Abdul Malik · Elisabeth Grohmann
Rais Akhtar *Editors*

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Natural and anthropogenic determinants

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Preface

Environmental deterioration has shown an increasing relationship with the rise and spread of human diseases. The World Health Organization believes that almost one third of global diseases can be directly related to environmental risk factors. In fact, environmental deterioration plays a large role in the emergence of infectious diseases. Particularly, in developing countries with poor access to sanitation, safe and sufficient water supply as the human population continues to grow, the population density increases; this leads to an abundance of vectors/parasites and other infection-forming conditions. Extreme temperatures, climate-related disturbances, air and water pollution have a direct influence on the spread of infection and disease. Environmental exposures to chemicals and toxins are a major contributor to diseases.

The health effects of global change are often indirect and difficult to assess, and the evidence of quality of the health-related outcomes varies widely. Furthermore, the health science needs to understand that global environmental change is increasingly interdisciplinary and requires collaboration among meteorologists, chemists, biologists, agronomists, geographers, geologists and health scientists. Environmental deterioration exaggerates the imbalance between population and resources and worsens the severity of poverty. In other words, interactions between poverty, population growth and environmental degradation impede sustainable economic development and worsen population health. It is important for health scientists to anticipate the potential consequence of environmental change and act accordingly. It is irony that serious environmental problems are often unknown or unrecognized.

The increasing incidences of air pollution, water pollution, land and soil pollution, solid and hazardous waste pollution, deforestation, soil erosion, silting and flooding are illustrations of environmental quality deterioration. Deteriorating quality of the environment slowly, but steadily poses a threat to human security. To counter the threat caused by environmental quality deterioration that impinges on human security, an environmental management system already exists. However, the various efforts undertaken by the relevant government agencies do not seem to be successful in stopping further environmental quality deterioration as the actions taken are not really coordinated and integrated especially when it comes to implementation of laws and regulations and, thus, the threat to human security is not really checked.

This book discusses the natural and anthropogenic determinants of the environment; climate change and other issues and their impact on human health. The book covers ecology of antibiotic resistant microorganisms, pesticide and heavy metal (arsenic) problems in natural environment; molecular advances in understanding of microbial interactions; ecological studies of human and animal health and diseases; food security, climate change and technological developments. This book is not intended to serve as an encyclopaedic review of the subject. However, the various chapters incorporate both theoretical and practical aspects and may serve as baseline information for future research through which significant development is possible.

The content of this book is divided into four main areas: Environmental Quality Deterioration and Health; Pollution and Health; Climate Change and Health; and Water Quality, Exposure and Health. The book has 18 chapters, with each focused on a specific topic to cover diverse perspectives. Chapter 1 gives an overview on Environmental Deterioration and Human Health. Other Chapters include Environment and Health in Italian Cities; Environmental Concerns of the Tanning Industry; Environmental and Health Effects of Textile Industry Wastewater; Applications of *Bacillus thuringiensis* for Prevention of Environmental Deterioration; Impact of Insecticides on the Environment and Human Health; Spread of Antibiotic Resistance in the Environment; Organic Chemicals of Emerging Environmental Concern–Persistence and Bioavailability; Application of microorganisms in bioremediation of environment from heavy metals; Organochlorine Pesticide Residues in Foodstuffs, Fish, Wildlife and Human Tissues from India; Management of Municipal Solid Waste Landfill Leachate: A Global Environmental Issue; Climate Change and Migration: Food Insecurity as a Driver and Outcome of Climate Change related Migration; Climate Change and Vector Borne Diseases in Latin America; Climate Change and Geoenvironmental Problems in Indian Desert; Geo-ecology of Malaria in India; Spring Water Quality and Human Health in Foothill Settlements of Pir Panjal Range in Anantnag and Kulgam, Kashmir, India; Dietary Exposure to Arsenic as Main Anthropogenic Factor; and Land Use Changes and their Impact on Water Resources in Himalayas.

With great pleasure, we extend our sincere thanks to all our well-qualified and internationally renowned contributors from different countries for providing the important, authoritative and cutting edge scientific information/technology to make this book a reality. All chapters are well illustrated with appropriately placed tables and figures and enriched with up to date information. We are also thankful to the reviewers who carefully and timely reviewed the manuscripts. Dr. Abdul Malik is also thankful to the Department of Biotechnology, Govt. of India, New Delhi for DBT CREST award/fellowship during the preparation of the book.

We are extremely thankful to Springer, Dordrecht, The Netherlands for completing the review process expeditiously to grant acceptance for publication. We appreciate the great efforts of the book publishing team, especially of Dr. Alexandrine

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We express sincere thanks to our family members for all the support they provided and regret the neglect and loss they suffered during the preparation of this book.

Aligarh, India — Abdul Malik
Freiburg, Germany — Elisabeth Grohmann
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Contents

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Dr. Abdul Malik is Associate Professor and Former Chairman (Head), Department of Agricultural Microbiology. Dr. Malik has been awarded several International fellowships, awards and honours including DBT CREST Award, DAAD fellowship (Germany), BOYSCAST overseas fellowship, Jawahar Lal Nehru Memorial Fund award etc. Dr. Malik spent one year as visiting professor/scientist at the University of Freiburg, Germany working on a project focusing on GFP-based monitoring of plasmid transfer in anthropogenic contaminated soils. He has collaborative projects with TU Berlin, Germany and University of Minho, Braga, Portugal. He has received research grants from several funding agencies of the Govt. of India including DST, CSIR, UGC as Principal Investigator. Dr. Malik has edited five books published by leading international Publishers. His major areas of research are Environmental Microbiology, Ecotoxicology and Agricultural Microbiology. Dr. Malik has published a number of research papers in leading scientific journals of the world with high impact factor.

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Part I
Environmental Quality Deterioration and Health

Chapter 1
Environmental Deterioration and Human Health: An Overview

Farhana Masood, Elisabeth Grohmann, Rais Akhtar and Abdul Malik

Abstract Ever since people have utilised natural resources, environmental quality has started to deteriorate. The increasing incidences of air pollution, water pollution, land and soil pollution, solid and hazardous waste pollution, deforestation, soil erosion, silting and flooding are illustrations of environmental quality deterioration. The deteriorating quality of the environment slowly, but steadily, poses a threat to human security. These threats include increasing exposure to infectious diseases, water scarcity, food scarcity, natural disasters and population displacement. Taken together, they may represent the greatest public health challenge humanity has ever faced. There always seem to be intermediaries connecting the change in the ecosystem and human health. For example, such environmental changes as climate change, land degradation and aquifer depletion seriously affect agricultural production. Agricultural production is a major determinant of nutritional status and population health. Hence, human health is affected by producing or consuming agricultural products and not directly by land degradation or aquifer depletion. However, there are some environmental changes that directly affect the quality of human health, such as a rise in temperature, which causes thermal stresses, respiratory problems and deterioration of aquatic ecosystems leading to waterborne diseases. Other health impacts of the ecosystem degradation may be exacerbated by changes in

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other systems and processes, such as proliferation of bacteria, distribution of vector organisms or quality and availability of water supplies. The significant changes in health conditions and emergence of new diseases require understanding and are calling for new solutions in implementation of environmental health policies.

Keywords Agriculture · Climate · Environmental quality deterioration · Human health

1.1 Introduction

Environmental factors, including climate change, ranging from natural disasters to environmental degradation have a negative impact on exposed and especially vulnerable countries, cities and populations around the world. Nevertheless, climate change cannot be addressed in isolation from environmental degradation, as both are very closely interlinked.

Climate change represents a range of environmental hazards and will affect populations in both the developed and developing countries, and particularly the regions where the current burden of climate-sensitive diseases is high.

The rising temperature, heavier rainfall and changes in climate variability would encourage insect carriers of various infectious diseases to multiply and move further in regions free of the disease. In some areas, higher rainfall will wash out breading pools, thereby decreasing mosquito populations. Sudden rainfall due to El Nino Southern Oscillation in 1994 created flooding conditions and, because of poor drainage in the Thar Desert, resulted in the creation of breeding places. This has resulted in a very high morbidity and mortality due to malaria in the region (Akhtar and McMichael 1996). Thus, climate change will perturb the world's various aspects of physical and biological systems, which, in turn, influence human health. Diseases other than malaria and dengue may increase as a result of climate change including chikungunya fever, cholera, diarrhoea and rodent-borne diseases as reported in *Lancet* that called climate change 'the biggest global health threat of the 21st Century' (Epstein 2009).

Research conducted in some geographical regions reveals a sobering scenario of the environmental deterioration due to current climate change. Increases in average temperature, maximum temperatures and duration of heat waves have already been experienced in both the developed and developing countries. The European heat wave of 2003 that killed more than 40,000 people in central and western Europe are a good example (Akhtar 2010).

Presently, it is estimated that the developing countries suffer 97 % deaths every year due to natural disasters and also face much larger economic losses than developed countries in terms of percentage of gross national product (UNISDR 2002). However, the 2003 European heat wave, the Katrina hurricane disaster in southern USA in 2005, Hurricane Sandy in 2012 and snowstorms in central and eastern USA during early 2013 confirm that even developed countries are in danger of natural disasters.

These examples reveal that climate change will disproportionately impact developing countries and the poor all over the world.

Intergovernmental Panel on Climate Change (IPCC) has also projected that in the tropics and subtropics, where some crops are near their maximum temperature tolerance and where rain-fed agriculture dominates, yields are likely to decrease due to even small changes in climate, which could lead to an increased risk of undernutrition and malnutrition. By 2020, in some countries, yields from rain-fed agriculture could be reduced by up to 50 %. Agricultural production, including access to food, in many African countries is projected to be severely compromised (IPCC 2007a, b, c).

Chemical products are used in virtually every man-made product and play an important role in the everyday life of people around the world. However, harmful exposure to and excessive use of chemical products can lead to health problems, such as skin diseases, chronic bronchitis, nervous dysfunctions and cancers, besides damaging the environment. In southern districts of Punjab, Bathinda, Faridkot, Moga, Muktsar, Ferozepur, Sangrur and Mansa, known together as the Malwa region, farmers and their families are facing cancer and health problems. The lush fields hide a scary tale. Farmers live in a disturbing cesspool of toxicity, a result of excessive and unregulated use of pesticides and chemical fertilizers (TOI 2011).

Climate change will also affect the health of the urban population. It represents a range of environmental hazards and will affect the population where the current burden of climate-sensitive diseases is high, such as low- and middle-income countries. Understanding the current impact of weather and climate variability on health of the urban population is the first step towards assessing future impacts. Improving the resilience of cities to climate change also requires improvements in the urban infrastructure including provision of safe drinking water and access to sanitation (Kovats and Akhtar 2008).

In view of the above, the Government of India's document of the 11th five-year plan focuses on the protection of the environment in any sustainable development-inclusive strategy. The document states that this aspect of development is especially important in the light of dangers of increased environmental degradation. Population growth, urbanisation and anthropogenic development employing energy-intensive technologies have resulted in injecting a heavy load of pollutants into the environment (GOI 2007–2012).

Global climate change is, thus, a significant addition to the spectrum of environmental health hazards faced by humankind. The global scale makes for unfamiliarity, although most of its health impacts comprise increases (or decreases) in familiar effects of climatic variation on human biology and health. For a long time, traditional environmental health concerns have been focused on toxicological or microbiological risks to health from local environmental exposures. However, in the early years of the twenty first century, as the burgeoning human impact on the environment continues to alter the planet's geological, biological and ecological systems, a range of larger-scale environmental hazards to human health has emerged.

As a human-generated and worldwide process, global climate change is a qualitatively distinct and very significant addition to the spectrum of environmental health hazards encountered by humankind. Climate change is the best known of the human-induced global environmental changes and includes the following:

- Greenhouse gas emissions into the lower atmosphere, causing changes to the climate
- Stratospheric ozone depletion (emissions of chlorofluorocarbons, other halogens and nitrous oxide)
- Ocean acidification (increased CO_2 uptake, threatening viability of marine productivity)
- Loss of biodiversity: loss of species, local populations and resultant ecosystem disruption
- Nitrification of soils and waterways, from increase in human-generated bioactive nitrogenous compounds
- Degradation of world's fertile land
- Depletion of freshwater (including aquifers—the 'fossil water' stores)
- Exhaustion of many great fisheries

During the first decade of this century, nearly all indices of human-induced climate change (including rates of sea-level rise, atmospheric carbon dioxide (CO_2) concentration, sea-ice melting and frequency of very severe weather disasters) have increased. Change in world climate would influence the functioning of many ecosystems and the biological health of plants and creatures. Likewise, there would be health impacts on human populations, some of which would be beneficial. For example, some mosquito-borne diseases such as malaria may recede where conditions become too hot or dry for mosquitoes. Warmer winters in some temperate-zone countries may lessen the otherwise frequent mid-winter deaths due to heart attacks and strokes. Some regions, in all continents, will experience gains in agricultural yields—at least in the earlier stages of climate change. Overall, scientists consider that most of the health impacts of climate change would be adverse (McMichael et al. 1995, 1996). This assessment will be greatly enhanced by the accrual of actual evidence of early health impacts, which epidemiologists anticipate will emerge over the coming decade.

Climate change is likely to have major effects on human health via changes in the magnitude and frequency of extreme events: floods, windstorms and droughts. Climate change projections are based on the anticipation of increasing means or norms. Global or regional climate models are not easily able to forecast future climate variability, whether daily, inter-annual or decadal. Changes in extreme events can be forecast by estimating changes in probability distributions (Downing et al. 1996; Palmer and Raisenen 2002; Campbell-Lendrum et al. 2003; Maheepala and Perera 2003). Evidence is mounting that such changes in the broad-scale climate system may already be affecting human health, including mortality and morbidity from extreme heat, cold, drought or storms; changes in air and water quality; and changes in the ecology of infectious diseases (Patz et al. 1996; Kovats et al. 2001; Stott et al. 2004).

1.2 Potential Health Impacts of Climate Change

The great moral dilemma posed by climate change is clearly revealed in the differences in risks posed to health and survival, both between and within populations and between present and future generations. The risks to human health provide one of the strongest signals of the profound significance of climate change as a threat to the planet's life support processes. The World Health Organization (WHO) estimates that 150,000 lives have been lost annually over the last 30 years that are directly attributable to climate change; this number is based on a partial list of outcomes for diseases, flooding and malnutrition and it represents a conservative estimate (Patz et al. 2005).

Three broad categories of health impacts are associated with climatic conditions: impacts that are directly related to weather/climate, impacts that result from environmental changes that occur in response to climatic change and impacts resulting from consequences of climate-induced economic dislocation, environmental decline and conflict (McMichael et al. 2001). Changes in the frequency and intensity of heat events and extreme rainfall events (i.e. floods and droughts) will directly affect population health. Indirect impacts will occur through changes in the range and intensity of infectious diseases and food- and waterborne diseases and changes in the prevalence of diseases associated with air pollutants and aeroallergens.

