suggested the use of transgenic hairy roots developed by *Agrobacterium rhizogenes* in phytoremediation of organic and inorganic pollutants. Wu et al. (2006b) demonstrated the engineered plant-microbe symbiosis for rhizoremediation of inorganic mixtures. About 40 % Cd accumulation by sunflower roots with engineered rhizobacterium (*Pseudomonas putida* 06909) was achieved. While studying the ability of GM plants in phytoremediation of heavy metals and metalloid contaminated soil or sediments, Kotrba et al. (2009) observed successful promotion of Cd, Pb, Cu, As and Se phytoextraction by transgenic approaches. Brim et al. (2006) reported that the engineered *Deinococcus radiodurans* strain cloned with *tod* and *xyl* genes of *P. putida* was able to degrade organic contaminants.

Weyens et al. (2009) reported a successful field-scale phytoremediation of 90 % by poplar trees grown with TCE-degrading engineered endophyte (*Pseudomonas putida*) at a TCE-contaminated site. Weyens et al. (2013) achieved increased accumulation of Cd and toluene by inoculating the willow tree with Cd-resistant, and siderophore- and IAA-producing engineered *Burkholderia vietnamiensis* BU61 as a donor of the pTOM-TCE plasmid. Hu et al. (2012) reported 84 % PAH removal by the use of genetically engineered higher eukaryotic lines. Sood et al. (2010) developed novel yeast (*Candida digboiensis*) strain that could remove 72 % heneicosane in 8 days at pH 3.0, and 40 mg of eicosane in 50 ml minimal salts medium in 10 days. Paul et al. (2005) suggested the production of suicidal GMOs for safe and efficient remediation. Brim et al. (2006) developed a radiation-resistant *Deinococcus radiodurans* strain, by the cloned expression of *xyl* and *tod* genes of *Pseudomonas putida* for toluene degradation, and achieved complete oxidation of toluene under both complex and minimal nutrient conditions. Ripp et al. (2000) conducted a field study in USA using *Pseudomonas fluorescens*, carrying a naphthalene-degrading plasmid (pUTK21) mutagenized by transposition insertion of *lux* gene, to remediate PAH-contaminated site. Recently, Cao et al. (2012) recommended the use of a stable GMO producing rhamnolipid for pyrene removal from the contaminated soil. Wide array of studies employed GMOs and plants for the degradation of contaminants at lab-scale (Table 15). All that is required is to broaden the utility of GMOs and plants for large-scale pollutant clean ups.

4.4 Microbial Consortia in Photo-Hetero Microbial System

One of the most vital components of bioremediation is microbes. More commonly, bacteria, yeast, seaweeds, algae, fungi and actinomycetes that are isolated from the contaminated sites are evaluated for their efficiency in contaminant degradation at laboratories, and once they are confirmed to possess the catabolic genes that degrade the target contaminant, they are reinoculated into the real contaminated sites (Filali et al. 2000). In most studies, single species that could survive in the laboratory conditions where a feasible environment is provided will find it too complex to survive and get adapted to natural environments when the site constitutes complex pollutants at high concentrations. In such a case, microbial consortium can be developed so that multiple interactions among the microbial population can take place which can make the microbes more robust to the environmental fluctuations.

The first and foremost advantage of using microbial consortia is the ability of a microbe to detect and respond to the presence of another microbe either by exchanging dedicated molecular signals or by trading metabolites. This will lead to the second important merit of division of labor. As a result, microbial consortia perform several functions at a time with accelerated speed that are impossible for individual strains or species. Consortia of bacteria, bacteria and fungi or bacteria and algae are currently being developed and utilized for environmental implications (Sannasi et al. 2006; Subashchandrabose et al. 2011). One of the problems that rest with the consortia is the issue of compatibility between the two organisms that are brought together. It is expected that one must not hinder the growth of the other. Use of algal–bacterial consortia is much more beneficial than bacterial consortia, or bacterial–fungal consortia in the remediation of pollutants (Subashchandrabose et al. 2011). It is because, cyanobacteria or microalgae release a variety of light weight compounds and extrapolymeric compounds composed of nucleic acids, lipids, proteins, excretion products and fermentation products that serve as microbial growth substrates which, in turn, enhance the degradation potential of aliphatic and aromatic contaminants by the bacteria (Kirkwood et al. 2006). Fuels, non-halogenated VOCs, SVOCs, herbicides, heavy metals, pesticides and radionuclides could be treated by microbial consortia. To overcome the limitations pertaining to the use of microbial consortia at real contaminated site in the presence of mixed high contaminant levels, ‘engineering microbial consortia’ (Brenner et al. 2008) could be developed and used in the near future. Cost estimates are not available for this system.

Thavamani et al. (2012) demonstrated the potential of a bacterial consortium (*Alcaligenes* sp., *Pseudomonas* sp., *Pandorea* sp. and *Paenibacillus* sp.) for field-scale bioremediation of high molecular weight PAHs (pyrene and BaP) with heavy metal (Cd) tolerance in a long-term PAH-contaminated soil. More than 90 % anthracene, phenanthrene and fluoranthene, 77 % pyrene and 48 % BaP were degraded during the 60-day incubation. A consortium composed of bacteria—three gram-positive genera, *Micrococcus*, *Arthrobacter* and *Bacillus*; and six gram-negative genera, *Agrobacterium* sp., *Xanthomonas* sp., *Chryseomonas* sp., *Flavobacterium* sp., *Serratia* sp. and *Pseudomonas* sp.—all isolated from metal-contaminated site, reduced 38–52 % Cr, 17–28 % Cu and 3–17 % Pb at a pH range of 6.0–8.0 (Sannasi et al. 2006).

Recently, Gojgic-Cvijovic et al. (2012) achieved 82–88 % and 86–91 % TPH degradation in petroleum sludge and polluted soil, respectively, by the use of bacterial consortium (*Pseudomonas* sp., *Achromobacter* sp., *Bacillus* sp. and *Micromonospora* sp.). PAHs bioremediation was reported with a bacterial consortium enriched from the contaminated soil (initial PAH concentration was 9362.1 μg/kg) collected from the US EPA Superfund site by Mao et al. (2012). Addition of 10–20 % suspension from bacterial consortium (*Mesorhizobium* sp., *Alcaligenes* sp. and *Bacillus* sp.) was able to remove 20–35 % PAHs in 56 days. Pino and Penuela (2011) tested the simultaneous degradation of chlorpyrifos and methyl parathion by the consortium composed of *Pseudomonas putida*, *Proteus vulgaris*, *Bacillus* sp., *P. aeruginosa*, *Acinetobacter* sp., *Citrobacter freundii*, *Stenotrophomonas* sp.,

Table 15 Transgenic plants and microorganisms in bioremediation

Recipient plant/organism	Introduced gene	Contaminant	Reference
Arabidopsis thaliana	*ArsC*—Arsenate reductase gene	As	Dhankher et al. (2002)
Nicotiana tabacum	*CYP76B1*–Cytochrome P450 Monoxygenase gene	Herbicide	Didierjean et al. (2002)
Brassica juncea	Selenocysteine lyase	Se	Pilon et al. (2003)
B. juncea	γ-*ECS*, *GS*—Glutamycysteine synthetase and Glutathione synthetase gene	Atrazine, Dinitrobenzene, Phenanthrene, Metolachlor	Flocco et al. (2004)
A. thaliana	*hGSHS*—Homoglutathione synthetase	Herbicide	Sugiyama and Sekiya (2005)
A. thaliana	*NfsA*—Nitroreductase gene	Nitroreductase	Kurumata et al. (2005)
Poplus nigra	*YCFI*—Yeast protein	Cd, Cr, Cu	Bittsanszky et al. (2005)
N. tabacum	*GstI-6His*—Glutathione S-transferases gene	Alachlor	Karavangeli et al. (2005)
Lycopersicon esculentum	*tpxI*—Peroxidases gene	Phenol	Wevar Oller et al. (2005)
Deinococcus radiodurans	*merA* gene	Hg	Brim et al. (2000)
N. tabacum	*Gly* I, *Gly* II—Glyoxalase gene	Zn	Singla-Pareek et al. (2006)
A. thaliana	*XplA* and *XplB* from *Rhodococcus rhodochorus*	RDX	Rylott et al. (2006)
N. tabacum	*Bphc* from PCB-degrading bacteria	PCB	Novakova et al. (2009)
N. tabacum	*rh1A*, *rh1B*—Rhamnosyl transferase gene	Al	Brichkova et al. (2007)
N. tabacum	*DbfB*—Biphenyl dioxygenase	Chlorobiphenyls	Mohammadi et al. (2007)
A. thaliana	*BrMT1*—Metallothionein type 1 gene	Cd	Kim et al. (2007)
Populus trenula x, *Populus alba*	*CYP450 3EI* from rabbit	TCE, VC, CCl_4, Chloroform	Doty et al. (2007)
N. tabacum	*Dh1A*, *Dh1B*—Haloalkane dehalogenase gene	Dichloroethane	Mena-Benitez et al. (2008)
Oryza sativa	*CYP1A1* from human	Chlorotoluron, Norflurazon	Kawahigashi et al. (2008)
E. coli	*MerR*/*CadC*/*ZntR*/*Pmer*/*PcadA*/*PzntA* gene	Cd, Zn, Hg, Pb	Bondarenko et al. (2008)
E. coli	*As III* S-adenosylmethionine methyltransferase gene	As	Yuan et al. (2008)
A. thaliana	*743B4*, *73C1* genes	TNT	Gandia-Herrero et al. (2008)

N. tabacum	*TvGST* gene	Anthracene	Dixit et al. (2011)
Populus tremuloides	*pnrA* from *Pseudomonas putida*	TNT	Van Dillewijn et al. (2008)
N. tabacum	*Tpx 1* and *tpx 2* from *Lycopersicon esculentum*	Phenol	Sosa Alderete et al. (2009)
A. thaliana	*merP*	Hg	Ruiz and Daniell (2009)
A. thaliana	*MerP*—Metal tolerant and accumulation gene	Hg	Hsieh et al. (2009)
Caulobacter crescentus	*RsaA-6H*—Fusion protein	Cd	Patel et al. (2010)
Pelargonium sp.	*HPS*/*HPI*—Fusion protein	Formaldehyde	Song et al. (2010)
N. tabacum	*ppk*/*mer*, *T*/*merB*	Hg	Nagata et al. (2010)
C. crescentus, *Sphingomonas desiccabilis*, *Bacillus idriensis*	*arsM* gene	As	Liu et al. (2011)
Pseudomonas aeruginosa	*rhlABRI*—Cassette that produces rhamnolipid	PAHs	Cao et al. (2012)

Flavobacterium sp. and *Klebsiella* sp. isolated from highly polluted soils in Moravia, Columbia. In culture media augmented with each of the pesticide, the consortium was able to remove 72 % methyl parathion and 39 % chlorpyrifos. When glucose was supplemented, about 97–98 % of the pesticide was degraded in 120 h by the bacterial consortium. Kumar et al. (2012) identified *Pseudomonas*, *Bacillus*, *Pannonibacter* and *Ochrobacterum* species from the paper mill and agro-based pulp which were capable of reducing COD up to 86.5 % in black water and 66 % in black liquor and black water at a pH of 6.8 and 35 °C when enriched with phosphorous and nitrogen along with trace elements. Congeevaram et al. (2007) found that a consortium of *Micrococcus* sp. and *Aspergillus* sp. was able to remove 90 % Ni(II) and Cr(VI) around pH 5.0, and tolerant to a Cr level of 10,000 mg/L. Within 42 days, about 95.3 % BaP was degraded when *Mucor* sp. and *Bacillus* sp. were co-immobilized on vermiculite (Su et al. 2006).

A new bioremediation method for petroleum-contaminated soil using AM fungi and bacteria was investigated by Chen et al. (2009) at Petro China of Chandqing, Shaanxi, China. Both *Glomus caledonium* and *Bacillus subtilis* removed 92.6 % TPH in 60 days. Caceres et al. (2008) reported the transformation of an organophosphorous pesticide, fenamiphos, to non-toxic fenamiphos sulfone by a consortium of five different cyanobacteria and microalgal species. Munoz et al. (2005) showed the complete degradation of acetonitrile by the consortium of *Chlorella sorokiniana* and *Comamonas* sp. in a column photobioreactor. Zhong et al. (2011) demonstrated MTBE degradation by a mixed microalgal–bacterial system (*Methylibium petroleiphilum* and *Chlorella ellipsoidea*). There are many studies that confirmed the efficiency of algal–bacterial system in the degradation of phenols, hydrocarbons and heavy metals as listed in Table 16. The current requirement is to increase the use of these microbial consortia at full-scale and develop different formulations like immobilized mixed cultures in a nutritious substrate that would assure more remedial success as well as cost-effectiveness when commercialized as a product.

5 Challenges and Prospects

An in-depth revisiting of the available literature on techniques applicable for in-situ remediation indicated that the application of remedial tools is growing rapidly day-by-day, of which bioremediation has taken upper hand over physical and chemical treatment systems although physico-chemical techniques like EK remediation are successful. It is because, chemical and physical techniques are almost energy intensive and evolve greenhouse gases which increase the intensity of global warming, and are not considered to be ecologically and economically secure. However, existing bioremedial strategies also suffer from a number of limitations such as lesser degradation potential of microbial community during on-site remediation, less bioavailability of pollutants on temporal and spatial scales, and lack of benchmark standards for efficiency and pollutant toxicity testing of bioremediation for their increased field applicability (Table 17). As a result, currently focus is

Table 16 Degradation of environmental pollutants by microbial consortia

Consortia	Pollutant and Removal %	Reference
Bacterial consortium		
1. *Pseudomonas* sp., *Serratia* sp., *Flavobacterium* sp., *Chryseomonas* sp., *Xanthomonas* sp., *Agrobacterium* sp., *Bacillus* sp., *Arthrobacter* sp., *Micrococcus* sp.	Cr(VI) 38–52; Cu(II) 17–28; Pb(II) 3–17	Sannasi et al. (2006)
2. *Alcaligenes* sp., *Pseudomonas* sp., *Pandorea* sp., *Paenibacillus* sp.	HMW and PAHs 48–90	Thavamani et al. (2012)
3. *Acinetobacter* sp., *Pseudomonas putida*, *Bacillus* sp., *P. aeruginosa*, *Citrobacter freundii*, *Stenotrophomonas* sp., *Flavobacterium* sp., *Proteus vulgaris*, *Klebsiella* sp.	Chlorpyrifos, Methyl parathion 39–72	Pino and Penuela (2011)
4. *Mesorhizobium* sp., *Alcaligenes* sp., *Bacillus* sp.	PAHs 20–35	Mao et al. (2012)
5. *Pseudomonas* sp., *Achromobacter* sp., *Bacillus* sp., *Micromonospora* sp.	TPH 82–91	Gojgic-Cvijovic et al. (2012)
Bacterial–Fungal consortium		
1. *Mucor* sp., *Bacillus* sp.	BaP 95.3	Su et al. (2006)
2. *Micrococcus* sp., *Aspergillus* sp.	Cr(VI) 90; Ni(II) 90	Congeevaram et al. (2007)
3. *Glomus caledonium*, *Bacillus subtilis*	TPH 92.6	Chen et al. (2009)
4. *Sphingobacterium* sp., *Bacillus cereus*, *Achromobacter insolitus*	Phenanthrene 25–100	Janbandhu and Fulekar (2011)
Bacterial–Algal consortium		
1. *Chlorella sorokiniana*, *Sphingomonas yanoikuyae*, *Pseudomonas migulae*	Phenanthrene 15	Munoz et al. (2003)
2. *Chlorella* sp., *Scenedesmus obliquus*, *Stichococcus* sp., *Phormidium* sp., *Rhodococcus* sp., *Kibdelosporangium aridum*	Ni and Cu 62; Zn 90; Fe 64; Mn 70	Safonova et al. (2004)
3. *Pseudoanabaena* sp., *Pseudomonas* sp.	Phenol 95	Kirkwood et al. (2006)
4. *Selanastrum capricornutum*, *Mycobacterium* sp.	BaP 73	Warshawsky et al. (2007)
5. *Phormidium* sp., *Oscillatoria* sp., *Chroococcus* sp., *Burkholderia cepacia*	Diesel 99.5	Chavan and Mukherji (2008)
6. *Scenedesmus obliquus*, *Sphingomonas* sp., *Bacillus cepacia*, *Pseudomonas* sp., *Pandoraea pnomenusa*	Naphthalene, Phenanthrene and Fluorene 100	Tang et al. (2010)

rendered to develop advanced green remedial procedures which facilitate the emergence of new, promising bioremediation techniques like MFCs with high cost-benefit ratio where they perform a dual role of contaminated site clean up as well as electricity generation.

Most of the emerging technologies are only biological and the widely researched technologies for advancement and commercialization are also related to the family of bioremediation. Currently, there is a possibility to integrate successful physico-chemical methods with biological tools to accelerate the remedial efficiency at real contaminated sites. Also, emerging technologies like MFCs are not widely implemented at field-scale as they require system designing (define the components, modules, interfaces and data needed for setting up the MFC system). In such cases, appropriate models for implementation at full-scale are required to be engineered. Similarly, nanoremediation has prospects to synthesize eco-friendly green nanoparticles utilizing the natural resources which are so far not implemented at field-scale. Also, regulations are to be developed for the field application of transgenic plants and microbes so that they could be harnessed for large-scale risk-based remedial approaches. Photo-hetero microbial systems can be studied in-depth for their potential to produce economically viable products like biofuels, enzymes, etc. that could ensure an economical return when environmental clean up is done.

In relation to the vision to develop a less energy intensive and a non-greenhouse gas evolving remedial technique to support the ease of global living beings, it is highly necessary to develop and use a battery of bioassays to monitor and test the efficacy of remediation during the operation of each remedial technique in order to ensure the system efficiency and economy (Megharaj et al. 2000). Since remedial technologies available for emerging contaminant removal are scarce, research should be focused more on the development of large-scale advanced emerging technologies to ensure risk-based clean up of emerging priority pollutants. Hence, application of the principle of less energy intensive, function-directed, no greenhouse gas evolving remedial technology with high cost-benefit ratio is adequate to minimize the risks caused by the persistence and further spreading of priority and emerging pollutants in the ecosphere.

6 Summary

A global hot topics of concern are ‘pollution’ and ‘remediation’. World-wide annual release of billion pounds of chemical toxins into the bionetwork, and global population risk of around 2.0 billion people by complications caused by persistent priority pollutants like pesticides, petroleum hydrocarbons, heavy metals, halogenated materials, nitroaromatic compounds, solvents and phthalate esters, as well as by newly emerging, noxious contaminants such as flame retardants, pharmaceutical and personal care products, illicit drugs and industrial byproducts are the currently spoken issues of alarming distress for the livings in the biome.

Currently, decontaminating the pollutants in the environment is a major policy priority in most developed and developing countries as people are exposed to toxicants at dangerous levels that cause deleterious health effects (Ludlow and Roux 2012). Several physical, chemical, thermal and biological remedial options are available for removing the pollutants from the ecosystem. Of them, a number of strategies are available to remove the pollutants in-situ, and the available in-situ

Table 17 Advantages and disadvantages of the existing in-situ remediation techniques

Technology	Advantages	Disadvantages
Thermal		
1. Steam injection/Conductive/Radio frequency/Vitrification	• Potentially rapid remediation • High temperature treatments increase VOC removal efficiency from clay soils • Less site monitoring • Can enhance the efficiency of other in-situ remedial measures such as air sparging	• Unsuited for deeper depths (>65 m) • Initial capital cost is high • Potential to be expensive • Operating difficulties by soil debris • Unsuited for unsaturated soil • Interferences by soil properties • Need for extensive characterization of the site to determine the preferred path of treatment (for ex., steam injection)
2. Electrical resistance heating	• Adaptable to treat all soil types • Suited for sedimentary bedrocks • Depth independent • Effective in fractured zones	• Heat loss on small sites • Interference by co-contaminants
3. Thermal desorption	• Shorter treatment time • Appropriate to treat contaminant mixtures • Applicable to remediate heterogeneous sites	• High extensive material handling needs • Damage of processor unit • Material binding problems • Need for stabilization • Chance of contaminant migration to non-impacted areas • Difficulty in treating near occupied sites • Post-treatment effects on soil properties (for ex., soil shrinkage, sterility)

(continued)

Table 17 (continued)

Technology	Advantages	Disadvantages
Physical/Chemical		
1. Soil flushing	• Effective in soils with low silt or clay content • Reusability of recovered fluids • Simple design and operation	• Lengthy remediation time • Costly above ground treatments • Hydraulic control requirement • Extractant post treatment requirement • Surfactant adherence to soil • Contaminant mobility problems • Underground injection control regulations and land disposal restrictions limit selection and use of flushing solution • Requires greater understanding of the site geology • Not suited to treat mixture of hazardous substances
2. Fracturing	• Effective to treat low-permeable and fine-grained soils • Enhanced mass transfer of the contaminant in dense soils • Reduced treatment cost	• Unsuited for seismic bedrocks • Potential for contaminant spread • Fractures close in non-clayey soil • Lack of idea on trapped free product
3. Electrokinetic separation	• Most effective in clays • Compatible with most of the techniques • Early treatment response • Highly targetable (treat specific area) • Viable method to treat inorganic and organic compounds in porous media • Competitive in cost and remedial efficiency over other methods • Less energy intensive over *ex*-situ methods	• Decreasing efficiency with increasing soil moisture and unfavourable site conditions (cation exchange capacity, salinity, organic content, etc.) • Interference by buried soil metals • Formation of undesirable products in soil by redox reaction • Not suited for contaminant mixtures with varying concentrations • Not suited to treat non-polar contaminants • Post-treatment disposal requirements

4. Physical barriers	• Passive treatment system • Reduced exposure to contaminants • Relatively less maintenance and operational cost • Site is able to be in use while treatment is occurring • Barriers may last long	• Large rocks below ground may present a problem during construction • Installation requires excavation, produces substantial quantities of spoils that must be disposed of • Lengthy time for cleanup and monitoring • Reactivity of the barrier may get significantly reduced by environmental stress • Assessment of performance is difficult
5. Soil vapor extraction	• Cost-effective • Applicable to remediate large sites in short time • Minimal soil disturbance • Easy installation • Compatible with other techniques	• Reduced removal rates in soils with high organic & moisture content • Residual treatment before disposal • Unsuited for saturated zone, low permeability or heterogeneous soil • Limited applicability only to volatiles • Not suited to remediate mixture of chemicals
6. Multi-phase extraction	• Minimum disturbance to site operations • Proven performance in low-permeable soils • Short treatment times • Can be combined with other technologies • Can be used under buildings and other locations that cannot be excavated	• Expensive to implement at sites with medium to high permeable soils • Requires specialized equipment with sophisticated control capacity • Requires monitoring and control during operation
7. Air sparging	• Best stimulator of pollutant biodegradation • Supports microflora at contaminated sites • Easy implementation • Less costly • Remediate broad range of volatiles in short time • No post-treatment requirements	• Inappropriate for silt & clay sediments • Inefficient for non-strippable toxins • Inefficiency in high permeable zones • Flow of dangerous vapors • Influence of site specific conditions • Risks of contaminant migration

(continued)

Table 17 (continued)

Technology	Advantages	Disadvantages
Biological		
1. Natural attenuation	• Natural process • Reduced remediation cost • Reduced long-term risks • Minimal disturbance above ground • No disorder to existing soil biological communities • Post-disposal site is not required	• Reliability is not predictable • Slow process • Program duration affects cost • Need for regular and long-term monitoring • Natural events like storms or human activities may cause resuspension of contaminated sediments • Integration of several disciplines (microbiology, chemistry, hydrogeology, etc.) is needed
2. Bioventing	• Economic • Efficient in treating unsaturated soils • Creates biologically active soils • Short treatment time • Simple • Low maintenance	• Unsuitable for low permeable, clayey soils • Inefficiency in saturated zone and sites with shallow contamination • Not suited to treat sites with high contamination
3. Bioremediation (Bioaugmentation and biostimulation)	• Natural process • Cost-effective • Less energy requirement • Minimal site disruption • Less manual supervision • Toxic chemicals are destroyed • Low capital expenditure • Reduced exposure to public or site personnel	• Slow process • Chance of incomplete degradation resulting in toxic by-products • Process is sensitive to the level of toxicity and environmental conditions • Not suited to completely remove heavy metals • Not suited to biodegrade almost all chemicals • Unsuited for soils with low permeability • Gaps in the understanding of microbial ecology, gene expression and physiology • Performance evaluation is uncertain

4. Phytoremediation	• Less expensive • Green approach • Aesthetically pleasing • After plant establishment, there are chances to flourish wildlife • Easily monitored • Preserves environment in more natural state	• Limited to shallow sites with low levels of contamination • Restricted to sites with contamination as deep as the roots of the phytoremediating plants • Retarded remediation efficacy in sites with high contaminant concentration • Complete treatment shutdown if selected plants are dormant or root growth rate is very slow • Need for post treatment of used plants • Chances for air pollution by burning of plant leaves that were used to phytoremediate a field • Slow treatment • Food chain could be adversely affected by bioaccumulation of contaminants into the plants • Need for large surface area • Contaminant transfer from soil to air • Seasonal interferences • Mass transfer limitations

physico-chemical techniques like EK remediation, heating, etc. are the most promising for on-site contaminant clean up. Bioremediation that harnesses the potential of microbes is widely adopted for full-scale contaminant removal either by biostimulation or bioaugmentation or phytoremediation. However, the successful physico-chemical techniques are not advantageous as they are energy intensive and pave way for global warming by letting out greenhouse gases into the atmosphere. On the other hand, though bioremediation is cost-effective and eco-friendly, it suffers from limitations due to the low bioavailability of pollutants on spatial and temporal scale, poor performance of microbial groups in real contaminated sites, and lack of bench-mark values for evaluating the efficacy and toxicity reduction by bioremediation for their widespread field applications. Considering the above constraints of the existing technologies, advanced techniques using MFCs, nanomaterials, transgenic microbes and plants, and photo-hetero microbial systems have been recently developed which are mostly biological with more prospects of high remedial efficiency in short span along with the potential to harness electricity and by-products like biofuels that add to the economy. However, the in-situ emerging technologies are not widely employed at field-scale due to the lack of system designing for large-scale implementations and regulatory limitations. Therefore, the current prospect as well as a challenge in the field of environmental remediation is to develop a regulated, less energy intensive, no greenhouse gas evolving remediation technology with high cost-benefit ratio for field-scale remediation of soil/sludge/sediment/groundwater/surface water/leachate/air emissions along with the development of bioassay techniques for determining the toxicity and efficiency of each remedial technology at the time of operation.

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Ex-Situ Remediation Technologies for Environmental Pollutants: A Critical Perspective

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Abbreviations

°C	Degree celsius
$	Dollar
>	Greater than
<	Less than
%	Per cent
2,4-D	2,4-Dichlorophenoxyacetic acid
A	Australian
Al	Aluminium
AOP	Advanced oxidation process
As	Arsenic
B	Boron
Ba	Barium
BDD	Boron-doped diamond
BTEX	Benzene toluene ethylbenzene and xylenes
BTF-PCO	Biotrickling filtration and photocatalytic oxidation
CCl_4	Carbon tetrachloride
Cd	Cadmium
CH_4	Methane
Cl_2	Chlorine
cm	Centimetre
Co	Cobalt
CO_2	Carbon-di-oxide
COD	Chemical oxygen demand
Cr	Chromium
CTMAB	Cetyltrimethyl ammonium bromide
Cu	Copper
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DNAPL	Dense non-aqueous phase liquid
EDTA	Ethylenediaminetetraacetic acid
EK	Enhanced electrokinetics
EPA	Environmental Protection Agency
Fe	Iron

F-gases	Fluorinated gases
FRTR	Federal Remediation Technologies Roundtable
g	Gram
GDP	Gross domestic product
h	Hour
H_2O_2	Hydrogen peroxide
H_2S	Hydrogen cyanide
HCH	Hexachlorocyclohexane
Hg	Mercury
Hz	Hertz
IEM	Ion-exchange membrane
IrO_2	Iridium oxide
kW	Kilowatt
L	Litre
lb	Metric pound
m^2	Square metre
m^3	Cubic metre
MFC	Microbial fuel cells
mg	Milligram
min	Minute
Mo	Molybdenum
N	Nitrogen
N_2	Atmospheric nitrogen
NAPL	Non-aqueous phase liquid
NO_2	Nitrogen dioxide
nZVI	Nano zero-valent iron
O_3	Ozone
$OH^{\bullet}$	Hydroxyl radical
P	Phosphorous
PAHs	Polycyclic aromatic hydrocarbons
Pb	Palladium
Pb	Lead
PBDE	Polybrominated diphenyl ethers
PCB	Polychlorinated biphenyl
PCDDs	Polychlorinated dibenzodioxins
PCDFs	Polychlorinated dibenzofurans
PCE	Perchloroethylene
PCNs	Polychlorinated naphthalenes
PCP	Pentachlorophenol
Pd	Palladium
PFCs	Perfluorochemicals
PFOA	Perfluorooctanoate
PFOS	Perfluorooctane sulfonate
POP	Priority organic pollutant
QACs	Quaternary ammonium compounds
s	Second

S/S	Solidification/stabilization
Sb_2O_5	Antimony pentoxide
Se	Selenium
SnO_2	Tin dioxide
SO_2	Sulfur dioxide
SVOC	Semi-volatile organic compounds
t	Metric ton
TCE	Trichloroethylene
TCPP	Tris(chloroisopropyl)phosphate
Ti	Titanium
TMB	Trimethyl benzene
TNT	Trinitrotoluene
TOC	Total organic carbon
TPH	Total petroleum hydrocarbons
U	Uranium
US	United States
UV	Ultra-violet
VOC	Volatile organic compounds
W	Watt
WHO	World Health Organization
Zn	Zinc

1 Introduction

Pollution and the global health impacts from toxic pollutants are presently of great concern. World-wide, one serious problem of half the population is polluted drinking water. Such pollution causes nearly 250 million cases of water-based diseases and 0.005–0.01 billion deaths annually. In US alone, more than 70 % of the cancer risk from exposure to air toxicants is contributed by diesel emissions (WHO 2013). Currently, more than 100 million people are at risk from exposure to a list of toxic organic and inorganic pollutants (Fig. 1) such as pharmaceutical and personal care products, illicit drugs, hormones, steroids, polychlorinated naphthalenes (PCNs), perfluorochemicals (PFCs), synthetic musks, quaternary ammonium compounds (QACs), veterinary products, polychlorinated alkanes, benzothiazoles, polydimethylsiloxanes, bisphenol A, triclosan, industrial compounds/byproducts, food additives, pesticides, heavy metals, chlorinated solvents, polycyclic aromatic hydrocarbons, engineered nanoparticles, etc. Exposure to toxicant pollution can causes immense health impacts (Fig. 2) such as physical and mental disorders, organ dysfunction, neurological disorder, cancer, reduced life expectancy, weakening of the body's immune system, and in some cases death (Godduhn and Duffy 2003; Perera and Herbstman 2011; Mates et al. 2010; Yu et al. 2011; Huang et al. 2012).

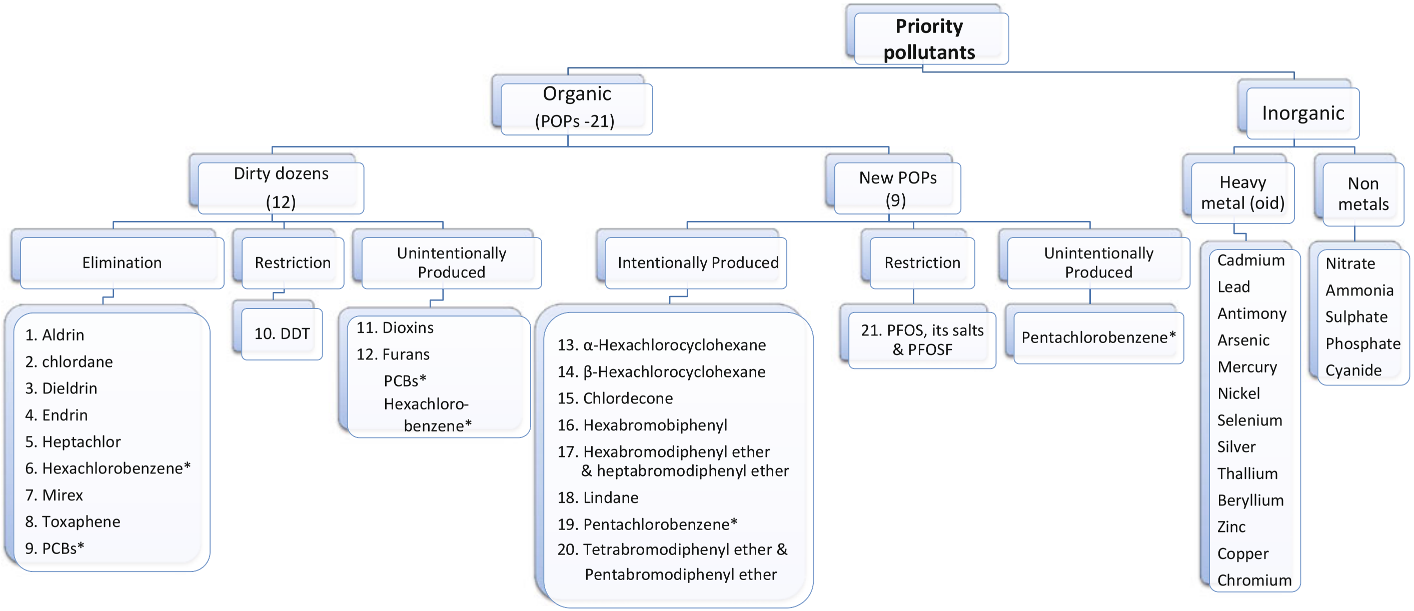


Fig. 1 Priority organic and inorganic pollutants of global issue: a comprehensive framework. *Source*: Stockholm Convention (2010); US EPA (2012). *POPs* priority organic pollutants, *PCB* pentachlorobenzene, *PFOS* perfluorooctanesulfonic acid, *PFOSF* perfluorooctanesulfonyl fluoride, *asterisk* listed twice under the annexes; *numbers* in parentheses indicate the total number of pollutants

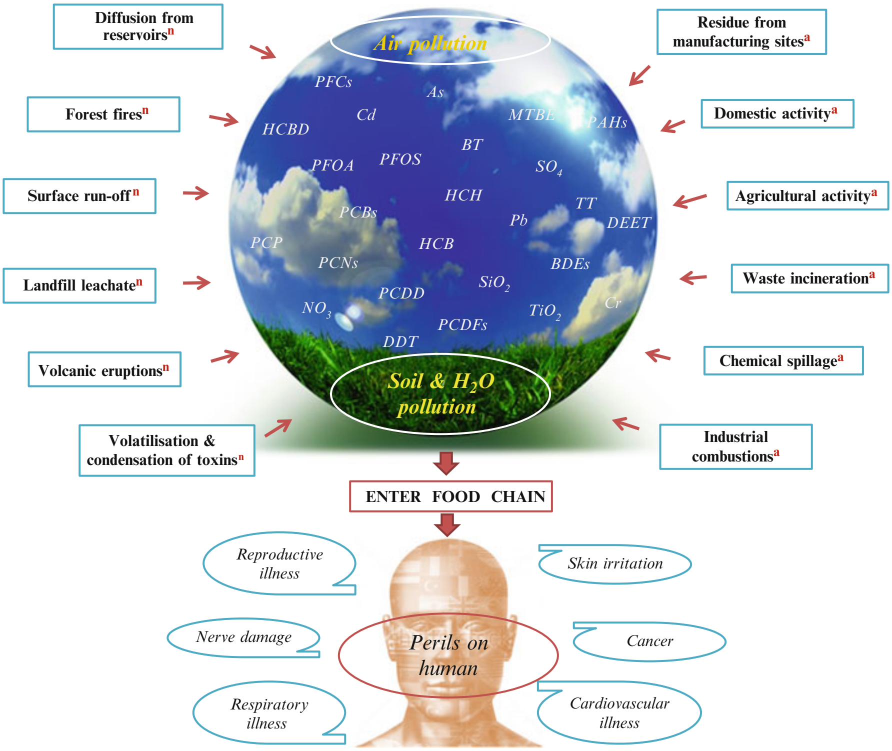


Fig. 2 Priority noxious wastes in the biosphere: causes and consequences. [n]natural source; [a]anthropogenic source; *PCP* pentachlorophenol, *Cd* cadmium, *As* arsenic, *BT* benzotriazole, *PFOS* perfluorooctane sulfonate, *PFOA* perfluorooctanoate, *HCBD* hexachlorobutadiene, *PCBs* pentachlorobenzene, *HCH* hexachlorocyclohexane, *HCB* hexachlorobenzene, *MTBE*, methyl tertiary butyl ether, SO_4 sulfate, *Pb* lead, *TT* tolyltriazole, *PCDFs* polychlorinated dibenzofurans, *PCDD* polychlorinated dibenzo-*p*-dioxins, *DEET* diethyl-meta-toluamide, *PAHs* polyaromatic hydrocarbons, *Cr* chromium, TiO_2 titanium di oxide nanoparticles, SiO_2 silicon nanoparticles, *BDEs* brominated diphenyl ether, NO_3 nitrate, *DDT* dichloro diphenyl trichloroethane, *PCNs* polychlorinated naphthalenes

Notably polychlorinated dibenzofurans and dibenzodioxins are highly persistent chemicals, and some of the congeners, mostly those with lateral chlorine substitutions at certain positions, are extremely toxic and carcinogenic to humans. Pesticides are often used in public health and agricultural programs globally. Solvents such as carbon tetrachloride and trichloroethylene (TCE) contaminate the surroundings due to large-scale anthropogenic applications. Pharmaceutical and personal care products and food additives are used in our day-to-day life. Recently, the use of nanoparticles in sunscreen lotions and tooth pastes has increased. In most cases, the negative ecological consequences of the toxic chemicals, when released, have been observed to exceed the benefits of their use and necessitate the need for their removal or mineralization (Landis and Yu 2003).

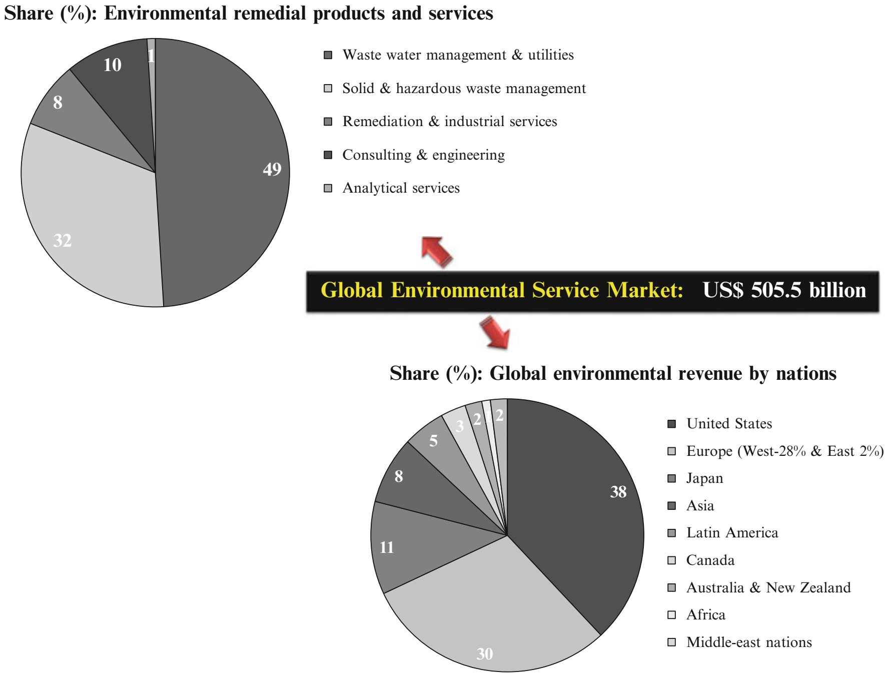


Fig. 3 Global remediation market scenario in 2010: per cent contribution by different nations and services. *Source*: EBI online (2013); US ITC (2013)

Remediation of pollutants, whether by physical, chemical, biological means or any combination thereof constitute the only options to remove them. Globally, the remediation sector annually contributes US$505.5 billion to revenue (Fig. 3), of which 30–50 % of profit is derived from managing solid and hazardous wastes and wastewaters. The major global contributor to environmental income of the sector is the US, followed by Western Europe (EBI 2013; US ITC 2013). This shows that the remedial sector is economically important and contributes significantly to GDP, as does other sectors like agriculture. Many remediating technologies are available, and selecting the most suitable one for any application depends mainly on the site characteristics and the objectives of the task. Since there is a strong demand for developing a promising technology that aids in minimizing treatment cost and maximizing the benefits, current research is focused on developing new remedial measures by integrating the principles of successful existing techniques. This is paving the way for emerging technologies such as ultrasonics, sonophotocatalytic oxidation, etc. Normally, it will be easier to choose the right technology for implementation only when reviews of the existing and emerging ones are available. Moreover, comparing available technologies helps one to understand the merits and demerits of each one.

Several techniques are suited as both *in-situ* and *ex-situ* options and such techniques are well established as *ex-situ* measures, where remedial efficiency is fairly high. For instance, advanced oxidation processes, incineration, dehalogenation, solidification, ion-exchange, sorption by natural materials (e.g., modified clays), constructed wetlands and bioslurries are suited for the remediation of a broad range of contaminants. It is our goal to present a comprehensive survey of such existing and emerging options that are suited for both *in-situ* and *ex-situ* remediation of contaminated sites. Since off-site remediation is the prime objective of the current review, the major aspects addressed for each technology involved in *ex-situ* applications include (1) technology profile, (2) merits, (3) drawbacks, (4) success stories, (5) recent advancements, and (6) future research directions.

2 Ex-Situ vs. In-Situ Remediation

The two main types of remediation are *ex-situ* and *in-situ. Ex-situ* involves physically extracting media from a contaminated site and moving it to another location for treatment whereas *in-situ* remediation involves treating contaminants on-site. At an *ex-situ* site, if the pollutant exists only in soil, the soil is excavated. If pollution has reached the groundwater, it is then pumped and both the polluted soil and water are removed. *Ex-situ* and *in-situ* techniques each have specific benefits and costs. The prime benefit of *in-situ* techniques is that contaminated soil need not be removed or transported. The downside of *in-situ* techniques is that they are less efficient at contaminant removal than *ex-situ* remedial options. In addition, *in-situ* remediation techniques are favored over *ex-situ* ones, because the excavation incurs a high cost and individual excavators are exposed to adverse health risks of contaminants. Despite the high cost, *ex-situ* treatment generally requires less time to achieve efficient contaminant cleanup, is easily monitored and achieves more uniformity. After *ex-situ* treatment, decontaminated soils may be used for landscape purposes.

3 Existing *Ex-Situ* Remedial Options for Contaminated Soil and Groundwater: Technology Profile and Recent Advances

3.1 Dig-and-Dump (Landfills and Engineered Landfills)

Dig-and-dump is the most used and conventional *ex-situ* remediation technology. Dig-and-dump/excavation-and-disposal generally targets “hot spots”, in which contaminants at a polluted site exceed pre-set risk levels, and therefore require remediation. In dig-and-dump, contaminated soils are excavated and transported to landfills or environmentally acceptable locations for disposal. Often polluted soils must be moved to secure landfills. A secure ‘landfill’ is a plot or site that is carefully engineered to receive dumped wastes. Landfill types are quite variable, and include inert waste landfills, solid waste landfills, and hazardous waste landfills, with an assumed annual disposal rate of between 5000 and 230,000 t waste/year. Generally, a secure landfill has four critical elements: a natural hydrogeological setting, a cover or "cap", a leachate collection system, and a bottom liner. The materials used in bottom liners are made either of plastic or clay or a composite of both; such liners are layered on a bathtub shaped depression in the ground and is designed to prevent waste from escaping into the environment. Covering or capping the landfill helps prevent leachates, and are augmented with a pipe system (leachate system) in the landfill to collect leachate. Any leachate that is pumped is treated at a waste treatment plant (US EPA 2012).

One upgraded form of engineered landfill is called the 'bioreactor landfill'—it is a sanitary landfill spot used to transform and stabilize toxins via microbial processes within the first 5–8 years of bioreactor operation. The advantages of bioreactor landfills include an ability to: (a) reduce greenhouse gas emission into the environment, (b) produce end-products that do not require landfilling, (c) steep decline in the landfilling cost, (d) decrease leachate treatment cost (capital and operating), and (e) reduce contaminant concentrations during landfill operation. A bioreactor landfill can either be aerobic or anaerobic or hybrid (aerobic-anaerobic), wherein accelerated degradation of waste is achieved by decreasing the cost of long-term monitoring (Warith 2002; US EPA 2012). The main drawback of landfills, either conventional or bioreactor types, is that they generate greenhouse gases that have a drastic environmental impact. Landfills also pose a risk to humans during their excavation, because the hazardous wastes that are deposited in them are not pretreated. The final drawback is that the cost of transporting the excavated contaminated material to a final destination is very high (Campbell 2009).

EPA charges landfill operators different levels of license fees, and requires financial assurances from operators, depending on the proposed facility's location and nature. There is a strict legal liability for unauthorised disposal of wastes that may reach a daily maximum penalty of US$60,000 per individual. Moreover, damage costs can be assessed by regulators for (a) greenhouse gas emissions, (b) air pollution, (c) leachate releases, and (d) amenity impacts. More recently, governments have increased the cost of waste disposal at existing and new landfills, and have strengthened regulations. For example, the total waste disposal costs at urban and rural landfills in Australia range between A$42–102 and A$41–101 per t waste, respectively (BDA Group 2009).

In a field investigation, Osako et al. (2002) observed the mobility of polychlorinated dibenzofurans/polychlorinated dibenzodioxins (PCDFs/PCDDs) in a landfill area replete with municipal solid waste residues. Al-Yaqout and Hamoda (2003) also found that considerable quantities of leachate are formed at a landfill site. Baumann et al. (2006) witnessed heavy metal transport that was in direct contact with groundwater at a landfill site. According to VanGulck and Rowe (2004), when suspended on solids landfill leachate can form bio-rocks (clogs). Some researchers have reported methane emissions from solid waste landfills (Scheutz and Kjeldsen 2004; Kumar et al. 2004). Scheutz et al. (2009) illustrated the need for developing new technology to mitigate methane emission from a landfill site via improved oxidation processes. In Southern Spain, Zamorano et al. (2008) suggested that the biogas produced from urban landfills could be used to generate electricity (approx. 4,500,000 kW/year). Although landfills have several negative environmental impacts, these may be overcome by applying the results of further investigations and utilizing more advanced technologies.

3.2 Pump-and-Treat

In pump-and-treat, the groundwater is pumped and then treated using granular activated charcoal. Generally, the pump-and-treat approach requires 50–100 years to reach remedial goals, and in most cases the goals are never achieved (US EPA 1996). Moreover, disposal of contaminants that become bound to activated carbon after treatment becomes a problem (Bau and Mayer 2006). Because of these drawbacks, surfactant-enhanced remediation, metallic iron technology, permeable reactive barriers, etc., have emerged as alternatives to traditional pump-and treat-systems.