Changes in climatic conditions and increases in weather variability affect human well-being, safety, health and survival in many ways. Some impacts are direct acting, immediate, familiar and therefore easily understood as relevant to future climate change. Other effects are less immediate and typically occur via more complex causal pathways. Similarly, impacts would vary geographically as a function both of environment and topography and of the vulnerability of the local population. Impacts would be both positive and negative (although expert scientific reviews anticipate predominantly negative). This is no surprise since climatic change would disrupt or otherwise alter a large range of natural ecological and physical systems that are an integral part of Earth's life support system. Through climate change, humans are contributing to a change in the conditions of life on Earth. The more direct impacts on health include those due to changes in exposure to weather extremes (heat waves, winter cold); increases in other extreme weather events (floods, cyclones, storm surges, droughts); and increased production of certain air pollutants and aeroallergens (spores and moulds). Decreases in winter mortality due to milder winters may compensate for increases in summer mortality due to the increased frequency of heat waves.

Earth has warmed by around 0.6 °C since the mid-1970s, and there is clear and measurable evidence that most of that warming resulted due to a human-induced increase in concentration of greenhouse gases in the lower atmosphere (IPCC 2007). The resultant additional 'greenhouse' absorption of infrared energy, radiating out from Earth's solar-warmed surface, is the overwhelming cause of current global climate change. Further, because of the great but slow momentum in the climate system, there is already an additional human-induced warming of approximately 0.5 °C to be 'realised'. Then, given the likely range of future emissions, climate scientists estimate a further total warming within the range of 1.8–4.0 °C by 2100.

1.2.1 Direct Effects on Health

1.2.1.1 Heat Waves

Heat is an environmental and occupational hazard. The risk of heat-related mortality increases with natural ageing, but persons with particular social and/or physical vulnerability are also at risk (Kovats and Akhtar 2008). There are important differences in vulnerability between populations, depending on climate, culture, infrastructure (housing) and other factors. Episodes of extreme temperature can have significant impacts on health and present a challenge for public health and local government services. Global climate change is likely to be accompanied by an increase in the frequency and intensity of heat waves, as well as warmer summers and milder winters. The impact of extreme summer heat on human health may be exacerbated by increases in humidity (Gaffen and Ross 1998; Gawith et al. 1999). Populations in developing countries are much more affected by extreme events. Relative to low socio-economic conditions, the impact of weather-related disasters in poor countries may be 20–30 times larger than in industrialized countries.

The health effects of exposure to heat and cold have been studied in several populations (Curriero et al. 2002; McMichael et al. 2003). Physiological and biometeorological studies have shown that high and low temperatures affect health and well-being. High temperatures cause clinical syndromes like heat stroke, heat exhaustion, heat syncope and heat cramps. Higher temperatures (heat waves) result in an increase in cardiovascular and respiratory diseases especially in temperate countries. Most temperate countries have a strong seasonal pattern, with mortality increasing in winter. Populations with tropical climates have considerably less seasonality in mortality patterns. Heat waves kill people, primarily by causing heart attacks, strokes, respiratory failure and heat stroke. Temperature extremes also affect physiological functioning, mood, behaviour (accident-proneness) and workplace productivity, especially in outdoor workers and those working in poorly ventilated hot factory conditions (Kjellstrom 2009). There has been more research on heat waves and health since the Third Assessment Report (McMichael et al. 2001) in North America (Basu and Samet 2002), Europe (Koppe et al. 2003, 2004) and East Asia (Qiu et al. 2002; Ando et al. 2004; Choi et al. 2005; Kabuto et al. 2005). A variable proportion of the deaths occurring during heat waves are due to short-term mortality displacement (Hajat et al. 2005; Kysely 2005). Research indicates that this proportion depends on the severity of the heat wave and the health status of the population affected (Hemon and Jougla 2004; Hajat et al. 2005).

1.2.1.2 Cold Waves

Cold waves continue to be a problem in northern latitudes, where very low temperatures can be reached in a few hours and extend over long periods. Accidental cold exposure occurs mainly outdoors, among socially deprived people (alcoholics, the homeless), workers and the elderly in temperate and cold climates (Ranhoff 2000). Living in cold environments in polar regions is associated with a range of chronic conditions in the non-indigenous population (Sorogin et al. 1993) as well as with acute risk of frostbite and hypothermia (Hassi et al. 2005). In countries with populations well adapted to cold conditions, cold waves can still cause substantial increases in mortality when there is electricity or heating system failure.

1.2.1.3 Sea-Level Rise

Sea level is rising faster than in the 1980s–1990s (Rahmstorf et al. 2007); it is a result of two main consequences of global warming: first, thermal expansion of ocean water and, second, the melting of land-based glaciers and ice sheets (particularly the massive Greenland glacier, which is now apparently melting faster, and via previously unstudied physical processes, than in the late decades of the twentieth century). Whereas the IPCC (2007a) had predicted a rise of around half a metre (with a range of uncertainty) up to the middle of this decade, some recent estimates indicate that a rise of 1 m, or more, could occur by the end of this decade. Further, even if atmospheric concentrations of greenhouse gases stabilize in the next few decades, the sea level will continue to rise for many centuries as the slow processes of heat distribution throughout the oceans proceed. Sea-level rise poses both direct and indirect risks to well-being and health and to social stability.

The direct risks resulting from rising sea level include physical hazards from coastal inundation, more extensive episodes of flooding and increasingly severe storm surges (especially at times of high tide). Damage to coastal infrastructure (roads, housing and sanitation systems) would all pose direct risks to health. A range of indirect risks to health include the salination of freshwater supplies—a particular problem for many small islands, as their aquifer 'cells' of water are encroached upon—the loss of productive farm land and changes in breeding habitats for coastal-dwelling mosquitoes.

1.2.1.4 Floods

Floods are low-probability, high-impact events that can overwhelm physical infrastructure, human resilience and social organisation. Floods are the most frequent natural weather disaster (EM-DAT 2006). Floods result from the interaction of rainfall, surface run-off, evaporation, wind, sea level and local topography. Water management practices, urbanisation, intensified land use and forestry can substantially alter the risks of floods (EEA 2005). Windstorms are often associated with floods.

Flood health impacts range from deaths, injuries, infectious diseases and toxic contamination to mental health problems (Greenough et al. 2001; Ahern et al. 2005). In terms of deaths and populations affected, floods and tropical cyclones have the greatest impact in South Asia and Latin America (Guha-Sapir et al. 2004; Schultz et al. 2005). Populations having poor sanitation infrastructure and high risks of infectious disease often experience increased rates of diarrhoeal diseases after flood events. Increases in cholera (Sur et al. 2000; Gabastou et al. 2002), cryptosporidiosis (Katsumata et al. 1998) and typhoid fever (Vollaard et al. 2004) have been reported in low- and middle-income countries. Flood-related increases in diarrhoeal disease have also been reported in India (Mondal et al. 2001), Brazil (Heller et al. 2003) and Bangladesh (Kunii et al. 2002; Schwartz et al. 2006).

1.2.2 Indirect Effects on Health

1.2.2.1 Drought, Nutrition and Food Security

The causal chains through which climate variability and extreme weather influence human nutrition are complex and involve different pathways (regional water scarcity, salinisation of agricultural lands, destruction of crops through flood events, disruption of food logistics through disasters and increased burden of plant infectious diseases or pests). Both acute and chronic nutritional problems are associated with climate variability and change. Major drought effects on human health include deaths, malnutrition (undernutrition, protein-energy malnutrition and/or micronutrient deficiencies), infectious diseases and respiratory diseases (Menne and Bertollini 2000).

Drought and the consequent loss of livelihoods is also a major reason for population movements, particularly rural to urban migration. Population displacement can lead to increases in communicable diseases and poor nutritional status resulting from overcrowding, and a lack of safe water, food and shelter (Choudhury and Bhuiya 1993; Menne and Bertollini 2000; del Ninno and Lundberg 2005). Drought events are also associated with dust storms and respiratory health effects. Droughts also cause scarcity of water. The effect of climate change on food crop yield production globally appears to be broadly neutral, but climate change will probably intensify regional food supply inequalities (Perry et al. 2004; Patz et al. 2005).

Decreased availability of water due to climate change could affect populations in the subtropics where water is already scarce. Currently about a third of the world's population (1.7 billion people) lives in water-stressed countries, and this number is supposed to increase to 5 billion people by 2025 (Kovats et al. 2000; McCarthy et al. 2001; Kovats et al. 2003). Decreases in annual average stream flow are anticipated in central Asia and southern Africa, and the food supply may be affected (Woodward et al. 2000; Patz et al. 2002).

1.2.2.2 Infectious Diseases

The ecology and transmission dynamics of infectious diseases are complex and, in at least some respects, unique for each disease within each locality. Some infectious diseases spread directly from person to person; others depend on transmission via an intermediate 'vector' organism (e.g. mosquito, flea, tick), and some may also infect other species (especially mammals and birds). Many important infectious diseases, especially in tropical countries, are transmitted by vector organisms that do not regulate their internal temperatures and therefore are sensitive to external temperature and humidity. Climate change may alter the distribution of vector species, increasing or decreasing the ranges, depending on whether conditions are favourable or unfavourable for their breeding places (e.g. vegetation, host or water availability). Temperature also can influence the reproduction and maturation rate of the infective agent within the vector organism, as well as the survival rate of the vector organism, thereby further influencing disease transmission (Patz et al. 2005). The most important climatic factors for vector-borne diseases include temperature and precipitation, but sea-level elevation, wind and daylight duration are additional important considerations. Temperature also has an effect on food-borne infectious diseases. For example, higher than average temperatures contribute to an estimated 30 % of reported cases of salmonellosis across much of continental Europe (Kovats et al. 2004).

1.2.2.3 Effects of Social and Economic Disruptions

The impacts of climate change include severe social disruptions, local economic decline and population displacement that would affect human health (Woodword A 2003; Kovats et al. 2005). Of particular concern is the impact of a rising sea level (estimated, with a wide band of uncertainty, at around 0.5 m over the coming century) on island and coastal populations currently living not far above the shoreline. Population displacement resulting from sea-level rise, natural disasters or environmental degradation is likely to lead to substantial health problems, both physical and mental.

1.3 Conclusions

It is now established that climate changes are occurring at an increasingly rapid rate. Evidence has grown that climate change already contributes to the global burden of disease and premature deaths. Climate change plays an important role in the spatial and temporal distribution of malaria, dengue, tick-borne diseases, cholera and other diarrhoeal diseases; is affecting the seasonal distribution and concentrations of some allergenic pollen species; and has increased heat-related mortality. Increase in temperature and changes in rainfall patterns can increase malnutrition; disease and injury due to heat waves, floods, storms, fires and droughts; diarrhoeal illness; and the frequency of cardiorespiratory diseases due to higher concentrations of ground-level ozone. There are expected to be some benefits to health, including fewer deaths due to exposure to the cold and reductions in climate suitability for vector-borne diseases in some regions. Current national and international programmes and measures that aim to reduce the burdens of climate-sensitive health determinants and outcomes may need to be revised, reoriented and, in some regions, expanded to address the additional pressures of climate change. Measures implemented in the water, agriculture, food and construction sectors should be designed to benefit human health.

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Chapter 2
Environment and Health in Italian Cities: The Case of Taranto

Tiziana Banini and Cosimo Palagiano

Abstract Like "heterotrophic organisms," cities live on the basis of a strong imbalance between the relevant inflows of matter and energy and outflows of waste and emissions, which can extend over large areas. The data of the *ecological footprint* of cities have quantified emblematically this imbalance. The rapid growth of urbanization, especially in developing countries, is a matter of serious concern.

Unsustainable by definition, cities generate environmental impacts of all kinds, with intensities that vary according to the characteristics of the areas in which they develop. Italian cities are a significant case study, for the high density of population and economic activity, the shortage of green areas, the internal mobility largely centered on the private car, as well as for the frequent breaches of the rules and laws oriented to protect the environment.

Air pollution is one of the major environmental problems, especially in some cities of the country where industrial activities with high environmental impact are located. After a critical review of the literature focused on the relationship between environmental depletion, air pollution, and health conditions in Italian cities, this chapter explores the case of Taranto, a city of Southern Italy with serious problems of pollution and public health due to the presence of a large industrial area.

Keywords Cities · Italy · Industrial pollution · Environmental degradation · Human health · Taranto

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2.1 Introduction

Cities are the main topic of political and scientific debate on environmental degradation and sustainability (Allegrini and De Santis 2011). Compared to parasitic organisms (Odum 1971), which can live only by taking nourishment from other organisms, cities have an extremely unbalanced metabolism, including inflows of matter and energy from many different parts of the world and outflows of waste and emissions, which can extend over large areas and generate damage to the environment and to human health (Decker et al. 2000; Kennedy et al. 2007; Kennedy et al. 2011). Studies on the ecological footprint of cities have emblematically shown just how great this imbalance is (Rees and Wackernagel 1996; Wackernagel et al. 2006), beginning with the examples of Santiago de Chile (Wackernagel 1998), London (Best Foot Forward 2002), and Liverpool (Barrett and Scott 2001). The rapid growth of urbanization, particularly in developing countries, is a matter of serious concern. Unsustainable by definition, cities generate environmental impacts of all kind, whose intensity varies according to the environmental and social features of the territories they occupy. As a major cause of the increase of greenhouse gas emissions and the consequent effect on the thermal balance of the Earth, cities are also favored sites for finding solutions to air pollution and climate change (Dodman 2009).

Urban environmental problems are often made worse by the presence of industrial areas, which for historical, economic, and urban dynamic reasons are often very close to densely populated areas or areas used for commercial activities or tourism (e.g., the case of locating industries on the waterfront).These industrial activities create artificial ecosystems that become subsystems within the urban ecosystems, which constrain the city both at the local scale (especially as regards employment) and to the global logic of production, strongly influencing decisions, including the permanence of the industrial plant in the city (Bai 2007).

The recent scientific literature has focused on the issues of environmental justice and of the socially unequal impact of pollution. These studies try to detect whether and to what extent air pollution is produced and suffered by social groups, according to variables related to age, ethnicity, income, or deprivation. In addition, they try to answer the question of how social groups are aware of the pollution generated by their behavior (King 2010). Studies like these have been carried out in some New Zealand cities, showing how pollution affects social groups, so that those who produce the most pollution suffer the least exposure to particulate air pollution, while the most disadvantaged social classes suffer increased exposure to pollution and higher incidences of related diseases (Pearce et al. 2006; Pearce et al. 2011). Some studies in Britain reached the same conclusion, highlighting how the economically disadvantaged social groups produce less pollution but experience the highest pollution levels (Mitchell and Dorling 2003). Another study, also in Britain, showed strong correlations between degraded living environments, especially those where there were high levels of spatial aggregation, and high levels of air pollution (Briggs et al. 2008). The location of housing near the freeways in two West Coast American metropolitan areas (Seattle and Portland) has also been considered as one of the variables that can affect health: The most vulnerable populations living in these risk areas (in particular, those living 330 meters from the highway) suffer higher levels of pollution and are, therefore, exposed to greater health risks (Bae et al. 2007). The same conclusions were reached in Italian studies on younger age groups, who have higher incidences of respiratory problems when they reside in areas subject to intense air pollution and traffic (Galassi et al. 2005). Because of the close relationship between the residential context and the exposure to pollutants and related diseases, these issues were listed among the main topics to which geography can give a significant contribution (Curtis and Oven 2012; Reed and Colleen 2011).

Italy is a relevant case study not only because of its high population density, economic activities, and urbanization but also because of a lifestyle and mobility largely centered on the private car, as well as for its frequent breaches of the European Union's (EU) rules and laws, which have progressively emphasized the integration of environmental issues with economic and social ones (Dansero and Bagliani 2011).

Air pollution is among the most important environmental problems of Italy, especially in some cities which suffer pollution caused by industrial activities. After a critical review of the scientific literature on the relationship between environmental characteristics, air pollution, and health conditions in Italian cities, also in reference to the presence of industries which are at risk of a major accident, this chapter explores the case of the city of Taranto, which in recent years has become a protagonist in the national and international debate because of the historical presence of an industrial area with high environmental impact.

2.2 Urban Air Quality and the Impact on Human Health

In Italy, as elsewhere, the depletion of the environment derives not only from the high population density, economic activities, and urbanized areas but also from the lifestyle of the people, marked by a significant consumption of materials and energy from fossil fuels[1].

Air quality is compromised particularly in the cities, in reference to PM_{10}, $PM_{2.5}$, and other major pollutants (carbon dioxide, nitrogen oxides, sulfur oxides, ozone), which systematically exceed the level required by European legislation. In 2012, out of 95 cities monitored, as many as 51 exceeded the limit (35 days) for PM_{10}, while the $PM_{2.5}$ values were over the legal thresholds in 50 % of cities (Zampetti

[1] Italy is at the top of the European ranking for population density (201 inhabitants/km^2), after the Netherlands (492), Belgium (359), UK (254), Germany (229), and Liechtenstein (231) (http://epp.eurostat.ec.europa.eu). In the 12 metropolitan cities (Rome, Milan, Turin, Naples, Palermo, Florence, Bologna, Padua, Bari, Catania, Pescara, Genoa), the average of density of population is about 3,100 inhabitants/km^2, with a peak of 8,182 in Naples, 7,272 in Milan, and 6,972 in Turin. Taken together, these cities represent 0.9 % of the national area and include 8.8 million people, accounting for 14.5 % of the national population (ISPRA 2012).

and Minutolo 2013). The worst case was in the Po Valley (Northern Italy), due to the particular climatic conditions that facilitate the accumulation of pollutants in the air (Pinna 1991), so that among the top 20 Italian cities with the highest air pollution levels there are 18 northern cities, including Milan, Turin, and Padua, which are subject to the most critical conditions. As for the whole of Europe, ozone and particulate matter (PM) are the main pollutants posing a problem to human health and ecosystem balance (EEA 2011). While the concentrations of PM_{10} and $PM_{2.5}$ frequently exceed the limits during winter, forcing the periodic restriction of movement of private vehicles, the concentration of ground-level ozone tends to reach its highest values in summer (Parodi et al. 2005): In 2012, ground-level ozone exceeded the threshold levels in 44 out of 78 monitored cities. In this sense, Italy is one of the European regions with the highest annual average concentration of PM_{10} and $PM_{2.5}$ (EEA 2011) and has been found in breach of the European Court of Justice for having exceeded the limits (Directive 1999/30/EC) for long periods and in many areas, both in 2006 and in 2007 (Zampetti and Minutolo 2013)[2].

Major contributors to high levels of urban air pollution are traffic and the heating/air-conditioning of private, public, and commercial buildings. Overall, the emissions of sulfur oxides are produced mostly by industrial activities (78 %), while road traffic is responsible for 53 % of emissions of benzene, 52 % of carbon monoxide (CO), and 44 % of sulfur oxides (SO_X), and 27 % of PM_{10} (*Ibid.*). The general trend for using private cars for even short-range journeys contributes significantly to air pollution in urban areas. Italy has the highest motorization rate in EU-27 after Luxembourg, with 614 automobiles per 1,000 inhabitants (ISTAT 2012) and the car fleet mainly consists of the most polluting cars (Euro 0, I, II, III), compared to those of the new generation (Euro IV and V). This social habit of the wide use of the private car, however, is caused not only by the inefficiencies of the public transport system, subject to continual cuts due to the economic crisis, and the lack of bicycle lanes, especially in the cities of Central and South Italy (ISPRA 2012, p. 322–323), but also by the perception that riding a bike, going on foot, or using public transport exposes people to more sources of air pollution, as some studies confirm (Gulliver and Briggs 2004). The heavy private car traffic is augmented by commercial traffic using the road system, which is due not only to Italy's geomorphological diversity but also to the historical lack of investment in the rail network and the lack of navigable rivers and waterways.

The pedestrianization of the historic centers of cities, with the creation of limited traffic zones (ZTL, zona traffico limitato), has greatly helped in reducing emissions,

[2] For oxides of nitrogen (NO2), European legislation (Directive 2008/50/EC, implemented in Italy by Legislative Decree 155/2010) taken from the World Health Organization (WHO) guidelines (WHO 2006) establishes an annual average concentration of 40 µg/m3 and an hourly average concentration of 200 $\mu g/m^3$ not to be exceeded for more than 18 days a year. For $PM_{2.5}$, this threshold is 25 $\mu g/m^3$. For PM_{10}, it comes to a daily average of 50 micrograms/m^3, not to be exceeded on more than 35 daysyear^{-1}. For tropospheric ozone (O_3), the limit is set at a maximum of 25 days exceeding the daily threshold of 120 mg/m^3, calculated on the average of eight consecutive hours. For sulfur oxides (SO_2), the limit is equal to 20 g/m^3 average of 24 h and 500 mg/m^3 average of 10 min.

Table 2.1 Changes in emissions of major air pollutants between 2000 and 2010 in Italy. (Source: Zampetti and Minutolo 2013)

Pollutant	2000	2010	Change (%)
IPA (Kg)	115,020.72	152,627.68	32.7 %
Benzene (Mg)	I8,933.50	7,078.99	−62.6 %
PM10 (Mg)	208,970.78	202,063.62	−3.3 %
PM2.5 (Mg)	178,059.03	173,207.57	−2.7 %
CO_2 (Mg)	462,485,087.54	426,086,644.32	−7.9 %
CH_4 (Mg)	2,180,924.77	1,788,288.63	−18.0 %
N_2O (Mg)	127,706.97	87,798.39	−31.3 %
CO (Mg)	4,856,674.95	2,710,995.19	−44.2 %
NOx (Mg)	1,431,155.58	965,975.31	−32.5 %
NMVOC (Mg)	1,620,132.39	1,102,514.96	−31.9 %
SOx (Mg)	749,479.24	210,147.38	−72.0 %
NH_3 (Mg)	448,580.65	379,026.00	−15.5 %

as reported in a recent study carried out in Milan (Invernizzi et al. 2011). In addition, due to the increased energy efficiency of motor vehicles and the improvement of the refining processes of fossil fuels, which have reduced the presence of sulfur compounds, in the last 10 years there have been significant reductions in various pollutants, such as carbon monoxide (CO), benzene, and sulfur oxides (SO_X). For other pollutants, however, emissions have remained at the same level, as in the case of PM_{10}, $PM_{2.5}$, and carbon dioxide (CO_2), or there has been an increase, as in the case of polycyclic aromatic hydrocarbons (PAHs, Table 2.1).

The minimal reduction of the oxides and nitrogen dioxide is related to both the increase in the number of high-power vehicles in circulation and the fact that the emission of these pollutants is also attributable to the processes of high-temperature combustion that occur in industrial plants. For PAHs, the increase is instead due to domestic heating (more than 50 % of national emissions) and industry (about 30 %), and only for a small part to vehicular traffic (2 %) (Zampetti and Minutolo 2013).

While the air quality in the northern regions is generally worse due to the increased traffic and the higher level of industrialization and urbanization, in the southern regions air quality is strongly influenced by the illegal disposal of hazardous industrial waste, as well as by the problem of municipal solid waste, which engenders substantial illicit trafficking run by the local eco-mafias. The traffic of hazardous waste arising from industrial activities is estimated at 7 billion Euro; in Campania, from 2006 to 2009, more than 13 million t of waste are estimated to have been illegally disposed of. The problem, however, covers the entire country and is linked to a vast global organization, involving several European, African, and Asian countries, especially Malaysia, China, and India (Legambiente 2012).

The recent increase in atmospheric temperature, which is perceived significantly in large urban centers, which are already affected by the heat island phenomenon (Colacino and Lavagnini 1982), further exacerbates the presence and accumulation of pollutants in the atmosphere, with relative impairment of the standards of air quality. The remarkable expansion of air-conditioning systems has contributed to this phenomenon; their presence in private homes, more than doubled over the last 10 years, especially in cities (ISPRA 2012, p. 389), is now added to that of other buildings (public offices, shopping malls, mega stores, etc.) and generates a significant increase in air humidity and, therefore, in the perceived temperature.

The environmental and climatic factors at a local and supra-local level also contribute to the concentration of pollutants. For Palermo, for example, a study has shown an increase of PM_{10} due to the presence of particles of iron (Fe) and aluminum (Al) deposited in the soil (Dongarrà et al. 2007). A study covering the period 2003–2005, the years when, especially in 2003, there was a considerable increase in summer temperatures, shows a correlation with the dust from the Sahara Desert and the resultant increase in mortality in Italy, especially in older age groups (Pederzoli et al. 2010). Another study comes to a similar conclusion examining the contribution of Saharan dust to concentrations of PM_{10} in Rome in 2001, showing an increase in the incidence of PM_{10} in some areas of the city (Gobbi et al. 2007). More generally, all the countries of southern Europe are subject to Saharan dust, causing an excess of the daily limits allowed by European regulations for PM_{10}; in the case of a study conducted in Tuscany, the contribution of Saharan dust has been estimated at 1–2 % (Nava et al. 2012).

The high levels of air pollution, as we know, are considered a major cause of acute and chronic diseases: irritation of the upper respiratory organs, chronic bronchitis, lung cancer, cardiocirculatory diseases, ischemic stroke, as well as allergies and asthma, especially in children (EEA 2011; Kampa and Castañas 2008; Villeneuve et al. 2012; Gasana et al. 2012). A study of 13 Italian cities, covering the period 2002–2004, showed that urban air pollution, in particular at a PM_{10} concentration of more than 20 μg/m^3, can be responsible for 8,220 deaths per year, equivalent to 9 % mortality for all causes of death (excluding accidents) in the population over 30 years and 1.5 % of the total mortality of the entire population (1,372 deaths) (Martuzzi et al. 2006). Another study, covering the period 1996–2002, on the short-term exposure to air pollutants, particularly NO_2, CO, and PM_{10}, ICR, found a direct correlation with the increase in daily mortality for all causes of death, cardiorespiratory mortality, and hospital admissions for heart and respiratory diseases. The same study found a strong correlation between pollutants, mortality, and hospital admissions in the summer, without finding differences or significant changes in children (0–24 months) and the elderly (> 85 years). Overall, the impact on mortality is between 1 and 4 % and 4.1 % for the gaseous pollutants (NO_2 and CO), while for PM_{10} values vary between 0.1 and 3.3 %. The peak of mortality varies depending on the type of pollutant: 2 days for PM_{10} and 4 days for CO and NO_2. The study also highlighted that the implementation of European legislation could prevent about 900 deaths (1.4 %) for PM_{10} and 400 deaths (1.7 %) for NO_2 (Biggeri et al. 2004). Another study conducted in the period 1988–1999 on eight Italian cities (> 400,000 inhabitants) had shown that 4.7 % of deaths (3,472 deaths) were attributable to PM_{10} concentrations above 30 mg/m^3, rising to 7 % (5,148 deaths) considering a concentration equal to 20 g/m^3. It also showed that around 4,500 hospital admissions each year for cardiovascular disease and respiratory tract diseases were due to air pollution, which rose to 7,000 with the threshold located at 20 μg/m^3 (Martuzzi et al. 2002).

The overall consideration is that in Italy, as elsewhere, the environmental risk from human activities is closely related to the production, stockpiling, and use of nonrenewable energy, which on a national scale is still 60 % of the total energy consumed (ENEA 2012), or rather below the standards set down by the 20–20–20 European Strategy, which requires the achievement, by 2020, of the threshold of 20 % of energy consumed from renewable sources, reducing consumption by 20 %, capable of being increased to 30 % (European Commission 2010). Compared to other European countries less endowed in terms of solar radiation, Italy is in a low position, which raises even more concern considering the huge potential it has. Here, the perception that people have of pollution (Gatto and Saitta 2009) plays a relevant role, which concerns not only information campaigns and the activity of associations and local committees but also the decision-making power held by certain social groups in managing environmental information and the ability/possibility of individuals to access this information (Bickerstaff and Walker 2003). Several studies, for example, have highlighted the different perceptions of risk between men and women and between whites and people of color (Flynn et al. 1994; Finucane et al. 2000).

The recent adoption of the EU Smart Cities and Communities initiative, aimed at reducing carbon emissions and improving the energy efficiency performance of the city, is touting a number of initiatives, in view of the objectives that the EU has set in relation to the Strategy 20–20–20 to be achieved by 2020 (−20 % in greenhouse gas emissions compared to 1990, at least 20 % of energy consumption from renewable sources, and −20 % of energy consumption)[3]. The Smart Cities strategy seeks to create virtuous circles for Europe to be regarded as an outpost of the world in terms of clean, efficient, and low-carbon technologies, generating new lifestyles, integrated projects, and positive effects in terms of employment and sustainable economic growth. While in immediate terms the Smart Cities strategy can prove useful in promoting the transition to a society with low environmental impact, in the long run different ways of thinking about mobility, production, and consumption have to be made, starting from energy sources and the methods of production and consumption of materials. The initiatives under way in many cities, both from the municipalities and citizens' associations, with or without the collaboration of environmental and cultural associations (ISPRA 2012), are an important point of departure.

[3] According to the Global Greenhouse Gas Standard, launched by United Nations Environment Programme (UNEP), UN-HABITAT, and the World Bank at the World Urban Forum in Rio de Janeiro in March 2010 as the first global system for calculating the greenhouse gas emissions in the cities, the Italian cities appear with CO_2 emissions per capita ranging from 4 tons of the province of Naples, at 9.7 of Turin, to 11.1 in the province of Bologna. At the international level, Rotterdam, with 29.8 million t of CO_2 per capita, is the city's biggest polluter (http://corriere.com).

2.3 Industrial Cities and Environmental Risk

In addition to the pressures produced by traffic, heating/air-conditioning systems, and the other standard urban factors, many Italian cities are subjected to high levels of pollution from the presence of industrial plants with a high environmental impact, including the plants at Rischio di Incidente Rilevante (RIR; major accident risk), or in other words, plants which, because of the presence of specific substances or categories of substances over certain predetermined thresholds can generate, in the case of an accident (emission of substances, fire, explosion, etc.) "a serious hazard, for immediate human health or the environment, either inside or outside the industrial plant" (Legislative Decree no. 334/1999).