Mackay et al. (2000) performed a field experiment at a Dover site in Delaware and observed that pulsed pumping is more advantageous than continuous pumping. Wang and Mulligan (2004) recommended the use of ‘surfactant foam technology’ to improve contaminant removal efficiency and cost-effectiveness of a current pump-and-treat system. At the Dover national test site, Delaware, a surfactant-based flood (sodium dihexyl sulfosuccinate, isopropanol, and calcium chloride) significantly reduced the tetrachloroethylene (TCE) concentrations (80 %) within 800 h in a pump-and-treat system (Childs et al. 2006). Utilizing a pilot-scale pumping system, Wei et al. (2010) successfully demonstrated effective remediation (50–99 %) of groundwater polluted with chlorinated organic mixtures by employing nanoscale zero-valent iron (ZVI). Consequently, the conventional pump-and-treat system no longer operates, and has been amended for integration with recently advanced techniques (nano, or surfactant treatments, reactive barriers, etc.).

3.3 Incineration

As pump-and-treat techniques have declined, incineration technologies to treat environmental wastes have grown in importance over the past 20 years. Incineration, combustion or thermal oxidation are different terms for a process in which hazardous wastes are subjected to very high temperature (750–1200 °C) treatments to affect their disposal. Incineration is carried out in different experimental units like: infrared combustors (electrically-powered silicon carbide rods are used to heat organic wastes up to temperatures of 1010 °C via infrared energy); fluidized bed combustors (utilizes high-velocity air with infrared as a heat source; incineration occurs at temperatures up to 850 °C); circulating bed combustors (high velocity air entrains circulating solids and destroys noxious hydrocarbons by creating a highly turbulent combustion zone at temperatures up to 850 °C); and rotary kilns (rotating cylinder that is slightly-inclined and refractory-lined, with an afterburner that burns at temperatures up to 980 °C) (FRTR 2012).

Commercial incinerators are generally designed as closed burning rotary kilns that are equipped with an air pollution control system, a quench unit and an afterburner (Pavel and Gavrilescu 2008). Such incinerators are used to remediate soils that are contaminated with dioxins, PCBs, chlorinated hydrocarbons and explosives. The application of this incineration technology will reduce bulky solids or wastes that are combusted to 5 % of their original volume, and 25 % of their original weight. These reductions are achieved even when the wastes possess high moisture content. It aids in the detoxification of combustible carcinogens, pathogenically-contaminated materials and toxic organic compounds. In addition, the amounts of greenhouse gases (CH_4 and CO_2) generated by incineration are less than those generated in landfills for the same wastes (Hutton 2009). Incineration is used to treat very large quantities of wastes. One other advantage of incineration is that energy can be recovered from incinerating wastes that will add to the economy (by producing steam, electricity and fuel). The above advantages justified using incineration at more than 150 superfund sites, and using energy generated from combusting wastes at off-site locations described below. Incineration also has disadvantages that limit its effectiveness and usefulness.

Incineration is expensive, both in initial capital costs to construct a facility, and also in operating costs. Incineration equipment requires maintenance and is rather unreliable, requiring practical repairs to routine waste-handling issues. To achieve targeted combustion temperatures, supplementary fuels are often required, and these can be expensive. One prime disadvantage is that incineration practices may cause drastic secondary environmental impacts (Santoleri et al. 2000). For instance, most waste combustion systems have gas or particulate emissions that are highly dispersible by wind (e.g., flue gases composed of noxious fumes, nitrogen gases, carcinogenic hydrocarbons, carbon monoxide, hydrogen chloride, odors and sulfur dioxide). Incineration also may generates leachates (i.e. discharges of residue that may contain abrasive suspended or dissolved solids, heavy metals and pathogenic organisms into soil/groundwater/surface water bodies) that pose health risks (Chandler et al. 1997). Moreover the release of inorganic wastes from incineration processes, such as the heavy metals zinc (Zn), lead (Pb), copper (Cu), arsenic (As), cadmium (Cd), are very difficult to control (Sabbas et al. 2003). Incineration processes have technical risks, i.e., shortfall in performance (higher maintenance expenses, reduced system capacity than expected), and a newly installed incinerator is affected by changes in waste characteristics that are common due to seasonal variations (Niessen 2002).

Despite the above-mentioned technical challenges, incineration has progressed from batch-fed, simple, refractory hearth systems, and as a result now has much wider applicability. Currently, incineration plants in the United States are subject to a series of regulations/federal requirements that are technology-specific as follows: NCA—Noise Control Act (noise), NPDES—National Pollutant Discharge Elimination System (discharge to surface water), RCRA—Resource Conservation and Recovery Act (generation, treatment, storage and disposal of hazardous wastes), CAA—Clean Air Act (air emissions), and TSCA—Toxic Substances Control Act (treatment and disposal of PCB). These regulations help to reduce the environmental impacts of this system. Also, the incinerated residues need to be subjected to a few treatments before reuse or disposal like thermal treatments (melting, vitrification and sintering), solidification/stabilization (solidification with hydraulic binders, chemical stabilization and ageing/weathering), and separation (crystallization/evaporation, adsorption, ion-exchange, chemical precipitation, immobilization, chemical extraction, washing, eddy-current separation and magnetic separation) (Sabbas et al. 2003). Incineration costs US\$0.74–1.25 per m^3 when it is chosen to remediate a specific contaminated site (US EPA 2012).

McKay (2002) standardized the municipal solid waste incineration system of dioxins, and concluded that effective dioxin reduction with minimized PCDD/PCDF formation could be achieved when incinerators are operated using the following process conditions: combustion residence time of >2 s, chamber turbulence of >50,000, incineration temperature of >1000 °C and post-combustion temperature of 200 °C, and with the use of air pollution control systems like activated carbon injection, bag filters and semi-dry scrubbers. More recently, many experiments were conducted with the objective of electrochemical oxidation/incineration of wastewater containing organics where the organic contaminants were completely oxidized to CO_2. The electrochemical incineration of chloranilic acid using Si/diamond (Si/BDD), Pb/PbO_2 and Ti/IrO_2 electrodes was studied by Martinez-Huitle et al. (2004). In this context, electrochemical oxidation of many organics was investigated for a few other anodic materials like SnO_2–Sb_2O_5, SnO_2, PbO_2 and IrO_2.

Chang et al. (2000) stated that the removal of mercury by municipal waste incineration is mostly low varying from 30 to 45 %. Studies have been conducted using anodic materials like Si/BDD and Ti/BDD which are considered to be the boundaries of the novel ‘electrode material technique’ (Polcaro et al. 2002). Rein (2009) reported that the energy inefficient incineration of NAPLs by flaming technology could be replaced by smouldering combustions since smouldering is self-sustaining with no requirement for any energy input after ignition. Grant and Major (2010) evaluated the efficacy of STAR (Self-sustaining Treatment for Active Remediation—Smouldering combustions) technology to treat soils contaminated with coal-tar at a former manufacturing plant in Newark, New Jersey. Ignition was achieved after 25 h of preheating. Maintenance of the peak ignition temperature of 1340 °C for about 9 days completely removed the contaminant mass. Similar studies were conducted by Pironi et al. (2009) and Switzer et al. (2009) where the treatment efficacy of STAR for removing 99.9 % PAHs and TPHs was confirmed. Pironi (2010) also recommended smouldering combustion as a suitable incineration approach to treat soils contaminated with NAPLs. He observed a mass removal of 99.5 % NAPLs when the materials were smouldered to a temperature of 600–1100 °C at pilot-scale.

Remedial studies conducted by implementing incineration at superfund sites are numerous, and were successful in remediating 99.9 % NAPLs (FRTR 2012) as listed in Table 1. However, incineration applications at real contaminated sites are currently scarce compared to those done in the 1990s. It is necessary to search for a

Table 1 Overview of the selected full-scale incineration studies conducted at superfund sites of US EPA

Remediation site	Contaminants of concern	Volume treated	Target temperature (°C)	Outcome	Efficiency (%)
1. Bayou Bonfouca, slidell, Louisiana^{R}	PAHs	129,204 m^3 sediment	871–982	Completed 18 months ahead of schedule^{+}	99.9
2. Baird and McGuire, Holbrook, Massachusetts^{R}	Dioxins, PAHs, pesticides, Pb, As	210,000 t soil and 1153 m^3 sediment	871	Ability to treat wide range of contaminants like dioxins, PAHs and pesticides in soils/sediments^{+}	99.9
3. Bridgeport refinery and oil services, Logan Township, New Jersey^{R}	PCBs, VOCs, benzene, Cd, methylene chloride, Zn, Pb, Ba, Cr, toluene	172,000 t lagoon, sediment and sludge	760	Inadequate design caused mechanical problems^{-} Demulsifying problems complicateddewateringofsediment^{-}	99.9
4. Celanese, Shelby, North Carolina^{R}	VOCs, TCE, Pb, Cr, PAHs, ethylene glycol	4660 t sludge and soil	815–1037	Remediation was successful as low volume was incinerated^{-}	99.9
5. Former Nebraska ordnance works, Nebraska^{R}	Explosives, propellants	10,006 m^3 soil and debris	621–982	Remedial goals achieved in short time period^{+}	99.9
6. Petro processors, Baton Rouge, Louisiana^{R}	Hydrocarbons, heavy metals, hexachlorobutadiene, hexachlorobenzene	810,828 L liquids and fumes	1093–1315	Best suited groundwater treatment system for liquid organics and air stripper fumes^{+}	99.9
7. Sikes disposal pits, Crosby, Texas^{R}	PAHs, BTEX, VC, chlorobenzene, EDC	496,000 t soil and debris	704–982	Complete remediation within the framed time limit in spite of voluminous treatment zone^{+}	99.9

^{R}Use of rotary Kilns; $^{+}$Significant; $^{-}$Problem suitable remedial option to combat greenhouse gas emissions resulting from this mechanism as its end product is nothing but CO_2. Otherwise, suitable *ex-situ* treatment techniques that are listed below could be implemented.

3.4 Oxidation

Oxidation is a promising remedial option where the target contaminant is not only destroyed but also the toxicity of the pollutant is considerably reduced either by chemical or biological or advanced processes. Chemical oxidation destroys the target compound and reduces the toxicity associated with it. The most commonly used oxidizing agents are permanganate, chlorine-di-oxide, chlorine, peroxides, hypochlorites and ozone (O_3) (FRTR 2012).

Recent treatment methodologies termed 'advanced oxidation processes (AOPs)' have the potential to treat all types of inorganic and organic pollutants (volatile, semi- and non-volatile). An oxidation system that can produce adequate $OH^•$ radicals entails complete mineralization, implying that the terminal degradation products are inorganic ions, short-chain organic acids and CO_2 that are typically amenable for biodegradation, and are less toxic. AOP generally uses a combination of oxidation agents, irradiation like UV/ultrasound and catalysts such as TiO_2, and is more powerful than the conventional chemical oxidation process (Mahamuni and Adewuyi 2010). Of the different types of oxidation processes, Fenton's (H_2O_2/Fe^{2+}) oxidation, TiO_2/UV system and H_2O_2/UV system are some of the most powerful ones, and can be used to destroy a wide range of organic contaminants in aqueous ecosystems due to their high oxidative potential and being subject to high scrutiny. Advanced oxidation technique can be either: (a) non-thermal heterogeneous systems with irradiation (solar energy/O_2/UV/TiO_2); (b) a non-thermal homogeneous system without irradiation (Fenton's reagent, $O_3/OH^•$, O_3/H_2O_2); (c) without irradiation (electro-Fenton); (d) hydrothermal or (e) sonochemical (electrochemical/catalytic/photocatalytic) oxidation. There are also supercritical water oxidation and wet-air oxidation types.

Generally, advanced oxidation processes potentially reduce toxicity of organic compounds without producing additional hazardous by-products or sludge which requires further handling. Without much discrimination, the AOP system can be used to react virtually with all types of aqueous pollutants because of the remarkably high reactivity of the $OH^•$ radicals. In some cases, disinfection could also be achieved when using this method. However, some drawbacks exist like high cost, technical demand and an inability to handle large quantities of pollutants.

Andreottola et al. (2008) found that about 90 % organolead compounds can be removed from the contaminated groundwater by the use of chemical oxidation with Fenton's reagent followed by filtration on activated carbon. In the treatment of leachate effluent, Abdul et al. (2009) compared the performance of advanced oxidation processes over granular activated carbon bio-sorption and found that Fenton's oxidation could remove only 80 % TOC; however, biosorption (including adsorption and biodegradation) could remove 85 % of the TOC in a few weeks. According to Rodriguez et al. (2008), catalytic (copper supported on carbon nanofibers) wet-air oxidation can remove about 74 % TOC in 180 min. Orescanin et al. (2012) developed and adopted an appropriate combined treatment approach for landfill leachate, the use of calcium oxide/electrooxidation, where about 99.7 % of the contaminant was removed.

Advanced oxidation catalyzed with nZVI particles, for example, ferrous iron (Fe^{2+}) successfully removed the organics in wastewater treatment studies (Ershadi et al. 2011). More recently, biological oxidation integrated with solar driven oxidation processes was established at a pilot plant equipped with a photocatalytic system and an immobilized biological reactor for winery wastewater remediation (Souza et al. 2012). Among the AOPs tested (Fe^{2+}/H_2O_2/UV and TiO_2/H_2O_2/UV), solar photo-Fenton process demonstrated the highest efficiency. Parida and Mohapatra (2012) identified a novel photocatalyst—carbonate intercalated Fe/Zn layered double hydroxide with dissimilar intercalated anions (carbonate, chloride and nitrate)—for enhanced photodegradation of azodyes. In a pilot-scale study, Vargas and Nunez (2010) found that advanced photooxidation (TiO_2/UV) could mineralize 90 % *p*-nitrophenol, naphthalene and dibenzothiophene in 180 min.

Tsai et al. (2010) demonstrated that iron electrode corrosion-enhanced electrokinetic-Fenton oxidation is a valuable approach for effective and efficient remediation of TPH-contaminated lands. To achieve an environmentally friendly and cost-effective remedial option for tannery sludge containing high Cr levels, Kilic et al. (2011) used biosurfactants as sorbents in comparison with chemical oxidation and observed that oxidation was 3× higher than sorption. Villa et al. (2010) noticed that soil remediation by use of combined processes like photo-Fenton oxidation and soil washing with surfactants could remove 100 % DDT, DDE and diesel. TiO_2-based advanced oxidation nanotechnologies are emerging as competitive promising processes for full-scale applications in near future (Choi et al. 2010). Currently, ultrasonolysis with other advanced oxidation process performs better compared to photocatalysis alone (Mohajerani et al. 2010). Many remedial studies have been conducted by employing the latest oxidation processes (Table 2), and this technology is advancing steadily through the introduction of either: firstly, new catalysts (supported noble metal nanoparticles as photo/sono catalysts); secondly, nanoparticles or surfactants; or thirdly, adopting integrated processes with existing remedial measures to achieve 100 % remediation in a very timespan. However, more emphasis is required on reducing remedial costs by linking this technology to the basic study of its ecotoxicological effects. This is because the recent oxidation methods are expensive, and using extensive chemicals or nanoparticles may damage the ecosystem which is still unexplored.

3.5 Adsorption

Adsorption is the most widely used, fastest, inexpensive technology for the treatment of groundwater, industrial wastewater, air emissions, chemical spills, and for removing a series of toxic chemicals such as BTEX, ethylbenzene, xylene, trichloroethene, tetrachloroethene, dichloroethane, PCBs, pesticides, herbicides, explosives, and anions like perchlorate and heavy metals. A process in which molecules

Table 2 Oxidation: Remedial studies

Pollutant	Method	Remediation (%)	Reference
Organolead compounds in groundwater	Chemical oxidation with Fenton’s reagent	90	Andreottola et al. (2008)
Landfill leachate effluent	Advanced oxidation process	80	Abdul et al. (2009)
Dyes in textile effluent	Wet air oxidation	70	Rodriguez et al. (2008)
Landfill leachate	Advanced oxidation combined with electrochemical and microwaves	90	Orescanin et al. (2012)
TCE	Oxidation with nano-Pd-Fe^0 particles	90	Al-Shamsi et al. (2013)
Chipboard production wastewater	Advanced oxidation using solar energy	70	Eduardo da Hora Machado et al. (2004)
Dyes in textile effluent	Advanced oxidation using TiO_2/H_2O_2/sunlight	100	Garcia et al. (2009)
Phenol in water	Combined biological treatment and photocatalytic oxidation	80	Suryaman et al. (2006)
Pharmaceutical wastewater	Solar photo-Fenton combined with biological treatment	90	Sirtori et al. (2009)
p-Nitrophenol, naphthalene and dibenzothiophene	Photodegradation (TiO_2/UV)	90	Vargas and Nunez (2010)
Phenanthrene and pyrene	Potassium permanganate	60	de Souza e Silva et al. (2009)
PAH-contaminated sediments	Chemical oxidation	90	Ferrarese et al. (2008)
Diesel-contaminated soil	Electrokinetic-Fenton oxidation	90	Tsai et al. (2010)
Phenols in agro-industrial wastewater	Fenton’s oxidation	60	Martins et al. (2010)
TCE-contaminated groundwater	Surfactant-enhanced persulfate/BOF slag oxidation	90	Tsai et al. (2010)
MTBE	Ferrous-ion activated persulfate oxidation	80	Chen et al. (2009a)
Chlorinated solvents	Sodium persulfate oxidation	80	Dahmani et al. (2006)
Chromium in tannery sludge	Oxidative remediation	70	Kilic et al. (2011)
PCB	Sulfate radical-based advanced oxidation processes	90	Rastogi et al. (2009)
Polyvinyl alcohol	Persulfate activated with heat, Fe^{2+} and ZVI	90	Oh et al. (2009)
Synthetic dyes	Electro-Fenton and photo electro-Fenton oxidation	80	Peralta-Hernandez et al. (2009)
SVOCs	Chemical oxidation	90	Wei et al. (2012)
Phenol	Catalytic wet peroxide oxidation	90	Valkaj et al. (2011)

of a gas or liquid are attached and then held at a solid surface by electromagnetic forces or chemical bonding is known as 'adsorption'. 'Absorption' is the intraphase distribution of a solute where a solute is absorbed or dissolved into the absorbing phase. When both absorption and adsorption occur simultaneously, and both cannot be distinguished, then it is termed 'sorption'. Adsorption can be categorized into physical, chemical and electrostatic. Chemical adsorption is also referred to as chemisorption (Bhandari et al. 2007). Ion-exchange is a form of adsorption that is detailed in the following section.

Activated carbon is the most common adsorbent which has been used extensively for water and air treatments followed by synthetic ion-exchange resins, activated alumina, sorption clays and forage sponge (open-celled cellulose sponge with an amine containing chelating polymer that selectively adsorbs toxic transition heavy metals). A full-scale system in which the dissolved organic chemicals in groundwater are adsorbed when pumped through a series of columns packed with activated carbon is designated 'liquid-phase carbon adsorption'. The reactor designs available for carbon adsorption systems are moving bed or pulsed and fixed bed. Fixed bed system is the one that is typically utilised. Activated carbon adsorption is effective for remediating sites contaminated even with smaller concentration of pollutants (<10 mg/L), and for polishing the treated water from other remediation systems (FRTR 2012). The carbon adsorption system is a rapidly deployable technique with very high remedial efficiency. However, one of the major problems is the transportation cost and decontamination of the spent carbon.

Shuibo et al. (2009) found that hematite (type of inorganic sorptive medium) can be used to efficiently remove U from aqueous solutions. Choi et al. (2008) developed an innovative remedial strategy employing a series of granular activated carbon composites impregnated with palladium/iron bimettalic nanoparticles which was able to physically adsorb 90 % PCBs in 2 days. Since the emphasis is to select a cost-effective, eco-friendly sorbent for removing environmental contaminants, currently more emphasis is given to biological means of sorption apart from physical or chemical. Gong et al. (2007) proved the advantage of activated carbon adsorption of PAHs. Organoclays performed best on hydrocarbon sorption (Carmody et al. 2007). The effects of different low-cost adsorbents like neem bark, saw dust, fly ash, fuller's earth, activated alumina, rice husk ash and clarified sludge (waste from steel industry) were studied by Bhattacharya et al. (2008). Activated alumina, rice husk and clarified sludge were the most effective tested sorbents for removing Cr(VI) from aqueous solutions. Nano-sized modified ZVI particles are efficient sorbents of As in aqueous solutions (Jegadeesan et al. 2005).

While studying the effect of integrated adsorption, chemical and physical processes for the remediation of landfill leachate, Rivas et al. (2005) found that integrating Fenton's oxidation, wet-air oxidation and adsorption on activated carbon could remove 80–96 % of the COD. Chitosan (a natural amino polysaccharide) was used as a sorbent to remove dye from aqueous solutions (Crini and Badot 2008). Oladoja et al. (2008) discovered that even castor seed shell can be used as a sorbent of dyes in contaminated wastewater. Some of the sorbing materials that have been investigated so far are summarized in Table 3. Studies revealed that several

Table 3 List of sorptive materials used for pollutant cleanup

Contaminant	Sorptive medium
Heavy metals (U, Cr, Zn, Pb, Co, As, Cd, Zn, Ni, Cu)	Hematite Clarified sludge, rice husk and activated alumina Nano-sized modified ZVI particles Granular activated carbon Biogenic manganese oxide Natural Jordanian sorbent (quartz, aluminosilicates, calcite, dolomite) Novel organoclays (ammonium organic derivatives with different chelating functionalities in the interspace of montmorillonite) Maize tassel Rice bran Vermiculite Brown seaweed Zeolite Phosphate-modified kaolinite clay Vegetable compost Polymetallic sea nodule Biogenic magnetic nanoparticles Iron oxide coated sand Manganese oxide coated lead Coconut shell Eucalyptus bark Natural siderite Diatomite Zeolite composite Nano-hydroxyapatite Acrylate-based magnetic beads Fuller's earth nZVI Biochar Nano-sized magnesium oxide powder Modified SBA-15 mesoporous silica Zeolite Red mud Psyllium and acrylic acid based hydrogels Gibbsite Multiwall carbon nanotube/ iron oxide magnetic composites Red algae
PCB	Granular activated carbon composites incorporated with Fe/Pd bimetallic nanoparticles
Phenol	Organoclays Activated clay Hydrophobic modified clay Almond shell residues
PAHs	Activated carbon Matrix modified organoclays
TPH	Organoclays

(continued)

Table 3 (continued)

Contaminant	Sorptive medium
Dyes	Chitosan Coniferous pine bark powder Castor seed shell Jackfruit leaf powder Activated carbon Cyclodextrin polymer Bentonite Broad bean peel Citric acid modified wheat straw Sepiolite, fly ash Apricot shell activated carbon Palygorskite-supported ZVI
Tetracycline	Carbon nanotubes
Nitrate	Nano-alumina
Herbicide (2,4-D)	Organo-palygorskite
Cd	Red algae

agrowastes such as barks of trees, saw dust, bran (wheat, rice), husks (wheat, rice, blackgram), shells (groundnut, coconut, hazelnut, walnut, cotton seed), waste leaves (tea, *Cassia fistula*), stalk (cotton, grape, sunflower), peels (apple, banana, orange), and others (coffee beans, biochar, water hyacinth, soybean hulls, sugarcane bagasse, jatropha deoiled cakes, maize corn cob, sugar beet pulp, etc.) can be used as sorbents to remove the contaminants, especially heavy metals (Sud et al. 2008). Cr(VI) was successfully remediated by Sarkar et al. (2010) through adsorption by bentonite-based Arquad® 2HT-75 organoclays. Modified clays are recently being developed for sorption of heavy metals. Shu et al. (2010) developed CTMAB modified bentonite and kaolinite for the sorption of chlorobenzenes. Recently, Beckingham et al. (2012) reported that steam-activated poultry litter biochar (commercial black carbon that is produced from organic wastes by pyrolysis mechanism) could remove >99.7 % Hg over a wide range of pH. They suggested that the biochar amendments are effective for sites contaminated with mixed organic and inorganic chemicals as they could sorb the priority pollutants with the benefit of carbon sequestration. Even nanoparticles are increasing in importance recently as effective sorbents of pollutants. For example, nano-alumina developed by Bhatnagar et al. (2010) was used to remove nitrate from water. Iron oxide nanoparticles were also employed to sorb As from soil (Shipley et al. 2011). Thus, the sorption studies are many, and constitute the most promising and cheap remedial options for remediating contaminated soils and groundwater. However, the combined effects of biosorption with other remedial techniques are not yet much explored, and should be the focus of future research.

3.6 Ion-Exchange

Exchange of cations or anions between pollutants and the media is referred to as ion-exchange. Ion-exchangeable materials are generally resins (natural polymers with a variety of ionic functional groups for attachment of exchangeable ions) (FRTR 2012). When liquids are passed over a resin bed, ions in resins (i.e., cations and anions) and contaminated materials are exchanged, and the metallic ions remain in the resins. Resins can be regenerated for reuse when their capacity has been exhausted; sometimes the resins are only adapted for single use. So far both anionic and cationic resins have been used (Alexandratos 2008).

Ion-exchange systems can remove dissolved metals, radionuclides, nitrate, ammonia and silicates from liquid media (Vilensky et al. 2002; Rengaraj et al. 2003). This technology is widely adopted for decontaminating the hotspots of concern as the resins are considered to be a rapidly developing twentieth century scientific tool. Their promising applicability to biomolecular separations and catalysis, chromatography, hydrometallurgy, wastewater treatments, environmental remediation and water softening has been confirmed (Harmer and Sun 2001; Mergen et al. 2008). Ion-exchange resins are highly adaptable and environmentally compatible since they are insoluble and the loading/regeneration/reloading mechanisms allow them to be used for many years in most cases. Ion-exchange technology has been in industries from late 1990s and is commercially available.

Typically grease, oil and organic or inorganic biological compounds found in various traces (humic and fulvic acids) in the treated media clog the ion-exchange resin (Beril Gonder et al. 2006). The resin can be damaged by the interference of unfavorable soil factors like high pH, oxidation and suspended solid concentrations. Generally, wastewater is generated during the resin regeneration and requires additional treatment and disposal that increase the cost (Pintar et al. 2001). There are also concerns with respect to the treatment size, odor, noise generation and disposal issues after the use of resins. However, remediation practices by making use of ion-exchange technology mainly for perchlorates and heavy metals are being developed to reduce the risks they pose to the public (Srinivasan and Sorial 2009). The cost involved for operating a typical ion-exchange technology to treat 4000 L of water is nearly US$0.3–0.8 (FRTR 2012).

Recently, Awual et al. (2012) showed that ‘weak base anion-exchange adsorbents’ (Diaon WA30 and Diaion WA20) are the most effective in removing As(V) from drinking water with faster adsorption rates and excellent adsorption capacity. Similarly, Awual et al. (2011, 2013) reported that ion-exchange resins, polyallylamine fibres and primary amine could selectively take up phosphate and As(V) from contaminated groundwater systems at higher flow rates even in the presence of competing anions such as sulphate, bicarbonate, nitrate and chloride. Kim et al. (2005) studied the effect of ion-exchange membrane (IEM)-enhanced electrokinetic (EK) soil processing on metal removal, and observed that nearly 96 % Cd and Pb was removed by this integrated mechanism within 4 days. One limitation of EK remedial system alone (soil hydroxide is precipitated near the cathodic side of the electrodes) was overcome by the use of IEMs.

Gu et al. (2002) conducted a pilot-test at Edwards's Air Force Base, California, to remove perchlorate from polluted groundwater using bifunctional ion-exchange resin and $FeCl_3$-HCl for the regeneration of resins. The bifunctional ion-exchange resin bed treated nearly 40,000 empty bed volumes of groundwater, and about 100 % perchlorate was successfully removed in 6 months. Gu et al. (2007) also carried out a field experiment in California, the objective being to treat perchlorate-polluted water using perchlorate destruction and highly regenerable, selective ion-exchange tools which could enhance the treatment efficiency as well as minimize secondary waste production. Bifunctional anion-exchange resin (Purolite A530E) and $FeCl_3$-HCl (as the resin generation system) were used for the full-scale study. In 2 years of treatment, there was no deterioration in the resin performance, and around 92–97 % of perchlorate was destructed in the 3700 empty bed volumes of groundwater with equal resin regeneration. A similar study was conducted by Bae et al. (2010) who successfully removed >95 % perchlorate and nitrate from drinking water with the help of ion-exchangeable resin (IX resin—Purolite A530E, Rohm and Haas PWA2) column system. Though the ion-exchange resin system is considered to be a promising technology for removing perchlorate from waterbodies, it is just a separation mechanism where wastewater solutions containing perchlorate after ion-exchange treatments need further treatment. To overcome this drawback, Batista et al. (2002) proposed a technology combining ion-exchange and biological reduction for perchlorate removal.

Woodberry et al. (2007) conducted a field trial (see Table 4) at Thala Valley tip, Casey Station, Antartica, and found that iminodiacetic acid chelating ion-exchange resins could help in reducing 92–100 % of heavy metals in the following order of selectivity: $Cd \sim Zn > Ni \sim Cu > Fe$ within 1 year of treatment. Extensive investigation into the remediation of perchlorate-contaminated waterbodies was done successfully by Gu et al. (2007) using ion-exchange technology. Tang et al. (2011) stated that 93 % of Cr(VI) could be adsorbed onto the cationic hydrogel when integrated with multiple-pulse flushing system. Dilip et al. (2008) found that chromatographic resins are potent in removing mercury and perchlorates from groundwater. Though ion-exchange technology is well tested and is found to be the most efficient for perchlorate and heavy metal removal from the waterbodies, there are still a few major complications with respect to its full-scale implications.

Future research should focus more on exploring suitable solutions to solve the biggest disposal problem of the used resins which are concentrated in the contaminants. The problem caused by most frequently occurring anions that are at higher levels than the contaminants resulting in the competitive adsorption on the resin should be resolved to improve contaminant recovery. It is possible to disperse nanoparticles in a polymer-like, functionalized ion-exchange resin that would render a feasible hydraulic property as suggested by Alonso et al. (2011). Developing 'ion-exchanger supported nanocomposites' will also open up a new opportunity to control the behavior of hybrid nanocomposites by synergistically altering or enhancing the adsorption competencies for diverse hazardous metal ligands (anionic and cationic).

Table 4 Performance overview of selected *ex-situ* remedial options at field- and pilot-scale

Site	Contaminants	Remediation (%)	Type	Reference
Ion-exchange				
1. Edwards air force base, California	Perchlorate	100	P	Gu et al. (2002)
2. Thala valley tip, Casey Station, Antartica	Cd, Zn, Ni, Cu, Fe	>91	F	Woodberry et al. (2007)
3. Clearwater bay, Hong Kong	Cr	93	P	Tang et al. (2011)
Pyrolysis				
1. Portsmouth DOE facility, Ohio	TCE	>90	F	Heron et al. (2000)
2. Visalia superfund site, Visalia, California	Creosote, PCP	99	F	US EPA (2012)
3. Savannah river site 321-M solvent storage tank area, Aiken, Georgia	PCE, TCE	90	F	FRTR (2012)
Soil washing				
1. Out-of-station oil distribution and storage station, Mexico	Heavy metals	93	F	Iturbe et al. (2004)
2. Old wood preservation site, Sweden	As, PAHs	60–75	P	Elgh-Dalgren et al. (2009)
3. Grand manan island, New Brunswick, Canada	Heavy metals	95	F	US EPA (2012)
4. Botany industrial park, Australia	Mercury	>90	F	Orica Australia (2010)
Enhanced reductive dehalogenation				
1. LLNL site, San Francisco	PCE, TCE	93–98	F	Mcnab and Ruiz (2000)
2. US DOE., Gaseous diffusion plant, Piketon, Ohio	TCE	80–90	F	Korte et al. (2000)
3. Active manufacturing facility site, Trenton, New Jersey	TCE	96	F	Elliott and Zhang (2001)
4. Vinyl chloride plant, Rotterdam Botlek, Netherlands	DCA	>90	F	Dyer et al. (2003)
5. Residential area, Lake Huron, Oscoda, Michigan	TCE	98	F	Ramsburg et al. (2004)
6. Naval air station, Jacksonville, Florida	Chlorinated VOCs	65–99	P	Henn and Waddill (2006)
7. Vilvoorde, Belgium	TCE, DCE	>90	F	Lookman et al. (2007)
8. LabMet, Ghent university, Belgium	TCE	90	P	Hennebel et al. (2009)
9. Former manufacturing facility site, US	TCE, PCB	98	F	He et al. (2010)
10. Housatonic river, Massachusetts	PCB	>90	F	US EPA (2012)

Solidification/stabilization				
1. Selma pressure treating site in Selma, California	PCP	95–99	F	Bates et al. (2000)
2. College Station, Texas	PCE	93	F	Hwang and Batchelor (2001)
3. US EPA National risk management research laboratory, Jackson, Tennessee	Dioxin, PCP, Creosote	95–99	F	US EPA (2012)
4. Artistic glass factory site, Island of Murano, Venice, Italy	Heavy metals	99	F	Scanferla et al. (2009)
5. California Gulch superfund site, Leadville, Colorado	Heavy metals	>95	F	FRTR (2012)
6. Camp Stanley storage activity site, Texas	Pb	99	F	FRTR (2012)
7. Frontier hard chrome superfund site, Vancouver, Washington	Cr	98	F	FRTR (2012)
Constructed wetlands				
1. Lake Bloomington, USA	N, P	42–53	F	US EPA (2012)
2. Site at Czech Republic	Heavy metals	90	F	Kropfelova et al. (2009)
3. SAFIRA research site, Germany	Chlorinated hydrocarbons	75	P	Wu et al. (2012)
4. Ramona LAKE, California	Nitrate	23–35	F	Karpuzcu and Stringfellow (2012)
5. Site at Midwestern USA	Chlorinated ethenes	>90	F	Kadlec et al. (2012)

F field-scale, *P* pilot-scale

3.7 Pyrolysis

Pyrolysis/molten solid processing/plasma arc technology is an emerging soil remediation technology where the chemical decomposition of hazardous materials occurs by thermal energy in the absence of oxygen at an operating temperature above 430 °C under pressure (Venderbosch et al. 2010). Pyrolysis transforms the targeted compounds into a gas or an insignificant amount of solid or liquid residues containing ash and fixed carbon, i.e. it yields char, organic liquids, fuel gas and water (Rofiqul Islam et al. 2008). Though complete oxygen-free atmosphere is not obtained, this process is operated with oxygen level that is less than the stoichiometric quantity. If the targeted waste is composed of volatile or semi-volatile materials, then thermal desorption also occurs. Organic and inorganic contaminants such as SVOCs, pesticides, dioxins, PAHs, PCBs, cyanides, mercury, paint wastes, synthetic rubber processing wastes, refinery wastes, creosote-contaminated soils, mixed wastes (radioactive wastes and others), hydrocarbon-contaminated soils, coal tar wastes as well as wood-treating wastes are generally removed by the pyrolysis process (Mohan et al. 2006; Arvanitoyannis et al. 2007).

High pollutant-cleaning efficiency within a short period of time is achieved by adopting the pyrolysis mechanism. One major advantage is that there is no evolution of CO_2 during the course of pollutant treatment in this technology which helps to combat global warming (Inguanzo et al. 2002). However, combustible off-gases like CO, H_2, CH_4 and other hydrocarbons are produced during the course of operation which requires further treatment. Equipment that is commercially used for pyrolysis includes rotary kilns, fluidized bed furnaces (high velocity air is used for circulation and suspension of waste particles in a combustion loop operated at 430 °C) and molten salt destructions (use of molten salt incinerator as a reaction medium to destroy hazardous wastes).

Operation of a pyrolysis system is typically stable for a broad range of wastes. It is effective in reducing the volume and weight of the target materials. The emissions from the pyrolysis system are well below the regulatory limit values. There are also efficient material recovery and energy production opportunities emerging from this system. Even the operational cost of pyrolysis mechanism is quite low as it does not require any supplementary fuel for its operation or continuous monitoring or maintenance (US EPA 2012). The system is highly flexible in its design and operation. Furthermore this method can be implemented in small-scale or large-scale at real contaminated sites. Yet, there are a few limitations for the applicability and effectiveness of this system. This method involves drying soil to achieve a low moisture content of <1 % before combustion, and if the soil has high moisture content then it increases the treatment cost. Stabilization is usually required if the treated medium is composed of heavy metals. Damage of the processor unit occurs in the case of high abrasive feed. This technology is promising only in remediating the organic pollutants from oily sludges and soils, and cannot effectively destroy or physically separate inorganics from polluted zones. Moreover, studies available for this technology in the field of remediation are scarce as presented in Table 4. The overall cost is expected to be nearly US$300 per t of the soil treated (FRTR 2012).

While conducting a field study of steam stripping and hydrous pyrolysis oxidation (SS/HPO) of a TCE DNAPL spill at Portsmouth DOE facility site in Ohio, Heron et al. (2000) observed that within 2 months >90 % of TCE was removed when the TCE DNAPL spill was boiled and vaporized at approximately 72–74 °C. At present, studies are conducted to manage the disposal problems of phytoremediation crops with the help of the pyrolysis process. Stals et al. (2010) tried to destroy the phytoremediating plant that accumulated heavy metals (Pb and Cd) via the pyrolysis process at a temperature of 723 K. Pyrolysis of phytoremediating plant yielded char (as soil amendment) and oil (as source of fuel), and only 35 % of the target element was recovered in the char, indicating that it is both an economical and eco-friendly technique.

Zhang et al. (2009) remediated 99.1 % Cr(VI) from a chromite ore processing residue by mixing the residue with sewage sludge and subjecting it to a pyrolysis temperature of 600 °C in 10 min reaction time. Thuan and Chang (2012) investigated the degradation of PCP from the contaminated soils of Taiwan by low temperature pyrolysis. More than 90 % PCP was removed within 40 min at a pyrolysis temperature of 350 °C. Also, the PCP decay rate was observed to increase constantly from 0.2 to 1.9 per minute in the range of the pyrolysis temperature (200–400 °C). Nkansah et al. (2011) reported that hydrous pyrolysis with Pd/C/nafion/formic acid at 300 °C, H_2O_2 at 380 °C and Nafion-SiO_2 at 300 °C could convert anthracene into derivatives that are easily oxidized or reduced within 1, 6 and 8 h of treatment time, respectively.

Currently, the heterogeneous catalysis system is regarded as an effective tool to mineralize toxic organic compounds, and it constitutes a potential environmental remedial system. Semiconductors like aluminium doped zinc oxide films and zinc oxide that could present efficient photocatalytic property were recently produced using the spray pyrolysis process. Bizarro (2010) observed that zinc oxide films created by spray pyrolysis process could remove 80 % methyl orange dye within 1.25 h by its increased photocatalytic activity. When the contaminated soil was mixed with 5–10 % of woody biomass (sawdust) and subjected to a pyrolysis temperature of 400 °C for 1 h, about 93, 91 and 43 % reduction was observed in the concentrations of Cd, Zn and Pb, respectively (Debela et al. 2012).

3.8 Soil Washing

Soil washing is also known as mechanical scrubbing, soil scrubbing, physical separation or attrition scrubbing. This approach can be either *ex-situ* or *in-situ*. It is a water-based approach for treating excavated soils and is extensively practiced in Europe but less so in the USA (US EPA 2012). This technology uses coupled aqueous-based separation unit and physical separation operations to minimize the toxin levels of an age-prone contaminated site to site-specific objectives. Soil washing systems do not significantly alter or detoxify the pollutant; instead they mechanically concentrate the hazardous materials into a much smaller soil mass or transfer the contaminant from soil into washing fluids for successive treatments (Dermont et al. 2008). On the whole, soil washing involves mechanical screening, crushing, physical processes (soaking, spraying and tumbling attrition scrubbing), treatment of coarse and fine-grained soil fractions (aqueous-based leaching and physical separation), and management of the generated residues. Though it is considered as a stand-alone approach, more frequently it is combined with other remedial systems to complete the off-site treatment process.

Soil washing is highly applicable to treat a diverse array of pollutants like heavy metals, SVOCs, PCBs, PAHs, pesticides and petroleum as well as fuel residues (Park et al. 2002; Juhasz et al. 2003; Isoyama and Wada 2007). Soil washing particularly permits the recovery of metals from coarse soils. If the recovery of metal is not desired, then solubility enhancement along with the adjustment of soil parameters like pH, redox potential, etc. are the only options. Since hydrocarbons tend to sorb smaller soil particles, physical separation/soil washing helps to separate smaller soil fractions (constituting silt and clay particles) from larger ones, and tend to reduce the soil volume which can further be treated by incineration or bioremediation after which it can be disposed in accordance with government guidelines. Large volume of treated soil can then be used as backfills since it is considered to be non-toxic (RAAG 2000; Chu and Chan 2003). Soil washing is considered to be very cheap as it reduces the volume of the contaminated soil requiring further treatment, and the reduction in soil volume minimizes the expenditure involved in post-remedial treatments done before disposal. Also, it is a proven suitable option in sandy or gravel soils (Urum et al. 2003).

On the other hand, this technology fails to treat soils with high silt and clay (>40 %) fractions. This *ex-situ* treatment does not work for soils that are not feasible for homogenization, i.e. in soils with different types and contaminant concentrations. Also, this technique is unsuitable for multicomponent soil mixtures with high clay and humic acid content where access of leaching solutions to contaminants is highly restricted. Even metal contaminants with lower solubility may take a very longer contact time and excessive amounts of reagents to solubilize. It costs around US$170 per t to decontaminate a site with this technique.

Budianta et al. (2010) proposed a new approach of *in-situ* soil washing by the sedimentation method where soil particles are separated hydraulically based on their particle size and density when high air pressure was injected into mixing water-sandy soil ground. In this method it was advised that there is a probability for the occurrence of both washing and separation processes along with remediation. Kos and Lestan (2003) proposed the use of biodegradable chelates and permeable barriers to induce the phytoextraction of Pb coupled with soil washing. They achieved an approximately 27 % increase in metal removal by the use of biodegradable chelates and permeable barriers. Iturbe et al. (2004) conducted a field experiment to remediate an out-of-service oil distribution and storage station contaminated with PAHs, BTEX, MTBE, diesel and gasoline in Mexico by using biopile and soil washing methods between 1966 and 2000. Washing approximately 1600 m^3 soil using non-ionic surfactant and biopiling (operated for 66 days) removed more than 93 % of the total contaminants in 500 days.

Villa et al. (2010) studied the use of combined processes (photo-Fenton oxidation and soil washing) to remediate soil contaminated with DDT, DDE and diesel. Soil washings using triton X-100 aqueous solution removed nearly 100 % diesel, 80 % DDE and 66 % DDT. Further treatment for 6 h using a solar photo-Fenton system removed around 99, 95 and 100 % DDT, DDE and diesel, respectively. In a pilot-scale experiment conducted in Sweden, Elgh-Dalgren et al. (2009) reported that a combination of biodegradable non-ionic surfactant (AG), chelating agent (MGDA) and elevated pH could remove 60–75 % As and PAH with only 10 min washing at an elevated temperature of 50 °C. Qui et al. (2010) found >95 % removal efficiency of cationic (Cu, Pb and Zn) and anionic (As and Cr) metals that co-exist in the soil within 24 h by the use of soil washing with Na_2EDTA and oxalate.

Jeon et al. (2010) investigated the TPH removal efficiency from clayey soil (oil reservoirs, Incheon, South Korea) after a soil washing process, using the EK remediation mechanism. It emerged that the surfactant-enhanced EK process with NaOH as electrolyte and isopropyl alcohol as a circulating solution could remove >30 % TPHs from low-permeability soils subjected to soil washing within the first 100 h of treatment by utilising 485 KWh/t energy. A similar study was conducted by Gomez et al. (2010) to evaluate the enhancement in the recovery of phenanthrene from polluted soil using sequential washing with cyclodextrin-enhanced electrochemical treatment. Soil washing with aqueous solution of 1 % hydroxypropyl-β-cyclodextrin removed 70 % phenanthrene in 7 days, and the second step of EK separation totally degraded the left-out phenanthrene in a day.

Davezza et al. (2012) confirmed the alkylphenol and benzoate removal efficiencies using surfactant-assisted soil washing and photocatalysis within 1–2 h of treatment. The combined effect of electrochemical treatment and EDTA-based soil washing was also reported by Pociecha et al. (2011), where 85–95 % removal of Cd, Zn and Pb was achieved in 10 and 30 min of soil washing and EK separation treatment time. Peng et al. (2011) stated that liquid/solid ratio, surfactant concentration, washing time and stirring speed are the critical factors that determine the effectiveness of PAHs removal by means of surfactant-enhanced soil washing.

Many technologies combined with soil washing have successfully remediated the contaminated soils as listed in Table 5. Huang et al. (2010) reported that the combined technique of chemical washing and phytoextraction is highly effective in treating sites contaminated with many metals. They conducted a pot culture experiment using crops like *Sedum alfredii* and *Zea mays* along with soil washing by mixed chelators to remove metals from a contaminated soil, and found that ethylenediaminedisuccinic acid enhanced the metal phytoextraction by both crops. Concerning the removal of 80–85 % of Cd, Zn and Pb, 40 % was contributed by phytoextraction and the remaining 45 % by chemical washing. Jansson et al. (2010) observed 81–85 % dioxin removal from soil with 70 % ethanol washing at 60 °C in 30 min, and concluded that ethanol washing is a cost-effective technique compared to other conventional remediation technologies that are commonly used for removing PCDD/Fs.

Table 5 Recent coupled soil washing remedial practices

Year	Researchers	Technology	Contaminant	Remediation (%)
2003	Kos and Lestan	Phytoextraction coupled with EDTA soil washing along with usage of permeable barriers	Heavy metals	55–65
2004	Kos and Lestan	Chelator-induced phytoextraction coupled with *in-situ* soil washing	Cu	<50
2003	Urum et al.	Biosurfactant-enhanced soil washing	Crude oil	75–85
2005	Giannis and Gidarakos	Washing-enhanced electrokinetic remediation	Cd	85–95
2009	Elgh-Dalgren et al.	Soil washing with chelating agents and surfactants	As, PAHs	75–85
2010	Villa et al.	Soil washing and Fenton oxidation	Pesticides, hydrocarbons	85–95
2010	Gomez et al.	Soil washing followed by electrokinetic remediation	Hydrocarbons	>95
2010	Huang et al.	Phytoextraction and soil washing	Heavy metals	55–65
2012	Davezza et al.	Surfactant-assisted soil washing with photocatalysis	Pesticides	85–95
2011	Pociecha et al.	Electrokinetic separation combined with EDTA soil washing	Heavy metals	85–95
2011	Sung et al.	Combined mild soil washing and compost-assisted phytoremediation	Heavy metals	65–75
2012	Begum et al.	Biodegradable aminopolycarboxylate chelant soil washing	Heavy metals	85–95

Though the washing technique utilizes surfactants and chelating agents for removing hazardous organic mixtures from contaminated soil media such as sediments/soils, a major issue rests with the proper disposal of the surfactant extractant or chelating solution containing the wastes after washing. To overcome such a limitation, Liu et al. (2011a) integrated nanotechnology with photocatalysis (utilization of La–B co-doped TiO_2 nanoparticle in the photocatalysis of a simulated complex system containing non-ionic surfactant Triton X-100 and PCP under solar and visible light irradiation) and removed the wastes from the washing solutions. More strategies using this technology should be the subject of future studies.