RIR industries are regulated by the Seveso Directive, which takes its name from the town that suffered most from the results of the accident that occurred in 1976 in the industrial plant of ICMESA located in Meda (Milan hinterland), which caused the emission of a cloud of dioxin that still today shows significant effects on the health of the local population (Consonni et al. 2008). The "Seveso" Directive was issued a few years later (Directive 82/501/EEC) and was amended by the "Seveso II" (Dir. 96/82/EC) and "Seveso III" (2003/105/EC)[4] (Ceci et al. 2012), which govern the activities of the RIR plants.

The Seveso Directive does not establish a minimum distance between the RIR industrial plant and residential areas, leaving the decision to the member states "to maintain appropriate distances" between plants and "residential areas, buildings and areas of public use, the major transport routes as far as possible, recreational areas and areas of particular natural interest or sensitivity from the environmental point of view and to establish for existing establishments technical measures…to reduce the risks to people" (Article 12 Dir 2003/105/EC). The European Commission, through the *Major Accident Hazards Bureau* (MAHB), has developed some guidelines for the allocation and use of land in areas where RIR plants are situated (http://mahbsrv.jrc.it), in support of the implementation of Article 12 of the Directive (see http://ipsc.jrc.ec.europa.eu/?id=694), which have been adopted in Italy by a Decree of the Ministry of Public Works, May 9, 2001.

In Italy, however, the distance between the RIR plants and residential, commercial, and/or hospital areas is often insufficient to avert the consequences of a major accident (ISPRA 2012). In most cases, industrial plants are located close to densely populated residential areas, as in the case of Taranto, which in addition to the presence of three plants subjected to the Seveso Directive, including Ilva SpA (MATTM 2012), is one of the 57 Sites of National Interest (SIN) for environmental reclamation that exist in Italy (Fig. 2.1)[5]. Several epidemiological studies have been

[4] The Seveso II Directive requires the manager of the establishment to notify the quantity and type of work related to hazardous substances included in the Appendix and the reports on the activities of risk prevention and management of major accident emergency. Directive 2003/105/EC extended the legislation to other industries and has included additional requirements on the safety of facilities and participation of workers and citizens.

[5] "The concept of 'polluted site' was firstly introduced in Italy with the definition of 'environmental high risk areas' (Rule 349/86). Later, the decree 471/99 stated that a site is considered polluted

Fig. 2.1 Sites of National Interest (SIN) for land reclamation in Italy. (Source: Pirastu et al. 2011)

produced on these areas to detect the incidence of mortality from diseases related to pollutants (Fano et al. 2005; Pirastu et al. 2011).

Another problem relates to the activities carried out by RIR plants; they must, in fact, meet a series of requirements: In addition to the obligation to notify the competent authorities about the activities performed by the establishment (hazardous substances and their quantities, analysis of the environment of the establishment, possible causes of accidents, etc.) and the preparation of a Safety Report, they must prepare an Internal Emergency Plan (by the manager of the factory) and an External Emergency Plan (by the competent governmental authority) to respond quickly to the need to safeguard public health and the environment (Legislative Decree no. 334/1999, Legislative Decree no. 238/2005; Dir 2003/105/EC)[6].

A survey conducted in 2010, however, showed a lack of enforcement (Legambiente 2013): Besides the fact that only 29 % of the municipalities surveyed (with at least one RIR industry in their territory) responded, 86 % said they had identified the areas of damage, but only 49 % specified the vulnerable and/or sensitive struc-

if the concentration of even just one index pollutant in anyone of the matrices (soil or subsoil, surface or ground waters) exceeds the allowable threshold limit concentration. The boundaries of Italian polluted sites (IPS) were defined (Decree 152/06) on the basis of health, environmental and social criteria" (Pirastu et al. 2011, p. 20).

[6] The External Emergency Plan requires the delimitation of three areas of risk: (1) *areas of maximum exposure* (threshold of high mortality in the immediate vicinity of the plant), (2) *area of damage* (threshold of irreversible damage), and (3) *area of attention* (subject to effects that are generally not serious). These areas are identified according to the type of damage (explosion, fire, toxic cloud, etc.), the hazard to human health, and the environmental features of the area where the industrial plant is located (seismic, hydro-geological risk, etc.) (DPCM 2005).

tures, only 50 % provided information to the citizens about the plans, and only 36 % proposed the organization of emergency exercises and among these only 16 % with the involvement of the population. The regional variability, however, is considerable, so that some regions are very much behind with the Legal Compliance (Abruzzo, Basilicata, Campania, Sicily, Marche, Lazio) and some regions appear more efficient (Emilia Romagna, Friuli Venezia Giulia, Tuscany, Umbria).

In December 2012, 1,143 RIR plants were operating in Italy, mostly concentrated in certain northern regions (Lombardy 288, Veneto 112, Piedmont 103, Emilia Romagna 99), while in the central and southern regions there were Lazio (69), Sicily (71), and Campania (70) (MATTM 2012). The local scale shows a scattered distribution of these enterprises, which affects the whole country, especially in petrochemical plants, oil refineries, or storage facilities of oil or liquefied petroleum gas (LPG): In addition to Ravenna and Porto Marghera (Venice), hosting the greatest number of RIR industries, we focus our attention on the industrial centers and ports of Genoa, Naples, Taranto, and Brindisi (Fig. 2.2).

Overall, the majority of RIR plants are engaged in the storage of mineral oil (26.5 %), chemical and petrochemical industries (25.6 %), and storage of liquefied gas (22 %) (www.isprambiente.gov.it), confirming the vulnerability of the Italian territory, especially of the coast, to activities related to the production, processing, and use of fossil fuels, although many studies have highlighted the major impact that comes from petrochemicals (Gatto and Saitta 2009), the emission of metals (arsenic, chromium, cadmium, etc.; Stigter et al. 2000), and volatile organic compounds (Cetin at al. 2003), benzene, vanadium, and benzo[a]pyrene (Iturbe et al. 2004).

The major accident database (International Beacon Registration Database, IBRD), established by the Ministry of the Environment to collect, process, and disseminate data and information of environmental interest, including information about accidents, had collected, a few years ago, about 5,000 national and international incidents, although they do not refer to RIR industries alone (Ricchiuti et al. 2007). At the European level, the computer system Major Accident Reporting System (MARS), established by the European Commission to collect data on accidents and to allow an exchange of information between the member states, as determined by the Seveso II Directive, has surveyed more than 450 major accidents. The European Environment Agency, in the list of the 622 most polluting industrial plants on the continent, included more than 60 Italian companies, with Ilva of Taranto placed second (EEA 2011), for environmental damage estimated at 0.75 billion Euro (Table 2.2).

These costs, however, are underestimated, since they refer only to air pollutants, without considering the pollution of the subsoil, soil, and aquifers; for this reason, the impact of coal and minerals that affect the environment of Taranto and Brindisi, two of the main Italian RIR locations, is not considered (Attardi et al. 2012)[7].

[7] The Ilva of Taranto, in particular, according to *European Pollutant Release and Transfer Register* (E-PRTR) for 2004, generates atmospheric emissions of 9.6 million t of carbon dioxide (CO_2), 446,000 tons of carbon monoxide (CO), 350 kg of cadmium (Cd), 468 tonnes of methane (CH_4), 27,800 tons of oxides of nitrogen (NO_x/NO_2), 40,600 tons of sulfur oxides (SO_x/SO_2), 1,500 tons

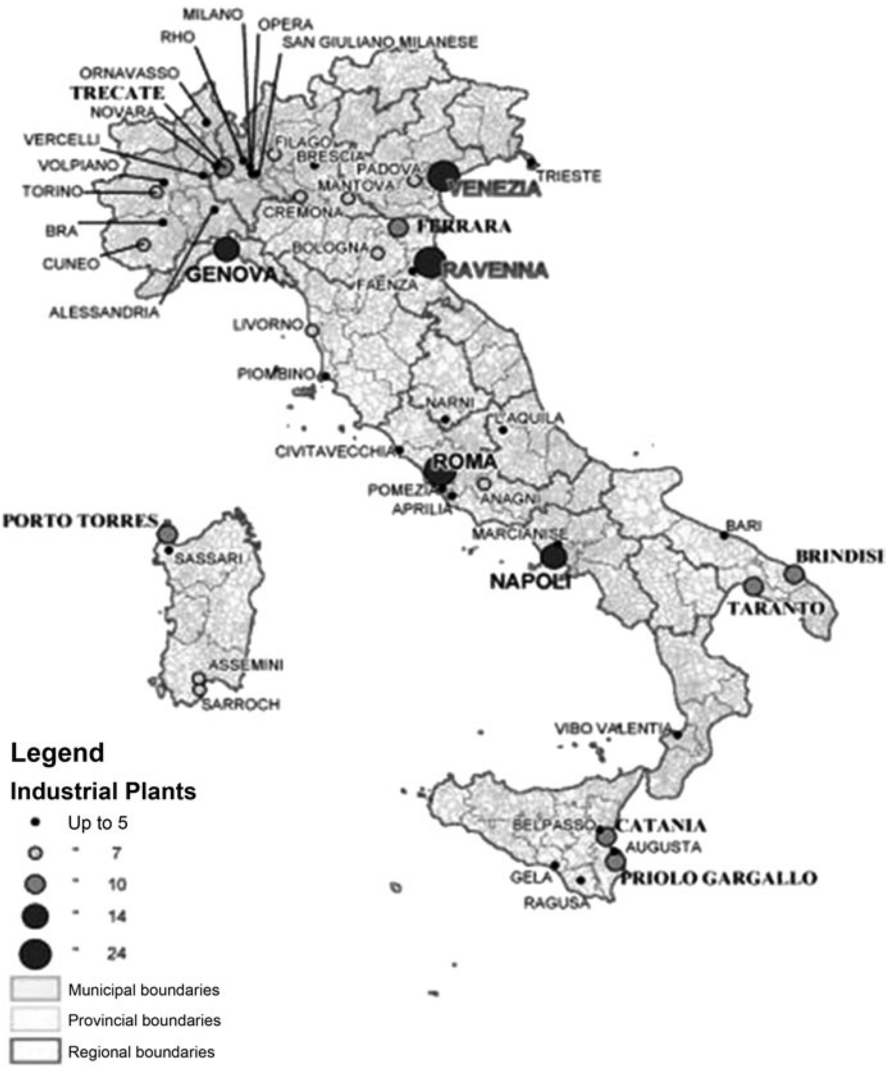

Fig. 2.2 Municipalities with four or more industrial plants subject to Articles 6/7 and 8 of D.lgs.334/99 (December 2012). (Source: http://www.isprambiente.gov.it)

Any discussion of the problems of these industries involves a different perspective from those of the manufacturing industry: For the latter, it is possible to rethink the logic of production in a circular manner, from cradle to grave (Richards and

of non-methane volatile organic compounds (NMVOC), 183 t of benzene, 754 t of chlorine (HCl), 1.14 tons of mercury (Hg), and other pollutants, which in many cases (carbon dioxide, cadmium, chlorine, carbon monoxide, chromium, mercury, etc.), compared to the data of 2001, were increased (http://prtr.ec.europa.eu).

Table 2.2 The first 15 air-polluting activities in Italy in the year 2011. (Source: Attardi et al. 2012)

Location	Activity	Environmental damage costs in Euro	Environmental damage costs in percentage
Brindisi	Energy—Thermal power stations and other combustion installations	1243	17.9%
Taranto	Production of pig iron or steel meltins and continuous casting	746	10.8%
Sarroch	Energy—Mineral oil and gas refineries	582	8.4%
Taranto	Energy—Thermal power stations and other combustion installations	511	7.4%
Sassari	Energy—Thermal power stations and other combustion installations	559	8.1%
Venezia	Energy—Thermal power stations and other combustion installations	407	5.9%
Quiliano	Energy—Thermal power stations and other combustion installations	417	6.0%
San Filippo Del Mela	Energy—Thermal power stations and other combustion installations	393	5.7%
Augusta	Energy—Mineral oil and gas refineries	386	5.6%
Sannazzaro De' Burgondi	Energy—Mineral oil and gas refineries	350	5.0%
PrioloGargallo	Energy—Mineral oil and gas refineries	313	4.5%
Portoscuso	Energy—Thermal power stations and other combustion installations	269	3.9%
Civitavecchia	Energy—Thermal power stations and other combustion installations	233	3.4%
Milazzo	Energy—Mineral oil and gas refineries	303	4.4%
Ferrera Erbognone	Energy—Thermal power stations and 0titer combustion installations	226	3.3%

Pearson 1998), while for those operating in the sectors of extractive industries, petrochemicals, energy, metallurgy, iron and steel, and chemicals, there is a fundamental problem related to the collection, processing, and consumption of environmental components that are formed in geological time (minerals, hydrocarbons, etc.) and the related environmental impact that results from their combustion, suggesting a radical reflection on the systems of production and consumption (Banini 2010). The contribution of geography to how sustainability can be understood, pursued, and achieved can be significant (Sneddon 2000; Bradshaw 2010), starting at the local level and the rethinking of the energy sources used, which, as motors of the social and economic system, involve the entire reorganization of the territory in a sustainable way (Bagliani et al. 2010).

2.4 The Ilva of Taranto

A huge iron and steel industry like that of Taranto, which extends for 1,545 hectares (3,818 acres), devastates the landscape and greatly damages health. The ideas behind the locating of an industry like this in this area are political and economic: the entrance of Italy into the European Coal and Steel Community (ECSC) which came into force on July 23, 1952; although Italy has no coal or iron mines, Italian politicians decided to be signatories to this treaty both to strengthen the heavily damaged Italian economy after the Second World War and to gather the old enemies together. Thus, they thought by producing more steel, the raw material of the war industry, they could protect themselves against any future aggression.

The Taranto state industry was the fourth largest steelworks in Italy, after those of Cornigliano, Piombino, and Bagnoli. The location was chosen because of the following reasons: It is close to the sea and to a natural large harbor with a wide flat hinterland; it has a great supply of limestone; it was in Southern Italy, the most depressed area in the country, with a considerable supply of labor; Taranto is open to the markets of raw materials and oil from Mediterranean and South Asiatic countries, which in turn demand steel and piping for their development; and the need for water, important for this type of industry, is met by the rivers of Basilicata, a nearby region, which has too much water for its needs.

On the basis of these considerations the 4th Steelworks Centre was established on April 10, 1965, although the foundation stone was laid on July 9, 1960; the pipe shop was the first to run in 1961, the first blast furnace was put into operation on October 21, 1964, and the second on January 29, 1965.

Giuseppe Saragat, the president of the Italian Republic at the time said: "I am here today to celebrate the opening of a great factory, the complex of the 4th Steelworks of Italsider. Also, on this occasion I would like to guarantee the Italians of the Mezzogiorno that the State is fully aware of the crucial situation in Southern Italy, and will spare no effort to change this" (*La Stampa*, April 11, 1965, p. 5).

The building of this huge plant, however, had serious effects on the local environment. The spectacular view of a landscape of ancient olive groves was wiped out by bulldozers and replaced by buildings, towers, and chimneys. Some other problems soon appeared: (1) The traffic pattern became much denser; (2) land prices went sky-high; (3) the facilities were less than satisfactory; (4) the crime rate increased; and (5) the factory was too close to the housing estate called Tamburi (Fig. 2.3)[8].