3.9 *Dehalogenation*

This treatment technology is used to dehalogenate (remove halogens) halogenated compounds. The treatment could be either chemical or biological. During chemical dehalogenation, contaminated soils and reagents are mixed, and heated in a treatment vessel (Soesilo and Wilson 1997). Reagents could be either sodium bicarbonate (base-catalyzed decomposition process—BCD) or polyethylene glycol (alkaline polyethylene glycol or glycolate technology—APEG). Biological dehalogenation involves degradation of halocompounds by microorganisms (van Pee and Unversucht 2003). Dehalogenation was successful in removing PCBs, PCDD/Fs and pesticides from soil. It has been recently reported that the BCD process could treat as high as 45,000 mg/kg PCBs at field-scale and APEG is amenable to small-scale PCB treatments (FRTR 2012). This technique is unsuited for treating chlorinated volatile organic compounds. Some concerns with the chemical dechlorination process are as follows: large volumes of reagent are required to treat soils with elevated concentrations of chlorinated compounds; it is difficult to treat volatile contaminants and dust when the contaminated soil is very moist; pretreatment requirements removing the debris from soils that are greater than 60 mm dia; toxicity and persistence of chemical reagents like glycol ethers are evident; and it is very expensive to treat large volumes of soils that are high in clay and moisture content.

Currently, environmental and economic concerns of chemical dehalogenation are overcome by the alternative use of biological dehalogenation mechanisms (Furukawa 2003; Bedard 2004). Biological dehalogenation includes many classes like reductive dehalogenation, oxidative dehalogenation, dehalogenation by methyltransfer, dehalogenation by hydration, dehydro dehalogenation, intramolecular substitution, thiolytic dehalogenation and hydrolytic dehalogenation (Van Pee and Unversucht 2003). Of these, the most important and widely studied broader class of biological dehalogenation mechanism is reductive dehalogenation. It is mostly done by anaerobic bacteria such as *Dehalococcoides*, *Dehalobacter*, *Anaeromyxobacter*, etc., and is becoming significantly important in remediation research (Smidt and de Vos 2004). In addition to the presence of specific dehalogenators (anaerobic microbes), environmental factors such as available carbon or electron sources strongly affect the rate of contaminant dehalogentation as has been first established for PCBs (Nollet et al. 2005).

In many studies, microbiological reductive dechlorination of chlorinated organic molecules is proved to be important for bioremediation of polluted groundwater (McNab and Ruiz 2000). There exists an electrochemical dehalogenation mechanism where chlorinated hydrocarbons and chlorofluorocarbons are dechlorinated by electrolysis using appropriate solvents. Photo-assisted and irradiation type dehalogenations were also reported (Shih and Wang 2009). Moreover, Guo et al. (2010) had described mechano-chemical (tribochemical reaction) reductive dehalogenation of PCBs, DDT, HCH, TCE and dioxins using ball mills as an innovative reductive dehalogenation technology.

So far, many significant methods that could enhance the efficiency of reductive dehalogenation were explored. The more sophisticated microbial dehalogenation types involve the use of microwave-induced and UV-photolytic process (Li et al. 2012a), nanoparticle iron (Zhuang et al. 2011), and ZVI (Xiu et al. 2010). In most cases, metals as such or in the form of nanoparticles or biocells are used as electron donors in dehalogenation processes as summarized in Table 6. The expenditure

Table 6 Topical reductive dehalogenation methods

Electron donor	Halogenated waste	Remedial efficiency (%)	Reference
Iron powder	PCBs, DDT, Triallate	95	Lampron et al. (2001); Agrawal et al. (2002); Gander et al. (2002); Clark et al. (2003); Volpe et al. (2004); Aristov and Habekost (2010)
ZVI	PCBs, PBDEs	95	Kluyev et al. (2002); Clark et al. (2003); Habekost and Aristov (2012)
Ultrasonically-produced air stable nano iron	Chloroethene	85	Tiehm et al. (2009)
Fermenting substrates (formate and lactate)	TCE	90	Azizian et al. (2010)
Subcolloidal Fe/Ag particles	Chlorinated benzene	90	Xu and Zhang (2000)
Rhodium nanoparticles	Mono- and polyhalogenated arenes	90	Hubert et al. (2011)
Nanoscale iron	TCE	95	Elliott and Zhang (2001); Nyer and Vance (2001)
Bimetallic copper-aluminium	Halogenated methane	75	Lien and Zhang (2002)
Palladium iron nanoparticles	Chlorohydrocarbons	90	Hildebrand et al. (2009)
Bioinorganic palladium cells	PBDE, TCPP	90	Deplanche et al. (2009)
Biogenic palladium nanoparticles	TCE	90	Hennebel et al. (2011)
Bimetallic palladium-iron	Chlorophenol	90	Graham et al. (2006)
Palladium chloride and triphenylphosphine	Halopyrazoles	85	Chen et al. (2012)
Yeast extract	DCB	85	Fung et al. (2009)

for field-scale treatment ranges between US\$200 and 500 per t for the chemical dehalogenation process (FRTR 2012), but no specific cost estimates for other dehalogenation types exist.

Habekost and Aristov (2012) suggested that reductive dechlorination and debromination of PBDEs and PCBs occurs efficiently with ZVI at reasonably high temperatures (350–600 °C) in a nitrogen atmosphere. Tiehm et al. (2009) produced nano-sized air-stable ZVI particles by passing ultrasound to a Fe(CO) solution in edible corn oil and coating the resulting nano-iron with a non-crystalline carbon cover after dispersing it in a carbon matrix. The nano-sized ZVI particles were able to dehalogenate 80 % chloroethene in 5 days. Since most of the reductively dechlorinating bacteria such as *Dehalococcoides* and *Desulfuromonas* need molecular hydrogen as an electron donor, hydrogen formed by ZVI increases chloroethene elimination. Formate and propionate are valuable fermenting substrates for reductive dehalogenation (Sleep et al. 2006; Aulenta et al. 2007; Azizian et al. 2010). Elliott and Zhang (2001) and Nyer and Vance (2001) proved the efficiency of nano-iron to dehalogenate more than 95 % halogenated wastes. More than 99 % heterogeneous dehalogenation of PCBs and DDT was achieved with iron powder in a nitrogen atmosphere at 500 °C by Aristov and Habekost (2010).

According to Waller (2010) and Wagner et al. (2012), bioaugmentation of *Dehalococcoides* containing cultures is a successful technique for the clean up of chlorinated ethene and brominated benzene-polluted groundwater. Also, Bunge et al. (2003, 2008) and Fennell et al. (2004) reported the dioxin dehalogenating efficacy of *Dehalococcoides* sp. Hubert et al. (2011) observed that rhodium nanocatalyst either as suspension or supported on silica like particles could effectively decontaminate 87–95 % mono- and polyhalogenated arene like endocrine disruptors in water. Lien and Zhang (2002) demonstrated the effect of bimetallic Cu/Al to degrade 77 % halogenated methanes in groundwater. About 97 % chlorinated herbicide (triallate) was reductively degraded by the contact of electrolytic iron powder in a batch system at 25 °C in the absence of oxygen (Volpe et al. 2004). Even the use of Pd nanoparticles (Windt et al. 2005) or yeast extract (Fung et al. 2009) enhanced the treatability (85–90 %) of reductive dehalogenation. Cupples et al. (2005) demonstrated that *Desulfutobacterium chlororespirans* could dehalogenate bromoxynil-like brominated herbicide and its metabolite. Graham et al. (2006) achieved more than 90 % degradation of chlorophenols using magnetically-stabilized fluidized-bed reactor composed of Fe/Pd media in polluted solid slurry under a nitrogen purge at pH 5.8.

Recently, Chen et al. (2012) paved the way for a new and efficient method for dehalogenating more than 83 % halopyrazoles using $PdCl_2$ and triphenylphosphine as catalysts. Pd/Fe nanocatalysts were explored for the selective dehalogenation process in wastewaster systems by Hildebrand et al. (2009). About 64 % reductive dechlorination of PCB mixture aroclor (50 mg/L) was achieved in 160 days by the natural attenuation and bioaugmentation of *Dehalococcoides* (Bedard et al. 2007). Intrinsic community (natural attenuation) + acetate + hydrogen (biostimulation) aided reductive dechlorination of PCE (80 μM) and helped to achieve 100 % PCE transformation to ethane in 76 days (Himmelheber et al. 2007). Deplanche et al. (2009) demonstrated the effective reductive debromination (>90 %) of flame retardants like PBDE and TCPP by palladized cells (bioPd) of sulphate-reducing bacterium, *Desulfovibrio desulfuricans*, which was five times more effective than using commercial Pd as catalyst. Furthermore, Hennebel et al. (2011) attained nearly 93 ± 4 % hydro-dehalogenation of persistent groundwater contaminants like TCE in microbial electrolysis cells with biogenic Pd nanoparticles. Shih and Wang (2009) reported 90 % PBDE degradation with less than 60 min of UV and solar irradiation exposures.

Reductive dehalogenation using nano-scale bimetallic iron and Pd particles (Elliott and Zhang 2001), use of Pd-catalyzed and polymer coated ZVI suspensions (Henn and Waddill 2006), application of palladized iron (Korte et al. 2000), bioPd in membrane reactor (Hennebel et al. 2009), reductive dehalogenation with Tween 80 (Ramsburg et al. 2004), and dehalogenation by the use of carboxymethyl cellulose-stabilized iron nanoparticle (He et al. 2010)—all revealed that halogenated pollutants could be removed efficiently by enhanced dehalogenation mechanism at field/pilot-scale as listed in Table 4. Thus, the studies concerning dehalogenation are many at bench-scale and this technology is being explored at the molecular level to generate further innovations. Overall, the coupling of promising technologies like nanotechnology, irradiations, bioaugmentation, etc., is innovative and aims to sustainably remove halogenated pollutants. This process needs to be explored more fully at full-scale.

3.10 Solid-Phase Bioremediation

Solid-phase *ex-situ* biological remediation techniques including biopiles, landfarming and composting are described in detail below.

3.10.1 Biopiles

Biopiles, also identified as biomounds, bioheaps, biocells and static pile composts, combine both landfarming and composting, and this technology is increasingly applied to treat excavated soils contaminated with petroleum products through the use of biodegradation. In biopiling, contaminated soils are piled or heaped, and then the microbiological processes are stimulated by aeration followed by addition of water and nutrient besides controlling heat and pH (US EPA 2012). This technique is similar to landfarming as it also works above ground, and the system uses oxygen (generally from air) to stimulate the population of aerobic microbes that helps in degrading the petroleum compounds adsorbed to the soil fractions. It differs from landfarming in that it provides a control over the maintenance of optimum levels of moisture, temperature, pH, aeration and nutrients favoring microbial survival and activity which promotes rapid biodegradation (McCarthy et al. 2004). While landfarming systems are aerated by plowing or tilling, biopiles are aerated most frequently by forcing air artificially to move by injection or extraction through slotted or perforated pipings placed throughout the pile.

Compared to landfarming or composting, mass transfer efficiency of air, nutrient and water in biopiles potentially offers a better pollutant removal strategy. In biopiles, structural materials like sand, straw, sawdust, woodchips and dry manure are used to enhance the mass transfer efficacy (Mohee and Mudhoo 2012). Generally, biopiles are operated up to a height of 0.9–3.1 m and could be enclosed with an impervious lining to prevent run-off or evaporation or volatilization and to promote soil heating. Efficiency of biopiles is poorer in clayey soils compared to sandy soils as the contaminant mass transfer is quite difficult in clayey soils due to its tendency to form agglomerates that limit the soil permeability (Rezende et al. 2012).

Petroleum products, pesticides, halogenated VOCs/SVOCs and non-halogenated VOCs can be degraded by biopiles. At the time of air injection/air extraction/pile turning itself, lighter petroleum products like gasoline are removed. Heavier petroleum products such as heating oil and lubricating oil are broken down by biodegradation which generally takes more degradation time compared to the lighter ones. The effectiveness of a biopile system depends on soil characteristics, contaminant characteristics, followed by climatic conditions (Giasi and Morelli 2003). Optimal biodegradation occurs between 20 and 40 °C at a pH range of 6–8 with adequate moisture and oxygen levels. This is an easy to implement, simple, cost-effective (US$30–90 per t of contaminated soil), short-term (6 months to 2 years) as well as full-scale technology that is effective over a series of diverse pollutants. Compared to landfarming it requires less land area for contaminant treatments (Li et al. 2004). It is effective even for organic constituents that have very slow biodegradation rates.

Biopile can be designed as a closed system in order to control vapor emissions. It can also be engineered to be possibly effective for any combination of petrochemical compounds and physical settings. Though biopile is an eco-friendly, cost-effective technology, it does have a few limitations. Biopiling is not effective for very high contaminant concentrations (>50,000 mg/kg), especially with significantly heavy metal concentrations of >2500 mg/kg which will inhibit microbial growth. Though the land area required for implementing this process is quite less compared to landfarming, it is quite high compared to the other *ex-situ* technologies. It is very difficult to achieve more than 95 % degradation in most cases when using this technology. Moreover, volatile constituents are evaporated rather than biodegraded which makes it necessary to treat the generated vapors before their discharge into the atmosphere.

Roldan-Martin et al. (2006) described the utilization of biopile technology for remediating oil sludge with TPH concentration up to 300 mg/kg sludge, where 60 % degradation was achieved after 3 months of treatment. After 1 year, Mohn et al. (2001) observed a reduction in the total petroleum hydrocarbons from 2109 to 195 mg/kg and 196 to <10 mg/kg soil TPH (30–49 % TPH degradation) when the biodegradation was stimulated by the addition of ammonium chloride and sodium phosphate in biopiles assembled at two field sites in the Arctic tundra. Liu et al. (2009) confirmed the usefulness of bioaugmentation combined with biosurfactant (rhamnolipid) and nutrient enhancements to treat diesel-contaminated soils using biopiles. Chien et al. (2009) recommended the application of appropriate substrates like organic amendments (chicken manure) or commercially available microbial inocula to enhance the decay rate of petroleum hydrocarbons to 85 % in *ex-situ* field-scale biopiles.

Humidifying air for the remediation of petroleum hydrocarbon-polluted soil by heated/aerated biopile structure reduced the TPH concentration from 11,000 to 300 mg/kg in 10 months at Kingston, Canada (Sanscartier et al. 2009). A wind-powered biopile unit was used at Savitok Point, North-West Territories, Canada, to remediate approximately 15,000 m^3 TPH-contaminated soil, and a reduction of about 7000 mg/kg TPH over a 2 year time frame (ESG 2001) was observed. Reimer et al. (2003) reported 60 % TPH degradation when the temperature of petroleum hydrocarbon-contaminated soils in the Arctic was maintained at 15 °C by injecting heated air into the biopile. Filler et al. (2001), on the other hand, used heating cables and blankets for enhancing the contaminant volatilization efficiency in a biopile system. A pilot study was conducted by Genovese et al. (2008) to evaluate the effect of bioaugmentation in a biopile. Augmentation with a 300 L culture containing 10^8 cells/mL of *Rhodococcus* sp., *Pseudomonas* sp. and *Acinetobacter* sp., followed by nutrient spray on the biopile, led to the reduction of 90 % BTEX and heavy aliphatic hydrocarbons in 15 days.

Delille et al. (2007) observed the performance of nutrient-enriched biopiles (amended with fish compost) in a pilot study that helped in achieving TPH regulatory standard (100 mg/kg) in diesel oil-contaminated soil in Antartica in less than 12 months. Wu and Crapper (2009) designed a hydraulic-based approach to stimulate a biopile in the context of its ambient temperature. When a 27 m^3 biopile was operated for 22 weeks, it was able to remove 80 % TPH at full-scale (Iturbe et al. 2007). A 28 m^3 pneumatically-aerated bioreactor set up in static biopile amended with manure oil compost (40 %) and garden waste compost (20 %) successfully removed 68.7 % petroleum hydrocarbons within 3–4 months treatment time (Kriipsalu and Nammari 2010). Seabra et al. (2006) demonstrated that it was possible to remediate even crude oil-contaminated clayey soils (39,442 mg/kg TPH concentration) to acceptable levels by rice hull amendments and periodic pile mixings within 16 weeks. While studying the effect of different strategies like bioaugmentation, biostimulation, and bioaugmentation plus biostimulation to enhance the petroleum hydrocarbon degradation in biopiles, Liu et al. (2011b) recorded >80 % TPH degradation after 140 days operation of a biopile subjected to the bioaugmentation approach (introduction of selected consortium and kitchen waste).

Coulon et al. (2010) conducted a field study at a former dockyard in Scotland to compare the remedial effect of biopile and windrow turning technologies of a bunker C fuel-contaminated soil. It was witnessed that windrowing was most effective for treating the bunker fuel soils because the soil was more friable and biopiling is amenable to treating coarse soil textures. Gallego et al. (2011) performed a field-scale clean up study of a jet fuel-polluted soil using biopiles by adding a slow release fertilizer, a surfactant and an oleophilic fertilizer. They observed a reduction in TPH concentration from 500 to 5000 mg/kg within 5 months when the C:N ratio was maintained at 10:1. In an *ex-situ* field-scale biopile study involving a Siberian soil polluted with mazut (heavy residual fuel oil), Beskoski et al. (2011) observed the biological reduction of about 96, 97, 83 and 55 % of aliphatic, aromatic, asphaltene and isoprenoid fractions, respectively, after 150 days of biostimulation with softwood sawdust and bioaugmentation with microbial consortia (isolated microbes from the polluted soil).

A composting field trial of a soil polluted with lubricating and diesel oil by Jorgensen et al. (2000) showed a reduction of 70 % mineral oil content over a period of 150 days. Wang et al. (2011) observed only 20–44 % TPH removal after 220 days when it was biostimulated with excess quantities of urea which indicated the suppression of microbial activity and diversity by large quantities of nutrient amendments. Lin et al. (2010) showed that biosurfactant addition helped in achieving 90 % TPH removal at field level in 100 days of biopiling which suggests that hydrocarbon bioavailability, desorption and mass transfer are the limiting factors of *ex-situ* petroleum hydrocarbon degradation. Field studies related to biopiling are copious (see Table 7). The present requirement is to explore the use of more natural waste materials as nutrient amendments in order to enhance the soil and microbial health along with the establishment of field-scale treatment trials of coupled *ex-situ* biological/physical/chemical treatment techniques with biopiling to achieve 100 % degradation in a short time.

Table 7 Full-scale studies of *ex-situ* solid-phase biological treatment technologies

Site	Pollutant	Competence (%)	Effect	Reference
Biopiles				
1. Military radar sites, Komakuk beach and Cambridge bay, Arctic tundra^{F}	TPH	30–49	☻	Mohn et al. (2001)
2. Savitok point, North West territories, Canada^{F}	TPH	88	☻ ☻	ESG (2001)
3. Mexican refinery, Mexico^{F}	TPH	80	☻ ☻	Iturbe et al. (2007)
4. Canadian forces base, Kingston, Canada^{F}	TPH	97	☻ ☻	Sanscartier et al. (2009)
5. Renova AB, Klapp, Sweden^{P}	TPH	68.7	☻	Kriipsalu and Nammari (2010)
6. Former dockyard, Scotland^{F}	TPH	22	O	Coulon et al. (2010)
7. Fire fighting practice (airport) site, Spain^{F}	TPH	90	☻ ☻	Gallego et al. (2011)
8. Mazut reservoir site, Siberia^{F}	TPH	55–96	☻ ☻	Beskoski et al. (2011)
9. Outdoor oil sludge storage site, Shengli oilfield, Shandong province, China^{F}	TPH	20–44	O	Wang et al. (2011)
10. Aged fuel spilled site, Taiwan^{F}	TPH	90	☻ ☻	Lin et al. (2010)
Landfarming				
1. Petroleum refinery, San Francisco, Argentina^{F}	TPH	84	☻ ☻	Belloso (2001)
2. Haliburton Pad, Prudhoe Bay field, France^{F}	Diesel	84	☻ ☻	US EPA (2012)
3. Territory of Kokuyskoye oil field, Russia^{F}	Crude oil	88	☻ ☻	Kuyukina et al. (2003)
4. Service city pad, Alaska^{F}	Diesel	48–71	☻	US EPA (2012)
5. Wood treatment site, KwaZulu–Natal, South Africa^{P}	Creosote	68–83	☻ ☻	Atagana (2003)

(continued)

Table 7 (continued)

Site	Pollutant	Competence (%)	Effect	Reference
6. Factory site, South Africa^{F}	Creosote	76–87	☻ ☻	Atagana (2004)
7. Northeast shore of North Salt Lagoon, Barrow, AK^{F}	BTEX	>90	☻ ☻	McCarthy et al. (2004)
8. Oil refinery site, Murica, Spain^{F}	TPH	80	☻ ☻	Martin et al. (2005)
9. Petroleum development, Oman^{F}	TPH	90	☻ ☻	Al-Mahruki et al. (2006)
10. Former lindane manufacturing site, Spain^{F}	HCH	82–89	☻ ☻	Rubinos et al. (2007)
11. Arctic location, Canada^{F}	TPH	>80	☻ ☻	Paudyn et al. (2008)
12. Site with stormwater sediments, France^{P}	TPHs, PAHs	53–97	☻ ☻	Petavy et al. (2009)
13. Nigeria delta, Nigeria^{F}	TPH	14–82.2	☻ ☻	Mmom and Deekor (2010)
14. Resolution island, Nunavut, Canada^{F}	TPH	64	☻	Chang et al. (2010)
15. Site polluted with oil, Spain^{F}	PAHs	100	☻ ☻	Silva-Castro et al. (2012)
Composting				
1. Former gas-work site, Prague Czech Republic^{F}	PAHs	37–80	☻ ☻	Sasek et al. (2003)
2. Industrial facility site, US^{F}	Perchlorate	99	☻ ☻	US EPA (2012)
3. Shengali oil production plant site, China^{F}	TPH	31	O	Ouyang et al. (2005)
4. South China agricultural university, China^{F}	PAHs	64–94	☻ ☻	Cai et al. (2007)
5. Stauffer management company superfund site, Tampa, Florida^{F}	Pesticides	90	☻ ☻	FRTR (2012)

^{F}Field-scale study, ^{P}Pilot-scale study, ☻ ☻ successful study, ☻ partially successful study, O unsuccessful study

3.10.2 Landfarming

Landfarming is a successful, above-ground remedial technique that has been practiced for more than 100 years. Since the 1980s the petroleum industries worldwide have used it to treat hydrocarbons. Wood preserving wastes, coke wastes, diesel fuels and certain pesticides are also treated by landfarming (Paudyn et al. 2008). In this technology, contaminated soil/sediment/sludge is excavated and spread into lined beds of about 0.46 m thick and biological activity of the soil is triggered through the addition of moisture, nutrients and minerals. Only if the contaminated soils are deeper than 1.5 m is excavation carried out; if not (less than 0.9 m below ground surface), the soil microbial activity is triggered without excavation.

For successful landfarming, it is a prerequisite to maintain a temperature of 20–40 °C, pH of 6.5–7.5, moisture up to 40–85 % and C:N ratio of 9:1 (Khan et al. 2004). Also, bacteria that may potentially successfully degrade hydrocarbons are added regularly in order to aid speedy biodegradation. Aerating the soil is an important aspect of this technology because mixing is performed to aerate the soil. Mixing also increases the contact between organic contaminants and microorganisms thereby accelerating the aerobic microbial degradation at contaminated sites (McCarthy et al. 2004).

Depending on the degradation rate, petroleum-contaminated soils could be applied at regular intervals to the landfarm sites which help to more importantly maintain the soil biological activity and replenish the supply of hydrocarbons. Bulking agents and co-substrates are generally applied (Straube et al. 2003; Maila et al. 2005) to stimulate microbial metabolism. Landfarming is quite similar to biopiles in its characteristics, benefits and shortcomings, but only with little dissimilarity as stated in the previous section. Landfarming system is limited to treat heavier hydrocarbons. The higher the molecular weight of a chlorinated and nitrated compound, then the more difficult it is to degrade contaminants using this technology (Hejazi et al. 2003). Landfarming requires a large land area for treatments and it is difficult to achieve more than 95 % degradation. Moreover, treatment of the generated dust and vapors that evolve during the course of landfarming is required as they are toxic will probably cause air pollution. There is a risk that pollutants will migrate from the treatment zone to uncontaminated areas. However, landfarming is a simple and cost-effective eco-friendly technology like biopile which is also widely implemented at field level in most contaminated sites around the world (Hejazi et al. 2003; Martin et al. 2005). Remediating petroleum-contaminated soil by landfarming, takes about 6 months to 2 years for the decontamination process to be completed, and costs about US$30–60 per t soil (US EPA 2012).

Petavy et al. (2009) conducted a pilot-scale study to treat stormwater sediments contaminated with total hydrocarbons and PAHs, and obtained 53–97 % total hydrocarbon degradation and 60–95 % PAH degradation. Souza et al. (2009) recommended the amendment of rice hulls to accelerate the biodegradation efficiency of landfarming. Silva-Castro et al. (2012) studied the efficiency of combined bioaugmentation and biostimulation applications to remove hydrocarbons like PAHs through landfarming, and reported that when a consortium of four bacteria (*Bacillus pumilus, Alcaligenes faecalis, Micrococcus luteus* and *Enterobacter* sp.) is augmented into the PAH-contaminated soil with inorganic fertilizers (NPK), it remediated 100 % PAHs in 7 months. Besalatpour et al. (2011) reported about 57 % hydrocarbon degradation through the landfarming process after 4 months of treatment.

While assessing the potential of enhanced landfarming system to treat diesel oil-contaminated soils in bioreactors, Kuo et al. (2012) discovered that the use of additives (kitchen waste compost), bulking agent (rusk husk), activated sludge, and petroleum hydrocarbon-degrading bacteria could remove 92.4 % TPH in 25 days. Acuna et al. (2010) recommended the use of electro-bioremediation after landfarming treatment for unsaturated soils contaminated with hydrocarbons. Mmom and Deekor (2010) also showed 14.5–82.2 % TPH degradation by landfarming in the

Nigerian Delta at a soil pH of 5.5. Studies conducted at the Fahud petroleum development concession site in Oman revealed the significant improvement in landfarm performance through the use of a proper irrigation schedule, fertilization and weekly tilling (90 % degradation in 12–15 months) (Al-Mahruki et al. 2006). da Silva Souza et al. (2013) demonstrated the clastogenic effect of landfarming soil from petroleum refineries through sugar cane vinasse amendment.

A slurry-phase aerobic biotreatment of seriously polluted crude oil sediments at the Kokuyskoye oil fieldin Russia resulted in 88 % reduction of the crude oil levels after 2 months when combined with landfarming (Kuyukina et al. 2003). Atagana (2003) conducted a pilot-scale landfarming for creosote-contaminated site and confirmed that microbial supplementation and amendment of 10 % sewage sludge, poultry manure and cow manure could remove 68–83 % creosote in 6 weeks. Chang et al. (2010) evaluated the feasibility of landfarming biotreatment of petroleum-contaminated soils at Arctic regions (1–10 °C) and showed 64 % TPH removal in 60 days when the soil C:N:P ratio was maintained at 100:9:1 for 60 days. Belloso (2001) observed that bioaugmentation is effective in degrading 84 % total hydrocarbons in 12 months. Landfarming of a diesel fuel site at a remote Canadian Arctic region was successfully achieved (>80 %) under various temperature regimes (5, 9.3 and 18 °C) by aerating the contaminated field site by rotatilling for every 4 days over a 3 year period in the summer months (Paudyn et al. 2008).

Rubinos et al. (2007) demonstrated hexachlorocyclohexane (HCH) decontamination (82–89 % removal in 11 months) using landfarming at large-scale with moderate temperature (10–40 °C), and no deficit water and periodic tillage as these parameters reduced the heterogeneity in contaminant distribution and increased bioavailability. Martin et al. (2005) bioremediated (80 %) an oily sludge containing hydrocarbons using landfarming techniques in 11 months in a semi-arid climate. Thus, many field studies had been conducted by utilizing the potential of bioaugmentation and biostimulation to aid landfarming activities as listed in Table 7. However, it is necessary to: firstly, explore the applicability of landfarming for varied volatile contaminants other than hydrocarbons by overcoming the above mentioned limitations; and secondly, develop novel integrated landfarming techniques to sustain environmental remediation.

3.10.3 Composting

Composting is an *ex-situ* solid-phase remediation technology where organic contaminants like PAHs are transformed into stabilized, innocuous byproducts by microorganisms (under anaerobic and aerobic conditions). Composting is all about creating a suitable environment for the microorganisms, and it has been at the forefront of diversion and processing of organic wastes due to its relatively simple and robust process. Unlike landfarming, during composting a thermophilic condition (50–65 °C) is required to suitably compost hazardous organic compound-contaminated soils. Also, key parameters that must be monitored in the composting system include oxygen (10–15 %), moisture (50–55 %), C:N ratio (30:1), pH (6–9), and porosity (1–5 cm) (Semple et al. 2001). During composting, polluted soil is excavated and mixed with organic amendments/bulking agents such as hay, vegetative wastes, wood chips and manure to accelerate the thermophilic microbial activity and porosity of the mixtures to be decomposed (Coker 2006). Maximum remedial efficacy is achieved by maintaining temperature, irrigation and oxygenation control.

Process designs used in composting are: windrow composting (compost is placed in long piles known as windrows and periodically mixed with mobile equipment), mechanically agitated in-vessel composting (compost is placed in a reactor vessel where it is mixed and aerated), and aerated static pile composting (compost is formed into piles and aerated with blowers or vacuum pumps). Windrow composting that uses a sophisticated in-vessel technology is one of the most cost-effective composting alternatives (FRTR 2012). Thermophilic composting is capable of reducing the level of heavy oils, explosives and PAHs. Heavy metals are not treated by this technique though it could be reduced by dilution as higher concentrations of heavy metals become toxic to microbes. However, application of compost helps to remediate metal-contaminated soils. For example, van Herwijnen et al. (2007) remediated 80 % metal (Cd and Zn)-polluted soil with mineral amended composts. Increased Cu, Cd and As removal from the contaminated soils by the use of composts was shown by Cao et al. (2003a) and Gadepalle et al. (2009).

The factors that limit the effectiveness and applicability of the composting system are its need for substantial space and the post-treatment excavation requirement of contaminated soil. Management of odor and leachates that are generated at the time of composting is also a limiting factor. Otherwise, composting is a sustainable, simple technique which reduces pathogens, stabilizes the waste, reduces the mass of the waste and yields a product (van Herwijnen et al. 2007). It generally takes 6–18 months to complete a composting process. Composting cost is about US\$314–458 per m^3 (FRTR 2012).

Ouyang et al. (2005) conducted a field study in China comparing bioaugmentation and composting for remediation of oily sludge, and observed that bioaugmentation could decrease oil contamination in the soil sludge by 45–53 %, while composting was able to remove only 31 % of the total hydrocarbons after 30 days when saw dust was used as an additive, indicating that bioaugmentation of microbial preparations is an effective treatment mechanism for oily sludges. Ceccanti et al. (2006) found significant hydrocarbon reduction in soil treatments using a combination of compost and earthworms (*Eisenia fetida*), both regulating the biochemical equilibrium of the soil. Tandy et al. (2009) recommended co-composting as a sustainable management option for remediating mine soil polluted with metals (Cu, As, Zn and Pb). Cai et al. (2007) investigated the efficacy of four different composting systems to bioremediate sewage sludge contaminated with PAHs. Sewage sludge was mixed with rice straw to obtain a C:N ratio of 13:1 prior to the compositing. After 56 days of composting, the total concentration of 16 PAHs increased considerably in the order of intermittent aerated compost < continuous aerated compost < inoculated manual turned compost that indicated removal rates of 94, 85 and 64 %, respectively.

Jiang et al. (2006) indicated that composting with immobilized *Phanerochaete chrysosporium* is potent in that it bioremediated 90 % of PCP in 60 days when yard waste, straw and bran were used as amendments in aerated compost systems. The parameters (0.8:1.0 soil/green waste, 60 % moisture content, and 38 °C) for controlled in-vessel composting of PAH-contaminated media were standardized by Antizar-Ladislao et al. (2006). Compost-mediated removal of PAHs from a manufactured gas plant soil was undertaken by Sasek et al. (2003) in a thermally insulated composting chamber using mushroom compost consisting of gypsum, chicken manure and wheat straw. The removal of individual PAHs ranged from 37 to 80 % after 154 days of maturation. To treat acid-mine drainage at the former Wheal Jane Tin Mine, Cornwall, in the United Kingdom, Johnson and Hallberg (2005) constructed compost bioreactor (anaerobic cell/anaerobic wetlands—consisting of bulky organic material held in a water-tight membrane buried underground that is totally devoid of macrophytes) components of three composite passive clean up models (lime-diluted, anoxic limestone and lime-free drain) for 16 months. They observed more than 99 % removal of Zn and Fe in the lime-free system amended with 5 % hay, 95 % softwood sawdust and a small amount of cattle manure to act as a microbial inoculum.

In a field experiment conducted in South Korea, Namkoong et al. (2002) standardized the suitable mix ratio of organic amendments to contaminated soil for improving diesel oil degradation by composting as 1:0.5. Suthar and Singh (2008) tested the feasibility of using vermicomposting technology to remediate metals (44 % Zn, 34 % Fe, 46 % Mn and 26 % Cu) from distillery sludge, recommending that earthworms can enhance nutrient profile and mitigate metal toxicity in the sludge which might be useful in sustainable land restoration practices at a low-input basis. Another feasibility study of aerated in-vessel composting was conducted at bench-scale by Godoy-Faundez et al. (2008) as a biodegradation strategy to remediate polluted sawdust (fuel concentration of >225,000 mg/kg) and desert mining soils (fuel concentration of >50,000 mg/kg) in the Atacama region. After 56 days of treatments, about 35 and 50 % removal of pollutants was observed in the contaminated soil reactors and sawdust, respectively.

Joo et al. (2008) evaluated the efficiency of *Candida catenulata* CM1 during composting of a mixture containing diesel-contaminated soil and food waste. After 13 days of composting, 84 % of the original petroleum hydrocarbons were degraded in the composting mixtures compared to 48 % of reduction in control reactor without the inoculum. Lu et al. (2010) conducted a bench-scale trial to enhance the removal of residual toxins after composting in soil contaminated with higher concentrations of petroleum hydrocarbons by combining biodegradation with Fenton-like pretreatment and observed more than 80 % removal and reduction in toxicity of TPH in 577 days. Walter et al. (2005) reported PCP removal by composting in the presence of white-rot fungi. Singh et al. (2010) stated that degradation of 50:50 mixture of cattle dung and biosludge could be attained in 75 days when earthworms (*Eisenia fetida*) were inoculated at 25 g/kg biosludge collected from the beverage industry.

Contreras-Ramos et al. (2006) reported that vermiremediation by *Eisenia fetida* (150 mg/kg soil) along with the autochthonous microorganisms could accelerate the rate of PAH removal (51 % anthracene, 100 % phenanthrene and 47 % benzo[a] anthracene (BaP) in a spiked soil within 15 days. More than 60 % PAH remediation was observed by Zhang et al. (2011) in 60 days through composting with mixtures of organic wastes (leaves, branches and biowaste consisting of green vegetables such as cabbage, spinach and celery). Unlike biopile and landfarming, composting is not a widely adopted field-scale remedial option at contaminated sites in full-scale; however, a few lab studies involving compost reactors are available. This technique is commercially adopted only to develop end-product out of organic waste that is devoid of pathogens or pollutants which could be used as nutrient-rich additives to enhance agricultural productivity. It is vital to increase the remedial efficiency of composting technology to more than 90 % in most cases at field-scale by utilizing other cost-effective *ex-situ* techniques either before or after the composting process.

3.11 Slurry-Phase Bioremediation: Bioreactors

Slurry bioreactor is one of the best choices for the biological remediation of subsurfaces contaminated by recalcitrant pollutants under controlled environmental conditions. Bioreactor technique is an *ex-situ* biochemical processing system designed to remove pollutants in wastewater or pumped groundwater using microbes (Robles-Gonzalez et al. 2006). In this technique, contaminated solid or liquid material (water, sludge, sediment and soil) is processed through an engineered contamination structure (bioreactor—manufactured or engineered device that supports a biologically active environment) to achieve bioremediation. Generally, bioreactor treatment is performed using microbes attached on a solid growth support medium or in suspension in liquids. In suspended growth systems (sequencing batch reactors or fluidized beds), polluted groundwater is circulated in an aeration basin where a population of microbes aerobically degrade organic matter, and produce CO_2, biomass and water (Zaiat et al. 2001). The biomass is settled out in a clarifier, which is then either disposed off as sludge or recycled back to the aeration basin. In attached growth structures (trickling filters, rotating biological contractors and upflow fixed film bioreactor), microbes are grown as biofilms on a solid support matrix and the pollutants in the water are removed as they diffuse into the biofilm (Quijano et al. 2010; FRTR 2012). Solid support matrix has a larger surface area for microbial attachment which could serve as an absorptive medium such as activated carbon (having the ability to adsorb pollutants and slowly release them to the microbes for degradation) or plastic or ceramic packing or sand or gravel.

In a bioreactor, the microbial population is either derived from natural selection or from an inoculum of organisms or enrichment from the polluted media with specific pollutant degradation potential (Nano et al. 2003). The biodegradation rate is rapid and remedial goals are achieved in few months. Also, bioslurry systems are technically versatile, simple and more effective than conventional bioremedial approaches. Since it is a closed system, it allows better control of temperature, pH, aeration, nutrient and surfactant additions, control of VOC emissions, monitoring of reactions, and microbial supplementations. Bioslurries are used to treat SVOCs, VOCs, pesticides and PCBs (Kuyukina et al. 2003; Machin-Ramirez et al. 2008). It is more effective than bioremediation and it works for most petroleum types. However, it has serious handling problems in heterogeneous soils, and dewatering of fine particles after treatment is costly. It also requires extensive site and contaminant characterization along with an effective disposal method for non-recycled wastewaters. Treatment cost using bioslurries ranges from US$130 to 200 per m^3. Cost increases in the case of post-gas treatment requirements for volatile contaminants (US EPA 2012).

Villemur et al. (2000) used a three-phase, aerobic slurry system containing 30 % silicone oil and biodegraded 90–98 % chrysene, pyrene and BaP. Wang and Vipulanandar (2001) observed that 96–99 % naphthalene was rapidly degraded by aerobic slurry bioreactors in 4 days. Castaldi (2003) treated petroleum waste sludges containing four-ringed PAHs in continuous multi-stage slurry bioreactors that operated for a short time with insignificant loss of volatile compounds, and observed more than 90 % removal of chrysene, BaP and pyrene. Hudak and Cassidy (2004) treated an aged PCB-polluted soil in bioslurry reactors inoculated with *Pseudomonas aeruginosa* that produced biosurfactant (rhamnolipid), and observed 98 % PCB remediation after 6 days. The removal of 47.9 % phthalate in a contaminated soil was observed by Venkata Mohan et al. (2006) in 40 h when a bioreactor coupled with bioaugmentation was chosen as the remedial tool. Fava et al. (2003) demonstrated the ability of surfactants like cyclodextrin, saponin and triton X-100 to enhance the actual remediation in slurry-phase systems by 30 %.

Marcoux et al. (2000) and Janikowski et al. (2002) indicated the use of solvents such as dodecane, decene, undecanone, hexadecane, limonene, jasmine, corn oil, silicone oil and paraffin oil can enhance PAH biodegradation. Lanthier et al. (2000) had reported augmentation of dehalorespiring strains (*Desulfitobacterium dehalogenans* and *Desulfitobacterium frappieri*) that used organo-chlorinated materials as electron acceptors in slurry bioreactors. Nano et al. (2003) recommended the combined application of slurry and solid phase bioreactor systems to remediate diesel-contaminated soils along with the use of soil additives, sand and surfactants for rapid TPH degradation (>95 %) in a week. In et al. (2008) estimated the effect of co-substrates (molasses and starch) in anaerobic slurry-phase biological degradation of TNT and reported 87–97 % degradation, which was 50–60 % higher than contaminant degradation without co-substrate addition.

Venkata Mohan et al. (2008) studied the *ex-situ* remediation of stimulated pyrene-polluted soil in slurry bioreactors operated in periodic discontinuous batch mode under anoxic-aerobic-anoxic microenvironments with bioaugmentation, and highlighted a pyrene removal rate of 90 % in 5 days. In a two-phase partitioning bioreactor, Robles-Gonzalez et al. (2006) suggested the slurry bioreactor *ad-situ* biodegradation approach as a successful substitute for treating mineral agricultural soils characterized by high contents of organic matter and fine texture contaminated with 2,4-D. The study reported 95 % removal of the herbicide in 14 days with and without sucrose supplementation. In a solid–liquid two-phase partitioning bioreactor system, Rehmann et al. (2008) managed 80 % phenanthrene removal using isopropyl alcohol as the mobilizing agent. About 66–94 % HCH bioremediation in slurry batch bioreactor was achieved by the white-rot fungus (*Bjerkandera adusta*) in 30 days after inoculation (Quintero et al. 2007). Soil slurry augmentation of an immobilized bacterium (*Burkholderia cepacia*) with molasses achieved highest carbofuran removal of 96.97 % in a soil slurry-phase reactor in 4 days (Plangklang and Reungsang 2010).

Nasseri et al. (2010) noted the efficiency of bioaugmentation in a bioreactor to remove 87–92 % PAHs from contaminated soils. A successful TPH remediation of 95 % in 225 days was observed by the application of a continuously stirred tank bioreactor for remediating industrial wastewater effluents rich in hydrocarbons using a consortium of *Rhodococcus* sp., *Stenotrophomonas maltophilia, Ochrobactrum intermedium*, *Bacillus cereus* and *Aeromonas punctata* (Gargouri et al. 2011). Singh and Fulekar (2010) stated the potential of cowdung microflora as a source of biomass for benzene degradation (50 % in 168 h at an initial concentration of 5000 mg/L) in a two-phase partitioning bioreactor. When wheat straw pellets were used as the bulking agent, emerging pollutants like naproxen and carbamazepine were degraded by white-rot fungi (*Trametes versicolor*) to 38 % in 2 days in spiked sludge by solid and slurry-phase systems (Rodriguez-Rodriguez et al. 2010). Like aerobic bioslurry treatments, anaerobic systems have also been proved to remediate >95 % HCH, PCP, TCE, 2,4-D and TNT as presented in Table 8. Thus, many studies on bioreactor technology have proved that it is the most successful bioremediation technology for large-scale implementations.

3.12 Solidification/Stabilization

One of the best known waste fixation processes that offer reduction in mobility of pollutants in the environment through chemical and physical means is solidification/stabilization (S/S). It could be either *ex-situ* or *in-situ*. In this method, contaminants are enclosed or physically bound within a stabilized mass (solidification), or chemical reactions are induced between the stabilizing agent and pollutants to reduce their mobility (stabilization). Though mass reduction in contamination does not occur in this technique, reduced mass flux and mobility to receptors effectively removes the pollutant pathway. Distinct *ex-situ* innovative processes that have been developed in this method are vitrification/molten glass, soluble phosphates, sludge stabilization, radioactive waste solidification, portland cement, polyethylene extrusion, modified sulfur cement, emulsified asphalt batching, and bituminization. *Ex-situ* and *in-situ* S/S processes are usually applied to soils polluted by heavy metals and other inorganics. Mostly, this technology has limited effectiveness against pesticides and organics, except for vitrification and asphalt batching.

Ex-situ S/S is very effective for inorganics including radionuclides. Compared to biopiles or monitored natural attenuation, it has a short treatment time scale with an ability to remediate a wide range of mixed contaminants. It offers potential structure or geotechnical improvement in soil. Generally, environmental conditions affect the long-term pollutant immobilization. This treatment, however, is site-specific where residual long-term liability (contaminant mass remains) is observed. Inhibitory substances like free-phase solvents and oils limit the success of this system. Some

Table 8 Remedial effect of aerobic and anaerobic slurry bioreactors

Augments	Contaminant	Remediation (%)	Reference
Aerobic			
1. Consortia of *Corynebacterium aquaticum*, *Flavobacterium mizutaii*, *Mycobacterium gastri*, *Pseudomonas aeruginosa* and *Pseudomonas putida*	Pyrene	93	Cassidy and Hudak (2001)
2. Biosurfactant (Brij 30)	Pyrene	70	Schuur and Mattiasson (2003)
3. *P. aeruginosa*	PCB, TPH	98–99	Hudak and Cassidy (2004)
4. Molasses	TNT, TNB	90	Fuller and Manning Jr (2004)
5. *Rhodococcus* sp.	Fluoranthene, anthracene, pyrene	98–100	Dean-Ross (2005)
6. *P. putida*	Naphthalene	100	Piskonen et al. (2005)
7. *Bjerkandera adusta*	HCH	94	Quintero et al. (2007)
8. Consortia of bacteria (*Mycobacterium* sp., *Pseudomonas* sp., *Sphingomonas* sp., and *Rhodococcus* sp.) and fungi (*Phanerochaete chrysosporium*, *Bjerkandera adusta*, *Irpex lacteus* and *Lentinus tigrinus*)	Anthracene, fluoranthene, benz[a]anthracene	46–85	Li et al. (2009)
9. *Pseudomonas* sp.	BTEX	99	Collins and Daugulis (1999)
10. Isopropyl alcohol	Phenanthrene	80	Rehmann et al. (2008)
11. Cowdung	Benzene	50	Singh and Fulekar (2010)
12. *Trametes versicolor* and wheat straw	Naproxen, carbamazepine	38	Rodriguez-Rodriguez et al. (2010)
13. Molasses and immobilized *Burkholderia cepacia*	Carbofuran	97	Plangklang and Reungsang (2009)
14. *Aeromonas punctata*, *Bacillus cereus*, *Ochrobactrum intermedium*, *Stenotrophomonas maltophilia* and *Rhodococcus* sp.	TPH	95	Gargouri et al. (2011)
Anaerobic			
1. *Desulfitobacterium* sp. and zero-valent iron	TCE	100	Lee et al. (2001)
2. Anaerobic sludge	HCH	100	Quintero et al. (2007)
3. Sucrose	2,4-D	95	Robles-Gonzalez et al. (2006)
4. *Desulfitobacterium frappieri*	PCP	100	Lanthier et al. (2000)
5. Molasses and starch	TNT	87–97	In et al. (2008)

processes result in a significant rise in the contaminant volume (double the initial volume), and there it is necessary to explore the long-term effectiveness of this technology on the contaminants (RAAG 2000). It costs around US$132–263 to treat per m^3 contaminated site (FRTR 2012).

Bates et al. (2000) recorded a full-scale remediation of 95–99 % PCP at Selma pressure treating site in Selma, California using S/S technology. Alpaslan and Yukselen (2002) conducted a study on bioremediation of Pb-contaminated soils by S/S and achieved 88 and 99 % Pb immobilization with the use of lime and soil (1:21) followed by cement and soil (1:15), respectively. Singh and Pant (2006) concluded that solidification of As waste with cement is suitable for reducing the leachability of As. Dermatas and Meng (2003) observed that fly ash materials (pozzolanic-based S/S) along with quicklime could immobilize more than 90 % trivalent, hexavalent Cr and Pb present in artificially-polluted sandy clay soils. Hwang and Batchelor (2001) studied the effect of Fe(II)-based degradative S/S (modification of conventional S/S that used Fe(II) as a reducing agent for chlorinated organics) at field-scale for immobilizing inorganic contaminants, and found less than 7 % of the initial amount of PCE on a molar basis between 13 and 335 days of treatment.

Many amendments facilitated the stabilization of heavy metals such as As, Cr, Pb and Cu. Several studies (Kim et al. 2003; Moore et al. 2000; Lee et al. 2011; Yoon et al. 2010) demonstrated the effect of Fe(II), limestone + redmud, Portland cement + cement kiln dust and sulphate to effectively reduce the mobility of As. Also, clay minerals, hydroxyapatites, aluminium oxides, organic matter, alkaline materials like lime and fly ash were proved to be effective amendments that facilitate As stabilization (Garcia-Sanchez et al. 2002). Stabilization of Cr was reported in the presence of divalent iron + organic matter (Seaman et al. 2001), and alkaline materials like hydroxyapatite, fly ash and calcium carbonate (Kim and Dixon 2002). More than 75 % immobilization of Cu by the use of clay minerals, palygorskite (Alvarez-Ayuso and Garcıa-Sanchez 2003), fly ash stabilized sewage sludge (Su and Wong 2004), sugar foam (Garrido et al. 2005), peat (Balasoiu et al. 2001), sewage sludge with earthworms (Kizilkaya 2008), and coal fly ash (Ciccu et al. 2003) was documented.

Pb stabilization was successfully performed with the application of P-containing amendments like natural apatites, hydroxyapatites, rock phosphate, phosphoric acid and their combinations (Brown et al. 2005; Cao et al. 2003b; Raicevic et al. 2005; Ownby et al. 2005). Even alkaline compounds, rice husk, ash, biosolids, compost, zeolite, iron as well as manganese oxides were used as soil amendments to stabilize Pb (Castaldi et al. 2005; Brown et al. 2005; Yin et al. 2006). The optimal cement binder content (5 %) to solidify or stabilize more than 85 % As in abandoned mine tailings was suggested by Choi et al. (2009). More than 95 % S/S of hazardous radioactive wastes using alkali activated cements was achieved by Shi and Fernandez-Jimenez (2006). Chen et al. (2009b) reported 100 % immobilization of heavy metals by the application of enhanced carbonation coupled with CO_2 and Na_2CO_3 in cement-based S/S of heavy metal-bearing sediment.

Scanferla et al. (2009) developed and patented an innovative S/S technology using high performance additive (water reducers and superplasticizers) concrete technology and observed superior leaching of heavy metals (99 %) at field-scale. Leonard and Stegemann (2010) reported more than 90 % immobilization of hydrocarbons in petroleum drill cuttings using Portland cement along with the addition of high carbon power plant fly ash which act as a novel sorbent for organic pollutants. In stabilization technology, the aim of adding additives is to change the soil physico-chemical properties through ion-exchange, adsorption, precipitation, redox potential and pH control. These will alter the existing forms of inorganics in soil, thereby reducing the mobility and bioavailability of heavy metals. This approach has been one of the most successful technologies in that it is efficient in immobilizing more than 95 % inorganics at large-scale more cheaply (Table 4). The current focus is to enhance the efficacy of the present reagent-based stabilization, vitrification, plastic material stabilization, lime pozzolanic solidification and cement solidification techniques using several biodegradable, natural reagents or additives or bulking agents in combinations with the ones that are outlined in Table 9.

3.13 Constructed Wetlands

Constructed wetland treatment for wastewater is a long-term technology that is primarily microbial, and uses natural, geochemical and biological processes inherent in an artificial wetland ecosystem composed of vascular plants, algae, microflora and organic soils to facilitate the accumulation and removal of explosives, metals and other pollutants from influent waters. Though it is a green technology practiced since 1969, the long-term effectiveness of constructed wetlands is not well understood (Vymazal and Kropfelova 2009). Also, wetland aging along with temperature fluctuations causes a problem which contributes to a decrease in pollutant removal rates over time; indeed, constructing a wetland is financially not viable for many sites (US EPA 2012). However, many remediation studies have been conducted with this technology to remove heavy metals from wastewaters. It is estimated that the capital costs of wetland treatment are about 1.36 US$ per 1000 gal water (over a 10 year period) and US$0.45/4000 L water (over a 30 year period) (FRTR 2012).

Polomski et al. (2009) observed more than 85 % N and P removal by three floating marine macrophytes (*Eichhornia crassipes, Pistia stratiotes* and *Myriophyllum aquaticum*) in greenhouse-based bench-scale subsurface constructed wetlands. Vymazal (2009) reported the extensive application of constructed wetlands with horizontal subsurface flow for treating wastewater from agriculture, airports, highways, greenhouses and plant nurseries. Horne et al. (2000) emphasized the success of phytoremediation by constructed wetlands. Around 70 % Se was removed by constructed wetlands in 2 years from Se laden drainage water collected from Corcoran, California (Lin and Terry 2003). In Czech Republic, three horizontal flow wetlands were constructed between March 2006 and June 2008 for removal of 34 trace elements (Kropfelova et al. 2009). The highest degree of 90 % Al removal followed by 78 % Zn, 50–75 % Gallium, Fe, Ba, Cr, Mo, Pb, Cu, Sb and U, and low retention concentration of 0–25 % for B and Co was noticed by the end of the study.

Table 9 Bulking agents used for metal immobilization in solidification or stabilization systems

Bulking agent	Metal immobilized	References
1. Cement	Almost all metals	Chen et al. (2009b); Paria and Yuet (2006)
2. Rice husk and its ash	Pb	Yin et al. (2006)
3. Biosolids and compost	Pb, Cu, Zn, As	Brown et al. (2004); Castaldi et al. (2005); Chiu et al. (2006); Kumpiene et al. (2008)
4. Zeolite	Pb, Mn, Zn, Hg	Kumpiene et al. (2008)
5. Iron and manganese oxides	Cd, Cu, Ni, Pb, Zn	Contin et al. (2007); Garciia et al. (2004)
6. Peat	Pb, Cu	Kumpiene et al. (2007)
7. Fly ash and its geopolymers	Pb, Cu, Cr, Zn, As	Phair et al. (2004); Chen et al. (2009a, b); Ciccu et al. (2003); Seoane and Leiros (2001)
8. Cyclonic ashes and steel shots	Zn	Brown et al. (2005)
9. Ferrous sulphate	As	Kim et al. (2003); Hartley et al. (2004)
10. Red mud	Pb	Ciccu et al. (2003); Brown et al. (2005)
11. Limonite	As	Garcia-Sanchez et al. (2002)
12. Palygorskite	Cu, Zn	Kumpiene et al. (2008)
13. Calcium carbonate	Zn, Pb, Mn, Cu, Ni, Cd, Co, Sr	Kumpiene et al. (2008)
14. Aluminium oxide	As, Cu	Garcia-Sanchez et al. (2002)
15. Alkali silicate minerals	Zn, Pb, Cd, Cr	Shi and Fernandez-Jimenez (2006)
16. Sewage sludge	Cu, Zn	Sanchez-Monedero et al. (2004); Su and Wong (2004)
17. Gypsum	Pb, Cd	Lombi et al. (2002); Garrido et al. (2005)
18. Chitosan type biopolymer	Zn, Cu	Sherman and Randall (2003); Jothiramalingam et al. (2010)
19. Goethite, lepidocrocite, hematite and ferrihydrite	As	Nurmi et al. (2005)
20. Nano-sized iron	Cu, Cr, As	Kumpiene et al. (2006); Gil-Diaz et al. (2014)
21. Nanometallic Ca/CaO dispersion mixture	Pb, Cr	Mallampati et al. (2012)
22. Phosphates (apatites, hydroxyapatites, phosphate rock, diammonium phosphate and phosphoric acid)	Pb, As, Zn	Martinez et al. (2014)
23. Lime	Pb, Cu, As, Zn	Kumpiene et al. (2008)
24. Egg shell waste	Cu, Pb, As	Lee et al. (2013)

Nyquist and Greger (2009) reported 36–57 % decrease in Fe, Cu, Zn and Cd concentration by the use of emergent plants and constructed wetlands at the Kristineberg mine site in Sweden.

The accumulation of >85 % Cu, Cu and Zn, Al, Fe, Zn and Pb by phytoremediating plants (*Phragmites australis* and *Typha domingensis*) in constructed wetlands was reported by Ye et al. (2003), Ashraf et al. (2011) and Hegazy et al. (2011). Wu et al. (2012) conducted a long-term investigation (2005–2010) in two pilot-scale horizontal flow constructed wetland systems with Fe-rich solid matrix for treating sulphate-rich contaminated groundwater with lower concentration of chlorinated hydrocarbons, and observed 75 % pollutant removal at the SAFIRA research site in Bitterfeld, Germany. Chen et al. (2011) reported up to 70 % PCE dechlorination in two pilot-scale horizontal sub-surface flow constructed wetlands with vegetation (*P. australis*). Shelef et al. (2012) demonstrated 20–60 % salt phytoremediation by *Bassia indica* in a recirculating vertical flow constructed wetland system.

More recently, *Eleocharis macrostachya* used in constructed wetland prototypes showed a higher As mass retention of 87–90 % in 33 week test period (Olmos-Marquez et al. 2012). Zou et al. (2012) recommended employing a new vertical flow constructed wetland structure with drop aeration for treating rural wastewaters. A wetland system that had operated for 11 years in 12,800 m^2 area in the mid-western USA for remediating >90 % chlorinated ethenes rapidly developed into a healthy ecosystem with diverse vegetation, supporting over 60 bird species and several other animal species (Kadlec et al. 2012). Thus, most studies have indicated that planted wetland is a suitable option for treating metal-contaminated water, and long-term establishment of wetlands in a vast area could favor the survival of several micro- and macro-flora over a period of time. However, in high contaminant concentration such a possibility is not applicable, and there is a need to harness the merits of this technology (aesthetic, environmental friendly and sustainable characteristics) for remedial approaches by integrating this technique with several other physico-chemical techniques. They could in turn reduce the initial contaminant concentration and make this method successful.

4 *Ex-Situ* Technologies for Air Pollution Control

The recent pollutant release inventories published by environmental organizations and governments demonstrate that emission of atmospheric pollutants is continually rising with a steady increase in global warming leading to more threats to life forms. Of the total global air emissions in 2010, 77 % was CO_2 (US EPA 2012) followed by CH_4 (14 %), NO_2 (8 %) and F-gases (1 %). According to Rice (2007), one of the major contributors to global air emission (26 %) is energy production, distribution and use. Subsequently, road and non-road transport, industrial process, agriculture, accumulation of waste and forestry also contribute to between 3 and 19 % of the ever-increasing air pollution. If the current scenario of air emission is not controlled, by 2020–2050 there would be a drastic decrease in agricultural production, reduction in water

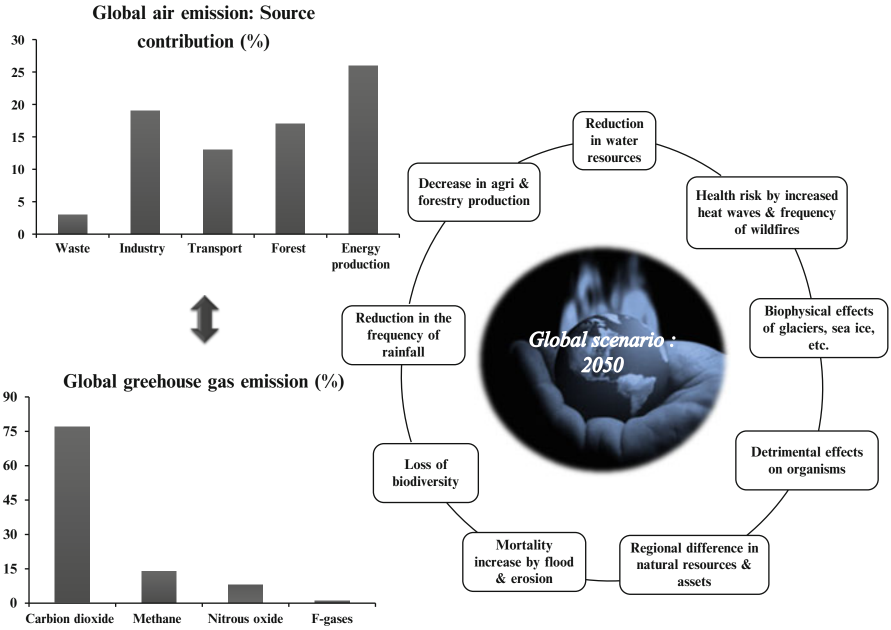
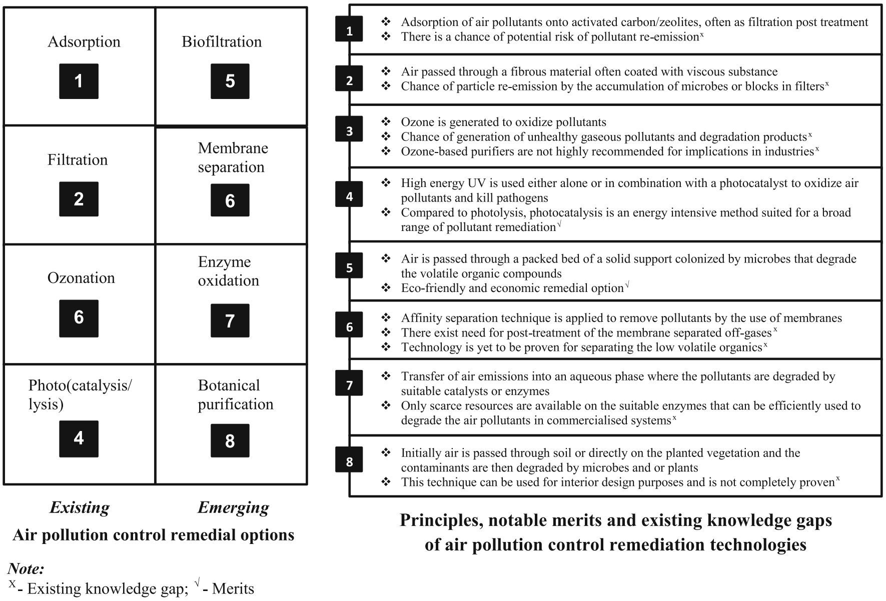


Fig. 4 Global air emissions and the sources for contribution in 2010 with the projected regional impacts. *Source*: US EPA (2012); Rice (2007)

resources, increased health risks by climate change, elevated detrimental effects on living organisms by the biophysical effects on natural resources, loss of biodiversity and increase in mortality by erosion or flooding or forest fires or volcanoes, etc. (Fig. 4).

One way to control air emissions is to treat the industrial or household waste gases by adopting any of the physico-chemical or biological remedial options such as adsorption or ozonation or incineration or biofiltration or oxidation (UV/photochemical/biocatalytic) or membrane gas separation, etc. before they are let into the atmosphere (Fig. 5). These air pollution control remedial techniques which can be done both *in-situ* and *ex-situ* are just as important as soil and groundwater remediation technologies, and hence are discussed in this review.

Activated carbon is commonly used as adsorbent in waste-gas treatments (Foo and Hameed 2012). Many odorous organics like BTEX, TCE, hydrogen sulphide, SO_2, acetone, mercaptans, etc. have been successfully removed by adsorption. Though adsorption has been employed for vapor/gas purification systems, it does have numerous drawbacks such as need for desorbate recovery at very low purity, high mechanical energy for pressurization, difficulty in maintenance of complicated set-up and high initial capital cost. Condensation is potentially effective for VOCs (99 % removal) having a boiling point over 40 °C. However, skilled technicians and a rigorous maintenance regime are required to handle the unit efficiently (US EPA 2012). Ozonation is not widely practiced commercially owing to its high cost, and the probability of ozone gas emission and its transformation into toxic intermediates (Li et al. 2012b).



- Adsorption of air pollutants onto activated carbon/zeolites, often as filtration post treatment
- There is a chance of potential risk of pollutant re-emission^{x}

- Air passed through a fibrous material often coated with viscous substance
- Chance of particle re-emission by the accumulation of microbes or blocks in filters^{x}

- Ozone is generated to oxidize pollutants
- Chance of generation of unhealthy gaseous pollutants and degradation products^{x}
- Ozone-based purifiers are not highly recommended for implications in industries^{x}

- High energy UV is used either alone or in combination with a photocatalyst to oxidize air pollutants and kill pathogens
- Compared to photolysis, photocatalysis is an energy intensive method suited for a broad range of pollutant remediation$^{\surd}$

- Air is passed through a packed bed of a solid support colonized by microbes that degrade the volatile organic compounds
- Eco-friendly and economic remedial option$^{\surd}$

- Affinity separation technique is applied to remove pollutants by the use of membranes
- There exist need for post-treatment of the membrane separated off-gases^{x}
- Technology is yet to be proven for separating the low volatile organics^{x}

- Transfer of air emissions into an aqueous phase where the pollutants are degraded by suitable catalysts or enzymes
- Only scarce resources are available on the suitable enzymes that can be efficiently used to degrade the air pollutants in commercialised systems^{x}

- Initially air is passed through soil or directly on the planted vegetation and the contaminants are then degraded by microbes and or plants
- This technique can be used for interior design purposes and is not completely proven^{x}

Fig. 5 Existing and emerging air pollution control remedial techniques. *Source*: US EPA (2012)

Membrane processes for gas separation are also gaining a greater acceptance in industries where semi-permeable membranes made of polymers (polydimethylsiloxane/ethylene oxide/polysulfone/polyimides/polycarbonates/polyperfluoro-dioxoles/cellulose acetate) or porous ceramics are used to separate the gas mixtures. Reverse selective membranes (solubility-controlled), carbon hallow fibers, carbon molecular sieve membranes, carbon nanotubes as membranes, mixed matrix membranes, zeolite membranes, facilitated transport membranes are the different types of recent promising membranes used in industries for the separation of H_2/N_2, H_2/CO_2, H_2/hydrocarbons, O_2/N_2, CO_2/hydrocarbons, H_2S/hydrocarbons, H_2O/hydrocarbons, He/hydrocarbons, He/N_2 and ethylene/N_2 (Bernardo et al. 2009). Though extensive research is being carried out on improving membrane materials to control air emissions, application of membrane processes coupled with the other separation techniques in hybrid processes may be exploited better in the future.

An emerging purification technique for both air and wastewater due to its high effectiveness and versatility at low temperatures is photocatalytic oxidation (Assadi et al. 2012). Catalytic and thermal oxidations are also used to treat air pollutants present in their environment (Zhou et al. 2012). Bioprocess techniques that are mostly used for air emission control are bioscrubbers, biotrickling filters and biofilters. The biofiltration process is carried out in anaerobic/aerobic bioreactors where a polluted air stream will be allowed to pass through a porous packed media that support the thriving microbial population which help to exhibit a biofilm-like process.

Generally, pollutant diffuses through the biofilm that holds the microbes (Kennes et al. 2009). The treatment efficiency of the biofiltration technique is above 90 %. A diverse range of inorganic and organic chemicals (carboxylic acid, hydrocarbons, aldehydes, alcohols, ketones, hydrogen sulphide and ammonia) have been treated in biofilters (Kennes et al. 2009; Soares et al. 2012). Moreover low capital and operational costs, low energy requirements, and use of less chemicals make biofiltration a feasible biological technology for air emission treatments compared to other techniques. Further, recent technical discoveries and scientific advances have led to the development of novel bioreactor configurations such as continuous-suspended growth bioreactors, foam-emulsion bioreactors, fluidized-bed bioreactors, monolith bioreactors, air-lift bioreactors, and two-liquid-phase biotrickling filters. These have been promising and successful for handling air pollutants with a high remedial potential (Rene et al. 2012).

He et al. (2012) conducted a pilot-scale study integrated with biotrickling filtration and photocatalytic oxidation (BTF-PCO) for treating organic waste gas in a paint plant constituted of ethyltoluene, xylene, ethylbenzene, toluene, ethyl acetate and TMB. Elola et al. (2009)) proposed a new concept of combining adsorption (Pd as adsorbent) and catalytic hydrodechlorination for the treatment of organochlorinated off-gases (92 % conversion). Altomare et al. (2012) were able to remove ammonia (99 %) in nitrogen-containing effluent by photocatalytic treatments. Cai and Sorial (2009) removed 99 % VOCs in a trickling-bed biofilter integrated with cyclic adsorption/desorption beds. Fredenslund et al. (2010) recommended the use of engineered biocovers for the full-scale reduction of greenhouse gas emissions from landfills. The removal efficiency of VOCs by BTF-PCO treatment even after 90 days operation was in the range of 95.8–98.2 %. According to Jiang et al. (2009), graphene sheets with designed subnanometer pores (membrane) can selectively separate H_2/CH_4 mixtures with numerous technological and energy applications including gas sensors, fuel cells and carbon sequestration.

Most recently, electric swing adsorption has been reported as a fruitful second generation technology to capture CO_2 (89.7 % capture) from flue gases of power plants to combat global warming (Thiruvenkatachari et al. 2013). For filtration of air emissions, natural media filtration technology (alternative to conventional gravel, sand and activated carbon filters) was recently adopted (Wanielista et al. 2012). Use of a membrane bioreactor was able to remove 99 % toluene from waste air within 12 h under continuous and intermittent feeding conditions (Alvarez-Hornos et al. 2012). Kumar et al. (2012) investigated the degradation of TCE vapors in a membrane biofilm reactor inoculated with *Burkholderia vietnamiensis*. The primary growth substrate was toluene which was loaded consecutively during 110 days of the system's operation. A supreme TCE volumetric elimination of 4.2×10^{-3} g/m^2/h was documented and 2–10 times greater than those reported in other gas-phase bioremediation trials. Biofiltration of methanol in organic biofilter was conducted by Ramirez-Lopez et al. (2010) using peanut shells as the medium which could remove up to 30 kg/m^3 methanol/day. Thus, more available tools that can make use of natural waste materials for remediation require more in-depth research. Overall, advanced adsorption, photocatalytic oxidation, trickling and membrane biofilters are very critical to aid air pollution control at full-scale, and investigations into the performance of integrated existing and emerging remedial technologies should be encouraged.

5 Emerging *Ex-Situ* Remediation Technologies

Contaminated ecosystems constitute a serious environmental problem, and it is difficult to treat pollutants with any one of the existing remedial techniques. For example, owing to the specific properties of the contaminants, remediation efforts devoted at macro-scale like pump-and-treat acquired limited success over time. In some cases, the *ex-situ* treatments become costly and fail to remove the contaminant from the source (Caliman et al. 2011). Under this pressure, some remediation techniques have been developed in the last few years for the decontamination of polluted sites, and many show promise in cleaning up contaminated soil and water.

Many countries have devoted resources to develop advanced and innovative remediation techniques, and as a consequence emerging technologies are finding a suitable platform for environmental clean up and can represent an important tool to overcome environmental risks in the near future. Most of the emerging technologies such as nanoremediation, microbial fuel cells, microbial consortia in photo-heterotroph microbial system, bio/photocatalytic pollution control, and genetic engineering are mostly being applied *in-situ* though they have greater prospects of *ex-situ* application. One recently emerging *ex-situ* remediation technology is ultrasonic technology which is described in more detail below. More efficient and economical *ex-situ* strategies are needed to remediate contaminated groundwater and soil.

5.1 Ultrasonic Technology

Ultrasound technology makes use of frequency over 18 kHz that forms the source in developing cavitation bubbles leading to high localized pressures (>50 MPa) and temperatures (>4726 °C), and induce chemical reactions that degrades the pollutants (Adewuyi 2001). Compared to incineration technology, ultrasound remediation of pollutants is worthwhile because of its less space requirement, faster remediation rates, less energy expenses, lower installation and maintenance cost followed by no sludge waste generation (Thangavadivel 2010). Effectiveness of the ultrasound technology in contaminant clean up depends on the transmitting medium characteristics, reactor characteristics, losses and attenuation in the medium as well as the standing wave effect if it is generated. Ultrasonic cleaning has an extensive range of industrial uses. Large-scale clean up of contaminated soil using audible frequency sonication of 100 Hz and a higher power low frequency ultrasound pilot-scale operation were reported in Canada and Australia, respectively (Mason et al. 2004).

One of the important constraints in this technology is the physical limitation of transducer materials and wave propagation physics where the transmitted power drops with increasing frequency. Also, when intense mechanical energy is applied to the soil particles, clays get dispersed into a stable colloidal suspension, and it becomes difficult to separate organics from it. Desorption efficiency by ultrasonic destruction is slow for finer particles compared to coarse particles, i.e. finer particles demand longer sonication time. However, ultrasonic thermal desorption is an ideal alternative to solvent flushing or conventional soil washing techniques that involve additional costs when trying to solve contaminant accumulation problems in silt and clay particles.

Studies by Kazi et al. (2006) and Abramov et al. (2013) demonstrated the applicability of ultrasonic technology to leach or desorb pollutants from sediments and soils. Mason et al. (2004) reported an enhanced soil washing process with low frequency ultrasound for PCB removal in polluted zones. Low frequency (20 kHz)-assisted economically-viable remediation technology was also reported for PAHs desorption by Meegoda and Veerawat (2002). Ultrasonic thermal desorption can successfully remove chlorinated solvents, petroleum hydrocarbons, heavy metals and pesticides. It costs around US\$31.1 per m^3 when a frequency of 31 kHz is used for on-site remediation.

Thangavadivel et al. (2011) used low frequency, high power ultrasound heated slurries with anionic surfactant (sodium dodecyl sulphate) to enhance DDT desorption from contaminated soils. DDT contaminated soil, prepared as slurry (10 % wt) after the addition of 0.1 % surfactant at pH 6.9 was heated to 40 °C for 30 min. With a frequency of 20 kHz and ultrasonic intensity of 932 W/L, desorption of DDT was found beyond 80 % in 30 s without solvent extraction. He et al. (2011) confirmed the potential of ultrasound and biomass (transgenic *Chlamydomonas reinhardtii*) for *in-situ* mercury removal from contaminated inorganic sediments. Flores et al. (2007) proposed an innovative approach, employing the coupled effect of applying ultrasonic energy with advanced Fenton oxidation processes, for the degradation of hydrocarbons in problematic soils. The coupled effect resulted in 92 and 87 % removal of toluene and xylene, respectively, in 2 days.

Pham et al. (2009) concluded that ultrasonically-enhanced electrokinetics could significantly remove ten times more hexachlorobenzene and phenanthrene than electrokinetics alone. Yazici (2005) removed 25 % cyanides and generated hydrogen peroxide even at an increased alkaline pH of 10.5 when the temperature was high (>30–50 °C). There are many ultrasonic thermal desorption studies summarized in Tables 10 and 11 which ensure that the developing ultrasonic desorption is a reliable remedial technology for emerging priority pollutants. However, this technology's field-scale implications are not documented which emphasizes further applications of this technique are required in the near future.

Table 10 Ultrasonic-enhanced soil remediation coupled with other technologies—case studies at laboratory-scale

Contaminant	Cleanup level (%)	Highlight	Reference
Terphenyl	99	Use of 0.1 % octyl-phenyl-ethoxylate—surfactant-enhanced technology	Meegoda and Veerawat (2002)
PAHs	90	Use of sunflower oil—surfactant-enhanced technology	US EPA (2012)
PAHs	90	Coupled effect of electrokinetic and ultrasonic technology	Ik Chung and Kamon (2005)
Alcohols	40–80	Propanol and ethanol were removed with *Cladosporium* strain as biosorbents	US EPA (2012)
Phenol	15	NaCl and CCl_4 were used as additives in the solution—biostimulation	Mahamuni and Pandit (2006)
DDT	80	SDS—surfactant-enhanced technology	Thangavadivel et al. (2011, 2012)
Phenanthrene	69.5	Combined application of nanotechnology with soil washing	US EPA (2012)

5.2 Microbial Fuel Cells, Nanoremediation and Others

Two emerging promising remediation technologies that are mostly applied *in-situ* and can be considered to be successful even in *ex-situ* are microbial fuel cell (MFC) technology and nanoremediation. Another interesting area of research is perhaps the study of photo-heterotroph microbial systems (briefly explained in the other review under *in-situ* remedial techniques). These emerging, innovative approaches are so far not applied *ex-situ*, and thus open interesting possibilities for *ex-situ* field remedial initiatives which require thorough investigation. Cross-disciplinary clean up approaches that are eco-friendly, efficient in that they remove >95 % contaminant in short time, are less energy intensive, and economical should be developed using emerging methods and promising *ex-situ* techniques like advanced photocatalytic oxidation, biocatalysis, etc., and explored under *ex-situ* conditions.

6 Future Research Needs

It is evident in this review that many *ex-situ* remedial approaches are available for cleaning up contaminated sites. Although some existing technologies like advanced oxidation processes, sorption, solid and slurry-phase bioremediation are well-established and are potentially suitable for *ex-situ* remediation of contaminated sites, they are not very feasible due to their energy and cost considerations (for example, advanced oxidation processes are expensive). Also, no single technique is applicable for all pollutant types and the diverse physical settings that exist at

Table 11 Ultrasonic thermal desorption technology for pollutant cleanup

POP	Frequency (kHz)	Power (W)	Temperature (°C)	Duration (min)	Cleanup (%)	Reference
1. Chlorophenol	20–850	140–475	36–39	120	100	Teo et al. (2001)
2. TCE	100	140	20	40	90	Yim et al. (2001)
3. Phenol	20–500	50	20	80	100	Entezari et al. (2003)
4. Chlorophenol	1.7	35	25	60	20.1	Hao et al. (2003)
5. Phenol	20–520	25–180	–	90	60	Kidak and Ince (2008)
6. PCP	40	600	20	120	60	US EPA (2012)
7. Phenol	22	120–240	31	60	50	Mahamuni and Pandit (2006)
8. Chlorophenol	20–800	30	20	88	50	Jiang et al. (2006)
9. Phenol	200	200	20	60	85	Melero et al. (2011)
10. TCE	20	600	10–24	10	40	Ayyildiz et al. (2005)
11. PFOS, PFOA	354–612	250	10	140	63	Cheng et al. (2009)
12. PAHs	20–500	30	20	40	90	David (2009)
13. DDT	1.6	150	24	9	90	Thangavadivel (2010)
14. Cyanide	35–130	500	25	90	64–74	Bonyadi et al. (2012)

different polluted sites. In most cases, more than one remedial technique is required to address most of the polluted site issues. Apart from the emerging technologies like ultrasonics, several clean up approaches that are both cost-effective and efficient need to be explored as potential methods in a remedial system. Further research and development would bring the emerging technologies to the market for full-scale implementation. Some of the crucial research gaps identified in the field of *ex-situ* remediation are as follows:

- Which combinations of technologies are appropriate for remediating various organic and inorganic pollutants in soil and groundwater ecosystems as well as air emissions?
- After remediation, does the use of some chemically-modified materials, nanoparticles, etc. remain bioavailable and cause a risk to the livings in the biome?
- Can the contaminants be degraded completely or transformed into less toxic forms by making use of microbes in the place of chemically-modified materials, nanoparticles, etc? If so, what is the extent of the metabolic cooperation among the microbial community? What is the structure and function of microbes in contaminated sites and their responses to different stimuli using environmental genomics and community fingerprinting?
- Is it practical to restore, to some extent, the natural functions of some polluted soils (multifunctional remediation) by the use of natural amendments and microbes?
- To what extent can existing and emerging techniques be modified or integrated to develop a feasible function-directed remediation technique that is better able to minimize the risk due to persistence and further spreading of pollutants?
- What are the efficient methods to decontaminate the emerging contaminants like pharmaceutical and personal care products, hormones, antibiotics, engineered nanoparticles, etc?

Answering these questions may lead to the development of new remediation techniques that are more reliable on an economic and environmental basis. This review also suggests the need for research on testing the feasibility of emerging *in-situ* techniques like MFCs, nanoremediation and photo-heterotroph microbial system as *ex-situ* remedial options as well. This is because MFCs have the dual property of remediation + electricity generation, and are most economical. Even nanoparticles can be synthesized by green strategies that will be more environmentally friendly. Large-scale implementation of these emerging technologies can be profitable tools for environmental entrepreneurs while providing options for previously difficult risk-based remediation projects for contaminated ecosystems.

7 Summary

Contaminated soil, groundwater and air emissions have been the subject of public concern and research, and the field of remediation has grown and evolved continually spending about US$505.5 billion/annum globally. To improve decontamination the remediation industry is continuously developing and adopting new technologies. Clean up of environmental pollutants involves a variety of *in-situ* and *ex-situ* techniques, ranging from physical, chemical, biological to advanced engineering technologies. Clean up activities may also address a wide range of contaminants when they are integrated. This review is an exploration of the *ex-situ* technologies for cleaning-up the contaminated soil, groundwater and air emissions, highlighting their principles, advantages, deficiencies and where gaps in the knowledge exist. Challenges and strategies for removing different types of contaminants, mainly heavy metals and priority organic pollutants, are also described. Included are technologies that are well-established like incineration, soil washing, biopiles, landfarming, bioreactors, oxidation, adsorption, dehalogenation, composting, solidification/stabilization, constructed wetlands, and emerging *ex-situ* technologies such as ultrasonic technology to treat the excavated soils or groundwater or air. It is evident that to attain more remedial efficiency some emerging *in-situ* techniques such as nanoremediation and MFCs may be studied in depth. Even the new technologies can be integrated with existing ones to improve the performance and overcome limitations of the existing remedial options.

Each technology in this review has been discussed as a complete package by starting with its basic principles, highlighting its advantages and disadvantages, field studies that have been conducted so far, recent advancements, and ending with suggestions for further research. This review highlights the fact that excellence in the research and technology process can be attained only when the remedial techniques are effective for a wide range of pollutants under different field conditions. Moreover, knowledge on the toxicological effects of the newly synthesized or modified materials that are used as key components in new and emerging technologies should be made available. The necessity to develop newer cost-effective, environmentally friendly, and reliable remedial techniques is high because contaminants are being discovered on a daily basis, and the load of contaminants in the ecosystem is increasing due to extensive industrialization. Thus, in order to pave the way for a healthy environment for future generations to enjoy, more challenging research focusing on the limitations of the existing as well as emerging remediation technologies during field-scale applications is demanded.

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Lead Exposure and Oxidative Stress: A Systematic Review

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1 Introduction

Lead is an environmental toxicant that can induce oxidative stress (OS) via reactive oxygen species (ROS) generation, which has been reported as an important mechanism underlying lead toxicity (Gurer and Ercal 2000; Pande and Flora 2002; Kasperczyk et al. 2004a; Farmand et al. 2005; Verstraeten et al. 2008; Wang et al. 2009; Martinez-Haro et al. 2011). OS occurs when the generation of ROS exceeds the antioxidant system's ability to defend cells against oxidized molecules. ROS is a term generally used to refer to free radicals derived from O_2 (e.g., superoxide anions [O_2^-] and hydroxyl radicals [OH^-]) or to non-radical species (e.g. hydrogen peroxide [H_2O_2]) (Halliwell and Cross 1994).

Epidemiological and experimental studies have evidenced the occurrence of adverse health effects at progressively lower levels of lead exposure (Davis et al. 1993). Lead-induced OS due to chronic lead exposure can initiate subsequent events that may lead to the development of hypertension and cardiovascular disease (Vaziri and Khan 2007). Lead has also been shown to affect the hematological system through red blood cell injuries caused by OS (Gurer-Orhan et al. 2004; EPA 2013). Lead-induced OS by ROS generation also represents a mechanism underlying lead neurotoxicity (Verstraeten et al. 2008). Jia et al. (2012) observed that lead promoted OS in the human mesangial cells, which can be an important mechanism underlying lead-induced nephrotoxicity. Moreover, lead has been proven to affect numerous systems throughout the body, including the hormonal, immune, and gastrointestinal systems, at different blood lead levels (BLLs) (EPA 2013).

In addition to an increase in ROS generation, a decrease in the activity of the antioxidant system or alterations of both could lead to lead-induced OS (Vaziri et al. 2003). Therefore, different antioxidant enzymes and molecules have been evaluated to analyze lead-induced OS in both clinical and experimental studies (Wang et al. 2007). Several studies have shown that the effect of lead on antioxidant enzymes and other components of the antioxidant system, such as superoxide dismutase (SOD), catalase (CAT), glutathione peroxidase (GPx), and reduced glutathione (GSH), depends on the level of lead to which the subjects are exposed. These divergent results have been observed in general and in occupationally exposed populations (Kasperczyk et al. 2004a; Ahamed et al. 2008; Mohammad et al. 2008; Kasperczyk et al. 2009; Grover et al. 2010; Wieloch et al. 2012). Malondialdehyde (MDA) and thiobarbituric acid-reactive substances (TBARS) are products of lipid peroxidation (LPO) that can occur in the presence of lead. Many studies have observed increased levels of MDA or TBARS related to higher BLLs, suggesting an increase in LPO as a consequence of ROS (Ercal et al. 2001).

In view of the influence of OS on lead toxicity and its relation to lead-related diseases, we performed a systematic review of the epidemiologic evidence on the association of lead exposure with OS in the general and in occupationally exposed populations. Although there are several studies on this subject in the literature, this systematic review seeks to discuss possible explanations for inconsistencies and similarities in studies conducted in different contexts and situations and with possible variations in the methodology for collecting and analyzing the variables of interest. Such an analysis is essential for expanding knowledge and identifying gaps in the relationship between lead and OS biomarkers.

2 Sources and Types of Epidemiological Evidence

The electronic databases PubMed (http://www.ncbi.nlm.nih.gov/sites/entrez?db=pubmed), TOXLINE (http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?TOXLINE), and Web of Knowledge (http://apps.webofknowledge.com.ez78.periodicos.capes.gov.br/WOS_GeneralSearch_input.do?product=WOS&search_mode=GeneralSearch&SID=3BpD4JEBm5kK9iK3Lm3&preferencesSaved=) were searched to identify observational studies that analyzed individual data about the relationship between BLL and OS by using key words (Appendix 1), with no language restrictions, through February 2014. Studies lacking original data, human research, case series, case reports, ecologic studies, or guidelines, and studies with no data on lead exposure or OS outcomes were excluded from the analysis. For multiple publications on the same population, we included the most recent publication or the one that included the largest sample population. Studies that analyzed different OS biomarkers on the same population were included in the review.

For lead exposure, we considered studies that used BLLs and aminolevulinic acid (ALA) for lead assessment. We excluded publications that had measured lead or OS biomarkers in biological matrices different than blood and urine.

A total of 1430 articles were identified (522 in PubMed, 443 in TOXLINE, and 465 in Web of Knowledge). Appendix 1 displays the selection process of the study.

The selected studies in the present review were evaluated according to the criteria described in the Tables 1 and 2.

3 Lead-Induced Oxidative Stress in the General Population

Twelve studies met our inclusion criteria (i.e., 6 case-control and 6 cross-sectional studies). Among these, 4 studies were from India, 2 were from Senegal and the others were from China, Poland, South Korea, United States and Argentina (Table 3).

All of the analyzed studies presented significant differences between BLLs and at least 1 biomarker of OS measured in the study, and aminolevulinic acid dehydratase (δ-ALAD) activity was found to be negatively correlated with BLLs in the 5 studies that measured this biomarker (Table 3). All case-control studies identified significantly higher BLLs between the case and control groups (controls, 1.4–10.37 μg/dL *vs.* cases, 2.36–28.2 μg/dL). BLLs were higher in case groups in which the participants had some diagnosed disease, such as, neurological disorders (BLL, 18.6 ± 7.93 μg/dL), aplastic anemia (BLL, 9.86 ± 2.04 μg/dL) and prostate cancer (BLL, 28.2 ± 22.0 μg/dL) (Siddiqui et al. 2002; Ahamed et al. 2008, 2011) than in

Table 1 Criteria for evaluating the design and data analysis of epidemiologic studies of blood lead levels and oxidative stress biomarkers on general populations

	Lead exposure was assessed at the individual level	Sampling method[a]	Outcomes were based on objective tests/standard criteria in ≥ 90 % of study participants	Authors presented internal comparisons within study participants	Adjustment[b]	Exclusion criteria and data collection were similar to all participants	Response rate among no cases was at least 70 %
Hong et al. (2013)	Y	Y	Y	Y	+++	Y	–
Wu et al. (2013)	Y	Y	Y	Y	+++	U	Y
Martinez et al. (2013)	Y	Y	Y	Y	++	Y	–
Wieloch et al. (2012)	Y	U	Y	Y	N	U	Y
Cabral et al. (2012)	Y	U	Y	Y	++	Y	Y
Ahamed et al. (2011)	Y	Y	Y	Y	+	Y	Y
Ahamed et al. (2008)	Y	Y	Y	Y	N	Y	Y
Jin et al. (2006)	Y	Y	Y	Y	N	U	–
Ahamed et al. (2006)	Y	N	Y	Y	N	U	–
Diouf et al. (2006)	Y	U	Y	Y	+++	U	-
Lee et al. (2006)	Y	Y	Y	Y	+++	Y	–
Siddiqui et al. (2002)	Y	U	Y	Y	++	U	Y

– not applicable, *U* unclear, *N* no, *Y* yes

[a] Include diagnostic criteria to identify cases and selection methods of controls

[b] Adjusted for sex (+), adjusted for sex and age (++), adjusted for other variables besides sex and age (+++)

Table 2 Criteria for evaluating the design and data analysis of epidemiologic studies of blood lead levels and oxidative stress biomarkers on occupationally exposed populations

	Lead exposure was assessed at the individual level	Sampling method[a]	Outcomes were based on objective tests/standard criteria in ≥ 90 % of study participants	Authors presented internal comparisons within study participants	Adjustment[b]	Exclusion criteria and data collection were similar to all participants	Response rate among no cases was at least 70 %
Rendon-Ramirez et al. (2014)	Y	Y	Y	Y	+	Y	Y
Mazumdar and Goswami (2014)	Y	Y	Y	Y	++	U	Y
Singh et al. (2013)	Y	Y	Y	Y	+++	Y	Y
Kasperczyk et al. (2013a)	Y	Y	Y	Y	+	Y	Y
Kasperczyk et al. (2013b)	Y	Y	Y	Y	++	Y	Y
Kasperczyk et al. (2013c)	Y	Y	Y	Y	++	Y	Y
Kasperczyk et al. (2013d)	Y	Y	Y	Y	+	Y	Y
Kasperczyk et al. (2012)	Y	Y	Y	Y	+	Y	Y
Feksa et al. (2012)	Y	Y	Y	Y	N	Y	Y
Conterato et al. (2013)	Y	Y	Y	Y	+++	Y	Y
Permpongpaiboon et al. (2011)	Y	Y	Y	Y	++	Y	Y
Malekirad et al. (2010)	Y	Y	Y	Y	+	Y	Y
Grover et al. (2010)	Y	Y	Y	Y	+++	Y	Y
Kasperczyk et al. (2009)	Y	Y	Y	Y	+	Y	Y
Mohammad et al. (2008)	Y	Y	Y	Y	++	Y	Y
Khan et al. (2008)	Y	Y	Y	Y	++	Y	Y
Ergurhan-Ilhan et al. (2008)	Y	Y	Y	Y	+++	Y	Y
Garçon et al. (2007)	Y	Y	Y	Y	+++	Y	Y
Patil et al. (2006a)	Y	Y	Y	Y	N	Y	Y
Patil et al. (2006b)	Y	Y	Y	Y	N	Y	Y

(continued)

Table 2 (continued)

	Lead exposure was assessed at the individual level	Sampling method[a]	Outcomes were based on objective tests/standard criteria in ≥ 90 % of study participants	Authors presented internal comparisons within study participants	Adjustment[b]	Exclusion criteria and data collection were similar to all participants	Response rate among no cases was at least 70 %
Han et al. (2005)	Y	Y	Y	Y	+++	Y	Y
Kasperczyk et al. (2004a)	Y	Y	Y	Y	N	Y	Y
Kasperczyk et al. (2004b)	Y	Y	Y	Y	+	Y	Y
Oktem et al. (2004)	Y	Y	Y	Y	N	Y	Y
Gurer-Orhan et al. (2004)	Y	Y	Y	Y	+++	Y	Y
Yucebilgiç et al. (2003)	Y	U	Y	Y	+	U	Y
Wasowicz et al. (2001)	Y	Y	Y	Y	N	U	Y
Ye et al. (1999)	Y	U	U	Y	+++	U	U
Tenchova et al. (1997)	Y	U	Y	Y	+++	U	U
Costa et al. (1997)	Y	U	Y	Y	+	U	Y
Chiba et al. (1996)	Y	U	Y	Y	+	U	N
Solliway et al. (1996)	Y	Y	Y	Y	+++	Y	Y
Sugawara et al. (1991)	Y	N	U	Y	N	U	U
Ito et al. (1985)	Y	Y	Y	Y	+	Y	N
Monteiro et al. (1985)	Y	U	Y	Y	N	U	Y
Roels et al. (1975)	Y	U	Y	Y	N	U	Y

— not applicable, *U* unclear, *N* no, *Y* yes

[a] Include diagnostic criteria to identify cases and selection methods of controls

[b] Adjusted for sex (+), adjusted for sex and age (++), adjusted for other variables besides sex and age (+++)

Table 3 Epidemiologic studies of lead exposure and oxidative stress in general populations

First author (year)	City, Country	Study objective	Study design Statistical analysis Adjustment	Population			Lead assessment	Blood lead level (mean ± SD in μg/dL[a])	Pb-induced oxidative stress biomarkers	Main results
				Setting	No. of cases/no cases	Age range or mean (years)				
Hong et al. (2013)	Seoul and Incheon, Republic of Korea	Investigate the interaction between dietary antioxidants and BLL on OS level	Cross-sectional GM, ANOVA, simple regression, Scheffe multiple comparison test, partial correlation, multivariate linear regression analysis Age, sex, education, BMI, smoke, alcohol intake, exercise and nutritional supplement.	Adults aged 40 years old or more	683	51.4	BLL	GM: 4.0	8-OHdG	The level of urinary 8-OHdG was greater in participants in the highest quartile of BLL (GM = 6.8μg/dL) than those in the lowest BLL quartile (GM = 2.4μg/dL)
Wu et al. (2013)	Taiwan	Explore the differences between the BLL or OS levels of immigrants and non-immigrants, and to explore the duration of immigrant residency in relation to BLL or OS levels	Case-control *t*-test, trend analysis, χ^2-test, linear and logistic regression Education, cigarette and environmental tobacco smoke exposure, alcohol intake and duration of residence.	Cases: nonpregnant immigrant women No cases: local non-immigrant and nonpregnant women of a similar age range	Cases: 239 (137 recent immigrants/102 less recent immigrants) No cases: 189	Cases: recent immigrants (27.9)/ less-recent (30.6) No cases: 30	BLL	Cases: recent immigrants (2.67)/ less-recent (2.40) No cases: 2.33	MDA, SOD	MDA concentrations were significantly associated with BLL and with the duration of residence in Taiwan. SOD activity was not significantly associated with BLL