[8] The name Tamburi (drums) refers to a nearby Roman aqueduct and possibly to the imaginary sound of its water. This area is inhabited by 10,000 people. Its actual expansion is due to the construction of public housing for the workers of the plant.

Fig. 2.3 The intrusive presence of Ilva in the urban area of Taranto. Note the location of the Tamburi estate

Taranto is a naval town, with an arsenal and a shipyard, but these activities, which once were a major source of income and prestige for the city, are now heavily reduced or nonexistent. Locating the steelworks here obviously went a long way to solving the unemployment problem of Taranto. The fishing industry, particularly of shellfish (the well-known *cozz*e—mussels), was seriously damaged because of water pollution (Fig. 2.4).

The turnover of the 4th Steelworks Centre of Taranto is 310 million Euro. In 1970, its production percentage was 41 % of the whole of Italsider. In 1980, this percentage rose to 79 %. The plant is the largest in Europe.

Nobody regretted the olives, the fish of the *Mar Piccolo* (Little Sea)[9], the lost landscape, and the good social relations, because the smoke from the chimneys was a symbol of modernity and growth.

[9] The city is built around two inlets called *Mar Grande* (Great Sea) and *Mar Piccolo* (Little Sea). The latter has suffered particularly from pollution by the production wastes of the plant. In the sweet water of a spring that once run through the sea—called, thanks to a legend, *Anello di San Cataldo*(Saint Cataldo's Ring)—delicious fish products grew. The Taranto harbor contains several

Fig. 2.4 The Italsider of Taranto. Note the chimneys close to houses and to mussel farming

Only Camillo Cederna, an Italian ecologist, one of the founders of the Association *Italia nostra* in 1955, wrote two papers for the newspaper *Corriere della Sera* against the building of the Steelworks. In the first, entitled "Taranto in the hands of Italsider" (April 13, 1972, p. 3), he describes Taranto as "a heavily damaged city, a Manhattan of underdevelopment and building speculation." In the second, entitled "Taranto strangled by its boom" in the same newspaper in the same year, he calls the Taranto industrialization "a barbaric process," and that "a state industry, despite a public investment of almost 2,000 billion lire, has not yet thought of protecting from pollution the poor inhabitants of the downwind housing estates."

In 1995, after some changes of ownership, the 4th Steelworks Centre of Taranto was bought by the Riva Group and changed its name to Ilva, the Latin name of the island of Elba, where in Roman times some iron and coal mines were sited. At present, in this plant, there are 11,454 workers, 1,386 office workers, and 19 managers:

fishing boats: 80 trawlers and other little boats. The sea is rich in many prized species, such as dentex, sea bream, groupers, mullets, anchovies, shrimps, and squids. Taranto is the major production area in the world for farmed mussels, with an annual production of 30,000 tonnes and 1,300 employees. In fact, the *cozza* (mussel) is the gastronomic symbol of the city. Mussel farming in Taranto is very ancient. After the Saracen raids in 927, this farming was renewed, thanks to Byzantine Emperor Nicephorus Phocas the 2nd, and in the second half of the nineteenth century two thirds of the city's 30,000 inhabitants made their living from fishery products.

a total of 12,859 people. Because of its economic importance, the Riva Group is partially subsidized by the state.

For many years, the Steelworks has produced a large amount of air and water pollutants both during the state period and the current private period. The air pollution is evident over the whole area: A dark red dust covers houses and cars everywhere. At various times, the plant management tried to control the pollution to some extent, but now the problem is no longer to be borne.

In 2012, at the Taranto attorney's office two civil actions were deposited, one chemical and the other epidemiological. Consequently, some managers and owners of the plant have been placed under investigation. They are accused of culpable and fraudulent disaster, food poisoning, fraudulent omission of care in the case of industrial accident, aggravated damaging of public goods, discharge and spill of dangerous materials, and air pollution. The 70 hectares (173 acres) of mineral dumps are the most polluted areas, where dust, benzopyrene, dioxin, and other dangerous pollutants are collected. The epidemiologic assessment established that during a period of 7 years 11,750 people have died (1,680 yearly) particularly from cardiovascular and respiratory diseases and 26,999 people (3,857 yearly) were hospitalized for cardiac, respiratory, and cerebrovascular diseases. In the districts nearest to the plant, 637 people (91 yearly) died and 4,536 (648 yearly) were hospitalized for cardiac and respiratory diseases because of excess of PM_{10} in the air. The epidemiologic assessment ends with the following words: "The continuous exposure to the air pollutants emitted by the Steelworks caused and causes degenerative phenomena of different systems of the human body, which lead to disease and death." In March 2012, the Minister of the Environment, Corrado Clini, produced a new Integrated Environmental Authorization (the previous one was issued by his predecessor in 2011), giving the plant the possibility to continue production, along with the goal of reclamation of the environment.

At this moment, there is a standoff between the two state powers, one legislative and the other judicial, with the results: (1) a partial standstill in production; (2) wastage of material produced; (3) many workers laid off; (4) strikes and protests by workers; (5) claims by citizens seriously damaged by the pollution; and (6) detention of some plant owners. The question will be settled by the constitutional court.

During these events, a huge gantry crane with its driver was blown into the sea by a powerful tornado, on November 28, 2012 (Fig. 2.5). The driver's body was recovered after some time. Tornados are frequent along the Italian coasts, but almost always of little importance. Among some powerful historical tornados in Italy, I can quote the most ancient, which occurred in the Gulf of Naples in the fourth century B.C. (Musti 2005). Another sign of this atmospheric instability is, e.g., the frequency in variation of fog in the last few decades in Italy (Palagiano et al. 2008).

According to a table edited by Cadeo et al., issued by the newspaper *Il Sole 24 Ore* in 2012, on the quality of life in 107 Italian provinces, Taranto is in last place with 391 points. The data were obtained according to six parameters: standard of living (94 points), business and work (95 points), services, environment, and health (94 points), population (103 points), public order (64 points), and free time (104 points). We do not know the criteria of a classification like this, but we can note

Fig. 2.5 Tornado which struck Ilva of Taranto on November 28, 2012

that the sum of the values for Taranto are negative because not one single parameter considered has a positive value.

The Sentieri Working Group issued a National Epidemiologic Study (Pirastu et al. 2011), where 44 areas in Italy are at environmental risk, as is shown on the map (Table 2.3). The relationship between the exposure to some pollutants and chronic diseases is set out here, with the Sentieri data. Table 2.1 is based on the results of the Sentieri research.

The Sentieri research concludes that for a total of 403,692 deaths (both men and women) there are in excess of 9,969 deaths, with an average of about 1,200 extra deaths per year (p. 30). The most polluted areas are in Central and South Italy. It is difficult to connect diseases to environmental pollution with certainty. But the most evident problem is the degradation of the landscape, due to uncontrolled industrialization and to the greed of private entrepreneurs. I think that new industrialization systems are needed, with less polluting industry, with much more attention paid to the environment and the city dwellers. In addition, a new economy has to be developed taking into account the safety of workers.

The problems of asbestos in Italy are very serious, because asbestos fibers can be everywhere (in old houses, in the transport systems, and also in our mountains). To build the high-speed railway line from Turin to Lyon in Val di Susa, it is necessary to bore a tunnel through a mountain, possibly containing asbestos. For this reason, many people oppose this enterprise, which particularly spoils the landscape.

In recent times, cities and landscapes have been seriously threatened by changes and pollution. New technologies can help to minimize soil consumption and pollution. Public and private administrators, as well as politicians, tend to give more

Table 2.3 The Italian polluted sites (IPSs). In *bold* the areas with more pollution sources. (Source: Piratsu et al. 2011)

Sites	Etiology	Diseases
Balangero, Emarese, Casale Monferrato, Broni, Bari-Fibronit, Biancavilla	Contamination from asbestos	Increases in malignant neoplasms
Pitelli, Massa-Carrara, Vesuvian littoral zone, Tito, Basento Valley industrial areas, Priolo	Other sources of environmental pollution in addition to asbestos	Increases in malignant neoplasm of pleura; in both genders in Pitelli, Massa-Carrara, Priolo, Vesuvian littoral zone (in these areas in 1995–2002 a total of 416 extra cases)
Gela, *Porto Torres*	Emission from refineries and petrochemical plants	Increases in mortality from lung cancer and respiratory diseases
Taranto, *Sulcis-Iglesiente-Guspinese*	Emission from metal industries	Increased mortality from respiratory diseases
Falconara Marittima, *Massa-Carrara, Milazzo, Porto Torres*	Air pollution	Congenital anomalies and perinatal disorders
Massa-Carrara, Piombino, Orbetelloj, Lower Valley of Chienti river, *Sulcis- Iglesiente-Guspinese*	Causal role of heavy metals, PAH.s and halogenates compounds	Mortality from renal failure
Trento-Nord, Grado and Marano, and Lower Valley of Chienti river	Role of lead, mercury organohalogenated solvents	Neurological diseases
Brescia	Widespread PCB pollution	Increase in non-Hodgkin's lymphomas

weight to employment figures at the expense of safeguarding the health of individuals. An industrial reorganization needs to establish light industries rapidly, which can easily follow market changes: Once wood was the most used material; then came the time of great steel production, followed most recently by plastic; new airplanes and cars are made of plastic. In addition, the agricultural activities for producing food must be renewed and improved. Finally, there is too much waste of food, energy, and materials in our Western countries!

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Chapter 3
Environmental Concerns of the Tanning Industry

Farhana Masood and Abdul Malik

Abstract Tanning industry wastes pose a serious environmental impact on water (with its high oxygen demand, discolouration and toxic chemical constituents), terrestrial and atmospheric systems. Tannery waste characteristically contains a complex mixture of both organic and inorganic pollutants. The major public concern over tanneries has traditionally been about odours and water pollution from untreated discharges. Important pollutants associated with the tanning industry include chlorides, tannins, chromium, sulphate and sulphides, organic chemicals pesticides, dyes and finishing agents. These substances are frequently toxic and persistent, and affect both human health and the environment. High pollutant loads, involving chromium, can interfere with key biological processes used in sewage treatment plants. These pollutants may also damage the ecology of the receiving waters in the vicinity of the discharge points. Direct contact with some industrial chemicals can cause disability, illness (toxigenic/carcinogenic) and death in humans. Chlorophenols are the most predominant phenolic compounds in the tanning industry and are well known for their biocidal activities and have been found to be toxic, possibly mutagenic to terrestrial biota. Chromium appears to be the most damaging of these wastes, and in its hexavalent form it has a high level of toxicity, with chronic effects associated with cancer. The main contaminants and pollutants related to the leather sector are discussed in this chapter.

Keywords Chlorophenols · Chromium · Environment · Tannery

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3.1 Introduction

Modern industry is, to a large degree, responsible for contamination of the environment. There are no reliable estimates of the quantity and types of hazardous waste generated in most developing countries. Approximately 10–15 % of the wastes produced by industry overall are likely to be hazardous, increasing at a rate of 2–5 % per year (Chaaban 2001; Mwinyihija 2007). Khwaja (1998) identified leather tanning and finishing, as one of the main industries producing hazardous wastes and pollution. The global leather industry is currently valued at more than US$ 75 billion (Mwinyihija 2010). Today, the main leather-producing country is China, followed by Italy, India and Brazil. Processing of the hides and skins within the tanning industry is still an environmental concern irrespective of advances and mechanisms suggested as a way forward in adopting cleaner technologies. Moreover, pollution from the leather processing industries, which has been deemed as the largest polluter in the world (Khwaja 1998), has a negative long-term impact on the economic growth potential of a country (especially those with low technological capacity) irrespective of the immediate profit accruals intended. Tanning industry wastes pose a serious environmental impact on water (with its high oxygen demand, discolouration and toxic chemical constituents), terrestrial and atmospheric systems (Song et al. 2000; Mwinyihija 2007). Tannery waste characteristically contains a complex mixture of both organic and inorganic pollutants. The major public concern over tanneries has traditionally been about odours and water pollution from untreated discharges. Important pollutants associated with the tanning industry include chlorides, tannins, chromium, sulphate and sulphides, organic chemicals pesticides, dyes and finishing agents. These substances are frequently toxic and persistent, and affect both human health and the environment (UNEP 1994; Mwinyihija 2007).

In particular, tannery industries contribute enormously to water deterioration by discharging in the environment large volumes of wastewaters and are regarded as one of the most polluting among all industrial sectors (Soupilas et al. 2008; Tigini et al. 2011). The effluent has a broadly fluctuating pH and high temperatures (Aber et al. 2010). The pH of directly discharged tannery effluent varies between 3.5 and 13.5. Low pH in waters results in corrosion of water carrying system and leads to metal dissolving in water, whereas high pH water leads to scaling of the sewers. Furthermore, large pH fluctuation is detrimental to some aquatic species. The large amount of proteins and their degrading products forming a major part of the wastewater can affect biochemical oxygen demand (BOD). In addition to deposition of solids, raw unsettled tannery wastewaters can cause encrustation (of calcium carbonate) and serious corrosion of metals as well as concrete sewers due to H_2S biological oxidation to H_2SO_4 (Balusubramanian and Pugalenthi 2000). High pollutant loads, involving chromium, can interfere with key biological processes used in sewage treatment plants. These pollutants may also damage the ecology of the receiving waters in the vicinity of the discharge points. Chlorophenols are the most predominant phenolic compounds in the tanning industry. Chlorophenols are well known for their biocidal activities and have been found to be toxic, possibly mutagenic to terrestrial biota (Jensen 1996). Chromium appears to be the most damaging of these wastes, and in its hexavalent form it has a high level of toxicity, with chronic effects associated with cancer (Lemos et al. 2001; Mitteregger-Júnior et al. 2007).

During the tanning process, chromium salt is used to convert hide into leather and the wastewater containing huge amount of organic matter, phenolics, tannins and heavy metals (mainly chromium as environmental pollutants) is discharged into the environment, which causes serious soil and water pollution along with serious threat to human health. Tannery wastes are ranked as the highest pollutants among all the industrial wastes (Camargo et al. 2003). As the tannery wastewater is being contaminated with high levels of metals (Cr, Zn, Mn, Cu), its use in irrigation contaminates the soil. Long-term irrigation can induce changes in the quality of agricultural soil and trace element inputs which sustained over long period (Barman et al. 2000; Gothberg et al. 2002; Sinha et al. 2005). Trace metal concentrations in the water and soils from areas with known long history of tanning activities are found to be several times higher than the average metal contents in the background areas (Thuy et al. 2000; Tariq et al. 2006).

3.2 Chemicals Used in Tanning

The major parts of the chemicals that are used are inorganic bulk chemicals. Around 20–50 % of the chemicals that are added are inorganic standard chemicals. The inorganic chemicals generally used are calcium hydroxide, sodium chloride, sodium sulphide, acids, carbonates and sulphates. Besides the inorganic standard chemicals, chromium sulphate is also widely used as a tanning agent, and the consumption of chrome tanning agents is often around 80 kg/ton salted hides (corresponding to around 15 kg chromium/ton salted raw hide). Around 10–40 % of the chemical consumption in a tannery is of organic chemicals. Examples of standard organic chemicals used are organic acids and their salts. Besides the main process chemicals, a great variety of chemicals are used for auxiliary process purposes. These auxiliary agents may demand special attention because of the problem of reactivity, toxicity, persistence, bioaccumulation, mobility and the generation of problematic metabolites. It is, therefore, important to know the quantities used and their characteristics. Globally, approximately 6.0 million tonnes of raw hides (on a wet salted basis) are processed to leather (EC 2012). In addition, around 650,000 of goat- and sheepskins are processed to leather (EC 2012). This indicates that, globally, around 3 million tonnes of chemicals are used to produce leather (Rydin 2012).