(continued)

Table 3 (continued)

First author (year)	City, Country	Study objective	Study design Statistical analysis Adjustment	Population			Lead assessment	Blood lead level (mean ± SD in µg/dL[a])	Pb-induced oxidative stress biomarkers	Main results
				Setting	No. of cases/no cases	Age range or mean (years)				
Martinez et al. (2013))	Cordoba, Argentina	Evaluate BLL in children to compare with other studies performed before Pb was banned in gasoline in 1996	Cross-sectional Mean, Shapiro-Wilk normality test, ANOVA, linear regression Socioeconomic profile and age	Children who attended in a hospital (randomly chosen) (84 female and 77 male)	161	1 month to 14 years	BLL, δ-ALAD	2.58 ± 0.30	SOD, CAT	SOD and CAT activities were not correlated with BLL or with δ-ALAD. Results showed a no linear correlation between these enzymes activities and BLL
Wieloch et al. (2012)	Mogilno, Poland	To prove whether anthropogenic pollution affects antioxidant defense mechanisms such as SOD and CAT activity	Case-control Arithmetic mean, multiple regression	Cases: volunteers from polluted area No cases: volunteers from unpolluted areas	79/82	<60	BLL	Cases: 2.36 ± 2.7 No cases: 1.4 ± 0.7	SOD, CAT, TAS	SOD activity of volunteers from polluted area was over two times higher than those volunteers from unpolluted area. CAT activity was lower in volunteers from polluted area than those from unpolluted area

Cabral et al. (2012)	Senegal	Determine the BLL and changes in OS biomarkers in children living in a contaminated area	Case-control Mean, Mann–Whitney *U*-test, linear regression	Cases: children living near an exposed site No cases: children living in the control site	Cases: 26 (17 boys and 9 girls) No cases: 32 (25 boys and 7 girls)	Cases: 8.9±4.0 No cases: 8.3±4.3	BLL, ALA, ZPP	Cases: 14.8 ± 9.7 No cases: 8.2 ± 3.2	MDA, GSH, GSSG, GSSG/GSH	MDA levels were significantly higher in children living in the exposed site versus the control site. GSH and GSSG/GSH showed no significant changes with raised BLL
Ahamed et al. (2011)	Lucknow, India	Evaluate the effect of BLL on OS parameters in children with aplastic anemia.	Case-control Mean, linear regression	Cases: children with aplastic anemia (15 male and 2 female) No cases: healthy children (45 male and 6 female)	17/51	3 to ≤12	BLL, δ-ALA, δ-ALAD	Cases: 9.86 ± 2.04 No cases: 4.23 ± 1.23	GSH, LPO, CAT	BLL were higher and ALAD was lower in study group than in controls. LPO and CAT activity were higher while GSH was significantly lower in study group than in control

(continued)

Table 3 (continued)

First author (year)	City, Country	Study objective	Study design Statistical analysis Adjustment	Population			Lead assessment	Blood lead level (mean ± SD in μg/dL^a)	Pb-induced oxidative stress biomarkers	Main results
				Setting	No. of cases/no cases	Age range or mean (years)				
Ahamed et al. (2008)	Lucknow, India	Determine BLL and oxidant/antioxidant status as a measure of lead-induced ROS generation in children with neurological disorders	Case-controls Mean, linear regression	Cases: children with neurological disorders (22 male and 8 female) No cases: healthy children (43 male and 17 female)	30/60	3–12	BLL, ALAD, ALA	Cases: 18.60 ± 7.93 No cases: 10.37 ± 5.08	MDA, GSH, SOD, CAT, GPx	BLL were higher and ALAD was lower in study group. MDA concentrations, SOD and CAT activities were significantly higher and GSH was lower in study group than in control
Jin et al. (2006)	Anshan, China	Investigate the role of OS in lead-induced toxicity in preschool children	Cross-sectional ANOVA, GM	Children living in urban area (217 male and 191 female)	408	3–6	BLL, ALAD	6.9 ± 1.8	MDA, SOD, GSH, GPx	ALAD was significantly lower in children with higher BLL. MDA were higher in children with BLL ≥10 μg/dL than in children with BLL <10 μg/dL. SOD and GPx activities and GSH levels showed no significant changes with raised BLL

Ahamed et al. (2006)	Uttar Pradesh, India	Determine the proportion of urban adolescents with BLL >10 μg/dL and its impact on selected OS parameters and ALAD inhibition.	Cross-sectional Mean, linear regression	Randomly selected urban adolescents (male)	39	15–18	BLL, ALA, ALAD	9.96 ± 3.63	GSH, CAT, MDA	ALAD was significantly lower while CAT and MDA were higher in adolescents with BLL >10 μg/dL. Differences in GSH levels were not statistically significant between groups
Diouf et al. (2006)	Khombole and Dakar, Senegal	Investigate BLL in Senegalese children and to present data on the relationship between BLL and changes in biological markers of heme biosynthesis and OS	Cross-sectional GM, ANOVA, Spearman correlation	Children living in rural area (92 male and 70 female) and in urban area (92 male and 76 female)	330 (162 in rural area and 168 in urban area)	8–12	BLL, ALAU	7.32 ± 5.33 (all children) Urban children: 9.97 ± 3.93 Rural children: 5.21 ± 5.86	GSSG/GSH ratio, SOD, GPx, GR	Urban children have higher BLL than rural children and boys have higher BLL than girls. GPx was correlated with BLL ($r = -0.235$) and was lower in children of both gender living in urban area. SOD presented no significant changes between groups

(continued)

Table 3 (continued)

First author (year)	City, Country	Study objective	Study design Statistical analysis Adjustment	Population			Lead assessment	Blood lead level (mean ± SD in µg/dL[a])	Pb-induced oxidative stress biomarkers	Main results
				Setting	No. of cases/no cases	Age range or mean (years)				
Lee et al. (2006)	United States	Examine associations of BLL with OS marker GGT.	Cross-sectional GM, linear regression Race, sex, age, education, poverty income ratio, BMI, smoking status and amount, alcohol intake	Randomly selected American population	10.098	≥20	BLL	2.80	GGT	Even after adjustment, serum GGT was positively associated with BLL
Siddiqui et al. (2002)	Lucknow, India	Determine BLL and possible relations of MDA and GSH status with lead exposure.	Case-control Mean, regression analysis	Cases: BPH and PCA patients admitted to a hospital No cases: men living in the same socioeconomic environment	Cases: BPH (40) PCA: (17) No cases: 20	53.1–71.0	BLL	Cases: PCA (28.2 ± 22.0) BPH: (23.4 ± 19.6) No Cases: 10.2 ± 10.0	MDA, GSH	BLL were significantly higher in PCA and BPH groups than in controls. GSH was significantly decreased and MDA was raised only in PCA group compared to controls

N number, *SD* standard deviation, *Pb* lead, *BLL* blood lead level, *OS* oxidative stress, *GM* geometric mean, *BMI* body mass index, *8-OHdG* 8-hydroxydeoxyguanosine, *MDA* malondialdehyde, *SOD* superoxide dismutase, *δ-ALAD* δ-aminolevulinic acid dehydratase, *CAT* catalase, *TAS* total antioxidant status, *δ-ALA* δ-aminolevulinic acid, *ZPP* zinc protoporphyrin, *GSH* glutathione, *GSSG* glutathione disulfide, *GSSG/GSH ratio* glutathione disulfide/glutathione ratio, *LPO* lipid peroxidation, *ROS* reactive oxygen species, *GPx* glutathione peroxidase, *ALAU* urinary d-aminolevulinic acid, *GR* glutathione reductase, *GGT* γ-glutamyltransferase, *BPH* benign prostate hyperplasia, *PCA* prostate cancer

[a] Units of measurement of blood lead levels were patronized into µg/dL

case groups in which participants had not been diagnosed with a disease (2.36 ± 2.7 μg/dL; Table 3) (Wieloch et al. 2012).

The most frequently used biomarkers for Pb-induced OS were as follows: GSH (Siddiqui et al. 2002; Ahamed et al. 2006, 2008, 2011; Diouf et al. 2006; Jin et al. 2006; Cabral et al. 2012), MDA (Siddiqui et al. 2002; Ahamed et al. 2006, 2008, 2011; Jin et al. 2006; Cabral et al. 2012; Wu et al. 2013), SOD (Jin et al. 2006; Diouf et al. 2006; Ahamed et al. 2008; Martinez et al. 2013; Wieloch et al. 2012; Wu et al. 2013), CAT (Ahamed et al. 2006, 2008, 2011; Wieloch et al. 2012; Martinez et al. 2013), and GPx (Diouf et al. 2006; Jin et al. 2006; Ahamed et al. 2008) (Table 3).

Three studies found significantly lower GSH levels in study groups (Siddiqui et al. 2002; Ahamed et al. 2008, 2011). Among these, the studies by Siddiqui et al. (2002) and Ahamed et al. (2008) identified a negative correlation between BLL and GSH levels ($r = -0.32$, $p < 0.05$ and $r = -0.31$, $p = < 0.05$, respectively). Three studies did not find significant changes in GSH levels with increase in BLLs (Ahamed et al. 2006; Jin et al. 2006; Cabral et al. 2012). Additionally, 2 studies evaluated the GSSG/GSH ratio. One of these found it to be elevated in the children living in the urban area compared to those living in the rural area (Diouf et al. 2006), while the other study did not find an association between GSSG/GSH ratio and BLLs (Cabral et al. 2012).

LPO was assayed by measuring the formation of MDA in 6 studies (Siddiqui et al. 2002; Ahamed et al. 2006, 2008; Jin et al. 2006; Cabral et al. 2012; Wu et al. 2013) and the formation of TBARS in 1 study (Ahamed et al. 2011). MDA concentrations were significantly higher in subjects with higher BLLs in all the studies, with a positive correlation between BLLs and MDA concentrations in the studies by Siddiqui et al. (2002), Ahamed et al. (2008) and Cabral et al. (2012), ($r^2 < 0.392$, $p < 0.01$; $r = 0.77$, $p < 0.05$ and $r = 0.37$, $p < 0.05$, respectively).

Two studies verified elevated SOD activity in the study groups when compared with the controls (Ahamed et al. 2008; Wieloch et al. 2012), and 4 studies found no significant changes in SOD activity with raised BLLs (Jin et al. 2006; Diouf et al. 2006; Martinez et al. 2013; Wu et al. 2013). CAT activity was also significantly higher in participants with higher BLLs in 3 studies (Ahamed et al. 2006, 2008, 2011) but was substantially lower in subjects with higher BLLs in 1 study (Wieloch et al. 2012).

There were no significant changes in GPx activity associated with increased BLLs in 2 studies (Jin et al. 2006; Ahamed et al. 2008), and in 1 study, there was a negative correlation between GPx activity and BLL ($r = -0.235$; $p < 0.01$) (Diouf et al. 2006). Also, the OS biomarkers, 8-hydroxydeoxyguanosine (8-OHdG) and γ-glutamyltransferase (GGT), were positively associated with BLLs in two studies (Lee et al. 2006; Hong et al. 2013).

4 Lead-Induced Oxidative Stress in Occupationally Exposed Populations

All the analyzed studies had case-control designs. Most of the studies were from the European and Asian continents, and 4 were from South America (Table 4).

MDA, SOD, CAT, GPx, and GSH were the biomarkers that were most studied for their association with BLLs and the ALAD index was most studied with respect

Table 4 Epidemiologic studies of lead exposure and oxidative stress in occupationally exposed populations

First author (year)	City, Country	Study objective	Study design Statistical analysis adjustment	Population	
				Setting	No. of cases/ no cases
Rendon-Ramirez et al. (2014)	Mexico	Study the antioxidant benefits of vitamin C and E supplementation and its effects on the enzymatic system.	Case-control Mean, *t*-test	Cases: recycling battery factory workers No cases: healthy workers non-exposed to lead (male)	15/19
Mazumdar and Goswami (2014)	Kolkata, West Bengal, India	Evaluate the effect of occupational lead exposure on hepatic function and hematological aberrations	Casecontrol Mean, *t*-test Age	Cases: plastic industry workers No cases: non-exposed (male)	47/42
Singh et al. (2013)	India	Assess the genotoxicity and OS due to lead in battery manufacturing workers	Case-control Mann Whitney *U*-test, ANOVA, Pearson correlation Sex, ses, age, diet, smoking and alcohol consumption	Cases: battery manufacturing industry workers No cases: Non occupationally exposed, matched subjects	Cases: 24 male and 6 female No cases: 23 male and 7 female
Kasperczyk et al. (2013a)	Miasteczko Śląskie, Poland	Explore the connection between lead toxicity and the activity of XO and MDA concentration	Case-control ANOVA, Levene's test, Shapiro Wilk's test, *t* test, Mann–Whitney *U*-test, Spearman	Cases: employees of a lead-zinc industry (workers with chronic diseases or receiving any drugs were excluded) No cases: healthy administrative workers nonoccupationally exposed to lead (male)	Cases: 125 (42 low tertile/41 medium tertile and 42 high tertile)/ No cases: 32

Age (mean ± SD or range years)	Lead assessment	Blood lead level (mean ± SD or range in µg/dL[a])	Pb-induced oxidative stress biomarkers	Main results
NR	BLL, ALAD	Cases: 73.0±11.0 No cases: 6.7±2.2	LP, TAC, SOD, GPx, GRx	LP, TAC, CAT and SOD were significantly higher in cases compared with controls. GPx activity was not different between the groups
Cases: 18–60 No cases: 20–62	BLL, ALA-U	Cases: 59.6±6.5 No cases: 12.3±3.2	LP	TBARS was increased in cases compared with controls
Cases: 36.90 ± 12.78 No cases: 37.80 ± 13.34	BLL	Cases: 57.17±18.4 No cases: 5.43±1.94	MDA	MDA was positively correlated with BLL ($r = 0.895$; $p < 0.001$). MDA were found to increase with the increasing duration of exposure and were higher in smokers and drinkers than in controls
Cases: 23–59 No cases: 28–57	BLL, ZPP, ALA-U	Cases tertiles: low- 26.10±4.52 medium- 36.20±2.60 high- 45.60±4.08 No cases: 7.88±2.44	XO, MDA	XO activity was significantly elevated in all BLL tertile compared to the control group and was significantly elevated in the high tertile of BLL. MDA concentration was increased in all tertile compared with control group. XO and MDA were positively correlated with BLL ($r = 0.26$ and 0.30; $p < 0.05$)

(continued)

Table 4 (continued)

First author (year)	City, Country	Study objective	Study design Statistical analysis adjustment	Population	
				Setting	No. of cases/ no cases
Kasperczyk et al. (2013b)	Southern region, Poland	Examine the association between occupational lead exposure and blood rheological parameters with respect to MDA, LPS and GSH concentrations in erythrocytes	Case-control Levene's test, Shapiro Wilk's test, *t*-test, Mann–Whitney *U*-test, Spearman	Cases: employees of lead-zinc manufacturing (workers with chronic diseases were excluded) No cases: healthy administrative workers (workers with former occupational exposure and with chronic diseases excluded) (male)	Cases: 210 (129 low exposed/ 154 high exposed) No cases: 73
Kasperczyk et al. (2013c)	Southern region, Poland	Investigate the influence of occupational lead exposure on LP and PC	Case-control Mean, Shapiro Wilk's test, Levene's test, ANOVA, Kruskal-Wallis, *t*-test, Mann–Whitney *U*-test, post hoc tests, χ^2 test, Spearman	Cases: healthy employees of lead-zinc manufacturing No cases: administrative workers (male)	Cases: 283 (79 low exposed/ 121 medium exposed/83 high exposed) No cases: 73
Kasperczyk et al. (2013d)	Southern region, Poland	Evaluate the influence of lead on GSH in erythrocytes in individuals exposed to lead and to evaluate OS, measured as the CP concentration in serum	Case-control Mean, Shapiro Wilk's, Levene's, Kruskal-Wallis, ANOVA, *t*-test, Mann–Whitney *U*-test, Spearman, χ^2 test	Cases: employees of metal work plants No cases: office workers or other healthy subjects with no history of occupational exposure to lead	Cases: 183 (102 low exposed/ 81 high exposed) No cases: 72

Age (mean ± SD or range years)	Lead assessment	Blood lead level (mean ± SD or range in µg/dL[a])	Pb-induced oxidative stress biomarkers	Main results
Cases: 41.0±9.23 No cases: 41.5±9.23	BLL, ZPP, ALA-U	Cases subgroups: low exposed- 32.31±5.54 high exposed- 45.92±4.03 No cases: 6.45±2.49	MDA, LPS, GSH	MDA and LPS concentrations were increased in the low exposed group by 55 % and 267 %, respectively, and in the high exposed group by 43 % and 254 %, respectively. GSH was significantly reduced in the low exposed group by 12 % and in the high exposed group by 11 %. MDA and LPS were positively correlated with BLL
Cases: 41.0±9.23 No cases: 41.5±9.23	BLL, ZPP, ALA-U	Cases subgroups: low exposed- 35.0 medium exposed- 35.0 to 45.0 high exposed- > 45.0 No cases: 6.45±2.49	CD, LHP, PC, MDA	CD, LHP, MDA, and PC levels were significantly increased by, respectively, 21 %, 352 %, 13 %, and 112 % in the low exposed group, by 25 %, 471 %, 36 %, and 94 % in the medium exposed group, and by 27 %, 370 %, 41 %, and 97 % in the high exposed group. BLL was positively correlated with CD, LHP, MDA and PC levels
Cases: low exposed- 40.5±10.42 high exposed- 43.9±7.44 No cases: 41.55±9.23	BLL, ZPP	Cases subgroups: low exposed- 38.4±5.44 high exposed-49.2±4.01 No cases: 6.45±2.49	CP	CP concentration increased 108 % in the low exposed group and 125 % in the high exposed group. CP was positively correlated with BLL and duration of lead exposure

(continued)

Table 4 (continued)

First author (year)	City, Country	Study objective	Study design Statistical analysis adjustment	Population	
				Setting	No. of cases/ no cases
Kasperczyk et al. (2012)	Southern region, Poland	Understand the influence of occupational lead-exposure on the gene expression and activity of SOD, CAT and GPx in leukocytes and erythrocytes	Case-control Mean, Shapiro Wilk's test, Levene's test, Student's *t* test, Mann–Whitney *U*-test	Cases: healthy workers of a lead-zinc industry No cases: healthy administrative workers (male)	45/17
Feksa et al. (2012)	Rio Grande do Sul, Brazil	Investigate the effect of lead on the activity of ALAD and PK and on GSH concentration	Case-control Mean, Student *t* test, linear regression	Cases: workers of manufacturing and recycling automotive batteries (male) No cases: volunteers with no history of lead exposure (male and female); excluded persons with severe CV, renal, hepatic, endocrine, metabolic or GI diseases or pharmacological treatment	Cases: 22 (all male) No cases: 21 (15 men and 6 women)
Permpongpaiboon et al. (2011))	Thailand	Explore the association between lead exposure and OS status as well as PON I activity	Case-control Mean, Mann–Whitney *U*-test, Pearson and Spearman correlation	Cases: earthenware factory workers No cases: people with no history of occupational lead exposure (male and female)	60/65

Age (mean ± SD or range years)	Lead assessment	Blood lead level (mean ± SD or range in µg/dL[a])	Pb-induced oxidative stress biomarkers	Main results
Cases: 24–58 No cases: 21–60	BLL, ZPP	Cases subgroups: low exposed group- 42.93±10.26; high exposed group-48.50 ±7.07 No cases: 5.71±1.99	GPx, GSSG, SOD, CAT	SOD activity of leukocytes was significantly increased (40 %) in the low exposed group. SOD activity in erythrocytes was elevated in both low (30 %) and high exposed (33 %) groups. GPx activity in erythrocytes was significantly elevated in the low and high exposed groups compared to the control group by 81 % and 67 %, respectively. CAT activity was not significantly changed
Cases: 20±50 No cases: 20±48 (men) 18±49 (women)	BLL	Cases: 1.88±0.39 No cases: 61.9±10.33	PK, GSH	GSH concentration was decreased in cases compared with controls. Pb significantly inhibited PK activity in a dose-dependent manner. BLL was negatively correlated with GSH and PK
Cases: 41.0 ± 1.1 No cases: 38.2 ± 1.3	BLL	Cases: 31.4 ± 2.5 No cases: 3.9 ± 0.2	CD, MDA, TAS, TP, OSI, PON I	CD, TP, MDA and OSI levels were significantly increased in lead exposed group compared to the control. BLL at 10 µg/dL significantly decreased PON I activity

(continued)

Table 4 (continued)

First author (year)	City, Country	Study objective	Study design Statistical analysis adjustment	Population	
				Setting	No. of cases/ no cases
Conterato et al. (2013)	Rio Grande do Sul, Brazil	Evaluate the BLL and the relationship with hematological and OS parameters	Case-control Mean, ANOVA, Duncan's test, Kruskal-Wallis, multiple comparison test, χ^2 test, Spearman	Cases: automotive battery-manufacturing workers and painters from automotive industry No cases: healthy workers nonoccupationally exposed (male)	Cases: 50 (painters)/ 23 (battery workers) No cases: 36
Malekirad et al. (2010)	Arak, Iran	Determine OS status and BLL.	Case-control Variance analyzes and Pearson correlation	Cases: zinc and lead mine workers No cases: farm workers selected from a village close to the mine, with no history of lead exposure (male)	67/67
Grover et al. (2010)	Hyderabad, India	Assess the genotoxicity of lead.	Case-control Mean, multiple linear regression analysis	Cases: lead recovery unit workers No cases: subjects from the general population with no history of lead exposure (male)	90/90
Kasperczyk et al. (2009)	Southern region, Poland	Determine BLL and ZPP levels and estimate the levels of OS biomarkers.	Case-control Mean, Shapiro-Wilk´s, Levene´s test, ANOVA, Mann–Whitney *U*- test, Spearman	Cases: employees of metal works No cases: office workers with normal blood pressure and not occupationally exposed to lead (male)	92–30

Age (mean ± SD or range years)	Lead assessment	Blood lead level (mean ± SD or range in μg/dL[a])	Pb-induced oxidative stress biomarkers	Main results
Cases: battery-workers -15 to 61 painters—21 to 54 No cases: 21 to 49	BLL, ALAD	Cases: battery-workers—49.8±4.0 painters—5.4±0.4 No cases: 1.5±0.1	Glutathione-*S*-transferase, GSH, GPx, SOD, CAT, TrxR, MDA, vitamin C, PC, MetHb	MDA was not correlated with BLL. GSH was higher in painters but not in battery-workers compared with controls. GPx and SOD were higher only in battery-workers compared with controls. CAT was decreased only in painters compared with controls and was negatively correlated with the duration of exposure
Cases: 39.7 ± 8.27 No cases: 41.4 ± 10.2	BLL	Cases: 9.6 ± 3.3 No cases: 5.1 ± 3.1	SOD, CAT, GR, MPO, 8-OHdG, TAC, LPO	BLL, SOD, GR and MPO were significantly higher in workers than in controls. LPO and CAT showed no significant difference and 8-OH-Dg concentration was lower in workers compared with controls
Cases: 34 No cases: 31	BLL, ALA, ALAD	Cases: 30.3 ± 2.1 No cases: 3.2 ± 0.3	SOD, CAT, GPx, MDA	BLL were significantly elevated in exposed than in controls. SOD, CAT and GPx were decreased in workers than in controls and MDA was raised
Cases: 41.9 ± 8.4 No cases: 41.2 ± 11.3	BLL, ZPP	Cases subgroups: Normotensive-41.8 ± 5.6; High-normotensive–41.4 ± 5.0; Hypertensive 1–45.3 ± 4.7; Hypertensive 2-42.7 ± 8.1 No cases: 7.73 ± 1.7	SOD, GPx, MDA	BLL, ZPP, MDA, GPx and SOD were significantly higher in Pb-normotensive group when compared to the normotensive control group. In hypertensive 1 group MDA raised by 48 % and GPx decreased by 30 %. In hypertensive 2 group MDA increased by 72 % and GPx decreased by 43 % in comparison to Pb-normotensive group

(continued)

Table 4 (continued)

First author (year)	City, Country	Study objective	Study design Statistical analysis adjustment	Population	
				Setting	No. of cases/ no cases
Mohammad et al. (2008)	Lucknow, India	Assess the antioxidant status of lead exposed residential and commercial painters	Case-control Mean, Pearson correlation, linear regression analysis	Cases: painters No cases: subjects of the same age group with no occupational lead exposure (male)	35/35
Khan et al (2008)	Wah Cantt, Pakistan	Determine the lead-induced OS and adverse health effects by biochemical markers in lead smelting industrial workers	Case-control Mean, median, Pearson´s correlation	Cases: lead smelting industrial workers No cases: office workers not exposed (male)	87/61
Ergurhan-Ilhan et al. (2008)	Isparta, Turkey	Investigate the effect of lead on the oxidative system in indirectly lead exposed male apprentices.	Case-control Mann–Whitney *U*-test, Pearson correlation Smoking, alcohol consumption and age	Cases: students working in auto-repair workshops No cases: healthy high school students (male)	25/24
Garçon et al. (2007)	France	Evaluate the usefulness of a set of early biological markers of OS or nephrotoxicity for the biomonitoring of workers	Case-control Mean, ANOVA	Cases: Non-ferrous metal smelter No cases: no exposed men matched by age, ses, smoking and drug us (male)	57/57

Age (mean ± SD or range years)	Lead assessment	Blood lead level (mean ± SD or range in μg/dL[a])	Pb-induced oxidative stress biomarkers	Main results
Cases: 32.1 ± 6.1 No cases: 32.8 ± 5.8	BLL, ZPP, ALAD	Cases: 21.9 ± 6.2 No cases: 3.1 ± 1.0	SOD, CAT, GSH, GSSG, MDA	BLL and ZPP were significantly higher, while ALAD was lower in painters than in controls. SOD and CAT activities were decreased in painters compared to controls. MDA was elevated in painters while GSH levels were decreased in painters compared to controls
Cases: 40 ± 10 No cases: 38 ± 11	BLL	Cases: 9.0–61.1 No cases: 1.0–21.7	MDA, GGT	BLL were significantly higher in exposed than in controls and were positively correlated with GGT and MDA concentration
Cases: 16.8 ± 1.2 No cases: 16.3 ± 1.0	BLL, ZPP, ALAD index	Cases: 7.9 ± 5.2 No cases: 2.6 ± 2.0	CAT, SOD, GPx, MDA, α-tocopherol, β-carotene	BLL, ZPP and ALAD index were significantly elevated in workers than in controls. MDA and GPx were increased; α-tocopherol and β-carotene were decreased in workers. SOD and CAT activities were unaltered, but there was a positive correlation between BLL and CAT, MDA and duration of lead exposure. Smoke was not correlated to any of the parameters analyzed
Cases: 44.1 ± 8.9 No cases: 43.5 ± 9.0	BLL, ZPP	Exposed: 38.7 ± 9.9 No exposed: 5.6 ± 3.5	MDA, SOD, GPx, GR, 8-OHdG, Se	BLL were higher in exposed group. ZPP and MDA were significantly increased in exposed compared to controls. SOD and GPx activities were not statistically different between the groups

(continued)

Table 4 (continued)

First author (year)	City, Country	Study objective	Study design Statistical analysis adjustment	Population	
				Setting	No. of cases/ no cases
Patil et al. (2006a)	Kolhapur, India	To examine the effect of BLL on heme biosynthesis, hematopoietic system and OS in workers exposed to lead	Case-control Mean, Pearson´s correlation	Cases: silver jewelry workers No cases: non-occupationally lead exposed healthy men	30/35
Patil et al. (2006b)	Kolhapur, India	Evaluate the activity of SOD and CAT in erythrocytes and MDA in plasma.	Case-control Mean, Pearson correlation	Cases: battery workers No cases: healthy subjects no lead exposed (male)	28/35
Han et al. (2005)	Ulsan, South Korea	Investigate the effects of welding fume exposure on correlates OS in the serum of asymptomatic shipyard welders	Case-control Mean, variance, correlation and regression analysis Smoking, age and lead exposure duration	Cases: shipyard welders No cases: unexposed office workers (male)	197/150
Kasperczyk et al. (2004a)	Miasteczko Slaskie, Poland	Estimate the activity of GPx, GR and MDA in erythrocytes	Case-control Mean, ANOVA	Cases: Zinc and lead steel works No cases: administration workers with normal BLL and ZPP levels	Cases: 75 low exposed/ 62 high exposed No cases: 35

Age (mean ± SD or range years)	Lead assessment	Blood lead level (mean ± SD or range in µg/dL[a])	Pb-induced oxidative stress biomarkers	Main results
20–40	BLL, PBG-U, ALAD, ALA-U, ZPP, PBG	Cases: 48.6 ± 7.4 No cases: 12.5 ± 4.1	MDA, SOD, CAT, ceruloplasmin	BLL were significantly higher in exposed than in controls. MDA was elevated while CAT and SOD were lower in cases than in controls
20–40	BLL, ZPP, ALAD ratio, ALA-U	Cases: 25.8–78.0 No cases: 2.8–22.0	SOD, CAT, MDA	BLL, ZPP and ALAD ratio were significantly higher in exposed group than in controls. MDA was increased in exposed while CAT and SOD were lower than in controls
34.7–37.2	BLL	Cases (all welders): 0.53 Nonsmokers cases: 0.51 Smokers cases: 0.54 No cases: 0.11 ± 0.24	TAS, aconitase, GPx, SOD, isoprostane	TAS, aconitase, GPx and isoprostane were significantly increased in welders compared to control group, but these group differences were not altered by age or smoking. Increasing age was related to lower levels of TAS and SOD and to higher levels of GPx. GPx presented lower levels in current smokers than in nonsmokers. There was no evidence of the influence of welding years in OS biomarkers
Cases: low exposed-40.5 ± 9.9 high exposed-41.7 ± 9.8 No cases: 39.4 ± 10.8	BLL, ALA, ZPP	Cases: low exposed-35.0 ± 9.3 high exposed-44.2 ± 8.1 No cases: 8.6 ± 2.4	GPx, GR, MDA	BLL and ZPP were significantly elevated in workers than in controls. GPx increased by about 79 % in low exposed compared to controls and was statistically lower in high exposed than in low exposed group. MDA were increased in high exposed workers and GR showed no significant changes between the groups.

(continued)

Table 4 (continued)

First author (year)	City, Country	Study objective	Study design Statistical analysis adjustment	Population	
				Setting	No. of cases/ no cases
Kasperczyk et al. (2004b)	Poland	Evaluate the activity of SOD and CAT and concentration of ROS in blood.	Case-control Mean, Mann–Whitney *U*-test, Spearman correlation	Cases: Zinc and lead steel workers No cases: administration workers not exposed to lead with normal BLL and ZPP levels	Cases: 43 low exposed/94 high exposed No cases: 35
Oktem et al. (2004)	Isparta, Turkey	To assess renal adverse effects and OS in long-term low level lead exposure	Case-control Mean, linear regression Smoking	Cases: auto repair workers, No cases: healthy controls subjects (male)	79/71
Gurer-Orhan et al. (2004)	Turkey	Investigate the importance of OS in lead-induced toxicity in hematological system of humans	Case-control Mean, Mann–Whitney *U*-test, linear regression analysis	Cases: battery plants workers No cases: age-matched subjects with no history of occupational exposure (male)	20/16
Yucebilgiç et al. (2003)	Turkey	Examine the relationship between lead and LP	Case-control Mean	Cases: accumulator production workers exposed to lead at least for 10 years No cases: healthy subjects not exposed (male)	Cases: 30 No cases: 20

Age (mean ± SD or range years)	Lead assessment	Blood lead level (mean ± SD or range in µg/dL[a])	Pb-induced oxidative stress biomarkers	Main results
Cases: low exposed-41.0 ± 9.8 high exposed- 41.3 ± 9.8 No cases: 39.4 ± 10.8	BLL, ZPP, ALA	Cases: low exposed-30.3 ± 2.9 high exposed-43.1 ± 5.2 No cases: 9.2 ± 2.7	SOD, CAT, MDA	BLL and ZPP were significantly higher in all exposed groups. MDA and SOD increased in exposed groups than in controls while there were no significant changes in CAT activity between the groups
15–19	BLL, ALAD index	Cases: 3.4–24.8 No cases: 0–3.0	MDA, GPx, SOD, CAT	BLL and ALAD index were significantly higher in the study group than in control. MDA and GPx were elevated in exposed group. SOD and CAT activities did not reached statistical significance between groups. Positive correlation was found between MDA, GPx and BLL
Cases: 35 ± 8 No cases: 32 ± 9	BLL, ZPP, ALAD	Cases: 54.6 ± 17.0 No cases: 11.8 ± 3.2	GSH, MDA, CAT, G6PD, GSSG	GSH, MDA, CAT, G6PD and GSSG were significantly correlated with BLL
25–45	BLL, Na^+ -K^+ ATPase, Ca^{+2} ATPase	Cases: 317.3 ± 47.6 No cases: 10.0 ± 1.8	MDA	MDA concentration was significantly greater in study group than in control group

(continued)

Table 4 (continued)

First author (year)	City, Country	Study objective	Study design Statistical analysis adjustment	Population	
				Setting	No. of cases/ no cases
Wasowicz et al. (2001)	Poland	Investigate BLL and cadmium, trace elements (Se, zinc, copper), TBARS and activity of antioxidant enzymes, to find out the existence of any association between them	Case-control Mean, Mann–Whitney *U*-test, variance and correlation analysis	Cases: lead-acid batteries workers (male) No cases: healthy students or administrative workers of the same region employed in industry (male and female)	43/52
Ye et al. (1999)	China	Explore the presence of OS in workers exposed to lead	Case-control Mean, ANOVA Smoking, alcohol consumption and duration of work	Cases: secondary smelter lead workers No cases: NR (male and female)	66/28
Tenchova et al. (1997)	Bulgarian	State the MDA concentration in lead exposed workers	Case-control Mean, correlation and regression analysis Smoking	Cases: battery workers No cases: subjects not exposed (male)	Cases: 46 No cases: 30
Costa et al. (1997)	São Paulo, Brazil	Characterize the involvement of ALA in lead poisoning.	Case-control Mean, linear regression	Cases: pottery manufacturing plant workers No cases: police preparatory school students (male)	60/30
Chiba et al. (1996)	Japan	Analyze the activity of GPx, SOD, CAT on blood of lead exposed man	Case-control Mean, correlation analysis	Cases: steel rope workers No cases: NR	63/7

Age (mean ± SD or range years)	Lead assessment	Blood lead level (mean ± SD or range in µg/dL[a])	Pb-induced oxidative stress biomarkers	Main results
Cases: 25–52 No cases: 36–51	BLL	Cases: 28.2–75.2 No cases: 3.7–18.0	GPx, TBARS, SOD	BLL were significantly increased in exposed group than in controls as TBARS concentration. GPx was lower in study group while SOD differences were not significant between the analyzed groups
NR	BLL, ALA	Cases: 10 to 33 No cases: 0.9 (median)	MDA, SOD	There was a positive correlation between BLL and MDA levels and SOD activity. Smoking and alcohol consumption did not significantly affect MDA and SOD
Cases: 38.6 ± 2.0 No cases: NR	BLL	Cases and no cases: 2.6–11.6	MDA	MDA concentration was significantly higher in exposed when compared to controls
18–53	BLL, ALA, PP-IX.	Cases: 53.4 ± 1.2 No cases: 6.3 ± 0.2	MetHb, SOD	SOD was positively correlated with BLL
NR	BLL, ALAD, ZPP, FEP	Cases: 17.8 ± 11.5 No cases: 5.7 ± 4.3	GPx, SOD, CAT, Se	ALAD was correlated with BLL (r = −0.79). SOD activities in plasma were not correlated with BLL, but CAT was significantly increased in higher BLL. GPx in the plasma did not change, while those in erythrocytes were lower with increase in BLL

(continued)

Table 4 (continued)

First author (year)	City, Country	Study objective	Study design Statistical analysis adjustment	Population	
				Setting	No. of cases/ no cases
Solliway et al. (1996)	Israel	Evaluate variables with the potential to serve as functional probes of the effects of lead exposure	Case-control Mean, linear regression analysis, ANOVA Smoking	Cases: battery factory workers No cases: subjects not exposed to lead (male)	34–56
Sugawara et al. (1991)	Japan	Determine whether leucocytes and platelets make some difference to the OS of erythrocytes in the presence of lead	Case-control Mean, correlation analysis	Cases: workers occupationally exposed to lead, No cases: NR	NR
Ito et al. (1985)	Japan	Verify if lead exposure increased LPO level and inhibited SOD activity in workers exposed to lead	Case-control Mean, correlation analysis	Cases: manual workers exposed to lead in a steel factory No cases: office workers (male)	712/155
Monteiro et al. (1985)	São Paulo, Brazil	To evaluate SOD and GPx activities in the erythrocytes of lead-exposed workers	Case-control Mean, *t*-test	Cases: 1. chemical plant workers 2. electric-cable manufacturing plant workers 3. lead exposed workers in other industries No cases: 1/2 office workers, sales department, infirmary, storehouse and gardening workers No cases: 3 residents of São Paulo	Cases 1: 12/26 Cases 2: 24/21 Cases 3: 26/27
Roels et al. (1975)	Belgium	Investigate the relationship between BLL, cadmium, ALAD, and GSH levels in erythrocytes	Case-control Mean, correlation coefficient, regression analysis	Cases: Cadmium and lead producing plant workers No cases: students and laboratory staff (male)	84/26

Age (mean ± SD or range years)	Lead assessment	Blood lead level (mean ± SD or range in µg/dL[a])	Pb-induced oxidative stress biomarkers	Main results
Cases: 44 ± 13 No cases: 42 ± 12	BLL, ALA-U	Cases: 23–63 No cases: 1–13	GPx	Erythrocyte GPx was significantly increased in lead exposed subjects
NR	BLL	Cases: 57.1 ± 17.6 No cases: NR	SOD, CAT, GPx, LPO	GSH levels and SOD, CAT and GPx activities were increased in workers
Cases: 18–59 No cases: 40–59	BLL, ALAD	Cases: 4.97 to 62.16 No cases: NR	LPO, SOD	LPO serum was significantly higher in workers than in controls and was greater with an increase of BLL. Inhibition of SOD activity by lead exposure also induced the raise of LPO levels
NR	BLL	Cases 1: 52 ± 21 No cases 1: NR Cases 2: 39 ± 19 No cases 2: 13 ± 8 Cases 3: 69 ± 26 No cases 3: NR	SOD, GPx	In all case groups SOD activity were significantly higher in the exposed workers. GPx activity was also increased in lead exposed workers except for exposed of the case group 2
Cases: 40.7 ± 1.3/ 43.2 ± 2.0	BLL, ALAD ratio	Cases: 27.14 ± 1.04 (subgroup I) 52.21 ± 1.66 (subgroup II) No cases: 13.26 ± 0.62	GR, GSH	ALAD ratio and GSH were highly correlated with BLL (r = −0.76) and (r = −0.42), respectively

(continued)

Table 4 (continued)

N number, *SD* standard deviation, *Pb* lead, *NR* not reported, *BLL* blood lead level, *ALAD* aminolevulinic acid dehydratase, *LPO or LP* lipid peroxidation, *TAC* total antioxidant capacity, *SOD* superoxide dismutase, *GPx* glutathione peroxidase, *GRx* glutathione reductase, *ALA-U* urinary δ-aminolevulinic acid, *TBARS* thiobarbituric acid reactive substances, *OS* oxidative stress, *ses* socioeconomic status, *MDA* malondialdehyde, *XO* xanthine oxidase, *ZPP* zinc protoporphyrin, *LPS* lipofuscin, *GSH* glutathione, *CP or PC* carbonyl protein, *LHP* lipid hydroperoxides, *GSSG* glutathione disulfide, *CAT* catalase, *PK* pyruvate kinase, *CV* cardiovascular, *GI* gastrointestinal, *PON I* paraoxonase I, *TAS* total antioxidant status, *TP* total peroxides, *OSI* oxidative stress index, *TrxR* thioredoxin reductase, *CD* conjugated diene, *PP-IX* protoporphyrin IX, *MetHb* methemoglobin, *FEP* free erythrocyte protoporphyrin, *GR* glutathione reductase, *MPO* myeloperoxidase, *8-OHdG* 8-hydroxydeoxyguanosine, *GGT* gamma glutamyltransferase, *ALAD ratio/index* logarithm of activated δ-aminolaevulinic acid dehydratase/nonactivated δ- aminolaevulinic acid dehydratase, *Se* selenium, *PBG-U* porphobilinogen in urine, *PBG* porphobilinogen, *ROS* reactive oxygen species, *G6PD* glucose-6-phosphate dehydrogenase, *Na* sodium, *K* potassium, *Ca* calcium, *ATPase* adenosine triphosphatase

[a] Units of measurement of blood lead levels were patronized into µg/dL

to Pb-induced OS in occupationally exposed populations. Several other biomarkers were less frequently used to study this relationship (Table 4). The results identified in the present review come from studies involving exposed subjects, most of whom worked in industries such as lead-smelting, battery, and recovery factories. In most studies, control groups comprised office workers or healthy people with no history of lead exposure.

Table 4 shows that MDA levels were the most frequently used biomarker for measuring LPO. Twenty studies found MDA levels to be significantly higher in lead-exposed groups (BLL, 5.4–317.3 µg/dL) than in the control groups (BLL, 0–12.5 µg/dL) (Tenchova et al. 1997; Ye et al. 1999; Yucebilgiç et al. 2003; Gurer-Orhan et al. 2004; Kasperczyk et al. 2004a, b, 2009, 2013a, b, c, d; Oktem et al. 2004; Patil et al. 2006a, b; Garçon et al. 2007; Ergurhan-Ilhan et al. 2008; Khan et al. 2008; Mohammad et al. 2008; Grover et al. 2010; Permpongpaiboon et al. 2011; Singh et al. 2013). Among these, 15 studies reported a significant positive correlation between BLLs and MDA concentrations ($r = 0.15$–0.80; $p < 0.05$). Only one study did not find significant association between BLLs and MDA concentration (Conterato et al. 2013). Four studies reported that TBARS were detected measuring LPO in body fluids. Three studies reported that the TBARS concentration was significantly higher in workers exposed to lead than in control groups (Ito et al. 1985; Sugawara et al. 1991; Wasowicz et al. 2001), and another study showed no significant differences among subjects with higher BLLs (Malekirad et al. 2010). A higher correlation of serum LPO was observed with the duration of lead exposure than with aging (Ito et al. 1985). One study measured the production of isoprostane to check the oxidation of tissue phospholipids and observed increased isoprostane levels in welders when compared with the control group; it also identified that age and cigarette smoking did not contribute to the 2.4-fold increase in the isoprostane levels observed in welders (Han et al. 2005). Two studies analyzed conjugated dienes, a primary end-product of LPO and both reported a positive correlation with BLLs ($r = 0.33$; $p < 0.05$ and $r = 0.694$; $p < 0.001$) (Permpongpaiboon et al. 2011; Kasperczyk et al. 2013c).

Twelve studies simultaneously analyzed SOD and CAT activities. Among these, 6 studies observed that SOD and CAT activities were significantly lower in groups exposed to lead (Sugawara et al. 1991; Patil et al. 2006a, b; Mohammad et al. 2008; Grover et al. 2010; Conterato et al. 2013). Four studies found that SOD activity was higher in exposed groups (Kasperczyk et al. 2004b, 2012; Malekirad et al. 2010; Conterato et al. 2013), and 1 of these studies reported that the increase was greater in the low lead-exposed subgroup (BBL, 35.0 ± 9.3 μg/dL) than in the high lead-exposed subgroup (BBL, 44.2 ± 8.1 μg/dL) (Kasperczyk et al. 2004b). No significant difference was noted in CAT activity in these studies (Kasperczyk et al. 2004b, 2012; Malekirad et al. 2010). No significant changes in SOD and CAT activities were observed in 2 studies (Oktem et al. 2004; Ergurhan-Ilhan et al. 2008), while another study reported no significant changes in SOD activity but identified increased activity of CAT between the case group and the control group (Chiba et al. 1996). However, the study by Ergurhan-Ilhan et al. (2008) found a positive correlation between BLL and CAT activity and the duration of lead exposure ($r = 0.448$; $p < 0.05$).

Monteiro et al. (1985), Kasperczyk et al. (2009) and Rendon-Ramirez et al. (2014) identified a significant increase in SOD activity in lead-exposed workers, while Gurer-Orhan et al. (2004) found a positive correlation between CAT activity and BLL ($r = 0.62$; $p = <0.0001$). An additional 2 studies observed a positive correlation of SOD with BLL ($r = 0.948$) (Costa et al. 1997) and a significant increase in SOD activity in exposed groups (Ye et al. 1999). However, SOD activity was lower in exposed subgroups with higher BLLs (40.2–62.2 μg/dL) than in exposed subjects with lower BLLs (4.97 μg/dL) (Ito et al. 1985). In addition, 1 study reported decreased levels of SOD activity in subjects who were older (Han et al. 2005).

GPx activity was analyzed in 15 studies (Table 4). Eight studies reported significantly higher levels of GPx activity in the lead-exposed groups than in the controls (Monteiro et al. 1985; Solliway et al. 1996; Oktem et al. 2004; Kasperczyk et al. 2004a, 2012; Han et al. 2005; Ergurhan-Ilhan et al. 2008; Conterato et al. 2013). Five studies reported lower GPx activity in the lead-exposed groups than in the control groups (Sugawara et al. 1991; Chiba et al. 1996; Wasowicz et al. 2001; Kasperczyk et al. 2009; Grover et al. 2010), and two studies reported no significant differences between GPx activity and BLL (Garçon et al. 2007; Rendon-Ramirez et al. 2014). GPx was also found to be substantially higher in the low lead-exposed group than in the high lead-exposed group (Kasperczyk et al. 2004a). Similarly, the activity of the enzyme dropped 30 % in a study group with a BLL of 45.3 ± 4.7 μg/dL when compared to another study group with a BLL of 41.8 ± 5.6 μg/dL, but there were no significant differences in GPx activity between those groups and the control group (BLL, 7.73 ± 1.7 μg/dL) (Kasperczyk et al. 2009). In the study by Han et al. (2005), GPx activity was found to be negatively correlated with age and was lower in current smokers than in non-smokers in both the exposed and non-exposed groups.

Six studies measured GSH levels as a biomarker of Pb-induced OS. In 3 studies, GSH levels decreased in the exposed group (Mohammad et al. 2008; Feksa et al. 2012; Kasperczyk et al. 2013b) and were negatively correlated with BLLs in the other study ($r = -0.423$; $p < 0.001$) (Roels et al. 1975). However, GSH levels increased in the exposed group and were also negatively correlated with ALAD levels in another study (Gurer-Orhan et al. 2004; Conterato et al. 2013).

Furthermore, two studies analyzed 8-OHdG in occupationally exposed subjects. One of these reported an inverse correlation between the biomarker and BLL, and the other found no significant association between them (Garçon et al. 2007; Malekirad et al. 2010).