In most developing countries, large quantities of tannery effluents are directly discharged to the nearby open lands where they adversely affect the quality of both soil and groundwater, rendering them unsuitable for viable human use (Farooque et al. 1984). Furthermore, this leads to deleterious health effects such as headache, stomachache, dizziness, night blindness, leprosy, dermatitis and other skin disorders

(Parikh et al. 1995). Chromium is extensively used as a tanning agent (Bosnic et al. 2000). Although a number of cleaner leather production technologies have been developed to abate the pollution load of tannery effluents due to chromium salts (Prentirs et al. 2003; Vitolo et al. 2003; Tariq et al. 2006), the metal still remains an irreplaceable tanning agent. It is known that chromium discharged from tannery effluents into the surface waters far exceeds the worldwide accepted regulatory limit of 0.5–15 mg/l (Buljan 1996).

3.2.1 Organic Matter

Organic matter associated with tannery waste will include biodegradable organic matter (e.g. proteins and carbohydrates). These organic compounds result in depression of the dissolved oxygen content of stream waters caused by microbial decomposition (Balusubramanian and Pugalenthi 2000; Song et al. 2000, Mwinyihija et al. 2006). Their impacts are primarily the loss of dissolved oxygen, which is detrimental to aquatic organisms. Secondly, their effect is on dissolved oxygen that is consumed by aerobic microbial oxidation of the waste; anaerobic decomposition becomes prominent and releases noxious gases (Pepper et al. 1996; Mwinyihija et al. 2006). The organic pollutants can be biodegraded when the dissolved oxygen is sufficient, but with insufficient oxygen, fish and other aquatic species may die, and without oxygen, decomposition becomes anaerobic, with formation of methane (Kapdan and Oztekin 2003). Moreover, recalcitrant compounds can exist, which are not biodegradable or have very slow biodegradation rate, increasing their bioaccumulation. These compounds are considered pollutants due to their toxicity and not by the consumption of dissolved oxygen (Ikeda et al. 2002; Gomes et al. 2010).

3.2.1.1 Chlorinated Phenols

The curing and storage phase of the hides and skins utilises various types of insecticides and anti-mould chemical compounds, which are eventually discharged into the tannery effluents. Most of these compounds belong to chlorophenols, which enter the environment through several pathways (Steiert and Crawford 1985). Pentachlorophenols (PCPs) (which are used to prevent fungal growth and decay by bacteria in leather preservation) and its salts are highly toxic and harmful to human health and aquatic systems and persist in the environment for long periods of time. Polychlorinated biphenyls (PCBs) are found in softeners and are highly toxic and impact adversely on terrestrial, aquatic and atmospheric systems. Apparently, PCP was one of the substances for which the European Union (EU) was established. Formaldehyde resins (normally used as glazing agents in the finishing process) are known to irritate the mucosal membrane, cause allergic dermatitis, and on long-term exposure are potentially carcinogenic. PCP causes uncoupling of oxidative phosphorylation, inhibition of glycolytic phosphorylation, inactivation of mitochondrial and myosin adenosine triphosphate (ATP), inactivation of respiratory enzymes and damage to mitochondrial structures (McCarthy et al. 1997; Tewari et al. 2012). The noxious influence of phenols and their derivatives concerns acute toxicity, histopathological changes, mutagenicity and carcinogenicity.

3.2.1.2 Enzymes

The tanning process uses enzymes (notably trypsin) as digesting agents for certain hide components prior to tanning. Enzymes vary widely in potential toxic hazard; exposure to trypsin in solid form may lead to a possible allergic reaction in certain individuals, and prolonged skin contact with trypsin solutions can lead to irritation and dermatitis. Besides trypsin (a pancreatic enzyme), other enzymes of fungal and bacterial origin are used in various pre-tanning processes. These may also present a hazard to health and should be handled with appropriate caution.

3.2.1.3 Oils and Grease

Floating grease and fatty particles agglomerate to form 'mats' which then bind other materials, thus causing a potential blockage problem especially in effluent treatment systems. If the surface waters are contaminated with grease or thin layers of oil, oxygen transfer from the atmosphere is reduced. If these fatty substances emulgate, they create a very high oxygen demand on account of their biodegradability.

3.2.2 Inorganic Matter

3.2.2.1 H_2S

The primary biochemical effects arising from H_2S exposure are inhibition of the cytochrome oxidase and other oxidative enzymes, resulting in cellular hypoxia or anoxia (Beauchamp et al. 1984; Glass 1990; Reiffenstien et al. 1992; Nicholson et al. 1998). Concentration-dependent toxicity occurs in humans following acute exposure. These clinical effects are consistent with organic brain disease resulting from anoxia and thus may persist for several years after the initial exposure.

3.2.2.2 Sulphide (S^{2-})

The sulphide content in tannery effluent results from the use of sodium sulphide and sodium hydrosulphide and the breakdown of hair in the unhairing process. Comparable in toxicity to hydrogen cyanide, even a low level of exposure to the gas induces headaches and nausea, as well as possible damage to the eye. At higher levels, death can rapidly set in and countless deaths attributable to the build-up of sulphide in sewage systems have been recorded.

3.2.2.3 Neutral Salts

Two common types of salts are to be found in tannery effluents.

Sulphates

Sulphates are a component of tannery effluents, emanating from the use of sulphuric acid or products with a high (sodium) sulphate content. Many auxiliary chemicals contain sodium sulphate as a by-product of their manufacture. For example, chrome tanning powders contain high levels of sodium sulphate, as do many synthetic re-tanning agents. Health hazards due to sulphate containing water intake are relatively mild. High levels of sulphate in drinking water may cause dehydration from diarrhoea in children, transients and the elderly. Generally, laxative effect at concentrations of 1,000–1,200 mg/l is observed, but no severity is found as body starts adapting to higher sulphate levels. The presence of sulphate in drinking water also results in a noticeable taste.

Chlorides

Chloride is an indicator of pollution when present in higher concentrations (Singh et al. 2009). Sodium chloride used as a dehydrating and antiseptic agent is the source of chloride (Mehdi 2005). Chloride is introduced into tannery effluents as sodium chloride usually on account of the large quantities of common salt used in hide and skin preservation or the pickling process. Being highly soluble and stable, they are unaffected by effluent treatment and nature, thus remaining as a burden on the environment. Increased salt content in groundwater, especially in areas of high industrial density, is now becoming a serious environmental hazard. Chlorides inhibit the growth of plants, bacteria and fish in surface waters; high levels can lead to breakdowns in cell structure. If the water is used for irrigation purposes, surface salinity increases through evaporation and crop yields fall. When flushed from the soil by rain, chlorides re-enter the ecosystem and may ultimately end up in the groundwater. The level of chloride in the effluent (5,100 mg/l) was fivefold higher than that prescribed by Bureau of Indian Standards (2009). The presence of very high amounts of chloride and sulphate is responsible for high hardness and it further increases the degree of eutrophication (Kannan et al. 2005).

3.2.2.4 Heavy Metals

The most commonly occurring metals at the discharge sites are lead, chromium, arsenic, zinc, cadmium, copper and mercury. The presence of these metals in the water and soil may cause serious threat to human health and ecological systems (Sundar et al. 2010). Problems of pollution by metals have aggravated and affected the ecological balance and caused serious health hazards because of the release on land as well as dumping on the surface water. Ultimately, metallic components leach to groundwater and lead to contamination due to accumulation and result in a series of well-documented problems in living forms (Malarkodi et al. 2007).

A large number of biologically active substances, including heavy metals, may have direct, indirect, primary or secondary effects on the immune system and are of interest to pathologists, immunologists and toxicologists. Heavy metals (e.g., chromium from the tanning industry) are of significant importance in altering the immune response via immunostimulatory or immunosuppressive mechanisms (Shrivastava et al. 2002). Metal compounds are not biodegradable. They can thus be regarded as long-term environmental features. Since they can also have accumulative properties, they are the subjects of close attention. Two forms of chrome are associated with the tanning industry. Depending on the chemical species, these metals have differing toxicities that are also affected by the presence of other organic matter, complexing agents and the pH of the water. Aluminium, in particular, appears to inhibit the growth of green algae, and crustaceans are sensitive to low concentrations. Cadmium, sometimes used in yellow pigments, is considered highly toxic. It is accumulative and has a chronic effect on a wide range of organisms. If present in drinking water, it can induce brittleness in bones. Heavy metals can pose health hazards if their concentrations exceed allowable limits. Even when the concentration of metals does not exceed these limits, there is still a potential for long-term contamination, and heavy metals are known to accumulate within biological system (Altaf et al. 2008). Hence, the effluent released is expected to have a higher amount of chemicals and toxic metals. The industry is also associated with a number of environmental and human health risks, including cancers among tannery workers. Work in a leather tanning industry involves exposure to a wide range of chemicals, some of them with suspected carcinogenic and mutagenic properties.

Chromium Salts

Chromium basic sulphate is the most widely used tanning substance today (UNEP 1994). Chromium is a micronutrient and Cr salts such as chromium polynicotine, chromium chloride and chromium picolinate (CrP) have been demonstrated to exhibit a significant number of health benefits in animals and humans (Anderson 2000). Hazards due to environmental contamination depend on its oxidation state (i.e. hexavalent stage of chromium (Cr^{6+}) is more toxic than the Cr^{3+} which precipitates at higher pH). Trivalent chromium is unable to enter into cells but Cr^{6+} enters through membrane anionic transporters. Intracellular Cr^{6+} is metabolically reduced to Cr^{3+}. Cr^{6+} does not react with macromolecules such as DNA, RNA, proteins and lipids. However, both Cr^{3+} and the reductional intermediate Cr^{5+} are capable of coordinated covalent interactions with macromolecules (Shrivastava et al. 2002). The tannery waste can have between 40 and 50,000 mg/l of total chromium (Hafez et al. 2002). Due to the difference in the toxic nature of both the forms of Cr, the discharge of Cr (VI) into surface water is regulated to below 0.05 mg/l by the United

States Environmental Protection Agency (USEPA), while the total Cr (including Cr (III), Cr (VI) and its other forms) is regulated to below 2 mg/l (Sharma and Adholeya 2011).

During the tanning process, the leather takes up about 60–80 % of the applied chromium and the rest of the metallic salts are usually discharged into effluent waters with serious environmental impact (van Groenestijn et al. 2002; Leghouichi et al. 2009). Cr (VI) induces acute and chronic toxicity, neurotoxicity, dermatotoxicity, genotoxicity, carcinogenicity, immunotoxicity and general environmental pollution. Once transported through the cell membrane, chromium (VI) is rapidly reduced to chromium (III), which subsequently binds to macromolecules. Accumulation of chromium takes place mainly in liver, kidneys, spleen and bone marrow after entering the system. Oversensitivity to Cr may cause skin diseases like epidermal dermatitis on little exposure to the element. Also, it induces respiratory carcinogenicity in humans exposed to chromium (VI) in occupational settings. The properties of waste solution obtained from chromium-based tanning process and its toxic effects on humans were discussed in detail by previous researchers (Barnhart 1997; Barceloux 1999; Bajza and Vrcek 2001; Kornhauser et al. 2002).

Chromium is considered as one of the priority pollutants in the USA by the USEPA, and in many other countries, primarily because the soluble Cr species, Cr (VI), is a respiratory carcinogen when inhaled and a mutagen as a result of its strong oxidizing nature (USEPA 1996a). In contaminated soils, in the absence of reducing agents, Cr (VI) is soluble in alkaline environments, posing a threat to surface and groundwater quality because it is more readily transported. For these reasons, regulatory authorities monitoring the contaminated sites have placed considerable emphasis on remediation and rehabilitation of Cr-polluted soils.

The leather industry alone accounts for 40 % of the worldwide Cr usage. Large-scale disposal of tannery wastes has significantly contributed to Cr contamination in soils and water worldwide. Most of the Cr reaches the soil by improper disposal of industrial wastes, spills or faulty storage containers (USEPA 1984). Approximately 50,000 tonnes of Cr-rich solid wastes are disposed onto land annually from tannery industries alone. The long-term disposal of tannery wastes has led to extensive contamination of agricultural soil and groundwater in several countries, including Australia, China, India, Bangladesh, Nepal, Pakistan, Spain and Brazil. About 50,000 ha of land have been rendered barren by this activity in India and Bangladesh alone (ACIAR 2000).

3.3 Environmental Impacts

Tannery industry is common in many parts of the world and it pollutes groundwater and ecosystems (Khwaja et al. 2001; Chattopadhyay et al. 2004; Gagneten and Ceresoli 2004; Apte et al. 2005; Mondal et al. 2005; Tariq et al. 2005; Zahid et al. 2006; Gowd and Govil 2008; Kumar and Riyazuddin 2008, 2010; Naeem et al. 2008; Leghouchi et al. 2009; Mahmoud 2009; Sankaran et al. 2010; Tarcan et al.

2010). These industries have been known to be a considerable source of groundwater pollution and to cause health problems among local people (Paul Basker 2000; Mondal and Singh 2010).

The processes of leather manufacturing have a high environmental impact, most notably due to the heavy use of toxic chemicals in the tanning process. The major environmental issues of tanneries are solid wastes and wastewater. In the course of processing of hides into leather about 20 % of the material results as solid wastes, consisting of leather scraps, hair, soluble proteins, curing salts and fleshing (animal fats, collagen fibres, meat, etc.). The effluents discharged from tanneries are large in volume, are highly coloured and contain heavy sediment load, toxic metallic compounds, chemicals, biologically oxidizable materials and large quantities of putrefying suspended matter. Solid wastes of tanneries are usually dumped improperly inside and around the factory area. Large pH fluctuation and high BOD value caused by tannery effluents can kill all natural life in an affected water body. Hydrogen sulphide formed due to the presence of sulphide in the effluent is highly toxic to many forms of life. Another toxic pollutant of great concern present in tannery effluents is chromium, which is known to cause perforations and bronchiogenic carcinoma to continuously exposed humans.

3.3.1 Water Consumption

Generally, water consumption is greatest in the pre-tanning areas, but significant amounts of water are consumed also in the post-tanning processes.

3.3.2 Water Discharge

Tannery and leather manufacturing process use large volumes of effluents (wastewater) containing a wide variety of chemicals. The principal pollutants in wastewater discharges are from the beam house operations and the subsequent tanning operations. Wastewater from tanyard processes, deliming and bating may contain sulphides, ammonium salts and calcium salts and is weakly alkaline. After pickling and tanning processes, the main wastewater contaminants depend on the tanning techniques used. Finishing wastewaters may contain lacquer polymers, solvents, colour pigments and coagulants.