5 Types and Utility of Biomarkers

The epidemiological studies evaluated in this review showed that lead exposure induces OS in occupationally exposed populations as well as in general populations. The most commonly used OS biomarkers used to verify associations with BLLs were MDA, GSH, and GPx levels and SOD and CAT activities. In all studies analyzed, at least one OS biomarker showed changes with increase in BLLs. In general, the associations depended on the OS biomarker, the population studied (general or occupationally exposed), the concentration of lead in the blood, the study design, and/or the duration of exposure. However, divergent results were identified regarding the association between BLLs and OS biomarkers.

Several experimental animal and *in vitro* studies have evidenced that lead exposure, even at low levels, can promote enhancement of OS. Figure 1 describes some of the mechanisms of lead-induced OS.

In the present review, we observed that most of the studies involved occupationally exposed populations (i.e., with higher BLLs), while few studies focused on

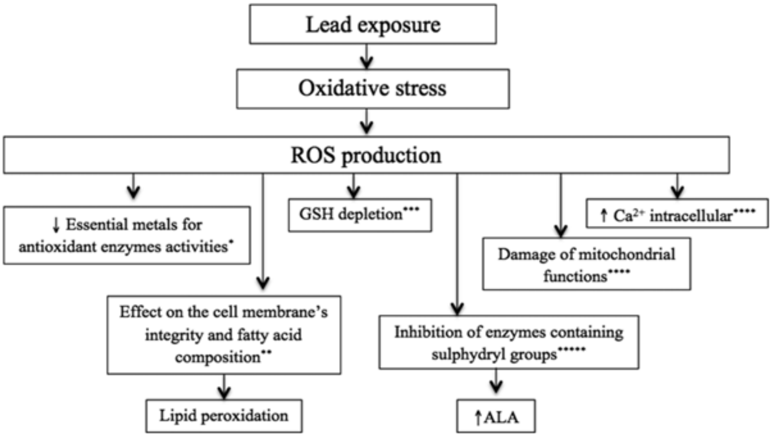

Fig. 1 Scheme of lead-induced oxidative stress. *ROS* reactive oxygen species, *GSH* glutathione, *ALA* aminolevulinic acid. *Mylroie et al. (1986), **Yiin and Lin (1995); Ercal et al. (2001), ***Loikkanen et al. (2003), ****Hermes-Lima (1995), *****Farmand et al. (2005)

general populations. Even at low doses, lead has been implicated in promoting OS, a relevant mechanism involved in the pathophysiology of lead-related diseases (Ni et al. 2004; Rodríguez-Iturbe et al. 2005; Lee et al. 2006; Ahamed and Siddiqui 2007; Nemsadze et al. 2009). Studies have pointed out that OS induced by lead causes reduction in the availability of active nitric oxide (NO), leading to hypertension, endothelial injury or dysfunction, arteriosclerosis, and cardiovascular disease (Vaziri and Gonick 2008).

Among the OS biomarkers studied in general populations, GSH was typically used to analyze associations with BLLs. GSH is a tripeptide containing cysteine that has a reactive thiol group (-SH) (Nemsadze et al. 2009), which interacts directly with ROS or can be involved as a cofactor in the enzymatic detoxification reactions for ROS (Ding et al. 2000). Three case-control studies found significantly lower GSH levels in case groups in which BLLs were higher (mean values, 9.86 ± 2.04–28.2 ± 22.0 μg/dL) than those for the controls (mean values, 4.23 ± 1.23–10.2 ± 10.0 μg/dL) (Siddiqui et al. 2002; Ahamed et al. 2008, 2011). However, in a cross-sectional study design, no significant changes were observed in GSH levels related to BLLs (Table 3), possibly because of the small sample size (n = 39) in 1 of the studies (Ahamed et al. 2006). GSH can also be oxidized to glutathione disulfide (GSSG) in the presence of ROS, resulting in a decrease in GSH and an increase in GSSG (Gurer-Orhan et al. 2004; Casado et al. 2007). Diouf et al. (2006) found that the GSSG/GSH ratio was higher in subjects with higher BLLs (9.97 ± 3.93 μg/dL) than in subjects with lower BLLs (5.21 ± 5.86 μg/dL). These data indicate that lead induces ROS formation due to increased GSSG levels and depletion of GSH levels. Similar results were also obtained in experimental studies (Schwartz et al. 2000; Martinez-Haro et al. 2011).

Regarding the decrease observed in GSH levels in lead-exposed subjects (Roels et al. 1975; Mohammad et al. 2008), experimental studies have also found a significant decline in GSH levels due to lead exposure (Wang et al. 2009; Martinez-Haro et al. 2011). In contrast, in the study by Conterato et al. (2013), GSH levels were elevated in lead-exposed workers with lower BLLs (5.4 ± 0.4 μg/dL) but not in workers with higher BLLs (49.8 ± 4.0 μg/dL). A possible explanation is that GSH synthesis increases as a protective mechanism when the cells are oxidized. However, when oxidation is very high due to elevated concentrations of lead, GSH synthesis cannot protect against OS; subsequently, GSH levels tend to drop (Schafer and Buettner 2001).

Lead is known to damage cell membranes, particularly erythrocyte membranes that have a high affinity for lead, by promoting LPO. The concentrations of MDA, one of the final product of LPO, commonly increase as the number of double bonds in the fatty acids increase due to lead exposure, thus making the cells more susceptible to damage than fatty acids with lesser double bonds (Gurer and Ercal 2000). In addition, lead can affect fatty acid composition by leading to elongation of the arachidonic acid (an essential unsaturated fatty acid in the membranes) and enhancing LPO (Yiin and Lin. 1995). These findings may explain the correlations identified between BLLs and MDA concentrations in the studies involving general populations. Jin et al. (2006) considered MDA the most sensitive OS biomarker because, when lead exposure induces overproduction of free radicals, antioxidant defense can be depleted and the radicals can react directly with biological macromolecules (e.g., lipids, proteins, and DNA), thus leading to an increase in peroxides as MDA.

Regarding the occupationally exposed populations, experimental studies have asserted that higher BLLs are associated with an increase in MDA or TBARS concentrations (Sandhir et al. 1994; Kaczmarek-Wdowiak et al. 2004; Jia et al. 2012). All the studies that enrolled workers exposed to lead reported elevated levels of LPO products, except for 2 studies that did not identify a statistical significance associated with higher BLLs (Table 4).

LPO is considered a basic cellular deterioration process that occurs due to the presence of polyunsaturated fatty acids in erythrocyte membranes that react with ROS such as hydroxyl radicals (OH^-) and superoxide anions (O_2^-) (Tappel 1973; Demopoulos et al. 1982; Cini et al. 1994). However, erythrocytes have different mechanisms in order to protect the cells from ROS damage and, consequently, MDA production. SOD, for example, is an effective intracellular antioxidant enzyme, which catalyzes the dismutation of O_2^- to molecular oxygen (O_2) and hydrogen peroxide (H_2O_2), which is a less reactive compound. The enzyme CAT is located on the peroxisomes and converts H_2O_2 to water and to O_2 (Matés et al. 1999).

The studies analyzed in the present review had divergent results with respect to antioxidant enzymes, which is in accordance with the literature data (Sandhir et al. 1994; Vaziri et al. 2003; Farmand et al. 2005; Wang et al. 2009; Martinez-Haro et al. 2011). As observed in 4 studies (Table 4), the association between increased MDA concentrations and lower SOD and CAT activities in subjects occupationally exposed to lead may be attributable, in part, to the fact that lead induces the expression of antioxidant enzymes and simultaneously binds to the sulfhydryl group, which inhibits CAT activity (Sugawara et al. 1991). Moreover, lead can interact with copper molecules, which inhibits SOD activity (Mylroie et al. 1986). It is noteworthy that short-term exposure to lead leads to an elevation in both superoxide (O_2^-) and H_2O_2 levels, while chronic lead exposure causes an increase in H_2O_2 but not superoxide levels. A possible explanation is that, initially, there is upregulation of SOD, resulting in H_2O_2 production, which in turn leads to reduction in superoxide (O_2^-) levels and increase in H_2O_2 levels in the chronic phase of exposure (Ni et al. 2004). Furthermore, increase in NO production, triggered by upregulation of endothelial NO synthase (Vaziri and Ding 2001), also plays a role in the decrease in superoxide levels, but is this case, SOD tended to increase. NO is highly attracted by superoxide and, as SOD expression is regulated by this anion, the lead-induced elevation in superoxide levels observed in some studies may contribute to the upregulation of SOD in cells chronically exposed to lead (Ni et al. 2004). Experimental studies suggest that an increase in SOD and CAT activities can be observed because some cells are resistant to lead as a result of the induction of an enzymatic response against OS. In addition, the excess ROS generation could induce enzymatic expression or it is possible that the lead ions could directly activate enzymatic actions (Dalton et al. 1999). Monteiro et al. (1985) connected the increased activity of SOD observed in lead-exposed workers to a protective mechanism against the deleterious effects of lead in erythrocytes. In addition, epidemiological studies have suggested that the disparities in the results are attributable to differences in the oxidant status of subjects and that they present a distinct antioxidant response (Han et al. 2005), which can also be correlated with the duration of lead exposure (Ergurhan-Ilhan et al. 2008).

Experimental studies have also shown divergent results regarding the association between BLL with CAT and SOD activities. Mylroie et al. (1986) and Nehru and Kanwar (2004) identified a decrease in SOD activity in both cerebral end cerebellar regions in Wister strain rats exposed to lead acetate, suggesting that lead induced deficiency of copper, an essential metal for SOD activity, leading to a reduced capacity of eliminating ROS and resulting in oxidative damage. CAT activity also decreased in the presence of lead, possibly because lead interferes with iron absorption and heme biosynthesis (CAT contains heme as a prosthetic group) (Nehru and Kanwar 2004). In contrast, the studies by Vaziri et al. (2003) and Farmand et al. (2005) showed upregulation of SOD and CAT activities in lead-treated animals, wherein an increased level of H_2O_2 was produced because of increase in the renal SOD level (Matés et al. 1999). The higher concentration of H_2O_2 stimulated expression of the gene encoding the CAT enzyme, representing a compensatory response to OS.

From the studies that involved general populations, Ahamed et al. (2008) showed that both SOD and CAT activities were significantly higher in the case group (BLL, 18.6 ± 7.93 μg/dL) and observed a negative correlation between BLL and GSH levels, suggesting that lead can cause an imbalance in the oxidant/antioxidant system in case groups. Ahamed et al. (2006) and (2011) also identified higher activity levels of CAT in case groups (Table 3). It was argued that the observed increase in CAT activity represented a defense mechanism against increased H_2O_2 levels during lead-induced OS. Wieloch et al. (2012) found the same results regarding SOD activity in case subjects living in a polluted area and reported that this increase occurred due to health conditions and environmental characteristics. Therefore, elevated SOD activity was considered as an antioxidant defense against environmental stress. However, in the same study, CAT was significantly higher in subjects from an unpolluted area. It may be that CAT is more sensitive to environmental influences and was lower in subjects living in a polluted area (i.e., subjects with higher BLLs).

GPx is a selenium-containing enzyme that uses GSH as a reducing agent to transform H_2O_2 and lipoperoxides generated in the tissues to O_2^- and is also involved in the antioxidant system (Matés et al. 1999; Gurer and Ercal. 2000). Lead reacts with selenium, an essential element for GPx activity, leading to the formation of an insoluble complex (lead selenide) and reducing selenium uptake (Schrauzer 1987; Whanger. 1992; Matés et al. 1999). Epidemiological studies that involved general populations and were performed by Jin et al. (2006) and Ahamed et al. (2008) did not detect significant changes in GPx activity with regard to BLL (Table 3). In an experimental study, Ni et al. (2004) reported the occurrence of H_2O_2 accumulation in lead-exposed endothelial and vascular smooth muscle cells and the enhancement of OS due to a lack of compensatory upregulation of GPx activity. However, Diouf et al. (2006) observed a negative correlation between BLL and GPx activity. Likewise, controversial results have been verified in the literature concerning GPx activity in occupationally exposed populations. Eight studies found increased GPx activities in lead-exposed subjects, another 5 studies showed reduced activities, and 2 showed no significant changes between the exposed and control groups (Table 4). Han et al. (2005) suggested that the increased OS due to lead exposure triggered upregulation of enzyme activity. The increase in GPx activity, also reported by Ergurhan-Ilhan et al. (2008) and Conterato et al. (2013), was suggested as a defensive mechanism against ROS damage in the erythrocytes of exposed workers. Solliway et al. (1996) and Kasperczyk et al. (2004a) observed a significant dose-dependent elevation in GPx activity in case groups. While GPx activity increased in exposed subjects with a BLL of up to 40 μg/dL, in subjects with BLLs over 40 μg/dL, inhibition of enzyme activity was seen (Kasperczyk et al. 2004a). However, Kasperczyk et al. (2009) reported a negative correlation between GPx activity and BLL. The divergent results may be attributable to the prolonged exposure to lead, which reduces enzyme activity and causes changes in H_2O_2 distribution. Sugawara et al. (1991) also noted reduction in GPx activity in the case group and suggested that this decrease may play an important role in the enhancement of LPO.

GPx activity was lower in the erythrocytes of lead-treated rats (drinking water containing 0.2 % lead acetate, administered for 5 weeks) than in the controls (Sivaprasad et al. 2003). In contrast, Mousa et al. (2002) who exposed goats to lead (5.46 mg lead acetate per kg body weight for 2 weeks) found an increase in the activity of GPx in erythrocytes on day 7 of lead exposure, indicating that lead induces antioxidant enzyme activities. However, the activities declined on day 14 to levels below the values recorded before lead exposure. According to the authors, this decline may be due to the exhaustion and overutilization of these enzymes by the OS products. The differences in GPx activity observed in experimental studies can be attributed to differences in the animal species used or to the fact that some studies analyzed GPx in the erythrocytes (Sivaprasad et al. 2003; Martinez-Haro et al. 2011), while other studies examined the activity of GPx in renal and aortic tissues (Farmand et al. 2005; Sobeková et al. 2009). The different doses of lead used in these studies represent another possibility that explains the divergent outcomes (Farmand et al. 2005). Some other factors that could also interfere with GPx are age, diet, pollution, environmental conditions, smoking habits, the abilities of the antioxidant system, and some ailments (Han et al. 2005; Kasperczyk et al. 2009). Furthermore, an insufficient increase in glutathione reductase (GR), an enzyme that is reported to restore GSSG to GSH for reduction by GPx, may have caused the lower activity of GPx (Kasperczyk et al. 2004a).

GGT, an ectoenzyme widely distributed in the human body, is responsible for the extracellular metabolism of GSH and had already been proposed as an useful biomarker of OS in clinical or epidemiological settings (Whitfield 2001; Lee et al. 2004). Although GGT has been considered to play an important role in antioxidant defense system, experimental studies have proposed that GGT may also be involved in ROS generation. The oxidant effect of GGT occurs when the enzyme is expressed in the presence of iron or other metals. It may be explained because cysteinylglycine, which is one of the products of GGT action, reduces Fe^{3+} to Fe^{2+}, which promotes the generation of free radical species (Karp et al. 2001; Lee et al. 2004). Lee et al. (2006) found a consistent positive association between BLLs and serum GGT in American adults, suggesting that even among people with low environmental exposure to lead, OS should be considered in the pathogenesis of lead-related diseases.

Finally, the 8-OHdG, one of the predominant forms of free radical-induced DNA lesions (Wu et al. 2004), was also analyzed as an OS biomarker in epidemiological studies. This biomarker is an oxidized form of DNA that can be quantified to indicate the extent of DNA damage. Among the three studies that measured 8-OHdG, Hong et al. (2013) analyzed data from Korean adults and found that the level of urinary 8-OHdG was greater in participants with higher BLLs (7.0 ± 1.9 μg/dL) compared to those with lower BLLs (2.5 ± 0.6 μg/dL). In contrast, Malekirad et al. (2010) identified an inverse correlation between 8-OHdG and BLLs in occupationally exposed subjects with increased BLLs (9.6 μg/dL ± 3.3), while Garçon et al. (2007) did not find a significant association in workers with higher BLLs (38.7 μg/dL ± 9.9).

6 Conclusions

The most frequently used OS biomarkers to evaluate Pb-induced OS were MDA, GSH, and GPx concentrations and SOD and CAT activities. Divergent results were observed since the OS biomarkers varied depending on the studied population (general or occupationally exposed), the physiologic and pathologic conditions of the participants, the study design, the BLLs and the time or duration of exposure, and the adjustment for confounders variables. Only MDA concentrations were significantly increased in groups with higher BLLs comparing with those with lower BLLs.

7 Summary

In the present review, it was confirmed that lead exposure can induce OS in general populations and in occupationally exposed populations. Even at low doses, lead promotes the generation of ROS resulting in oxidative damage. However, further studies involving general populations are necessary in order to provide additional data about lower BLLs and OS. Beyond that, it should be considered that other, less-studied OS biomarkers, such as GGT, 8-OHdG, and pyruvate kinase (PK), may become important OS biomarkers related to lead exposure.

Nevertheless, this review contributes to the characterization of the impact of lead exposure on public health and shows that lead causes ROS generation. Considering that OS is an underlying mechanism of several pathological conditions, it is important to propose regulatory actions regarding BLLs. In Brazil, an immediate intervention proposal should be considered for lowering BLLs in occupationally exposed populations (reference values up to 40 µg/dL and maximum permitted biological values of 60 µg/dL). In areas contaminated by lead industries, refineries, and former mining areas, which have already been identified in Brazil, the proposed interventions and decontamination practices previously suggested by researchers must be implemented in addition to regular programs for environmental and biological monitoring in these areas (De Capitani and Paoliello 2012). Application of these regulatory proposals and public health programs should be developed to prevent and reduce lead exposure below the current levels in adults and especially in children, who represent the group most susceptible to lead exposure.

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Appendix 1: Search Strategy

Search in PubMed

((((((((lead[Title/Abstract])) AND (((blood[Title/Abstract])) OR (ALAU[Title/Abstract])))) AND (((((poison*[Title/Abstract]) OR expos*[Title/Abstract]) OR occupation*[Title/Abstract]) OR contamination[Title/Abstract]) OR environmental[Title/Abstract]))) AND (((oxidative[Title/Abstract])) AND (((stress[Title/Abstract]) OR damage[Title/Abstract]) OR injury[Title/Abstract])))) OR (((((((lead[Title/Abstract])) AND (((blood[Title/Abstract])) OR (ALAU[Title/Abstract])))) AND (((((poison*[Title/Abstract]) OR expos*[Title/Abstract]) OR occupation*[Title/Abstract]) OR contamination[Title/Abstract]) OR environmental[Title/Abstract])))) AND (((((((((((((ALAD[Title/Abstract]) OR MDA[Title/Abstract]) OR SOD[Title/Abstract]) OR CAT[Title/Abstract]) OR 4HNE[Title/Abstract]) OR GPx[Title/Abstract]) OR G6PD[Title/Abstract]) OR GSSG[Title/Abstract]) OR GSH[Title/Abstract]) OR GR[Title/Abstract]) OR ZPP[Title/Abstract]) OR NADP[Title/Abstract]) OR NADPH[Title/Abstract]))

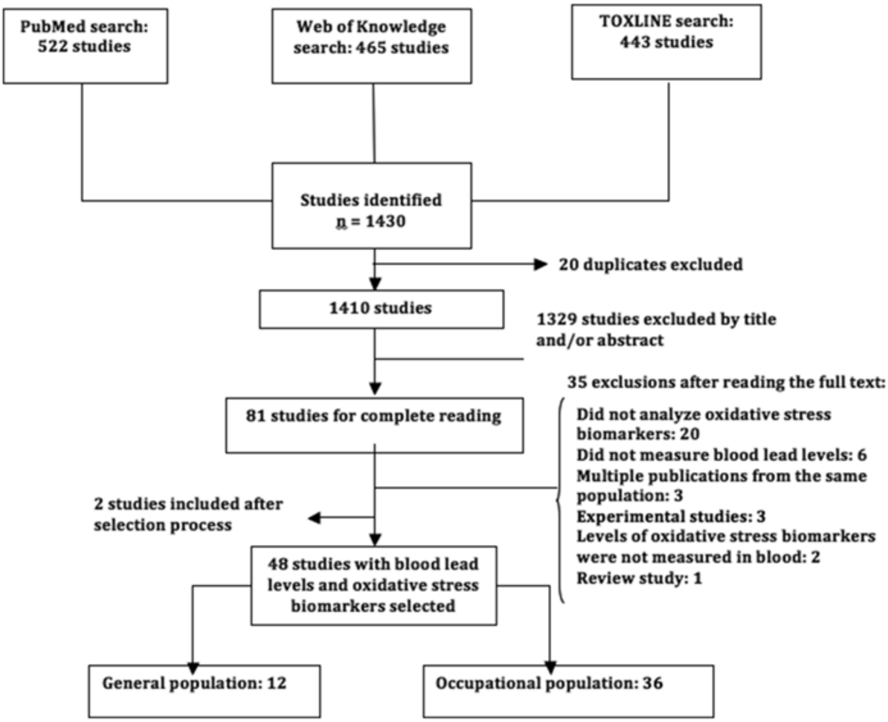
Search in TOXLINE

lead AND blood AND oxidative stress

Search in Web of Knowledge

lead AND blood AND oxidative stress

Databases: PubMed (http://www.ncbi.nlm.nih.gov/sites/entrez?db=pubmed); Web of Knowledge (http://apps.webofknowledge.com.ez78.periodicos.capes.gov.br/WOS_GeneralSearch_input.do?product =WOS&search_mode= GeneralSearch&SID= 3BpD4JEBm5kK9iK3Lm3&preferencesSaved=); TOXLINE (http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?TOXLINE).



Flow diagram of study selection process.

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Nanostructured Metal Oxides for Stoichiometric Degradation of Chemical Warfare Agents

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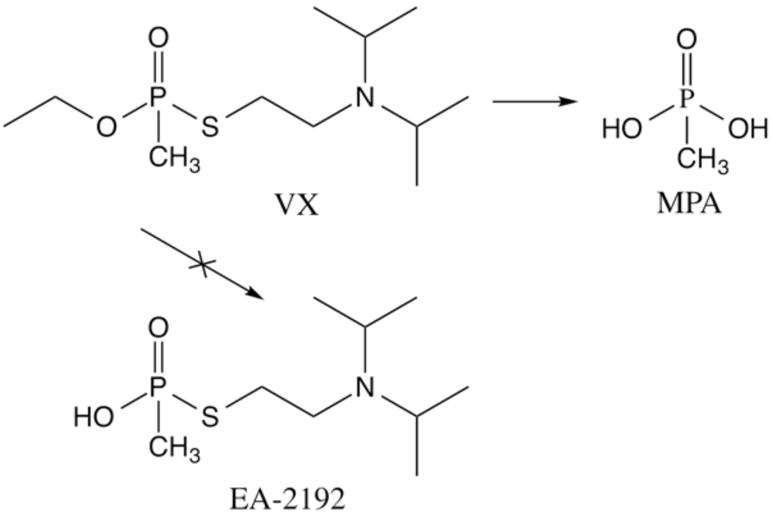

The nanostructure of reactive sorbents based on oxides of transient metals is crucial for degradation of chemical warfare agents

1 Introduction

Nerve agents (NA) are organic compounds (organophosphates) highly toxic to mammals. They are one of the most dangerous group of chemical warfare agents (CWAs) with rapid effects and penetration of the body by different entry routes. The chemically pure forms of G-agents, soman (O-pinacolyl methylphosphonofluoridate, GD), tabun (ethyl dimethylphosphoramidocyanidate, GA), sarin (*O*-isopropyl methylphosphonofluoridate, GB), and cyclosarin ((fluoro-methyl-phosphoryl) oxycyclohexane, GF) are colorless liquids with a water-like appearance, no noticeable odor, and are relatively soluble in both water and organic solvents. They possess high volatility, so the most likely pathway for substances to enter the body is the respiratory tract; the GD, GA, and GF can be regarded as contact hazards as well. V-agents, with VX as the main representative, are generally more persistent in the environment. In a chemically pure state, VX (O-ethyl S-[2-(diisopropylamino) ethyl] methylphosphonothioate) is a colourless liquid more viscous than water, with no noticeable odour. It has very low volatility and is poorly soluble in water, but highly soluble in organic solvents and fats. VR agent, as an isomer of VX, has very similar properties. Organophosphate compounds with a similar structure are known as effective pesticides (insecticides) in agriculture—parathion, parathion methyl, malathion, chlorpyrifos, dichlorvos, diazinon or fenitrothion belong to the most widely used and commonly available representatives of this group. Although their use has been restricted in many countries, some of them they are still applied in great quantities and represent a potential threat to human health. Organophosphates are used also in industry as plasticizers or hydraulic fluids, or in medicine as therapeutics or compounds for researching nerve functions.

Finding effective and safe decontamination methods has long been of great concern for defense against chemical and biological warfare (CBW) agents (Yang et al. 1992). In the wake of new threats, such as terrorist attacks on civilian society, it has been recognized that decontamination and clean-up must meet more stringent criteria, which calls for new methods and materials and places new demands on operational procedures and appropriate risk analysis. Currently, decontamination procedures are characterized by intensive use of chemicals that themselves must be often treated with care, and they pose problems with regard to logistics, personnel, time and damage to equipment and to the environment. At the same time, the threat of a wider range of toxic chemicals, emerging from, for example, accidental or non-accidental industrial release, calls for broad-spectrum decontamination methods that can be efficiently deployed in urban areas. The use of nanostructured oxides as reactive sorbents for CWAs is anticipated, given the cost of sensitive components of military equipment (electronic devices, computers etc.).

Diverse physical, chemical and biochemical principles are employed in current decontamination strategies, such as adsorption, chemical reactions (mainly oxidation and nucleophilic substitution), enzymatic decomposition and others. Conventional adsorbents such as activated carbon, coal, alumina or clays, offer certain advantages such as low toxicity and low environmental risk, along with easy handling, long shelf life and relatively low cost as well. However, they are unable to destroy the toxic chemicals and thus require extensive and expensive post-decontamination treatment.

It was found that some sorption materials, typically metal oxides, are able not only to adsorb (physically) various toxic chemicals but also to break them down chemically into non-toxic (or less toxic) products. If the size of the individual oxide particles decreases to tens or even units of nanometers, an increase in their specific reactivity is observed. This acceleration of the heterogeneous reactions taking place on the surface of the nanocrystals is attributed mainly to an increase in the proportion of highly reactive sites such as edges and corners of crystals and in the number of dislocations and defects of shape. An increase in the surface area plays also a significant role—it follows from empirically obtained knowledge that increasing the specific surface area proportionally increases the observed rate of decomposition reactions. However, even a very substantial increase in the surface area itself can hardly explain the enhanced reactivity of nano-sized oxide materials. The reactivity of nanocrystalline metal oxides may be demonstrated by titanium oxide (Stengl et al. 2011a): In Fig. 1, a high-resolution transmission electron micrograph of nanocrystalline titanium dioxide presents a Ti4+ cation shown in white. The cations inside the crystal, which are not shown, have a coordination number of 6; the cations on the surface, shown in blue, have a coordination number of five; the cations on the edges, shown in red, have a coordination number of 4; finally, the cations in the corners, shown in green, have a coordination number of 3. Surface defect gaps (see arrow) also reduce the coordination number of surrounding ions. Generally, the

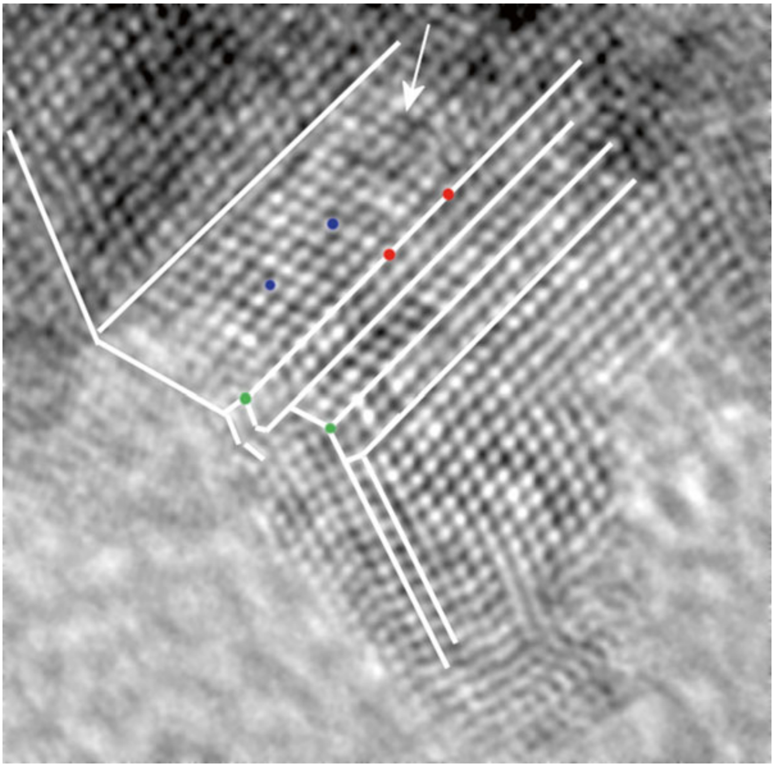

Fig. 1 The structure of a TiO_2 nanocrystal. Cations within the crystal (not shown) have a coordination number of 6, the cations on the surface (shown in *blue*) have a coordination number of 5, cations on the edges (shown in *red*) have a coordination number of 4, and cations in the corners (shown in *green*) have a coordination number of 3. Surface defect gaps (*arrow*) also reduce the coordination number of surrounding ions

lower the coordination number of cationic sites is, the higher is their reactivity (Sayle et al. 2008). This unique morphology of nanocrystals thus allows their high reactivity. It is assumed that the degradation of the chemical substance molecules occurs in two steps: the first is physical adsorption, and the second is chemical decomposition (Stark et al. 1996; Stark and Klabunde 1996).

In addition to the reactivity of the nanosized metal oxides, also other processes affecting the rate of conversion should be considered, namely the diffusion (external or internal) of substances to the active sites. As may be generalized from kinetic measurements, two stages with different kinetics may be distinguished on degradation curves (Stengl et al. 2011a): the initial stage characterized by a relatively rapid decrease in the concentration of the chemical agent is followed by a slower stage, where the decomposition rate is governed mainly by diffusion.

The first generation of nanostructured metal oxides was introduced by the Klabunde group in 1996 (Klabunde et al. 1996; Khaleel et al. 1999; Lucas et al. 2001;

Koper et al. 1997). Oxides of the alkaline earth elements, Al and Zn were the first representatives of the so- called reactive (ad)sorbents (the term "stoichiometric reagents" is used for this type of agent to distinguish them from "conventional" adsorbents). Reactive sorbents have been successfully used to destroy various types of CWAs (nerve agents sarin, soman and VX, as well as blistering agent HD). Their high degradation efficiency stems from their high surface area, porosity and nanocrystalline nature, which facilitates the formation of crystalline defects and other anomalies serving as reaction centers for chemical destruction. These types of nanocrystalline metal oxides were typically prepared from organic precursors using relatively laborious methods. More recently, some less expensive and environmentally friendly procedures have been developed to produce metal oxide- based reactive sorbents using simple and easily scalable "wet" synthetic routes. A wide range of new reactive sorbents with unique properties (extremely high surface area, high chemical reactivity and in some cases photocatalytic activity) has been introduced and tested for degradation of CWAs. Progress in this field during the last two decades is reviewed in this paper.

2 Nanostructured Oxides

2.1 Oxides of Alkaline Earth Metals

The nanostructured oxide of an alkaline earth metal, specifically MgO, with a particle size of 35 Å and a specific surface area of 1000 $m^2\ g^{-1}$ was prepared by a hypercritical drying method procedure (Utamapanya et al. 1991) and used for the degradation of dimethyl methylphosphonate (DMMP), a G agent simulant (Li and Klabunde 1991). The first mention of nanocrystalline MgO and CaO as stoichiometric reagents potentially usable for the decomposition of CWAs was published in 1996 (Klabunde et al. 1996). In the initial study, Wagner et al. (1999) described the decomposition of the solutions of sulfur mustard (HD), soman (GD) and VX at room temperature by nanostructured MgO which was listed as a reagent for the decontamination of sensitive components, military equipment and material. The mechanism for the decomposition of HD, GD and VX by nanocrystalline MgO (Wagner et al. 1999) and CaO (Wagner et al. 2000) is given in Fig. 2.

Nanocrystalline MgO decomposes HD into a mixture of divinylsulfide and thiodiglycol at a molar ratio of 1:1 (see Fig. 2). GD gives O-3,3-dimethyl-2-butyl methylphosphonic acid and methylphosphonic acid (see Fig. 2). Decomposition of VX leads to the formation of O-ethyl- methylphosphonic acid and methylphosphonic acid (see Fig. 2). In the decomposition of VX, it is important to avoid the toxic product S-2-diisopropyl(amino)ethyl-methyl phosphonothionate, E2192 (EA indicates that the agent is an experimental agent and is not actually in the U.S. arsenal). One of the products of the hydrolysis of VX in alkaline aqueous solution (Farquharson et al. 2005). As is evident from these diagrams, all three of these chemical substances, HD, GD and VX, decompose on the surface of MgO to form

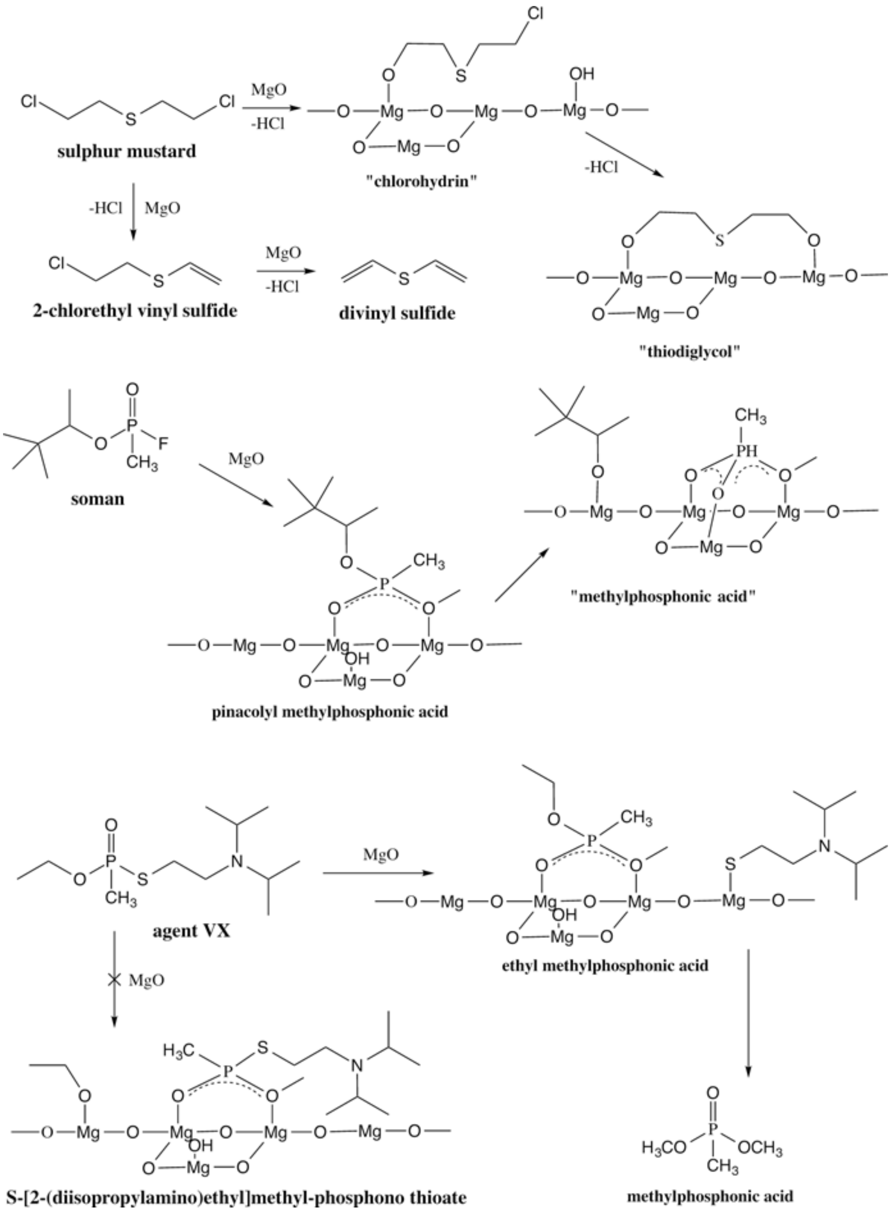

Fig. 2 Reaction scheme of the decomposition of HD, GD and VX on nanostructured MgO

non-hazardous products, which is very valuable for practical decontamination. Stengl et al. used an improved hypercritical drying method to prepare nanosized MgO with surface area greater than 1200 m^2 g^{-1} (Stengl et al. 2003). The highest percentage of the conversion of HD into harmless products after the completion of the reaction was 77 % (Stengl et al. 2004). The particle morphology and texture of the material are also important factors that depend on its specific surface area and porosity. Another factor that influences the adsorption of molecules of chemical substances and their subsequent degradation on the material surface is the acid-base character of the surface. Tang et al. (2008) studied the effects of acidic and basic sites on the surface of CaO, MgO, SiO_2 and Al_2O_3 on the degradation of HD. According to their results, it can be concluded that the surfaces of the base-point oxides Al_2O_3, MgO and CaO exist regardless of whether the oxide is of generally acidic, basic or amphoteric character. Furthermore, it was observed (Tang et al. 2008) that oxides such as CaO and MgO have a large amount of strongly basic sites, but no acidic sites, and that Al_2O_3 is a typical amphoteric oxide with acidic and basic sites. Nazari and Nazari (2010) presented a simple and easily performed method for the synthesis of MgO particles and described the destruction of the CWAs simulants malathion (Diethyl 2[(dimethoxyphosphorothioyl) sulfanyl]butanedioate) and DMMP. It was also found that the decomposition of HD may be accelerated at the acid and basic sites. An increase in the degree of conversion of GD and VX by the nanostructured mixed oxide $AlO(OH)\bullet ZrO_2$ (identified as sample AlZr_4) was caused by increasing the number of basic sites on the surface of the samples using a solution of NH_4OH, as presented in Fig. 3. The stoichiometric decomposition reaction (Klabunde et al. 1996) (unlike the photocatalytic reaction) is not dependent on exposure to light, but it is a surface-catalyzed hydrolysis reaction and involves the cleavage of chemical bonds. It should be noted that the macrocrystalline forms (particle size above 100 nm) of oxides of alkaline earth metals (Mg and Ca) and light metals (Al and Ti) (Wagner et al. 2007) have the ability to react with agents such as HD, GD and VX. However, the reactions on macrocrystalline oxides are generally slow and impractical for use in military decontamination.

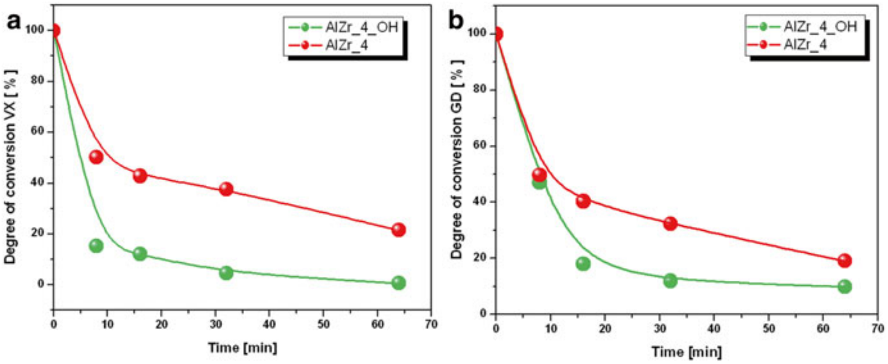

Fig. 3 The increase in conversion by increasing the number of basic sites (**a**) agent VX, (**b**) GD

2.2 Aluminum Oxide

Aluminum oxide is polymorphic. In its most common forms, it crystallizes as corundum, trigonal α-Al_2O_3, hexagonal β-Al_2O_3 and cubic γ-Al_2O_3. In nature, the monohydrate minerals boehmite γ -AlO(OH) and, rarely, diaspore α-AlO(OH) are formed, and the trihydrate gibbsite $Al(OH)_3 \bullet 3H_2O$ also forms. For decomposition of HD, GD and VX on nanocrystalline γ-Al_2O_3, TiO_2, metal titanium and aluminum (Štengl V et al. 2005) analogous degradation pathways have been suggested. Prasad et al. (2010) used alumina AP-Al_2O_3 and mixed alumina-transient metal oxide (AP-Al_2O_3–Fe_2O_3, AP-Al_2O_3–V_2O_5 and AP-Al_2O_3–CuO) prepared using an aerogel process (hypercritical drying procedure) for HD degradation. The value of the rate constant for HD degradation was determined to be 0.02 h^{-1} for alumina; for Al_2O_3–Fe_2O_3, Al_2O_3–V_2O_5 and Al_2O_3–CuO the values were 0.04, 0.03 and 0.03 h^{-1}, respectively. Nanoparticles of AP-Al_2O_3 in the size range 2–30 nm with a surface area of 375 m^2 g^{-1} were produced by the sol-gel method and were used for studying the kinetics of HD adsorption (Saxena et al. 2009).

2.3 Zinc Oxide

Zinc oxide (ZnO) crystallizes in two main structural forms, hexagonal wurtzite (Zn,Fe)S and cubic zincblende ZnS; in nature, crystalline zinc oxide occurs as the mineral zincite (Zn,Mn)O. Zinc oxide is widely used as an additive in numerous materials and products including plastics, ceramics, glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, batteries and fire retardants.

Prasad et al. used ZnO nanorods synthesized by a hydrothermal method (Prasad et al. 2007a) and ZnO from the sol-gel method (Mahato et al. 2009a) for HD and sarin degradation with rate constants of 0.36 h^{-1} and 0.08 h^{-1}, respectively. Houskova and Stengl (Houskovs et al. 2007; Houskova et al. 2007) prepared nanosized ZnO by homogeneous hydrolysis with thioacetamide heated at a temperature of 400 °C, which showed good decomposition of the HD, and its reactivity was superior to that of AP-MgO (Stengl et al. 2004). Mesoporous CuO-ZnO binary metal oxide was used as a decontaminant against HD (Kumar et al. 2013). These materials demonstrated superior decontamination properties against HD compared to single-component metal oxides and decomposed it to divinyl sulfide, chloroethyl vinyl sulfide and hemisulfur mustard.

2.4 Titanium Oxide

All three CWAs, i.e. neat HD, GD and VX, were hydrolyzed on the surface of TiO_2, and the reaction with VX is considerably rapid ($t_{1/2} < 30$ min) and approaches the rates attained in liquid decontaminant. Prasad et al. (2008) synthesized titania nanotubes from anatase TiO_2 and NaOH under hydrothermal conditions at 130 °C for 5 days. The decontamination reaction of HD has a linear curve, with a fast initial reaction that reaches a steady state at later stages of the reaction with a rate constant of 0.1156 h^{-1} and a half-life of 5.99 h, thus indicating the pseudo first order behavior of the decontamination reaction of HD on TiO_2 nanotubes, whereas parent TiO_2 exhibited a rate constant of 0.0214 h^{-1} and a half-life of 32.39 h. Sarin reacted in a similar fashion: the rate of the decontamination reaction was found to be 0.7536^{-1} and the half-life was found to be 0.92 h; on bulk titania, the rate of the reaction was 0.0711 h^{-1} and the half-life of the reaction was 9.75 h. Ag^+-, Cu^{2+}-, Ni^{2+}-, $CO_2{}^+$-, Mn^{2+}- and Ru^{3+}-modified titania nanotubes have been studied as powder decontaminants against HD. Thiodiglycol and 1,4-oxathiane were observed to be the major products except on Ru^{3+}-titania nanotubes, where a sulfoxide of mustard formed, thereby indicating oxidative decontamination (Prasad et al. 2009).

Homogeneous hydrolysis of titanium oxo-sulfate has been used to prepare anatase TiO_2 with high specific surface area, and the degrees of conversion for HD, GD and VX into non-toxic products after the completion of the reaction for 64 min were 96.5 %, 96.6 % and 98.8 %, respectively (Štengl V et al. 2005).

2.4.1 Zr^{4+} and Hf^{4+}-Doped Titania

The homogeneous hydrolysis mixture of titanium oxo-sulfate and zirconium oxo-sulfate with urea at 98 °C was used to prepare Zr^{4+}-doped anatase with high specific surface area. During hydrolysis, complexes such as $[Zr(OH)n]^{4-n}$ could prevent the formation of crystalline particles and thus lead to gel precipitation. Good results were obtained for the decomposition of HD, where ~95 % conversion was achieved within 32 min. Total degradation of GD and VX on Zr-doped titania occurred in 1 min (Stengl et al. 2008; 2009). Doping TiO_2 with Hf (see Fig. 4) also increased the degradation rate of GD and VX. Figure 5 presents the kinetics of degradation of VX and GD on nanostructured Hf^{4+}-doped TiO_2; complete decomposition occurred at 30 s. The degree of conversion of HD is 85 % per h.

2.4.2 Ge^{4+} and In^{3+} Doped Titania

Germanium-doped TiO_2 was prepared by homogeneous hydrolysis of aqueous solutions of $GeCl_4$ and $TiOSO_4$ with urea. The best degrees of degradation, 100 % for GD, 99 % for VX and 95 % for HD, were achieved with samples with 2 wt.% germanium (Stengl et al. 2012a). Novel In^{3+}-doped TiO_2 and TiO_2/In_2S_3 nanocomposites for stoichiometric degradation of CWAs were prepared by homogeneous hydrolysis with urea and thioacetamide, respectively. The best degree of conversion for stoichiometric degradation of HD (98.5 %) occurred with In^{3+} doped titania containing 0.54 wt.% In (Stengl et al. 2012b).

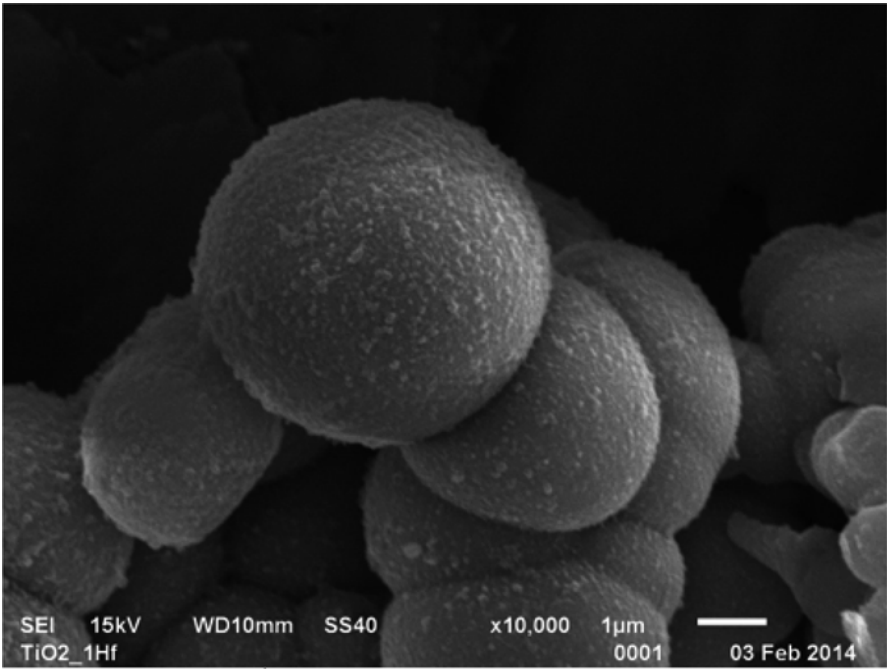

Fig. 4 SEM images of Hf $^{4+}$-doped TiO_2

2.4.3 Titania, Iron and Manganese Mixed Oxides

Titanium(IV)–manganese(IV) nanostructured mixed oxides were prepared by homogeneous hydrolysis of potassium permanganate and titanium(IV) oxo-sulfate with 2-chloroacetamide. The best decontamination properties for HD and GD were observed for the samples containing 18.7 % and 2.1 % Mn, where the degrees of conversion per h were 95.2 % and 89.3 %, respectively (Stengl et al. 2011b). Zirconium-doped mixed nanostructured oxides of Ti and Fe were prepared by homogeneous hydrolysis of iron and titania sulfate salts with urea in aqueous solution. The addition of Zr^{4+} to the hydrolysis of ferric sulfate with urea shifts the reaction route and promotes the formation of goethite FeO(OH) at the expense of ferrihydrite $Fe_5O_7(OH)\bullet 4H_2O$. The authors discovered that Zr^{4+}-doped oxo- hydroxides of Ti and Fe exhibit a higher degradation activity towards HD than any other yet- reported reactive sorbents. The reaction rate constant of the slower parallel reaction of the most efficient reactive sorbents is increased with an increasing amount of surface base sites (Stark and Klabunde 1996). Zirconium- doped nanostructured oxides of Fe, Al and Zn were prepared by homogeneous hydrolysis of the respective sulfate salts with urea in aqueous solution. The presence of Zr^{4+} dopant can increase both the surface area and the surface hydroxylation of the resulting doped oxides in addition to decreasing the crystallite size, thus potentially

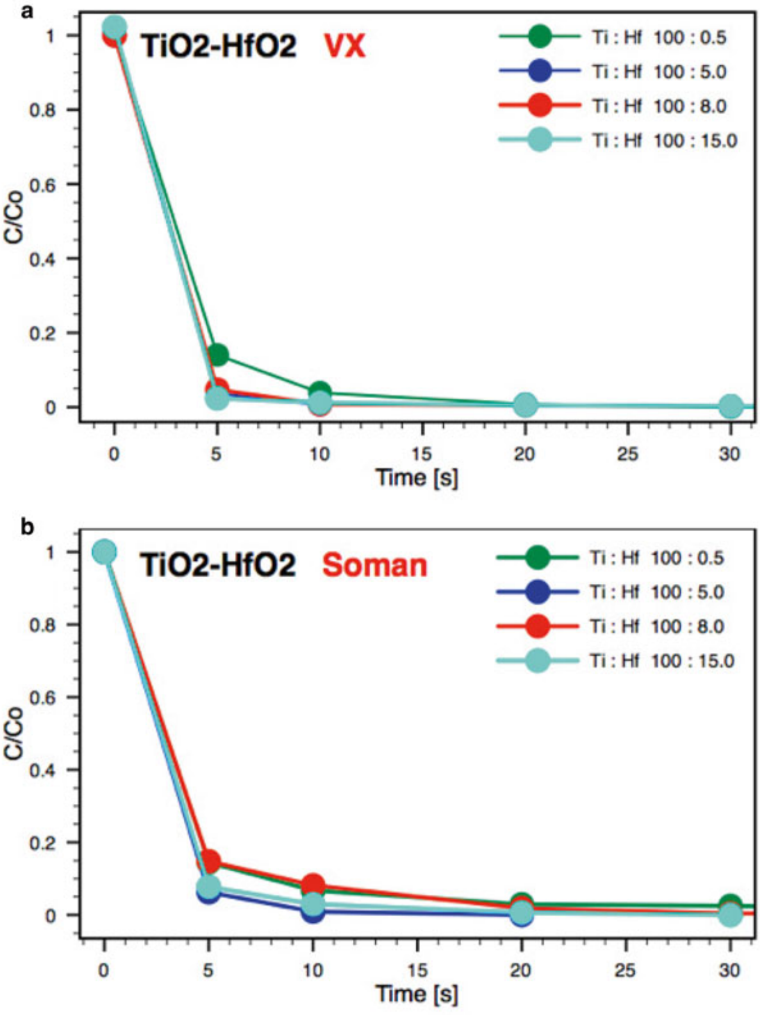

Fig. 5 Kinetics of degradation of (**a**) VX and (**b**) soman on Hf^{4+}-doped TiO_2 nanostructures

contributing to substrate adsorption at the oxide surface and thereby accelerating the rate of degradation of GD, HD, and VX. The addition of Zr^{4+} converts the product of the reaction of ferric sulfate with urea from ferrihydrite to goethite. We determined that the doped oxo-hydroxide Zr–FeO(OH) prepared by homogeneous hydrolysis of a mixture of ferric and zirconium oxo-sulfates in aqueous solution exhibit comparatively higher degradation activity towards CWAs. Degradation of GD or VX on Zr-doped FeO(OH) containing approximately 8.3 wt.% zirconium proceeded to completion within 30 min (Stengl et al. 2010).

Stengl et al. (2013) presented a procedure for the removal and detoxification of CWAs from corrosion-sensitive components using reactive sorption (adsorption and bond cleavage). The procedure consists of spraying a suspended sorbent over a contaminated surface followed by the mechanical removal of the spent sorbent after evaporation of the liquid phase. The procedure was tested using a video graphics array (VGA) card, HD and a nanostructured Zr^{4+}—doped TiO_2 sorbent obtained by homogeneous hydrolysis. After allowing 60 min for a suspension of the reactive sorbent to react with the contaminated VGA card, 99.3 % of the HD was removed, while the VGA card retained its functionality. The procedure does not require specialized instrumentation and is feasible for electronic devices, as it does not need corrosive and electrically conducting agents or nonvolatile solvents that would harm electronic circuits. The method could be applicable for the decontamination of a broad range of CWAs and pesticides.

2.5 Zero-Valent Iron and Iron Oxides

Nanoscale zero-valent iron (Zboril et al. 2012) particles and a composite containing a mixture of ferrate(VI) and ferrate(III) were prepared by thermal procedures. Both nanoscale zero-valent iron and the ferrate(VI)/(III) composite removed HD completely; reactions of GD and VX with Fe(VI) were rapid, and complete degradation was achieved within 10 min. On the contrary, the efficiency of GD and VX degradation by nanoscale zero-valent iron was found to be below 50 % in a reaction time of $\sim$1 h.

2.6 Zirconium Hydroxide

Commercial zirconium hydroxide (Mel Chemicals) was evaluated for its ability to detoxify CWAs GD, HD, and VX (Bandosz et al. 2012). The observed half-lives were 8.7 min, 2.3 h, and 1 min, respectively. The extraordinary reactivity of zirconium hydroxide toward VX is attributed to the complex chemistry associated with the surface of zirconia. The acidic bridging hydroxyl groups are proposed to protonate and hydrolyze VX in a manner analogous to ethyl methylphosphonic acid (EMPA) autocatalysis in solution.

2.7 Manganese Oxide (MnO_2)

Manganese(III, IV) oxide is a highly attractive inorganic material because of its physical and chemical properties and wide applications in catalysis, ion exchange, molecular adsorption bio sensors, and particularly, energy storage. Manganese(IV) oxide is polymorphic, with several different crystal structures such as α-MnO_2

(hollandite), β-MnO_2 (pyrolusite), δ-MnO_2 (birnessite), ε-MnO_2 (akhtenskite), γ-MnO_2 (nsutite) and amorphous MnO_2. Prasad et al. (2007b) used reactive sorbent based on nanosheets and nanotubes of manganese oxide for degradation of CEES with a rate constant of 0.148 h^{-1} and a half-life of 4.66 h, and for the detoxification of HD (Prasad et al. 2007c). Mesoporous manganese oxide MnO_2 nanobelts were prepared from Mn_2O_3 and NaOH by hydrothermal synthesis at 170 °C for 5 days. Decontamination reactions exhibited pseudo first order behavior, and the rate constant value and half-life were found to be 0.43 h^{-1} and 1.6 h, respectively, for GB; 0.01 h^{-1} and 69.32 h, respectively, for HD; and 0.02 h^{-1} and 34.66 h, respectively, for CEES (Mahato et al. 2010).

Manganese (IV) oxides were prepared by homogeneous hydrolysis of potassium permanganate with 2-chloroacetamide and direct reaction of potassium permanganate with manganese(II) sulfate in aqueous solution. The degree of conversion for HD and VX was very good for both samples and reached 95 % and 99 %, respectively. In contrast to HD and VX, degradation of GD was only 56 % on the cryptomelane-type MnO_2 and 18 % on the birnessite-type MnO_2 (Stengl et al. 2012c). The substituted iron(III)–manganese(III, IV) oxides ammoniojarosite $(NH_4)Fe_3(SO_4)_2(OH)_6$ and birnessite $K(Mn^{4+},Mn^{3+})_2O_4$ were prepared by homogeneous hydrolysis of potassium permanganate and iron(III) sulfate with 2-chloroacetamide and urea, respectively. The best activities for the degradation of HD (97.9 % in 64 min) and GD (97.9 % in 64 min) were observed for FeMn_75, which contained 32.6 wt.% Fe (36.8 wt.% Mn) and FeMn_37U, which contained 60.8 wt.% Fe (10.1 wt.% Mn), respectively (Stengl et al. 2012d).

2.8 Vanadium Oxide

Mahato et al. (2009b) synthesized nonstoichiometric $V_{1.02}$O2.98 nanotube samples from vanadium pentoxide and dodecyl amine under hydrothermal conditions at 180 °C for 7 days. The values of the kinetic rate constants for HD and GB degradation were calculated to be 0.11 and 0.1 h^{-1}. The products of the HD degradation were mustard sulfoxide and thiodiglycol, and GB gave isopropyl methylphosphonic acid. The results show that the nanostructure of $V_{1.02}O_{2.98}$ permits promising oxidative and hydrolysis reactions comparable with the existing solid decontamination systems such as nanosized MgO and Al_2O_3. Degradation of HD and its simulant 2-chloroethyl ethyl sulfide (CEES) were investigated on the surface of porous vanadium $_{\text{oxide}}$ VO_x nanotubes at room temperature; the study explored the roles of hydrolysis, elimination and oxidation reactions in the detoxification of HD and CEES, and the first order rate constant and t1/2 were calculated to be 0.026 h^{-1} and 26.6 h, respectively, for CEES and 0.052 h^{-1} and 13.24 h, respectively, for HD (Singh et al. 2011).

2.9 Ce^{3+} and Ce^{4+} Oxides

Cerium oxide belongs to the most important category of rare earths with numerous applications in such diverse areas as catalysis, (Wang and Lin 2004) fuel cell systems, (Babu et al. 2012) and glass polishing (Janoš and Petrák 1991). Crystalline cerium(IV) oxide exhibits a characteristic face-centered cubic (fluorite-type) structure, which is not disturbed by the presence of other lanthanides in concentrations of up to ca. 50 %. Typically, a portion of the Ce atoms exist in a reduced (trivalent) state in cerium(IV) oxide. The ability of Ce to switch between the two oxidation states is related to the unique catalytic activity and versatile applicability of cerium oxide. In recent times, cerium oxide has gained a great deal of attention because of its ability to interact with phosphate ester bonds in biologically relevant molecules including ATP and DNA. Currently, it is regarded as one of the most promising artificial enzymes, also called nanozymes (Wei and Wang 2013). These unique properties (enhanced catalytic activity, enzyme-mimetic ability) are usually attributed to the specifically designed nano-sized forms of cerium dioxide, nanoceria. The ability of cerium oxide to destroy dangerous organophosphate compounds has been discovered only recently (Janoš et al. 2014). Ceria-based reactive sorbents were effective in the degradation of organophosphate pesticides (parathion-methyl, chlorpyrifos, dichlofenthion, fenchlorphos, and prothiofos) and of some CWAs (the nerve gases GD and VX) under relatively mild conditions at ambient temperature. A highly reactive sorbent may be prepared not only from pure Ce compounds but also from cerium concentrates containing a certain amount of other lanthanides, and even from spent ceria-based glass-polishing sludges (Janoš submitted) (see Fig. 6).

Many synthetic routes have been used to prepare the catalytically active forms of nano-ceria, including sol-gel methods, thermolysis and homogeneous hydrolysis. It was shown that conventional precipitation/calcination methods may be adopted to produce ceria-based reactive sorbents with excellent degradation efficiency; a simple and easily scalable procedure involves the precipitation of sparingly soluble cerium carbonate (either with an ammonium bicarbonate solution or with a gaseous mixture of CO_2 and NH_3) with subsequent calcination in the presence of oxygen (air) (Janoš and Petrák 1991; Janoš et al. 2014; Janoš submitted). The properties of cerium oxide, such as its specific surface area, crystallinity, Ce^{3+}/Ce^{4+} ratio, the presence of surface functional groups and its reactivity with organophosphate compounds, may be finely tuned by the proper selection of calcination conditions.

It was suggested that organophosphate degradation in the presence of cerium oxide is governed by the S_N2 mechanism, a nucleophilic substitution in which the –OH groups on the sorbent surface attack the P atom in the organophosphate molecule. It was confirmed that the formation of the –OH groups is energetically favorable, especially in the vicinity of oxygen vacancies associated with the presence of non-stoichiometric "impurities", such as Ce^{3+} cations (Hayun et al. 2011). In accordance with the proposed reaction mechanism, the organophosphate

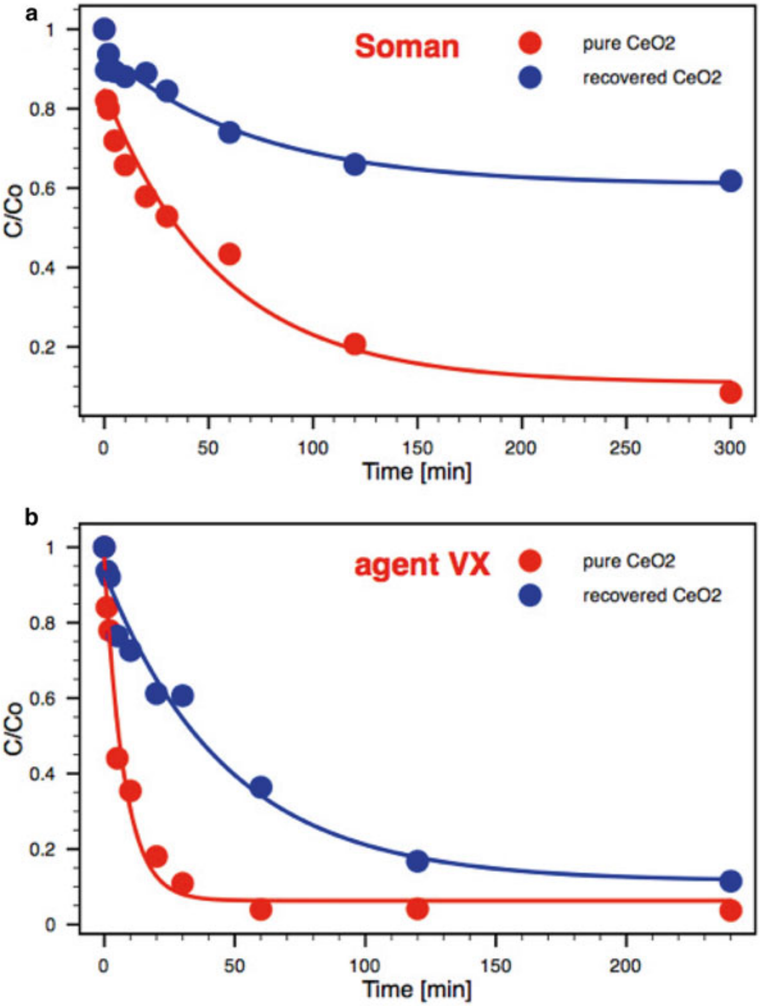

Fig. 6 Degradation of soman (**a**) and VX (**b**) on pure CeO_2 and on CeO_2 recovered from spent glass polishing slurry. Nonane was used as the reaction medium

degradation is promoted in aprotic solvents. As shown in Fig. 6, the almost complete degradation of VX was achieved in nonane within approximately 1 h (Janoš submitted). Both non-polar solvents (heptane, nonane) and polar aprotic solvents (acetonitrile, acetone) that are miscible with water can be used as reaction media (Janoš et al. 2014). This opens new possibilities for designing more versatile decontamination strategies.

Cerium oxide prepared from a carbonate precursor consists of relatively large clusters of irregularly shaped thin plates with diameters of several micrometers.

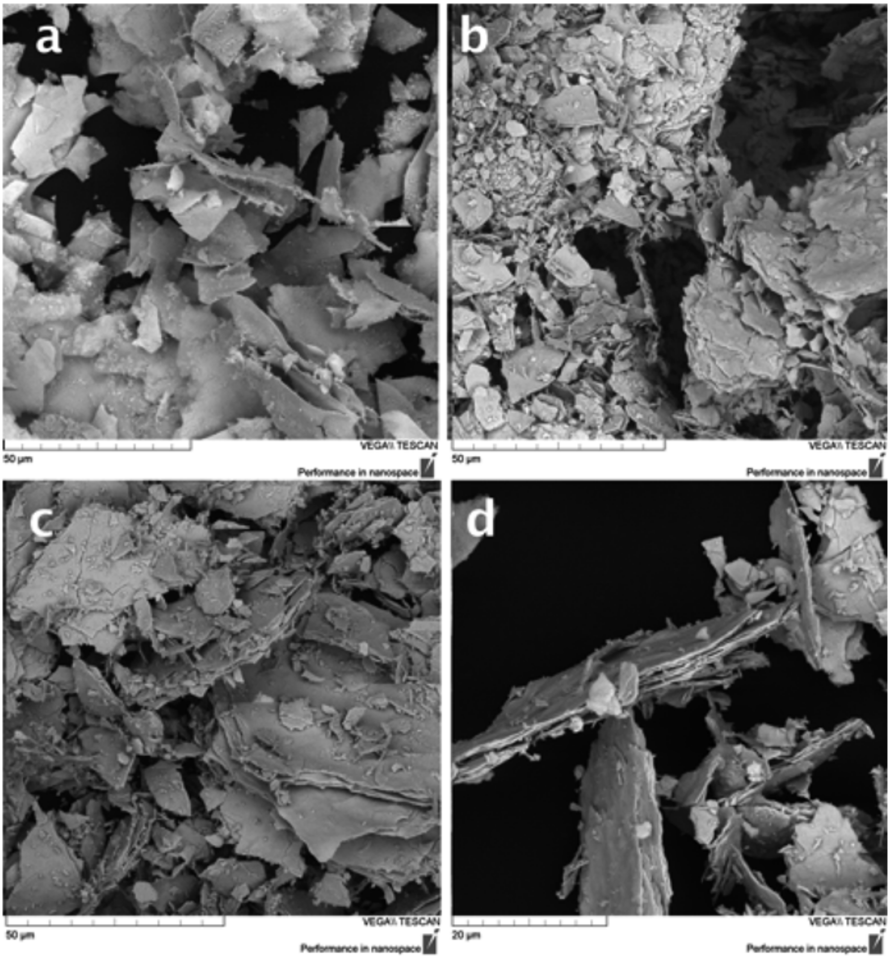

Fig. 7 SEM images of (**a**) cerium carbonate (precursor); (**b**) cerium oxide annealed at 500 °C; (**c**) cerium oxide doped with 5 % La; (**d**) cerium oxide doped with 5 % Pr

The characteristic layered structure of cerium oxide (with plate thickness on the order of nanometers), which is most likely a reason for its high degradation efficiency, is clearly visible in Fig. 7. The presence of minor amounts of other lanthanides (up to 5 % of La, Nd, and Pr, expressed as the respective oxides) does not significantly affect the physico-chemical properties or the degradation efficiency of cerium oxide (Janoš et al. 2014). Thus, relatively impure and low-cost cerium concentrates may be used for preparing effective reactive sorbents. A comparison of reactive sorbents based on nanostructured oxides for the stoichiometric degradation of HD is presented in Table 1.

Table 1 Comparing the effectiveness of selected reactive sorbents for sulfur mustard stoichiometric degradation for time degradation reaction 64 min

Reactive sorbents	Method of preparation	Degree of conversion 64 min [%]	k [s^{-1}]	k_1 [s^{-1}]	k_2 [s^{-1}]	Reference
MgO	Aerogel	68.0	5×10^{-4}		–	Stengl et al. (2004)
TiO_2-anatase	Urea hydrolysis	96.5	3.1×10^{-3}	–	–	Štengl et al. (2005)
Zn doped TiO_2	Urea hydrolysis	98.7	3.3×10^{-3}	–	–	Houskovs et al. (2007)
Zr doped TiO_2[a]	Urea hydrolysis	96.0	–	1.4×10^{-1}	$2–6 \times 10^{-3}$	Stengl et al. (2009)
In doped TiO_2	urea hydrolysis	98.5	–	2.2×10^{-2}	7.1×10^{-4}	Stengl et al. (2012b)
Ge doped TiO_2	Urea hydrolysis	97.7	–	1.9×10^{-1}	1.2×10^{-3}	Stengl et al. (2012a)
ferrihydrite	Urea hydrolysis	83.5	2.5×10^{-3}	–	–	Štengl et al. (2005)
Fe-Zr mixed oxides	Urea hydrolysis	95.0	5.1×10^{-3}	–	–	Stengl et al. (2010)
Al-Zr mixed oxides	Urea hydrolysis	74.0	1.9×10^{-3}	–	–	Stengl et al. (2010)
Zn-Zr mixed oxides	Urea hydrolysis	47.7	8.9×10^{-4}	–	–	Stengl et al. (2010)
Ti-Fe-Zr mixed oxides	Urea hydrolysis	99.5	–	4.5×10^{-2}	9.9×10^{-4}	Stengl et al. (2011a)
α-MnO_2	Chloroacetamide hydrolysis	95.1	–	1.4×10^{-2}	3.5×10^{-3}	Stengl et al. (2012c)
δ-MnO_2	Chloroacetamide hydrolysis	95.8	2.3×10^{-3}	–	–	Stengl et al. (2012c)
Ti-Mn mixed oxides	Chloroacetamide hydrolysis	95.2	–	4.7×10^{-2}	2.1×10^{-3}	Stengl et al. (2011b)
Mn-doped jarosite	Chloroacetamide hydrolysis	95.5	–	2.6×10^{-2}	3.9×10^{-4}	Stengl et al. (2012d)
Fe doped MnO_2	Chloroacetamide hydrolysis	97.8	–	1.4×10^{-0}	1.5×10^{-3}	Stengl et al. (2012d)
TiO_2-GeS_2	Thioacetamide hydrolysis	96.4	–	3.7×10^{-1}	6.7×10^{-4}	Stengl et al. (2012a)
TiO_2-In_2S_3	Thioacetamide hydrolysis	96.7	–	3.5×10^{-2}	1.1×10^{-3}	Stengl et al. (2012b)

[a] Time of degradation reaction 32 min

3 Conclusions

Further research is necessary to search for new, alternative and advanced technologies for CWA decontamination applications using nanostructured transient metal oxides. Previous work has shown that in many cases, the nanostructured metal oxides operate rather selectively and decompose each of the well-known types of warfare agents (HD, GD, GB, VX) with relatively good efficiency. Additional research in the field of nanostructured materials should focus on new materials for the degradation of CWAs with other chemical structures such as cyanophosphonates (tabun), agents containing an arsenic atom (lewisite, adamsite), new compounds based on phosphates (Novichok agents), derivatives of fentanyl and highly toxic halogenated oximes (phosgene oxime). New composite materials based on nanostructured transition metal oxides with graphene, carbon nanotubes or fullerenes have shown promise. In the future, these materials may become the basis for protective "self-decontaminating" materials to protect military equipment from the effects of toxic chemical and biological agents and to significantly facilitate and accelerate decontamination interventions.

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Ecological Recovery Potential of Freshwater Organisms: Consequences for Environmental Risk Assessment of Chemicals

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1 Introduction

The aim of environmental risk assessment (ERA) is to quantify the likelihood of adverse ecological effects resulting from exposure to chemicals and other anthropogenic stressors. The ecological impact relates to adverse effects on populations of non-target species, the communities they comprise and the ecosystem processes in which they function. The protection goals of environmental legislation that deals with chemical stress are usually described in general terms, and focus on sustainability of populations, communities and biodiversity (Brock et al. 2006; Hommen et al. 2010; Nienstedt et al. 2012). The conditions under which ecological recovery can be used as a decision criterion for the ERA of chemical stressors that involve short-term exposure of ecosystem is less clear, and evaluations are particularly needed.

Ecological recovery occurs when an impacted community or population returns to its pre-disturbance state or range of control systems. Disturbance is thereby defined as leading to the breakdown of a system's state, output or response function (Gerritsen and Patten 1985), whereas the cause of a breakdown is usually defined as a stressor (Niemi et al. 1990). A stressor may produce a defined disturbance of limited duration or cause long-term changes to ecosystem functions, referring to pulse or press disturbances, respectively (Bender et al. 1984). Ecological recovery can be classified as either (a) internal recovery due to population growth of surviving organisms or propagules in the stressed (patch of) ecosystem, or (b) external recovery due to the re-colonization of organisms from other sites, either caused by passive or active dispersal. Apart from life-cycle traits related to the mobility of the species of concern, re-colonization mostly depends on landscape patterns, such as the connectivity of habitats and the spatio-temporal configuration of the stressors and populations at risk (Kattwinkel et al. 2012; Niemi et al. 1990; Solomon et al. 2008). Internal recovery predominantly depends on the species' life-cycle traits, related to its ability to develop resistant life-stages (e.g., cysts), generation time and quantity of offspring produced (Brock et al. 2008; Kattwinkel et al. 2012). Furthermore, both the internal and external recovery of a population might be affected by shifts in biological interactions (competition, food availability and predation) in the stressed community (Liess and Foit 2010; Brock et al. 2008).

The aim of the current review is to derive recovery time estimates for a generic consideration of the resilience concept in the ERA of chemicals. We present a literature review on the ecological recovery of aquatic organisms that were exposed to chemical and physical stressors in both field and semi-field studies. In addition, we address the colonization of newly constructed freshwater habitats by water organisms, since this might serve as a worst-case scenario, where the possibility of internal recovery is excluded.

Ecological recovery depends on complex processes related to species, population, ecosystem and landscape properties. We focus in this review on five aspects of ecological recovery in aquatic organisms: (1) The variability in recovery times among different taxonomic groups of freshwater organisms; (2) a comparison of recovery times across taxonomic groups and ecosystem types; (3) variability in recovery times among different types of disturbance for similar taxonomic groups; (4) a comparison of field and semi-field studies; and (5) the relationship between effect magnitude, i.e., the decline in population size following disturbance, and recovery time.

2 Stressor Types, Case Studies and Recovery Estimates Covered by the Review

In this study, we address two general types of stress; chemical and physical. For chemical stressors, we distinguished between pesticides, other organic chemicals and metals. Common forms of physical disturbance comprise all types of man-made perturbation of substrates and communities. Man-made disturbances represented in the reviewed studies included simulated flood events of different sizes, as well as large-scale perturbation, such as resulting from logging activities. Physical stressor included natural perturbation such as drought and flood. Unlike the review by Niemi et al. (1990), in our study, physical disturbances (others than floods and droughts) predominantly concern small-scale disturbances of limited duration, such as alterations of stream beds by logging activities or the shuffling of substrates in studies investigating re-colonization.

In addition to the stressor types described above, we considered case studies that investigated the colonization of newly constructed water bodies as a worst-case scenario. These case studies of constructed water bodies covered newly established streams, stream sections or ponds as a result of restoration or opencast mining activities. We ignored other types of stressors such as acidification, and structural and saprobial degradation, which usually result in long-term shifts in community structure, biodiversity and ecosystem functions.

In this review, we considered studies that investigated recovery processes in both natural aquatic ecosystems and experimental aquatic ecosystems (micro- or mesocosms). Recovery or (re-)colonization refers to measurement endpoints such as abundance, biomass, taxa richness, diversity, community composition (e.g., index of

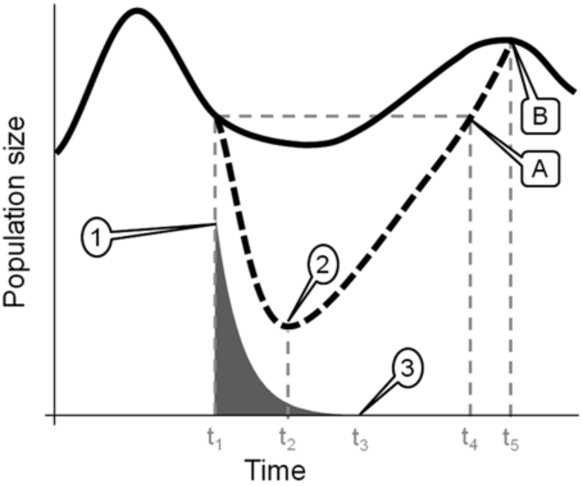

Fig. 1 Hypothetical illustration of recovery in terms of population size (*black lines*) upon disturbance (*grey shade*). The recovery period might start when a disturbance is initiated e.g., in case of short, explicit events (*1*), when a population reaches a minimum size (*2*) or when a stressor is removed from the system (*3*). An affected population (*black dashed line*) has recovered when it reaches the pre-disturbance size (A) or the population size of a reference (control) system (B). t_1–t_3 represent possible start times for a recovery period; t_4–t_5 correspond to different reference states (A, B) at the end of a recovery period

similarity or principle response curves), and the abundance of indicator organisms or the first occurrence of a species.

Recovery is here defined as the return of an ecological measure, such as the endpoints listed above, to its reference state (Fig. 1). The recovery time is calculated as the period between a certain starting point in time after the disturbance until the reference state is reached. The time point when the greatest effect (such as a decline in population abundance) occurred following a disturbance was considered to be the start of recovery whenever possible (t_2 in Fig. 1). However, in many cases, recovery times could only be estimated from the time when a stressor was introduced into the system (t_1 in Fig. 1) or from the end of an exposure period (t_3 in Fig. 1), e.g., in the case of restoration success after chronic metal pollution. In all of these cases, the stressor was not necessarily fully removed from the system at the considered start of the recovery process. In case recovery appeared during a sampling interval, recovery time was calculated based on the sampling date.

Taking a previously published review of case studies as a starting point (Niemi et al. 1990), the emphasis of our literature search was drawn to studies published in the period 1990–2010. On the basis of title and abstract, a total of 471 and 152 publications were collected for lotic and lentic systems, respectively. Out of these publications, case studies that included recovery and colonization information for freshwater populations or communities were selected on the basis of four criteria: (1) Appropriate description of the system or site characteristics available; (2) disturbance caused by a stressor of which the exposure is described clearly; (3) description and quantification of a pronounced effect that can be related to the described stressor; (4) data on recovery times are available, including pre-disturbance or reference data, or data indicating stable population establishment in newly constructed freshwater ecosystems. By applying these criteria, 397 publications were rejected. Finally, the selection included 150 articles for lotic systems and 76 articles for lentic systems, resulting in a total of 148 case studies and 908 recovery endpoints, i.e., records of recovery or colonization times for populations, functional groups or communities.

The studies considered in this review were predominantly performed in North America (54 %) and Europe (28 %). Only a few cases were found for Australia/Oceania, Africa, Asia, and South America. The duration of the original studies varied with the study objective and the type of stressor investigated. Studies were predominantly conducted with observation periods of 1–3 years (41 %) or shorter (40 %), whereas studies with longer observation periods were less frequent (19 %). Of the 908 recovery endpoints recorded, the total abundance of broad taxonomic groups (n = 408) and the abundance of taxa at the species to family level (n = 278) were used most often. Furthermore, taxa richness (n = 93) and the biomass of taxonomic groups (n = 74) were used in a number of studies to describe recovery processes. Community measures, namely community composition (n = 33), diversity (n = 21), and indicator organisms (n = 1), were used less frequently.

3 Variability in Recovery Times Among Taxonomic Groups

The majority of the recovery endpoints were identified for macro-invertebrates (n = 629). In comparison to Niemi et al. (1990), data for zooplankton (n = 133), algae (n = 50), and aquatic macrophytes (n = 51) increased in recent years. In addition, in our review, 45 entries for fish were included. Within the group of macro-invertebrates, most of the data on recovery times were available for Diptera (n = 114), Ephemeroptera (n = 64), Coleoptera (n = 43), Trichoptera (n = 42), and Heteroptera (n = 32). In a number of studies, recovery endpoints were clustered for functional groups (n = 221) including feeding groups, total abundance or the total biomass of macro-invertebrates. In contrast to planktonic micro-crustaceans, such as Phyllopoda and Copepoda, data were generally sparse for macro-crustaceans (e.g., amphipods and isopods), and other invertebrate groups such as molluscs.

In this review, recovery times for aquatic organisms varied from <1 month to >16 years, with an overall mean of 1.36 years and a coefficient of variation (CoV) of 2.09. When separating recovery times by taxonomic group, within-group variation could be reduced (mean CoV = 1.41), with the lowest variability in recovery times observed for planktonic taxa, e.g., algae, Phyllopoda and Copepoda, and the highest variability for several groups of macro-invertebrates (e.g., Oligochaeta and the insect groups Plecoptera, Trichoptera and Heteroptera) (Fig. 2). In part, this variability can be explained by differences in generation times among different taxa, which might vary from days, in the case of microalgae, to a few years, in e.g., fish

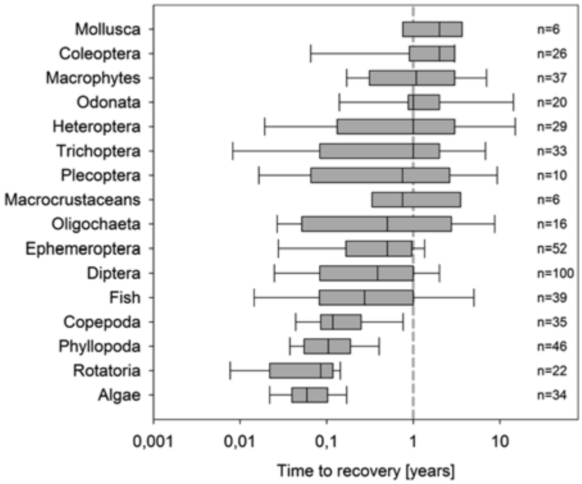

Fig. 2 Recovery times for selected taxonomic groups. *Boxes* represent quartiles and whiskers symbolize 95 % confidence intervals. Taxonomic groups are sorted by their median; *n* number of recovery endpoints

and some macro-invertebrate taxa (see e.g., Barnthouse 2004). Generation time is an important factor for internal recovery if a viable proportion of the population survives in the stressed ecosystem of concern, which in turn might depend on the effect size resulting from the disturbance. In the presence of source populations in nearby aquatic habitats, external recovery also depends on further characteristics such as the dispersal ability of a given taxon. In addition to information provided in the literature reviewed, we make use of information on life-history traits for different taxa derived from databases published by Heneghan et al. (1999), Liess et al. (2001, available online: http://www.systemecology.eu/spear/) and Usseglio-Polatera et al. (2000).

3.1 Algae

Within the group of algae, we considered phytoplankton and periphyton, whereas macro-algae such as species of the genus *Chara* are here classified as macrophytes. In most cases (60 %), algal recovery was observed in terms of total biomass or surrogate measures for biomass (e.g., Chlorophyll a). In reviewed lentic case studies, observations frequently included both phytoplankton and periphyton. In lotic systems, however, investigations were restricted to periphyton. Recovery times for algae ranged from 3 days to 20 weeks (Fig 1). Studies on the recovery of selected taxonomic groups, mostly Bacillariophyceae (diatoms) and Chlorophyceae (green algae), were commonly performed using artificial lentic systems. Mean recovery times were 3.9 and 4.4 weeks for taxonomic groups and total biomass, respectively. Rapid recovery was frequently observed, e.g., in case studies that investigated recovery after pesticide applications in artificial mesocosm studies (Brock et al. 2004;

Hatakeyama et al. 1994; Mohr et al. 2008; Peterson and Stevenson 1992). A longer recovery time was observed e.g., for a periphyton community exposed to heavy metals (Steinmann and McIntire 1990) and for a case where the colonization of bricks (placed at a closed canopy site) was completed by lotic diatoms within 20 weeks (Robinson and Rushforth 1987). Long-term changes in algal communities might be the consequence of the replacement of one species by another. For instance, in tundra ponds, a cryptomonad species became extinct during a crude-oil spill and was subsequently replaced by chrysophytes; the community did not return to its pre-disturbance composition during a study period of 6 years (Miller et al. 1978). As pointed out by Steinmann and McIntire (1990), community structure in turn might also affect periphyton recovery time. For example, the age of periphyton communities might have an influence, in that young periphyton communities have a higher resistance and recover faster than older ones (Kaufman 1982), as older communities are more complex and dynamically fragile (May 1975).

3.2 Zooplankton

Studies that report recovery times for zooplankton have predominantly focused on Phyllopoda (including Cladocera), Copepoda and Rotatoria, whereas few endpoints were available for Branchiopoda. Although post-disturbance reductions in population size larger than 90 % were frequently reported, zooplankton recovery usually appeared to be rapid. In the reviewed case studies, recovery was completed within 9 weeks in Rotatoria and 35 weeks in Phyllopoda, with a mean recovery times of 3.9 for Rotatoria and 8.1 weeks for Phyllopoda (Fig. 1). For Copepoda, the mean recovery time was 13 weeks, but longer recovery times of up to 1 year were also recorded. The slower recovery of Copepoda might be due to longer generation times in this group compared to other planktonic species. Generation times of zooplankton species generally vary between weeks, for instance in Rotatoria and Phyllopoda, and months in Copepoda (Barnthouse 2004; Kulkarni et al. 2013; Peterson 2001). As a consequence, most rotifers, cladocerans and copepods are characterized by large intrinsic growth rates (see e.g., Barnthouse 2004) and recover quickly by intrinsic means, if a viable part of a population is able to endure disturbance. This agrees with findings from field surveys (Melaas et al. 2001) and studies conducted in model ecosystems (Hanson et al. 2007; Liber et al. 1992; O'Halloran et al. 1999; Rand et al. 2000; van Wijngaarden et al. 2006). Longer zooplankton recovery times were observed in cases where populations went extinct upon disturbance (Lahr 1998; Ward et al. 1995). However, data for pond colonization indicate that re-colonization and passive dispersal can be effective (Frisch and Green 2007; Louette and De Meester 2004). Colonization by zooplankton largely relies on the presence of uncontaminated refuges (Lopez-Mancisidor et al. 2008b), the production of diapausing eggs (Hairston and Cáceres 1996) and their transport by wind (Brendonck and Riddoch 1999), by water flow in connected systems (Thorp et al. 1994) or animals (Bilton et al. 2001; van de Meutter et al. 2008).

3.3 Fish

In our review, recovery times for fish ranged between 1 day and 10 years and had a mean of 1.43 years. Data are predominantly based on lotic studies, including 44 endpoints, whereas recovery in lentic systems is less well represented ($n = 1$). In temperate climates, many fish species exhibit one reproduction event per year (for an overview see e.g., Ibrahim et al. 2014). As a consequence, short-term recovery of population size is only possible by external means, e.g. by re-colonization. Several examples have shown that de-faunated stream sections can be quickly re-occupied by eurecious and vagile species (Davey 2007; Lonzarich et al. 1998; Miller 2006; Olmsted and Cloutman 1974; Peterson and Bayley 1993; Sheldon and Meffe 1994), whereas the more slowly recovering species were classified as stenoecious and less vagile (Olmsted and Cloutman 1974). Galaxiidae, Gobiidae and some Cyprinidae, in particular minnows, were most resilient to disturbance (Davey 2007; Lonzarich et al. 1998; Greathouse et al. 2005), whereas Salmonidae were frequently among the least resilient species (Cowx et al. 1984; Hawkins and Sedell 1990; Milner 1987; Milner et al. 2000). Long recovery times were usually associated with dramatic large-scale effects (Hawkins and Sedell 1990; Lelek and Köhler 1990), habitat isolation (Hawkins and Sedell 1990; Lonzarich et al. 1998), or metal pollution (Diamond et al. 1993; Ryon 1992). In one case, the knockdown of a population was followed by the invasion of a new species with long-term consequences for community composition (Hanson and Waters 1974). In a comprehensive review of fish case studies, Detenbeck et al. (1992) concluded that lotic fish communities are least resilient following press disturbances, in the absence of mitigation efforts and alterations in habitat quality.

3.4 Macro-invertebrates

The group of macro-invertebrates is taxonomically heterogeneous. Therefore, in this section, we present recovery information according to different macro-invertebrate groups in the order of increasing median recovery times (see Fig. 2).

3.4.1 Diptera

The majority of aquatic Diptera are reported to have a multivoltine (≥ 3 generations per year) or bivoltine (two generations per year) life-cycle, although univoltine (one generation per year) species also exist. In the reviewed papers, recovery times for aquatic dipterans ranged between 1 day and 15 years, with an overall mean recovery time of 1.1 years (Fig. 1). Mainly Chironomidae, Chaoboridae and the lotic family of Simuliidae were investigated in the selected case studies. In lotic cases where re-colonization was possible via drift (Doeg et al. 1989; Matthaei et al. 1997) or migration from the hyporheic zone, which is the region alongside and beneath a stream bed

(Dostine et al. 1997), a rapid recovery was observed. Similarly, in insecticide-treated ditch sections, recovery times of Diptera were shorter in the presence of interconnected non-polluted ditch sections (Brock et al. 2010a) than in systems where the whole surface area was treated. For newly constructed lotic and lentic systems, as well as in systems contaminated with persistent compounds, dipteran recovery times appeared to be 1 year or longer (Barnes 1983; Christman and Voshell 1993; Fairchild et al. 1990; Melaas et al. 2001). In lentic systems, recovery might especially depend on external colonization sources. Where re-colonization from neighbouring sources was hampered (e.g., due to spatial isolation of newly constructed systems or by covering experimental ecosystems with gauze), full recovery of dipterans was not observed (Caquet et al. 2007; Tidou et al. 1992). In contrast, recovery of Diptera can be rapid when re-colonization from nearby external sources is possible (Caquet et al. 2007) and the stressor is not persistent. Furthermore, the partitioning and bioavailability of the chemical stressor in relation to the typical habitat of the dipteran in the aquatic ecosystem of concern might play an important role in its recovery time. For example, in experimental ditches sprayed with the hydrophobic and persistent insecticide lufenuron, Diptera predominantly dwelling in the water column (e.g., *Chaoborus*) showed a faster recovery than that of sediment-associated Diptera (e.g., *Chironomus*), which could be explained by differences in exposure dynamics between the water and sediment compartment (Brock et al. 2010b).

3.4.2 Ephemeroptera

In the papers reviewed, recovery times between 1 day and 8 years, with an overall mean of 0.9 years, were reported for Ephemeroptera (Fig. 1). The majority of Ephemeroptera exhibit a bivoltine to univoltine life-cycle, although multivoltine and semivoltine species are also common. Most recovery times for Ephemeroptera were reported for the Baetidae, for which most taxa have several generations per year. In lotic systems, Baetidae are often among the first to arrive after disturbance and can recover within a few days (Brooks and Boulton 1991; Dosdall and Lehmkuhl 1989; Dostine et al. 1997; Tikkanen et al. 1994), probably due to drift from undisturbed upstream reaches (Dosdall and Lehmkuhl 1989; Mackay 1992) or to survivors in the hyporheic zone (Dostine et al. 1997). Some aquatic stages of lotic and sediment-dwelling Ephemeroptera were reported to have a less-pronounced tendency to drift (e.g., *Ephemera danica*, Otto and Sjöström 1986). In a small headwater stream, methoxychlor exposure led to a reduction in aquatic insect abundance and biomass of about 90 %; ephemeropteran taxa were among the least resilient groups and did not recover until 3–5 years following the treatment (Yameogo et al. 1993). For other taxa with flying adults, recovery of Ephemeroptera in isolated aquatic systems benefits from the dispersal of reproductive adults, but recovery times are reported to depend on the number of generations that different taxa have. For example, in experimental ditches treated with the insecticide chlorpyrifos, *Cloeon dipterum* (Baetidae) with 2–3 generations per year showed a faster recovery than *Caenis horaria* (Caenidae) with 1–2 generations per year (van den Brink et al. 1996).

In general, the persistence of the stressor and prevailing environmental conditions can impact recovery times. Slow colonization in Ephemeroptera was observed for instance, after long-term heavy metal discharge (Ryon 1992, 1996; Smith 2003) or due to low ambient temperatures (Flory 1999; Flory and Milner 1999; Milner 1987, 1994; Milner et al. 2000). In addition, the partitioning and bioavailability of the chemical stressor in relation to the typical habitat of the ephemeropteran in the aquatic ecosystem of concern might play an important role in its recovery time. For example, in mesocosms treated with the pharmaceutical ivermectin (Sanderson et al. 2007) and the insecticide lufenuron (Brock et al. 2010b), both persistent chemicals that show a fast partitioning from water to sediment, it was observed that typical benthic Ephemeroptera had a relatively slow recovery compared with typical water column organisms, including species of Ephemeroptera that more frequently dwell in the water compartment between macrophytes.

3.4.3 Oligochaeta

The majority of aquatic Oligochaeta have a multivoltine or bivoltine life-cycle. Recovery in populations of Oligochaeta lasted for a mean of 2.2 years (Fig. 1). In Oligochaeta, recovery within 6 months was found in case studies investigating drought (Fuller et al. 2008; Harriman and Morrison 1982; Otermin et al. 2002) or small-scale physical disturbance, where migration from the hyporheic zone or neighboring patches was possible (Fuller et al. 2008; Otermin et al. 2002). In two cases of chemical pollution, no recovery within the study periods was reported for *Tubifex tubifex* (Liess and Schulz 1999; Swift 2002). If a proportion of the population of an oligochaete species with a short generation time survives in the stressed habitat, the recovery time might be short. However, these species appear to lack a high dispersal ability and therefore, (re-)colonization is expected to be slow (Barnes 1983; Koskenniemi 1994; Miller 2006).