Tannery effluents, being voluminous and highly puerile, when discharged untreated, damage the normal life of a receiving stream and seriously affect the groundwater table of that locality, if allowed to percolate into the ground for a prolonged period. Other major chemical constituents of waste resulting from the tanning industry are sulphide and chromium. These chemicals mixed with water are discharged from the tanneries. They pollute groundwater permanently and make it unfit for general consumption, including drinking and irrigation. It has been established that a single tannery can pollute groundwater within a radius of 7–8 km (Bhaskaran 1977). The total dissolved solids (TDS) value in groundwater can be as high as 39,100 mg/l. Sodium and chloride are the dominant chemicals present in groundwater, which make it unsuitable for any purpose (Mondal and Singh 2010). Among the dissolved constituents, Na^{+}, Ca^{2+}, Mg^{2+}, HCO_3^{-} and SO_2^{-4} are in excess of standard values for either drinking or irrigation. Of course, pollution in the area housing tanneries is also affected by geogenic and other anthropogenic activities (Mondal and Singh 2011).

3.3.3 Waste

Hair, offcuts and sludge are the main types of solid waste. Solids are usually disposed of to a landfill site. Dewatered sludges from tanneries can also be disposed of to controlled landfills without significant environmental problems being incurred. Tanning sludges should immediately be covered with inert material to avoid odour generation and insect infestation.

3.3.4 Soil and Groundwater Contamination

Soil and groundwater contamination occurs when chemicals and wastewater seep through the soil from unlined ponds, pipes and drains, or from dumps and spills. Important pollutants include chlorides, tannins, trivalent chromium, sulphate and sulphides as well as other trace organic chemicals and chlorinated solvents. Leather tanning produces thousands of tons of solid waste per year that are dumped in open fields and landfills. There is always a risk that toxic leachates of complex solid wastes may contaminate the surface- and groundwaters by runoff and percolation, posing a serious threat to the environment. A health survey of drinking water has proven that contamination by leachate from a pesticide waste dump occurs. As leachates are complex mixtures of toxicants, it is possible that various toxicants may synergistically interact inside the organism, which could induce greater toxicity than that generated by the substances individually. The presence of hexavalent chromium (Cr (VI)), a well-known mutagenic/carcinogenic metal, has already been reported in tannery waste-contaminated soils (Thangavel et al. 2002; Masood and Malik 2013). Leachates may contain various other heavy metals in addition to Cr, which, if absorbed through roots, may be transmitted to other organisms and to human beings through the ecological food chain (Dudka and Miller 1999).

During the past 20 years, a number of studies have examined the possibility that occupational exposure to hazardous chemical substances increases the risk for various diseases (Karipidis 2007). The incidence of environmental exposures on the general status of health has been increasingly acknowledged for numerous diseases (Melissa et al. 2006). The industrious hazardous waste may show effects in terms of death and morbidity. This may manifest as respiratory diseases, skin reactions, allergies, diminution of vision, corneal opacity, abortion, malformation of pregnancy, stunted growth, neurological disorders, mental depression, psychiatric changes, altered immune response, chromosomal aberrations and cancer (Kilivelu and Yatimah 2008). Health-related studies have shown that excessive intake of toxic trace metals results in neurological and cardiovascular diseases as well as renal dysfunction (Mehra and Juneja 2005). Hepatitis, cholera, dysentery and typhoid are the most common diseases, which affect large population (Aswathi and Rai 2005). It is understood through documented evidence that the primary pathways of toxic metal accumulation in humans are through the ingestion of contaminated water and food (Brown and Longoria 2009). Wastes may pose a problem to human health either through drinking water or indirectly through food chain or via fish (Chen et al. 2004). From the environmental point of view, there are different ways of avoiding or minimizing the pollution in tannery wastewaters These are:

1. Use of less contaminant raw materials. In this way, fresh hides can be processed avoiding the conversation salt
2. Replacement of some chemical by others with less pollution potential. This can be carried out according to the Integrated Pollution Prevention and Control (IPPC) procedure
3. Reduction of water consumption and reuse of wastewaters

3.4 Conclusion

There are many options of treating chromium from tannery effluent and some treatment techniques managed nearly 99 % of removal of chromium from the spent liquor. Usually, these kinds of technologies are complicated, expensive, energy intensive, can be applied on a specific region, others need skilled personnel and some technologies are not yet commercialised. However, technology like electrocoagulation could give very high removal of chromium (98 %) and reproducibility due to its low cost. Despite all these scientific attempts, tanning industry is still one of the major polluters of the environment worldwide. Therefore, to prevent the public health and environmental impact of tannery waste in general and chromium in particular, the environmental regulation like effluent discharge limit has to be stringent and organization should be powerful to the extent that they can take measure by applying polluter principle or precautionary principle to avoid the effect of toxicity and bioaccumulation.

Government assistance in the form of subsidies/low interest loans for investments in pollution prevention and control would ease the pollution burden. Activities such as combined treatment of municipal wastewater and tannery effluents, creation of information exchange for waste management, development of indigenous technologies or/and adaptation of environmentally sound technologies from abroad for tanning and production of leather products, installation of meters at tannery outlets with connections to the common effluent treatment plants and creation of eco-leather parks/complexes would satisfy sustainable development.

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Chapter 4
Environmental and Health Effects of Textile Industry Wastewater

Sana Khan and Abdul Malik

Abstract The textile production industry is one of the oldest and most technologically complex of all industries. The fundamental strength of this industry flows from its strong production base of a wide range of fibers/yarns from natural fibers like cotton, jute, silk, and wool to synthetic/man-made fibers like polyester, viscose, nylon, and acrylic. With escalating demand for textile products, textile mills and their wastewater have been increasing proportionally, causing a major problem of pollution in the world. Many chemicals used in the textile industry cause environmental and health problems. Among the many chemicals in textile wastewater, dyes are considered important pollutants. Worldwide environmental problems associated with the textile industry are typically those associated with water pollution caused by the discharge of untreated effluent and those because of use of toxic chemicals especially during processing. The effluent is of critical environmental concern since it drastically decreases oxygen concentration due to the presence of hydrosulfides and blocks the passage of light through water body which is detrimental to the water ecosystem. Textile effluent is a cause of significant amount of environmental degradation and human illnesses. About 40 % of globally used colorants contain organically bound chlorine, a known carcinogen. Chemicals evaporate into the air we breathe or are absorbed through our skin; they show up as allergic reactions and may cause harm to children even before birth. Due to this chemical pollution, the normal functioning of cells is disturbed and this, in turn, may cause alteration in the physiology and biochemical mechanisms of animals resulting in impairment of important functions like respiration, osmoregulation, reproduction, and even mortality. Heavy metals, present in textile industry effluent, are not biodegradable; hence, they accumulate in primary organs in the body and over time begin to fester, leading to various

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symptoms of diseases. Thus, untreated or incompletely treated textile effluent can be harmful to both aquatic and terrestrial life by adversely affecting the natural ecosystem and causing long-term health effects. Environmental hazards and health problems associated with chemicals used in textile industry are discussed in this chapter.

Keywords Dyes · Effluent · Environment · Heavy metals · Textile industry

4.1 Textile Industry: An Overview

Industrialization is considered to be the key for the development in economic terms. At the same time, it is also recognized to be the root cause for environmental pollution. Due to different types of industries, environmental pollution is one of the vital problems presently facing India and the world (Paul et al. 2012).

The textile and garment industry is one of the oldest manufacturing sectors in India. The industry plays an important role in the Indian economy. It is a significant contributor to many national economies, encompassing both small- and large-scale operations worldwide. In terms of its output or production and employment, the textile industry is one of the largest industries in the world (Verma et al. 2012). It is a major foreign exchange earner and, after agriculture, it is the largest employer with a total workforce of 35 mn. The industry covers a wide range of activities, which include the production of natural raw materials such as cotton, jute, silk, and wool, as well as synthetic filament and spun yarn. In addition, an extensive range of finished products is made. India accounts for about 14 % of the world's production of textile fibers and yarns. This includes jute, of which it is the largest producer. India is the second largest producer of silk, cellulose fiber and yarn and the fifth largest producer of synthetic fiber and yarn.

The modern world needs textiles for a vast array of applications, and from the carpets beneath our feet, to the clothes on our backs, to the architectural textiles shielding us from the elements—textiles are ubiquitous (Thiry 2011). Today, much of the textile and dyeing industry is located in developing countries, often with poor wastewater treatment. It can be said that India may be the major contributor of textile wastewater in South Asia. India has a large network of textile industries of varying capacity. The textile industries in India are mainly located in Mumbai, Surat, Ahmadabad, Coimbatore, Ludhiana, and Kanpur (Verma et al. 2012). Now, the industries are well developed and a large number of small textile-processing units are scattered all over the country (Garg and Kaushik 2007).

The environmental pollution caused by textile wastewater effluent poses a worldwide threat to public health and it gives rise to new initiatives for environmental restoration for both economic and ecological reasons. Textile industries have been placed in the category of most polluting industries by the Ministry of Environment and Forests, Government of India (Garg and Kaushik 2007). The effluent generated by the textile industry is one of the sources of pollution. Contamination of air, soil, and water by effluents from the industries is associated with a heavy disease burden (WHO 2002), and this could be part of the reasons for the current shorter life expectancy in the country (WHO 2003) when compared to the developed nations (Yusuff and Sonibare 2004). Moreover, textile industries are one of the most chemically intensive industries on the earth and one of the biggest users of water and also the major polluter of potable water (Verma et al. 2012). The most important chemical constituent used in textile industries is dye.

Throughout history, there have been several articles of clothing and dye colors that have had significant impacts on society. Historical records of the use of natural dyes extracted from vegetables, fruits, flowers, certain insects, and fish dating back to 3500 BC have been found. Earlier, fabric was being dyed with natural dyes. Synthesis of natural dyes was a long and tedious process. This was the common practice until the mid-1800s (Joseph 1977). These techniques were used to decorate clothing, utensils, and even the body. This was a religious as well as functional practice. These, however, gave a limited and a dull range of colors. Besides, they showed low color fastness when exposed to washing and sunlight.

WH Perkins in 1856 discovered the first synthetic dye, mauve. Synthetic dyes have provided a wide range of colorfast, bright hues (Kant 2012). Mauve was prepared using coal and tar. The vibrant color that was created not only had a tremendous impact on the fashions of the day but also spurred many other scientific discoveries. The synthetic dyestuff industry developed rapidly soon after this discovery with the introduction of another very important dye, magenta. The subsequent development of water-soluble azo dyes represented a landmark in the synthetic dye industry.

4.2 Processes in Textile Manufacturing

The most common textile-processing technology consists of desizing, scouring, bleaching, mercerizing, and dyeing processes (EPA 1997):

4.2.1 Sizing

This is the first preparation step, in which sizing agents such as starch, polyvinyl alcohol (PVA), and carboxymethyl cellulose are added to provide strength to the fibers and minimize breakage.

4.2.2 Desizing

This process is used to remove sizing materials prior to weaving. The nature of this process depends upon the type of size applied. Water-soluble size may simply be washed out, whereas water-insoluble size must first be subjected to chemical or enzymatic degradation.

4.2.3 Scouring

Natural impurities such as waxes, pectins, and proteins must be removed. This process removes impurities from the fibers by using alkali solution (commonly sodium hydroxide) to breakdown natural oils, fats, waxes, and surfactants, as well as to emulsify and suspend impurities in the scouring bath.

4.2.4 Bleaching

The step is used to remove unwanted color from the fibers by using chemicals such as sodium hypochlorite and hydrogen peroxide.

4.2.5 Mercerizing

Mercerization is a treatment specific to cotton. It is a continuous chemical process used to increase dye ability, luster, and fiber appearance. In this step, a concentrated alkaline solution is applied and an acid solution washes the fibers before the dyeing step.

4.2.6 Dyeing and Printing

This is the process of adding color to the fibers, which normally requires large volumes of water not only in the dye bath but also during the rinsing step. Textile materials can be dyed using batch, continuous, or semicontinuous processes. The kind of process used depends on many characteristics including type of material such as fiber, yarn, fabric, fabric construction and garment, and also the generic type of fiber, size of dye lots, and quality requirements in the dyed fabric. Among these processes, the batch process is the most common method used to dye textile materials (Perkins 1991). Depending on the dyeing process, many chemicals like metals, salts, surfactants, organic processing aids, sulfide, and formaldehyde may be added to improve dye adsorption onto the fibers. Whereas dying conveys a uniform color, printing allows a range of different colors to be applied. Usually between five and ten pastes are required for a single pattern. Color may be supplied by either pigments or dyes.

4.2.7 Finishing

Textile finishing represents the most variable area in the production process. A wide and ever-growing range of finishes are now available; these either improve the properties of the garment or provide “performance” properties.

4.3 Chemicals Used in Textile Industry

The textile industry has been condemned as being one of the world's worst offenders in terms of pollution because it requires a great amount of two components:

- Chemicals: As many as 2,000 different chemicals are used in the textile industry, from dyes to transfer agents.
- Water: This is a finite resource that is quickly becoming scarce and is used at every step of the process both to convey the chemicals used during that step and to wash them out before beginning the next step. Textile industries consume large volumes of water and chemicals for the wet processing of textiles. More textiles than ever are now manufactured and used, and chemicals are added for an ever-increasing number of purposes. The water becomes full of chemical additives and is then expelled as wastewater which in turn pollutes the environment: by the effluent's heat; by its increased pH; and because it is saturated with dyes, de-foamers, bleaches, detergents, optical brighteners, equalizers, and many other chemicals used during the process.

The chemical reagents used are very diverse in chemical composition, ranging from inorganic compounds to polymers and organic products (Mishra and Tripathy 1993; Juang et al. 1996). The chemicals used can be subdivided into:

1. Textile auxiliaries: This covers a wide range of functions, from cleaning natural fibers and smoothing agents to improving easy care properties. Included are such chemicals as:
   - Complexing agents, which form stable water-soluble complexes
   - Surfactants, which lower the surface tension of water so that grease and oil could be removed more easily
   - Wetting agents, which accelerate the penetration of finishing liquors
   - Sequestering agents
   - Dispersing agents
   - Emulsifiers
2. Textile chemicals (basic chemicals such as acids, bases, and salts).
3. Colorants, such as:
   - Dyes
   - Dye-protective agents
   - Fixing agents
   - Leveling agents
   - pH regulators
   - Carriers
   - Ultraviolet (UV) absorbers
4. Finishes.

4.3.1 The Most Important Constituents—Dyes: Structure and Properties

Dyes are natural and synthetic compounds that make the world more beautiful through colored products. Textile dyes represent a category of organic compounds, generally considered pollutants, discharged into wastewaters resulting mainly from processes of chemical textile finishing (Zaharia et al. 2009; Suteu et al. 2009a). It is estimated that over 10,000 different dyes and pigments are used industrially and over 7×10^5 t of synthetic dyes are annually produced worldwide (Zollinger 1987; Robinson et al. 2001; Ogugbue and Sawidis 2011). A dye is used to impart color to a material, of which it becomes an integral part. An aromatic ring associated with a side chain is usually required for resonance and thus to impart color. The characterization of dyes is based on their chemical structure and application. Dyes are composed of the atoms responsible for the dye color called chromophores as well as an electron-withdrawing or electron-donating substituent that causes or intensifies the color of chromophores, called auxochrome (Christie 2001). To be a dye, a compound must contain both the chromophore and auxochrome(s) (Verma et al. 2012). The most important chromophores are azo (–N=N–), carbonyl (–C=O), methine (–CH=), nitro ($–NO_2$), and quinoid groups. The most important auxochromes are amine ($–NH_3$), carboxyl (–COOH), sulfonate ($–SO_3H$), and hydroxyl (–OH) (Welham 2000). In general, azo dyes can occur in two tautomeric forms, azo (–N=N–) or hydrazone (=N–NH–). The latter is said to be more prone to oxidative fading, which is the most common photodegradation mechanism in the presence of light, moisture, and oxygen (Mirghani et al. 2008).