3.4.4 Macro-crustacea

We pooled Amphipoda, Decapoda and Isopoda into a single group of macro-crustaceans. The life cycle of this heterogeneous group varies from multivoltine to semivoltine. Amphipoda and Isopoda, however, overall have a bivoltine life cycle, whereas Decapoda overall can be characterised as univoltine. In the reviewed papers, reported recovery times for macro-crustaceans were scarce and ranged between 4 month and 5 years, with an overall mean of 1.7 years (Fig. 1). However, in 68 % of the studies included in the review for this group, macro-crustaceans did not recover within the study periods. As they lack terrestrial stages, movement within a system appears to be the most important re-colonization mechanism for macro-crustaceans. For example, in isolated lentic micro-/mesocosms treated with the insecticides chlorpyrifos (Van den Brink et al. 1996), lambda-cyhalothrin (Roessink et al. 2005) and gamma-cyhalothrin (Van Wijngaarden et al. 2009), the recovery of populations of *Gammarus pulex* was reported to be hampered when completely eliminated in the test systems. In contrast, the local elimination of *Gammarus pulex* in interconnected stream habitats by insecticide contamination was reported to be short-term, due to avoidance and migration to uncontaminated refuges followed by rapid re-colonization (Schulz and Liess 1999). In *Gammarus* species, seasonal upstream migration, which compensates for 50 % of yearly drift losses, has been suggested to be an important feature of population dynamics (Meijering 1971, 1977). It has also been reported that in isolated lentic microcosms, recovery of the macro-crustaceans *Asellus aquaticus* (Isopoda) and *Crangonyx pseudogracilis* (Amphipoda) is hampered following their elimination due to dichloroaniline and cypermethrin treatment, unless they are actively re-introduced into these systems (Maund et al. 2009).

3.4.5 Plecoptera

Plecoptera are reported to have a univoltine life cycle and almost exclusively inhabit lotic systems. In the reviewed case studies, the Plecoptera population recovered on average within 1.9 years, and the recovery time ranged between 1 week and 10 years (Fig. 1). Although Plecoptera species showed a rapid recovery due to drift dispersal from non-stressed upstream sections (Brooks and Boulton 1991; Harriman and Morrison 1982; Morrison 1990), they often exhibited slow or no recovery following large-scale disturbance or in habitats lacking refuges (Beketov et al. 2008; Yasuno et al. 1982), probably due to their poor adult dispersal ability. This general trend is supported by studies of newly established stream habitats (Flory 1999; Flory and Milner 1999; Malmqvist et al. 1991; Milner 1987, 1994; Milner et al. 2000).

3.4.6 Trichoptera

In the reviewed papers, recovery times for Trichoptera ranged between a few days and 15 years, with an overall mean recovery time of 2.2 years (Fig. 1). The majority of aquatic Trichoptera are reported to have a univoltine life-cycle, but bivoltine species are also common, whereas a few semivoltine Trichoptera species exist. Studies reporting the recovery of Trichoptera have mostly focused on lotic filter-feeding species belonging to the family of Hydropsychidae, whereas information on the common family of Limnephilidae is scarce. Rapid recovery of Hydropsychidae was found after pesticide application, flooding events and heavy-metal contamination (Malmqvist et al. 1991; Ryon 1992, 1996; Smith 2003; Specht et al. 1984; Yasuno et al. 1982; Whiles and Wallace 1992), whereas after large-scale disturbance (Ide 1967), in newly established lentic systems (Barnes 1983; Danell and Sjoberg 1982; Koskenniemi 1994) and for other trichopteran species (Ryon 1992, 1996; Smith 2003), long recovery times have been reported.

3.4.7 Heteroptera

Heteroptera are most common in lentic ecosystems. However, colonisation of bugs was also reported in pools of a lotic system shortly after establishing a river (Malmqvist et al. 1991). In the reviewed papers, aquatic bugs recovered on average within 3.5 years (Fig. 1). In contrast to this long recovery time, Heteroptera, in particular Notonectidae and Corixidae, are generally known as rapid colonizers, due to their high capability of flight (Barnes 1983; Solimini et al. 2003). However, the colonization success of aquatic Heteroptera also depends on the presence of suitable habitats and environmental conditions in the newly constructed aquatic systems (Danell and Sjoberg 1982). For example, no colonization of aquatic Heteroptera was found in newly constructed bog ponds (Mazerolle et al. 2006). In insecticide-treated experimental ditches (Brock et al. 2009), recovery times of adult *Plea minutissima* (able to fly) were considerably shorter than for the non-flying juvenile stages of this species, illustrating the importance of re-colonization in the recovery process. Despite their high dispersal ability and their bivoltine to univoltine reproductive strategy, rapid recovery can only be expected for Heteropera when habitat characteristics remain unaffected by stressors.

3.4.8 Odonata

The life cycle of Odonata varies from bivoltine to semivoltine. The majority of Zygoptera species (damselflies) is characterised by a univoltine life cycle, whereas most Anisoptera (dragonflies) have a semivoltine life cycle. Most of the studies included in this review, and which provided information on suborders, reported recovery processes of Zygoptera species (14 out of 17 studies), whereas less information was available for Anisoptera. Recovery times for aquatic Odonata ranged between 1 month and 15 years, with an overall mean recovery time of 2.9 years (Fig. 1). Odonata species in general have well-developed dispersal abilities in the form of flying adults (Corbet 1980). In Odonata, relatively short (<1.3 year) colonization times of newly constructed habitats and times to recovery after disturbance have been reported (Barnes 1983; Christman and Voshell 1993; Harrel 1985; Malmqvist et al. 1991; McDonald and Buchanan 1981; Solimini et al. 2003; Ward et al. 1995). However, as predators, Odonata rely on a sufficient supply of prey. Rapid recovery can thus be observed when sufficient prey organisms remain in the stressed ecosystem as a food resource. In contrast, slow Odonata colonization is reported for newly constructed ponds (Danell and Sjoberg 1982; Mazerolle et al. 2006), where prey populations had presumably not yet established.

3.4.9 Coleoptera

The majority of aquatic Coleoptera (beetles) is characterised by a univoltine lifecycle. Semivoltine species with a generation time longer than a year are also common and a few taxa are reported to be bivoltine. The mean recovery times reported for aquatic beetles was 2.2 years (Fig 1). However, for the majority of the studies included in this review (63 % of the cases), beetles did not recover within the study periods. In contrast, aquatic (adult) Coleoptera were frequently reported among the earliest colonists of new freshwater habitats (Barnes 1983; Collier and Quinn 2003; Dostine et al. 1997; Fairchild and Eidt 1993; Liess and Schulz 1999; Malmqvist et al. 1991; McDonald and Buchanan 1981; Scrimgeour et al. 1988). Following physical and chemical stress, no recovery within the study periods was found for long-lived beetles with a poor dispersal ability and in beetles that rely on certain habitats that were destroyed (Mazerolle et al. 2006; Molles 1985; Zwick 1992). The large variability in the capability of flight (Jackson 1952) and reproductive strategy among water beetles can complicate the prediction of recovery times for this group in general, although we found that variability in recovery times for this group is comparably low (Fig. 2).

3.4.10 Mollusca

In the reviewed papers, recovery times for Mollusca varied between 1 week and 8 years, with an overall mean recovery time of 2.5 years (Fig. 1). For Mollusca in lotic ecosystems, the colonization of newly constructed gravel bars appeared to be rapid (Bingham and Miller 1989; McClure 1985; Miller 2006), probably due to passive transport via drift from upstream sections. Longer recovery times of 12 and 26 months were reported for coal-ash exposure and crude-oil spill, respectively (Cherry et al. 1979; Harrel 1985), probably due to the persistent properties of the toxicants involved. Aquatic Mollusca have a univoltine life-cycle, but species with a multivoltine or semivoltine life cycle also exist. They generally lack good dispersal ability. Since colonization of new habitats relies on passive dispersal, it often takes molluscs several years to reach abundances in lentic systems similar to those of reference systems (Barnes 1983; Danell and Sjoberg 1982; Guiral et al. 1994; Koskenniemi 1994).

3.5 Macrophytes

Aquatic macrophytes can be classified into submerged and emergent plants. In the majority of macrophyte case studies, recovery was investigated with regard to area coverage or plant biomass, whereas a few studies also focused on the taxonomic composition of macrophyte communities (e.g., Biggs et al. 1998; Eichler et al. 1995; Gergs 2006). For the reviewed case studies, macrophyte recovery times ranged from 1 to 15 years, resulting in a mean recovery time of 2.75 years (Fig. 2). If parts of the plants or the entire aboveground plant parts are destroyed upon disturbance, recovery depends on the ability to re-grow from surviving rootstocks or shoots. Rapid recovery, usually below 1 year, was thus frequently found for submerged macrophytes such as Haloragaceae, Ceratophyllaceae, Characeae and Potamogetonaceae (Barnes 1983; Barrat-Segretain and Amoros 1996; Brooker and

Edwards 1973; Eichler et al. 1995). Long recovery times were usually associated with emergent plant recovery after dredging events (e.g., by Cyperaceae, Gergs 2006; Mazerolle et al. 2006) and colonization of new habitats (Danell and Sjoberg 1982). In cases where recovery was investigated at the community level, recovery times were also often long (Koskenniemi 1994; Mitchell 1980; Tanner et al. 1990). Macrophyte communities, however, might adapt to seasonal disturbances as was shown for ditches and streams in agricultural landscapes. Managing activities, such as periodic dredging to maintain hydrological function of ditches, have been shown to select for fast-growing species (e.g., Lemnids) and species that are able to re-grow from remaining rootstocks or detached shoots (Brock et al. 2010b; Twisk et al. 2003).

4 Contributions of Ecosystem Type, Landscape Characteristics and Community Processes

Factors relating to the ecosystem type and ecological infrastructure of the landscape are reported to trigger recovery processes (Poff and Ward 1990; Reice et al. 1990; Sedell et al. 1990). External recovery of a population depends on the degree of isolation of the stressed aquatic habitat and the presence of sources for recovery in other aquatic habitats. Lotic systems are usually well connected to undisturbed sections, if no barriers prevent organisms from within-stream migration. In contrast, lentic systems are usually less-well connected and terrestrial or aerial migration often appears to be the only re-colonization pathway. As a consequence, recovery is generally faster in lotic systems (overall mean recovery time of 0.90 years) compared to that in lentic systems (overall mean recovery time of 1.68 years). Of the case studies included in this review, 63 % were lotic, providing 54 % of the data and 37 % of the studies were conducted in lentic systems, accounting for 46 % of the recovery endpoints. Part of the variability in recovery times can thus be assigned to differences in system types. Classifying data by taxa and system type reduced the variation in recovery times compared to the entire data set (see above), with coefficients of variation of 1.25 and 1.22 in lotic and lentic systems, respectively (Fig. 3). Considering the importance of both internal recovery potential and migration ability for a given situation, recovery times might be shorter or longer than a species' generation time, depending on dispersal ability, the system type of concern and presence of source populations for re-colonization. Shorter recovery times in lotic compared to lentic ecosystems is more common for aquatic Diptera, Coleoptera and Trichoptera (Fig. 3), probably due to re-colonization of populations from non-stressed sections. Differences in recovery times were less pronounced for the groups of algae; Ephemeroptera and Oligochaeta (Fig. 3).

Part of the variability in recovery times also stems from the different taxonomic groups investigated in lentic and lotic systems. Within the group of algae, investigation of pelagic micro-algae is restricted to lentic systems, whereas recovery of periphyton is reported for both lentic and lotic systems. Moreover, zooplankton

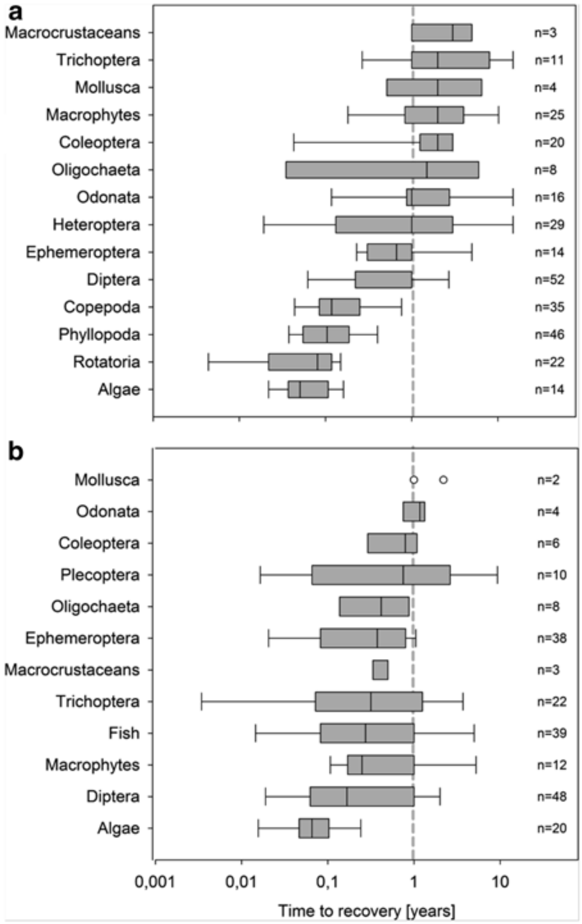

Fig. 3 Recovery times for selected taxonomic groups separated by system type: (**a**) lentic systems, (**b**) lotic systems. *Boxes* represent quartiles and whiskers symbolize 95 % confidence intervals. *Dots* represent data with n < 3. Taxonomic groups sorted by their median; *n* number of recovery endpoints

recovery is solely reported for lentic systems, whereas studies on lentic fish are generally lacking in this review. In the following, we therefore focus on the (heterogeneous) group of aquatic macro-invertebrates.

In lotic systems, the lowest macro-invertebrate recovery potentials were found for Mollusca, Coleoptera, Odonata and Plecoptera (Fig. 3b). At the low end of recovery times, Chironomidae were consistently recorded among the first macro-invertebrate colonizers of lotic ecosystems (Chadwick et al. 1986; Churchel and Batzer 2006; Milner 1994; Pires et al. 2000; Yasuno et al. 1982). Moreover, mayflies, especially Baetidae (mostly Baetis sp.) (Ryon 1992; Weng et al. 2001; Yameogo et al. 1993) and certain Leptophlebiidae (Sagar 1983; Scrimgeour et al. 1988) were frequently recorded as highly abundant and early colonizers of lotic systems. The early arrival of browsing and gathering dipterans and ephemeropterans mentioned above is consistent with their ability to exploit the early occurring food materials on and among bare substrates. Later in the recovery sequence of streams, grazers and shredders contribute to colonization. If colonists were not able to browse or gather, filter feeders appeared as alternative early feeding types. Accordingly, Simuliidae (Diptera), Hydropsychidae (Trichoptera) and some chironomids (e.g., *Rheotanytarsus* sp.) were found to re-appear quickly in disturbed stream patches (Chadwick et al. 1986; Malmqvist et al. 1991; Matthaei et al. 1996; Weng et al. 2001; Yameogo et al. 1993), whereas shredder-dominated communities, which are typical for first-order forest streams, appeared to recover slowly after disturbance (Mackay 1992). In general, shredders have often been reported as later colonizers compared to other detritivores and herbivores (summarized in (Mackay 1992), since they often have poor dispersal abilities.

For lentic systems, in particular Diptera, but also Epemeroptera, are recorded as early macro-invertebrate colonizers (Barnes 1983; Layton and Voshell 1991), which is also reflected by their overall low recovery times (Fig. 3a). In lentic case studies, the majority of benthic macro-crustaceans, Trichoptera, Mollusca and Coleoptera did not recover within 1 year. Subsequent colonization sequences largely depended on food availability for newcomers. For instance, early colonizing zooplankton and dipteran species can serve as food source for predatory heteropterans, e.g., of the genus *Notonecta*, and dytiscid coleopterans (Gergs 2006; Schmidl 1997), whereas detritivorous species, e.g., some Heteroptera such as *Hesperocorixa* sp. and *Sigara* sp., rely on certain macrophyte covers (Gergs 2006; Macan 1938; Savage 1989).

For both lotic and lentic systems, recovery times might depend on community processes, as recovery might be comparably faster if other resources, such as prey populations, remain unaffected by the stressor or show rapid recovery. In general, recovery times in terms of community biodiversity measures such as taxa richness, community composition and diversity indices were longer compared to recovery times recorded for the total abundance of macro-invertebrates or of high-abundance populations of single species (Fig. 4) indicating the importance of community processes. Studies that followed the recovery of single species have often focused on taxa that were relatively abundant. In contrast, the analysis of taxa richness, community composition or diversity indices also includes species that occur in low numbers and/or are erratic in time. It cannot be excluded that these low-abundance taxa are more vulnerable to stressors.

The analysis of the collected literature data indicates that taxonomy and the generation time of taxa alone cannot explain recovery patterns in the field and that habitat and landscape characteristics must be considered. Due to habitat connectivity, there is a trend for lotic systems to have a greater potential for faster recovery than lentic systems, even if the lotic species have relatively long generation times. Recovery in freshwater ecosystems might be faster if undisturbed stretches or refuges within affected reaches are present (Brock et al. 2010b; Cuffney et al. 1984; Schriever et al. 2007). Drift is one of the dominating re-colonization and recovery pathways within lotic systems (Brittain and Eikeland 1988); if only upstream migration is possible, then recovery appears to be slower. Only for fish is active movement more dominant than passive drift (Detenbeck et al. 1992). Within-stream

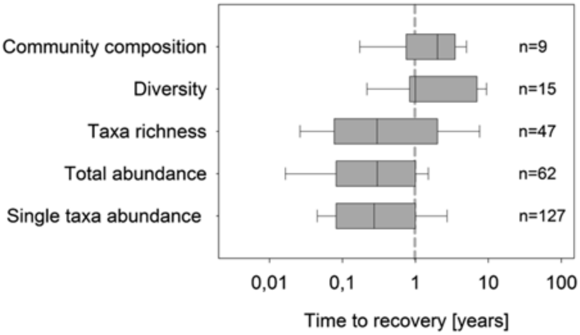

Fig. 4 Time to recovery in lotic macro-invertebrates as quantified for different populations and community measures. Total abundance covers the number or biomass in an entire community, irrespective of the species involved, whereas single taxa abundance refers to the number or biomass estimated from populations of a single taxonomic group. Taxa richness includes recovery of overall macro-invertebrates or recovery in selected taxonomic sub-groups, community composition includes principal response curves and indices of similarity; diversity integrates different diversity indices. *Boxes* represent quartiles and whiskers symbolize 95 % confidence intervals. Community measures are sorted by their median; *n* number of recovery endpoints

movement (either active or passive) was suggested as a major recovery pathway in 32 % of the case studies.

In both lotic and lentic freshwater ecosystems, aerial re-colonization of macrophytes and macro-invertebrates might be an important recovery pathway. Aerial re-colonization might be an active (e.g., in aquatic insects via flying adults) or a passive process (e.g., transport via waterfowl). In general, the spatial scale of disturbances, as well as habitat and landscape-related aspects such as the presence of refuges in the landscape of concern, and connectivity and distance to source populations in these refuges contribute to a population's rate of recovery (Niemi et al. 1990; Wallace 1990). Long-term effects and long recovery times were observed in large-scale disturbance events, when a species was fully eliminated and if barriers that hamper re-colonization were present (e.g., Hawkins and Sedell 1990).

5 Variability in Recovery Times among Stressor Types

In theory, for similar populations in similar landscapes, recovery times should be independent of stressor type as long as the stressor is removed and the food-web and habitat characteristics in the receiving system are not substantially altered by the stressor. To follow this hypothesis and examine the contribution of stressor type to the recovery time variation, we reduced variability due to taxa properties by focusing on aquatic macro-invertebrates, thus excluding groups that generally show rapid recovery (algae and zooplankton, see Fig. 2) and exhibit entirely different life strategies (macrophytes and fish). Macro-invertebrate studies included in this review

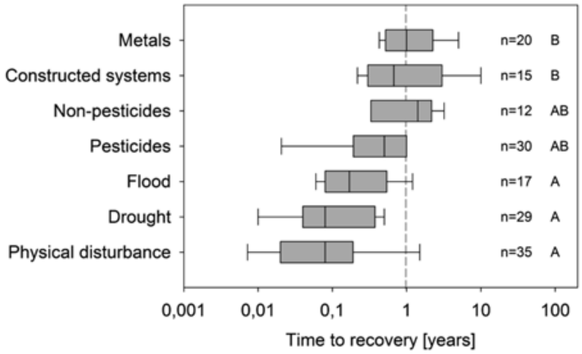

Fig. 5 Recovery times in lotic macro-invertebrates separated by stressor type. *Boxes* represent quartiles and whisker symbolize 95 % confidence intervals. *Capital letters* indicate significant difference ($p<0.0001$) in the Kruskal–Wallis test followed by a Dunn's post-hoc comparison; *n* number of recovery endpoints

concerned chemical stressors, including pesticides (n = 63, where n is the number of endpoints), non-pesticide organic chemicals (n = 12) and metals (n = 20), as well as further stressors such as flood (n = 17), drought (n = 30), other physical disturbances (n = 42) and newly constructed aquatic systems (n = 138). Lentic macro-invertebrate studies largely focussed on pesticides (n = 33), and the colonization of constructed aquatic systems (n = 123), and much less on metals, non-pesticide organic chemicals and physical disturbances such as flood and drought. However, the different stressors were well represented in lotic macro-invertebrate studies (Fig. 5). Contrary to the above hypothesis, we found that macro-invertebrate recovery times differed significantly among different stressors types (Fig. 5). Recovery times recorded for the stressor types metals and constructed systems, were significantly longer compared to those of the stressor types drought, flood and other physical disturbances. Recovery times for the stressors pesticides and non-pesticide organic chemicals were found to have an intermediate position and to be not significantly different from the two stressor types mentioned above (Fig. 5).

Floods, drought and other physical disturbances are explicit and relatively short events. According to the definition of Yount and Niemi (1990), this group of stressors can be defined as pulse-disturbance stressors and recovery is generally assumed to be rapid. For floods, the reduction in population abundance was usually above 90 % and spatial dimensions of river sections of 1 to ~80 km were reported in the literature. Droughts were characterised by durations of days up to six months and these events normally led to the total extinction of aquatic species, with the exception of propagules that survived in sediments and are adapted to overcome unfavourable conditions. Spatial dimensions of drought events are usually large for a river section of up to 45 km, with two small-scale exceptions of 30 and 100 m (Resh 1982; Sagar 1983). For physical disturbances, the duration of the event was always less than 1 day, the reduction in species abundance ranged from 30 to 100 %, and the spatial dimension comprised a few m up to several square km in two exceptional case studies (Hawkins and Sedell 1990; Meyerhoff 1991). In these two case studies, the large spatial dimension affected by the eruption of Mount St. Helens in the USA, together with extensive habitat alterations, might explain the exceptionally slow population recovery compared to that in other case studies for this group of stressor. Despite the large spatial dimensions of most flood and drought events, recovery times appeared to be relatively rapid. Flood and drought events are often attributed to regular endogenic features of the concerned systems (Reice et al. 1990) and lead to adapted communities (Sousa 1984; Wallace 1990; Yount and Niemi 1990), comprising species with short life-cycles and a high dispersal potential (Fisher et al. 1982; Gray 1981).

Stressors such as metals and several persistent organic chemicals can result in press disturbances which are generally followed by slow recovery of affected populations and communities. The impact of metals is characterized by durations of a few years to centuries in areas suffering from a long history of mining activities. These events led to a 50–90 % reduction in abundances for river sections up to 50 km. Non-pesticide chemical exposures were mostly accidental, an example being oil spills, and the time of exposure in reviewed case studies ranged from 1 day to 6 months. A 40–100 % reduction in species abundance and spatial dimensions of affected river sections up to 160 km have been reported. In general, for metals and non-pesticide organic chemicals, long recovery times were associated with large-scale disturbances and/or long-term persistence of stressors. Especially for metals and some non-pesticide organic chemicals, long-term persistence in sediments can be assumed. However, in many of the cases including long-term stressor persistence, recovery time was calculated from the time point at which the input of the stressor was stopped, which is not identical to the time of the removal of the stressor. For constructed water bodies, neither large spatial scales nor persistence of the stressor can be assumed, however, the issue more concerns the stressful environmental conditions associated with newly constructed 'virgin' habitats. Within newly constructed water bodies, a primary community must first establish, before species at higher trophic levels can successfully colonize the new ecosystems. Habitat alteration was previously found to be the most common impact associated with long recovery times (Niemi et al. 1990).

We found pesticide exposure lasting from less than 1 day to 105 days, including one study in which application was conducted over 11 times at intervals, in 3 years. The reduction in population abundance for the investigated species ranged from 70 to 100 %, with spatial exposure dimensions of river sections between 0.26 and ~5 km or areas between 0.0007 and 0.0900 km^2. The pesticides investigated were mainly insecticides that covered different modes of action. For the investigated pesticides, long recovery times in streams were usually associated with a large spatial scale of pesticide stress (Ide 1967), multiple applications over several years (Whiles and Wallace 1992), and a low dispersal ability of affected populations (Liess and Schulz 1999). Shorter recovery times in streams are reported to be associated with single applications (shorter-term exposures) and the possibility of rapid re-colonization (Caquet et al. 2007; Lopez-Mancisidor et al. 2008a; Yameogo et al. 1993).

These and other examples (e.g., Wallace et al. 1989; Whiles and Wallace 1995), show that pesticide applications might have characteristics of both pulse and press disturbances. They might be considered pulse disturbances when the compounds show rapid dissipation and are not frequently applied. These pulse disturbances are usually followed by rapid recovery. Pesticide exposures might turn into to press disturbances, characterized by slow recovery, when they occur in multiple events, such as repeated exposures to the same active ingredient or to different substances with a more or less similar toxic mode of action, or when the compound is persistent in the receiving aquatic ecosystem. The intensive and long-term use of pesticides such as insecticides, fungicides and herbicides, might result in press disturbances and long-term community shifts, as is presumed for surface waters of the fruit orchard region Altes Land in Germany (Heckman 1981; Schäfers et al. 2006) and streams in the region of Braunschweig, Germany (Liess and Von der Ohe 2005) and Brittany, France (Schäfer et al. 2007). In these cases, many aquatic species were presumably tolerant or became resistant to the agricultural chemicals, whereas others were eliminated from the habitat over a multi-year period of pesticide use. Regular pesticide disturbances thus might lead to systems that are organized in fundamentally different ways, similar to intermittent streams with periodical drought events such as endogenic features. It should be noted, however, that pesticide-use in agricultural landscapes often coincides with other types of stressors (e.g., habitat destruction; eutrophication; hydro-dynamic stress), thus, it might be difficult to distinguish the impact of pesticide exposure and other confounding stressors in field studies.

6 Comparison of Semi-field and Field Recovery Times

Within the ERA for plant protection products in Europe, artificial semi-field systems (microcosms or mesocoms) can be used as a higher tier tool to investigate the recovery of populations and ecosystem processes upon toxicant exposure (EFSA 2013). Species that are most commonly investigated in aquatic semi-field studies usually include algae, zooplankton (lentic systems) and macro-invertebrates. In semi-field studies, macrophytes are often included but not intensively investigated, except in herbicide studies. Micro- and mesocosm studies with fish are not recommended to evaluate pesticide effects for regulatory purposes (Giddings et al. 2002), and consequently are less common and absent in our dataset. Micro- and mesocosm tests are usually carried out using experimental ponds, ditches or streams. These allow controlled study designs, including replicated control systems (undisturbed references) and replicated treatments, with the chemical being the only influential factor. The study period of micro-and mesocosm studies performed with toxic chemicals for regulatory purposes, however, is usually not longer than 3–6 months (means of 5.00 and 3.75 months for lentic and lotic studies, respectively), so that recovery times of impacted univoltine and semivoltine organisms often cannot be demonstrated due to too-short observation times. In contrast to artificial systems, replicating controls and chemical treatments in natural systems is almost impossible. In field studies, the state of the disturbed system prior to disturbance, the state of similar but undisturbed systems, or theoretically derived system states, usually served as references for effects and recovery. An advantage of monitoring studies in the field, however, is that they can be more easily conducted for longer observation times (means of 1.2 years for natural lentic systems and 1.4 years for natural lotic systems), thus providing relevant information of recovery times for long-cyclic organisms (e.g., univoltine and semivoltine macro-invertebrates such as Trichoptera and Plecoptera). Despite these differences in study durations and focal species, the number of endpoints that failed to recover during the observation period was remarkably similar between semi-field and field studies. In lentic semi-field systems, 21 % of endpoints did not recover, compared to 24 % in lentic field systems, whereas in lotic systems, 36 and 35 % of the studied endpoints did not recover in semi-field and field studies, respectively. Note, however, that this apparent similarity might be an artifact, since lotic and lentic field studies have focussed on macro-invertebrates (with generally longer generation times) whereas in lentic micro-/mesocosms, the responses of both macro-invertebrates and zooplankton (with relatively short generation times) have been studied.

Due to their homogeneity and their spatial isolation, artificial systems (in particular lentic micro-/mesocosms and re-circulating lotic experimental ecosystems) are assumed to mimic worst-case conditions with regard to exposure, effects and recovery, particularly if re-colonization processes are excluded. It is thus important to know whether recovery times estimated for mesocosm populations are accurate or conservative predictors for the recovery of their field counterparts. Therefore, we compared field and semi-field recovery times for lotic and lentic systems, respectively (Fig. 6). Variability in recovery times is generally lower in artificial systems compared their natural counterparts, probably due to the homogeneity of the systems and the species investigated (Fig. 6). A remarkable observation is that overall recovery times of macro-invertebrates in lentic micro-/mesocosm experiments do not deviate significantly from those in lotic micro-/mesocosm experiments and studies in natural lotic and lentic systems (Fig. 6). Macro-invertebrates in natural lotic systems, however, recovered significantly slower from pesticide exposure than in natural lentic systems (Fig. 6). This latter observation is apparently the opposite

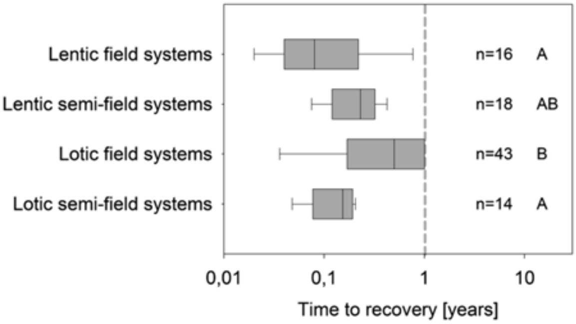

Fig. 6 Comparison of recovery upon pesticide exposure in artificial (semi-field) and natural (field) systems for macro-invertebrate endpoints. *Boxes* represent quartiles and whiskers symbolize 95 % confidence intervals. *Capital letters* indicate significant difference ($p < 0.0001$) in the Kruskal–Wallis test followed by a Dunn's post-hoc comparison; *n* number of recovery endpoints

of that from Fig. 3, where recovery lasted longer in lentic compared to lotic systems for most macro-invertebrate taxa, in particular for taxonomic groups dominated by uni- and semivoltine species. Differences in recovery times might be partly related to differences in investigated stressors. In the comparison of lotic and lentic systems presented in Fig. 3 (dealing with all stressor types), a large number of endpoints related to the colonization of newly constructed water bodies. The data presented in Fig. 6 refer to pesticide-stress only. However, the species that were involved in the original studies might also play a role. The majority of species investigated in lentic pesticide studies (69 %) belonged to Diptera, Ephemeroptera and Heteroptera, of which several representatives showed rapid recovery (see above). In contrast, Trichoptera species, which can show slower recovery (see Fig. 3), were largely absent from the natural lentic pesticide data included in this study, but comprised 39 % of the recovery-time endpoints recorded for natural lotic systems. Trichoptera populations, however, also occur in lentic freshwater ecosystems (e.g., Biggs and Brown 2010; Brock et al. 2010b), although often less frequently and in lower densities than in streams. Apparently, it is easier in lotic ecosystems to representatively collect a reasonable number of Trichoptera than in lentic ecosystems. Furthermore, Plecoptera, another group of insects with overall long recovery times, can be abundant in natural lotic systems, whereas they are virtually absent in non-flowing lentic ecosystems. The observation that recovery times for pesticide-stressed macro-invertebrates in natural lotic systems were significantly longer than their artificial lotic counterparts (Fig. 6) might be because observation periods in lotic micro-/mesocosm studies are usually too short to demonstrate recovery for affected univoltine and semivoltine insects and macro-crustaceans.

7 The Role of Effect Size in Recovery Time Estimation

Part of the variability in recovery times might be due to the size of effects caused by a stressor. To quantify disturbance scenarios, effects were commonly described as the percentage reduction of endpoints. In 55 % of the recovery endpoints collected from the literature, the effect was >90 %, and was less than 50 % in 3 % of all endpoints. In general, there is an expectation that recovery time will depend on the magnitude of an effect caused by a stressor; the larger the effect, the longer it might take a population to recover. This should be especially true for isolated systems where only internal recovery is possible and for species exhibiting low generation times and few offspring. In mesocosm studies, several chemical concentrations were usually tested, which led to effects of different magnitudes. In these test systems, the responses of Cladocera and Copepoda were frequently studied. Recovery times of 6 weeks or less were reported if the population size of Cladocera or Copepoda was reduced by less than 90 %, and with few exceptions, lower effect sizes resulted in shorter recovery times (O'Halloran et al. 1999; Rand et al. 2000; Solomon et al. 1989). In turn, for these zooplankton taxa, larger effects did not necessary result in longer recovery times. Maximum recovery times were found to

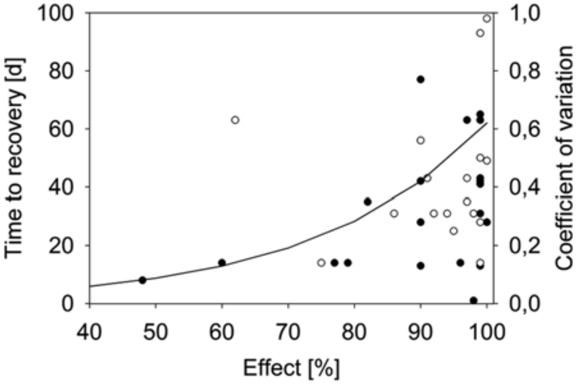

Fig. 7 Lentic mesocosm recovery times as a function of effect size for Cladocera (*black dots*) and Copepoda (*white dots*), as well as the coefficient of variation of recovery times for both groups (*line*). The *line* represents an exponential fit ($y = 0.012 \exp(0.039x)$, $r^2 = 0.95$) to the coefficients of variation for grouped effect magnitudes

increase with increasing effects (>90 %), but rapid recovery was also reported for Cladocera or Copepoda populations that were driven to the brink of extinction by chemical exposure (Fig. 7). The majority of reviewed papers dealt with a single magnitude of stressor effect in natural ecosystems and in 79 % of all cases, the population decline was larger than 90 %. However, we found a similar trend for aquatic macro-invertebrates as that described above for Copepoda and Cladocera, where an increasing magnitude of effects resulted in an increase in the variability in recovery times, as indicated by the CoV (Fig. 7).

8 Limitations for the Derivation of Recovery Times

The main obstacle for the evaluation of field data from the literature on recovery is that studies have been designed in different ways (different endpoints, taxonomic classification level, and reporting methods). Most studies were not conducted for long enough to determine full recovery. For example, most micro- or mesocosm experiments conducted with pesticides had observation periods shorter than 6 months and consequently, could often not provide recovery times for affected long-cyclic organisms (e.g., univoltine and semivoltine insects such as Trichoptera and Plecoptera). Another uncertainty in the estimation of recovery times relates to the start of the recovery process. As pointed out above, we assumed that ecological recovery started from the timepoint at which the maximum effect occurred. However, this does not necessarily mean that the stressor was always removed from a system at that time. For instance, Leeuwangh et al. (1994) found that zooplankton recovery started when insecticide concentrations in the water column had reduced to the range of the EC10 derived from acute single species tests. Moreover, a chemical stressor can quickly disappear from the water column, but persist in the sediment. In this case, aquatic populations that predominantly inhabit the water column might show rapid recovery, whereas typical benthic organisms that are in contact with the sediment might show long-term effects (Brock et al. 2010b; Sanderson et al. 2007).

The investigated study sites usually differed in several parameters, namely species composition, climate, connectivity of habitats and exposure to the stressor. All of these factors can influence recovery times. According to the high number of different parameters that affect recovery, a detailed analysis of single factors was not possible. The number of case studies that differed by only one factor was too low and a full dataset for all combinations of stressors could also not be achieved. Moreover, the statistical analysis of stressor types was biased towards ecosystem type. For instance, drought and flood events were almost exclusively observed in lotic systems, whereas the construction of new water bodies was largely restricted to lentic systems.

The recovery time data might be biased towards abundant and short-cyclic taxa. For instance, within the group of Ephemeroptera, species of the genus Baetidae, which generally have low generation times, were dominant in our data set, leading to a shorter overall recovery time for mayflies compared to estimates from non-baetid mayfly data. Furthermore, the studied endpoints in lentic ecosystems usually comprised both zooplankton (characterized by relatively short recovery times) and macro-invertebrates, whereas in lotic systems, the focus was more often only on macro-invertebrates (characterized by longer recovery times). Differences in species composition and taxonomic classification levels did not allow an evaluation of recovery for one given species across several datasets. Therefore, each dataset had to be analysed based on the lowest common denominator, i.e., often on family or higher taxonomic levels. Another factor limiting the derivation of recovery patterns is the fact that in frequently disturbed systems, communities might be selected for life-history traits (e.g., rapid development, continuous emergence, and diapausing eggs) that facilitate rapid re-colonization (Fisher et al. 1982; Gray 1981), e.g., for regular floods and droughts or pesticide use (Sousa 1984; Wallace 1990). This can lead to faster recovery rates for communities that are adaptive and a derivation of recovery times from these might be under-protective for undisturbed communities.

9 Risk Assessment, Ecological Recovery and Legislation

In the assessment and management of chemical stress in aquatic ecosystems, ecological recovery of impacted populations and ecosystem functions might play a role in retrospective risk assessment, and under certain well-defined conditions, in the prospective risk assessment of certain chemicals (for example pesticides).

Retrospective risk assessments of chemicals consider the impact from existing and/or past releases of toxic chemicals to the environment and usually a holistic, top-down approach is followed by a focus on the chemical and ecological status of the stressed ecosystem or watershed of concern (Artigas et al. 2012; Beketov and Liess 2012; Burton et al. 2012; Solomon et al. 2008; Suter et al. 2010). The EU Water Framework Directive (EC 2000) follows such a retrospective approach and aims to improve the ecological and chemical status of water bodies in Europe. If, for example, the aquatic ecosystem or water basin of concern is identified by chemical and biological monitoring to deviate from reference ecosystems and chemicals are identified as the main cause, measures have to be taken to improve the status of the impacted water body. The most important task of course, is to identify and diminish the main chemical stressors of concern. In addition, after these chemicals have declined below their level of impact (e.g., concentrations no longer in conflict with Environmental Quality Standards; EC 2011), information on the recovery potential of the impacted ecosystem might be necessary to further inform the managers which options for successful intervention are available. For example, if the impacted populations concern species characterized by complex life-cycles (e.g., uni-or semivoltine organisms) and a low re-colonization potential (for examples see Gergs et al. 2011), and the (previously stressed) ecosystem of concern is also isolated, additional measures might be required to facilitate a faster restoration, such as the re-introduction of affected populations. Furthermore, to prevent future problems and to maintain sustainable populations in the landscape, it might be required to improve the connectivity of aquatic ecosystems and/or ensure a sufficient protection of "ecological hot-spot" refuges in the landscape of concern.

Prospective ERA concerns the evaluation of the probability of adverse effects of chemical exposure in ecosystems prior to their marketing, use and release into the environment (Solomon et al. 2008). Consequently, a prospective risk assessment procedure always follows a more or less reductionist, bottom-up approach by making use of scenarios and models to estimate environmental exposure and by adopting a tiered effect-assessment procedure based on more or less standardized ecotoxicity tests and extrapolation techniques. For example, the prospective ERA for pesticides in Europe as performed under the umbrella of Regulation 1107/2009/EC (EC 2009) has its focus on shallow edge-of-field surface waters such as streams, ditches and ponds. On the basis of the pesticide-use in a certain crop and by assuming good agricultural practice, the peak exposure concentrations in surface water (PECsw;max), longer-term time-weighted mean concentrations in surface water (PECsw;twa) and annual concentration patterns of individual substances are predicted using FOCUS surface water scenarios and models (FOCUS 2001, 2007). These PECs should then be lower than the Regulatory Acceptable Concentrations (RACs) derived by means of an acute (RACsw;ac) and chronic (RACsw;ch) effect-assessment scheme. Currently, these RACs are largely based on extrapolations of experimental studies, including laboratory toxicity tests with standard and additional test species and micro- or mesocosm experiments (EFSA 2013).

In European environmental legislation of chemicals, ecological recovery of impacted populations of water organisms is usually not explicitly considered in the derivation of norm concentrations, except for pesticides in edge-of-field surface waters (Brock et al. 2006; EFSA 2010; Hommen et al. 2010). The effect-assessment schemes developed by EFSA (2013) allow the derivation of RACs based on two options: (1) the Ecological Threshold Option (ETO), accepting negligible population effects only, and (2) the Ecological Recovery Option (ERO), accepting some population-level effects if recovery takes place within an acceptable time period (the effect period should not exceed 8 weeks). Higher-tier approaches only (population and community level experiments as well as models) allow the derivation of an

ERO-RAC. In addition, in the population and community level experiments (e.g., mesocosm tests), the exposure regime tested should be realistic to worst-case (informed by the predicted exposure for edge-of-field surface waters), whereas sensitive taxa at risk (informed by lower-tier ecotoxicity tests) with a low recovery potential (on the basis of the target image of the aquatic ecosystem at risk) should be sufficiently represented in these test systems (EFSA 2013). These taxa are often referred to as focal species and potential candidates are described e.g., by Brock (2013), Gergs et al. (2011) and Ibrahim et al. (2014).

Since the exposure regime to pesticides (and other chemicals), as well as community composition (including ecological traits of populations) and connectivity between stressed and non-stressed habitats might differ between different types of ecosystem (e.g., lentic and lotic) and landscapes, it is often reported that the rate of ecological recovery is context-dependent (e.g., Barnthouse 2004; Brock et al. 2008; Caquet et al. 2007; Kattwinkel et al. 2012; Niemi et al. 1990). For this reason, it is of the utmost importance to gain further insight into the main factors that determine the recovery potential of aquatic populations and ecosystem functions, so that this knowledge can be used to scientifically underpin the prospective risk-assessment procedure for pesticides, as well as the measures to take to effectively restore aquatic ecosystems previously stressed by chemicals.

To address population-level effects, including recovery, at the relevant spatio-temporal scale, it is anticipated that in the near future, tailor-made decision support systems based on ecological scenarios and mechanistic population models (e.g., Galic et al. 2012, 2013; Gergs et al. 2014; Park et al. 2008; Preuss et al. 2010; van den Brink et al. 2007; Wang and Grimm 2010), will play a more important role in prospective ERA. Mechanistic population models to evaluate population recovery in freshwater ecosystems allow the integration of relevant landscape, ecological and ecotoxicological information, and specifically, the main factors that affect the ecological recovery of different taxa in lentic and lotic ecosystems. We anticipate that the data presented in this literature review can be used to inform risk assessors and risk managers to develop ecological scenarios for the application of mechanistic population models, and to select focal species to be addressed in these models. In turn, as demonstrated by Focks et al. (2014a, b), these scenarios and models can be used to explore the feasibility of the recovery option in the prospective risk assessment for chemicals in surface waters of specific landscapes and subject to different combinations and intensities of natural and anthropogenic stressors.

10 Summary

Environmental risk assessment (ERA) attempts to quantify the likelihood of adverse effects of chemicals on non-target species, the communities they comprise and the processes in the ecosystems they inhabit. The protection goals for ERA are usually described in general terms, with a focus on the sustainability of populations, communities and biodiversity. Although the effects caused by short-term exposure might be acceptable to some extent, the conditions under which ecological recovery can serve as a decision criterion in the ERA of chemical stressors remains to be evaluated. Ecological recovery refers to the return of the stressed community or population to its pre-disturbance or other reference states, either by internal means from the population growth of surviving organisms or propagules, or by external means from re-colonization. Ecological recovery thus depends on complex processes related to species characteristics, population dynamics and interactions, as well as ecosystem and landscape properties. For a generic consideration of recovery in the ERA of chemicals, we reviewed case studies, in which chemical and physical disturbances of natural and artificial aquatic systems were reported. We focused on five aspects that might cause variability in population recovery time: (1) taxonomic differences and life-history variability, (2) factors related to ecosystem type and community processes, (3) type of disturbance, (4) comparison of field and semi-field studies, and (5) effect magnitude, i.e., the decline in population size following disturbance. Reviewed recovery times for aquatic organisms varied from less than 1 month to longer than 16 years. In part, this variability can be explained by differences in generation times among different taxa, which might vary from days for planktonic species to a few years for some macro-invertebrate species and fish.

Variability in recovery also depends on variation in dispersal abilities among and within taxonomic groups. Recovery was particularly slow for molluscs, macro-crustaceans, some aquatic insect groups and macrophytes. Furthermore, we found recovery to be generally faster in lotic than in lentic systems, which can be ascribed to the higher connectivity of lotic systems. Part of the variability in recovery time among ecosystem types might also stem from the different taxonomic groups involved in case studies and differences in community processes. In addition, we found recovery times to vary with stressor types. Lotic macro-invertebrates recovered significantly faster in studies investigating drought, flood and other physical disturbances, compared to metal exposure and environmental conditions in newly established habitats. Recovery time after exposure to organic chemicals (pesticides and other substances) was not significantly different from that caused by the above mentioned stressor types. Pesticide applications might have characteristics of both pulse and press disturbances, depending on their dissipation and application frequency. However, the analysis of recovery times among stressor types was biased by species included in the case studies and adaptation processes within communities. For ERA on pesticides in Europe, recovery processes are investigated using artificial semi-field systems. It is therefore important to explore whether artificial systems provide appropriate recovery estimates for their natural counterparts. For macro-invertebrates, we could not demonstrate statistically significant differences in recovery times between lentic micro-/mesocosm experiments and lotic and lentic field studies. However, macro-invertebrate recovery was significantly faster in lotic artificial systems than in lotic field studies, probably due to differences in study periods, the endpoints investigated and species composition.

In general, semi-field studies provide reliable recovery information for short-lived organisms, but usually are not conducted for long enough to demonstrate recovery for heavily affected populations of univoltine and semivoltine insects and macro-crustaceans. We expected an increasing recovery time with an increasing effect magnitude, but found that this is not necessarily the case. Variability in observed recovery times, however, increases with larger reductions in population densities, again demonstrating that recovery time for similar populations might be context-dependent.

In summary, we addressed several factors in our review that affect recovery time, and, we believe, these factors should be incorporated into the risk assessment and management of chemicals. For retrospective assessments, information on the recovery potential of populations of vulnerable water organisms might be necessary for successful intervention to restore aquatic ecosystems. This information includes knowledge concerning stressor persistence, life-cycle properties of impacted species and connectivity of aquatic ecosystems in the landscape. When recovery in prospective risk assessment is considered, it needs to be ensured that vulnerable taxa are sufficiently represented in the test systems. In addition, a more comprehensive, mechanistic understanding of driving forces of recovery is needed.

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