In general, textile fibers can catch dyes in their structures as a result of van der Waals forces, hydrogen bonds, and hydrophobic interactions (physical adsorption). The uptake of the dye in fibers depends on the dye's nature and its chemical constituents. But, the strongest dye–fiber attachment is a result of a covalent bond with an additional electrostatic interaction where the dye ion and fiber have opposite charges (chemisorption) (Carmen and Daniela 2012).

Reactive dyes, including many structurally different dyes, are extensively used in the textile industry because of their wide variety of color shades, high wet fastness profiles, ease of application, brilliant colors, and minimal energy consumption (Wang et al. 2009). The three most common groups are azo, anthraquinone, and phthalocyanine dyes (Axelsson et al. 2006), most of which are toxic and carcinogenic (Acuner and Dilek 2004). All dyes used in the textile industry are designed to resist fading upon exposure to sweat, light, water, many chemicals including oxidizing agents, and microbial attack.

The textile azo dyes are characterized by relatively high polarity (log K_{ow} up to 3) and high recalcitrance. Recalcitrance is difficult to evaluate because of the dependence of degradation on highly variable boundary conditions (e.g., redox milieu or pH). Furthermore, azo dyes are relevant in terms of eco- and human toxicity, industrially produced in high quantities, and known to occur in hydrosphere. Azo dyes also have great structural diversity, high molar extinction coefficients, and medium-to-high fastness properties in relation to light as well as to wetness. Depending on pH value, azo dyes can be anionic (deprotonated at the acidic group), cationic (protonated at the amino group) or nonionic. Accordingly, knowledge of the acidity constants is indispensable for the characterization of azo dye behavior. Environmental partitioning is influenced by substituents as well as the number of carbon atoms and the aromatic structure of the carbon skeleton.

4.3.1.1 Textile Dye classification

Textile dyes can be classified in several ways. Previously, the dyes were divided into:

(a) **Natural dyes**, the dyes extracted from vegetable and animal resources and mainly used in textile processing until 1856
(b) **Synthetic textile dyes,** which were firstly discovered in 1856

Recently, textile dyes are mainly classified in two different ways:

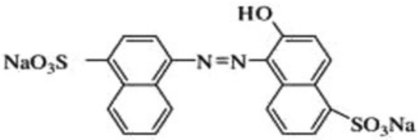
(a) Based on their application characteristics (i.e., Colour Index (CI) Generic Name such as acid, basic, direct, disperse, mordant, reactive, sulfur dye, pigment, vat, azo insoluble)
(b) Based on their chemical structure (i.e., CI Constitution Number such as nitro, azo, carotenoid, diphenylmethane, xanthene, acridine, quinoline, indamine, sulfur, amino- and hydroxy ketone, anthraquinone, indigoid, phthalocyanine, inorganic pigment, etc.)

Considering only the general structure, textile dyes are also classified as anionic (direct, acid, and reactive dyes), nonionic (disperse dyes), and cationic dyes (azo basic, anthraquinone disperse, and reactive dyes) (Robinson et al. 2001).

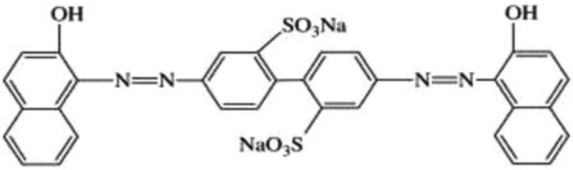
A systematic classification of dyes according to chemical structure is the CI (Table 4.1). This scheme is also useful for estimating the possible biodegradability of dyes (Wesenberg 2003).

The major textile dyes can be included in the two high classes: azo or anthraquinone (65–75 % of total textile dyes).

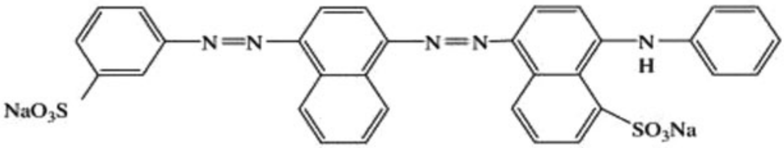
Azo Dyes The annual world production of azo dyes is estimated to be around 1 million t, and more than 2,000 structurally different azo dyes are currently in use (Vijaykumar et al. 2007). Azo dyes (Fig. 4.1), which are aromatic compounds with one or more –N=N– groups, constitute the largest class of synthetic dyes used in commercial applications (Zollinger 1991), constituting 60–70 % of all dyestuffs produced (Carliell et al. 1995). This linkage (–N=N–) may be present more than once and thus mono azo dyes have one azo linkage while there are two linkages in diazo dyes and three in triazo dyes. Azo dyes have one or more azo groups (R1-N=N-R2) having aromatic rings mostly substituted by sulfonate groups. These complex aromatic substituted structures make a conjugated system and are responsible for the intense color, high water solubility, and resistance to degradation of azo dyes under natural conditions (O'Neill 2000; Rajaguru 2000).



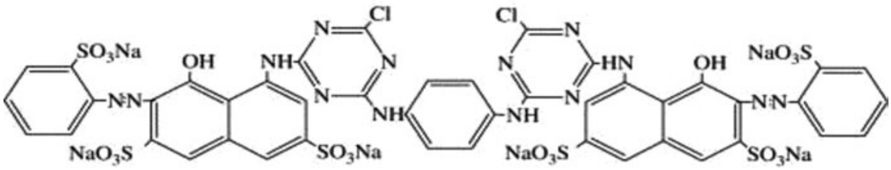
C.I. Acid Red 88 (AR-88), C.I. 15620, λ_{max} = 505nm



C.I. Acid Red 97 (AR-97), C.I. 22890, λ_{max} = 494nm



C.I. Acid Blue 113 (AB-113), C.I. 26360, λ_{max} = 554nm



C.I. Reactive Red 120 (RR-120), C.I. 25810, λ_{max} = 530nm

Fig. 4.1 Chemical structure and principal characteristics of some azo dyes

Azo dyes are synthesized via the following reaction. A primary amine (R-NH_2) is converted to a diazonium salt and this is reacted with another aryl unit.

Anthraquinone Dyes: Anthraquinone dyes constitute the second most important class of textile dyes, after azo dyes (Baughman and Weber 1994). These dyes have a wide range of colors in almost the whole visible spectrum, but they are most commonly used for violet, blue, and green colors (Christie 2001; Fontenot et al. 2003).

4.3.1.2 Toxicity of Dyestuffs

Dyes are the most important chemical constituents used in the textile industry, which impart color to yarn or cloth. Several adverse health effects and potential adverse effects have been defined for this group of substances. Wastewater effluent, generated from the textile industry, is a complex mixture of many polluting substances ranging from organ chlorine-based pesticides to heavy metals associated with dyes and the dyeing process. During dyeing processing, a large amount of the dyestuffs is released due to inefficiencies in the dyeing process and is directly lost to the wastewater, which ultimately finds its way into the environment. In addition, antimicrobial agents resistant to biological degradation are frequently used in the manufacture of textiles, particularly for natural fibers such as cotton (O'Neill et al. 1999; Couto 2009). For instance, azo dyes, which amount to around 60 % of textile dyes, display strongly adverse effects on the growth of methanogenic bacterial cultures (Hu and Wu 2001). This toxicity may be due mainly to the azo functional group itself rather than to the products of reductive cleavage (Razo-Flores et al. 1997). Therefore, the effluent is also resistant to biodegradation. The toxic effects of the azo dyes may result from the direct action of the agent itself or of the aryl amine derivatives generated during reductive biotransformation of the azo bond (Rajaguru et al. 1999). The azo dyes entering the body by ingestion can be metabolized to aromatic amines by the azoreductases of intestinal microorganisms. If the dyes are nitro dyes, they can be metabolized by the nitroreductases produced by the same microorganisms (Umbuzeiro et al. 2005). Mammalian liver enzymes and other enzymes may also catalyze the reductive cleavage of the azo bond and the nitroreduction of the nitro group. In both cases, if N-hydroxylamines are formed, these compounds are capable of causing DNA damage (Arlt et al. 2002; Umbuzeiro et al. 2005).

Unfortunately, heavy metals have often been used in dye fixatives and also in dyes (Mirghani et al. 2008). Typically, transition metals such as chrome, copper, nickel, and cobalt are used. These metals can form multiple bonds with organic dyestuffs and/or fibers (Walters 2005). Metals can be present in dyes for two reasons: first, metals are used as catalysts during the manufacture of some dyes and can be present as impurities; second, in some dyes the metal is chelated with the dye molecule, forming an integral structural element.

Toxic chemicals sometimes found in the dyeing process include:

- Dioxin—a carcinogen and possible hormone disrupter.
- Toxic heavy metals such as chrome, copper, and zinc—known carcinogens.
- Formaldehyde—a suspected carcinogen.
- Azo dyes group—which give off carcinogenic amines.

4.4 Characteristics and Composition of Textile Wastewater

In addition to the problem caused by the loss of dye during the dyeing process, the textile industry is generating large volumes of effluent. These effluents are complex mixtures of many pollutants, ranging from original colors lost during the dyeing process to associated pesticides and heavy metals (McMullan et al. 2001), and if these pollutants will not be properly treated, they can cause serious contamination of the water sources.

Textile industries utilize a huge amount of water. The amount of water used varies widely, depending on the specific processes operated at the mill, the equipment used, and the prevailing philosophy of water use (Verma et al. 2012). The daily water consumption of an average-sized textile mill having a production of about

8,000 kg of fabric per day is about 1.6 million liters. Sixteen percent of this is consumed in dyeing and 8 % in printing (Rita 2012). Textile industries typically generate 200–350 m^3 of wastewater per ton of finished product (Ranganathan et al. 2007; Gozálvez-Zafrilla et al. 2008) resulting in an average pollution of 100 kg chemical oxygen demand (COD) per ton of fabric (Jekel 1997). The dye house releases two types of wastewater, namely, dye bath water and wash water/rinse water. The dye bath water mainly consists of complex dyestuff and various intermediate complexes. It was noticed that in a typical factory the effluent from the dye bath had COD 5000–6000, total dissolved solids (TDS) 52,000, Suspended Solids 2,000 mg L^{-1}, and pH 9. After dyeing, the fabrics are washed by rinsing in water to remove the excess dye present. The wastewater generated due to this operation is commonly called "wash water" having COD 400–860, TS 4,000, TDS 3,200 mg L^{-1} and pH 8. Effluents contain a high organic load and biochemical oxygen demand, low dissolved oxygen concentrations, strong color, and low biodegradability.

During dyeing processes, the entire dye is not fixed to the fiber and a certain amount of the dye remains in dye bath, which is released with effluents. During textile processing, inefficiencies in dyeing result in large amounts of the dyestuff being directly lost to the wastewater, which ultimately finds its way into the environment. The amount of dye lost is dependent upon the class of dye application used, varying from only 2 % loss when using basic dyes to a 50 % loss when certain reactive dyes are used (O'Neill et al. 1999). Very low concentrations of dyes in effluent are highly visible and their presence is undesirable (Nigam et al. 2000). A huge amount of effluent from textile mills is being discharged on land or into watercourses. This effluent is characterized by high biological oxygen demand (BOD), COD, sodium and other dissolved solids as well as micronutrients and heavy metals.

Water is also needed for cleaning the printing machines to remove loose color paste from printing blankets, printing screens, and dyeing vessels (Wasif and Kone 1996; Vijaraghavan 1999). The other feature of this industry, which is a backbone of the fashion garment industry, is the large variation in the demand for type, pattern, and color combination of fabric resulting in significant fluctuation in waste generation volume and load.

4.5 Environmental and Health-Related Issues of Textile Wastewater

The environmental issues associated with residual dye content or residual color in treated textile effluents are always a concern for each textile operator that directly discharges, both sewage treatment works and commercial textile operations, in terms of respecting the color and residual dye requirements placed on treated effluent discharge (Zaharia et al. 2011).

Water pollution caused by industrial effluent discharges has become a worrisome phenomenon due to its impact on environmental health and safety. Textile industries contribute immensely to surface water deterioration and are categorized among the most polluting of all industrial sectors (Odjegba and Bamgbose 2012). Effluents from textile industries are complex mixtures of chemicals varying in quantity and quality.

These industries can generate both inorganic and organic waste mixed with wastewaters from the production processes, which leads to change in both biological and chemical parameters (Fig. 4.2) of the receiving water bodies (Gomez et al. 2008).

4.5.1 Environmental Issues

One of the most critical problems of developing countries is improper management of vast amount of wastes generated by various anthropogenic activities. More challenging is the unsafe disposal of these wastes into the ambient environment (Kanu et al. 2011). The key environmental issues associated with textile industry are water use, treatment, and disposal of aqueous effluent (Odjegba and Bamgbose 2012). Water scarcity is the most important sustainability issue facing the textile industry. The environmental risk is a function of environmental exposure (concentration and duration) and polluting potential (hazard characteristics or toxicity). Hence, reducing the emissions into the various environmental pathways can reduce the environmental risk (Shaikh 2009).

Textile wastewaters generated from different stages of textile processing contain huge amounts of pollutants that are very harmful to the environment if released without proper treatment (Verma et al. 2012). The extent of environmental pollution due to dye bath water is very high (Selvakumar et al. 2010). Environmental pollution caused by the release of a wide range of azo dyes through industrial wastewater is a serious problem in the present day (Mahmood et al. 2011). There are large numbers of mechanical and chemical processes involved in the textile industry and each process has a different impact on the environment. The presence of sulfur, naphthol, vat dyes, nitrates, acetic acid, soaps, chromium compounds, heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt, and certain auxiliary chemicals all collectively makes the effluent highly toxic. The mill effluent is also often of a high temperature and pH, both of which are extremely damaging (Kant 2012). Also, the accumulation of color hinders sunlight penetration, disturbing the ecosystem of the receiving water (Georgiou et al. 2003; Merzouk et al. 2010).

In addition when this effluent is allowed to flow in the fields, it clogs the pores of the soil resulting in loss of soil productivity. The texture of soil gets hardened and penetration of roots is prevented. The wastewater that flows in the drains corrodes and incrustates the sewerage pipes. If wastewater is allowed to flow in drains and rivers, it affects the quality of drinking water in hand pumps making it unfit for human consumption. The color in watercourses is accepted as an aesthetic problem rather than an eco-toxic hazard. Therefore, the public seems to accept the blue, green, or brown color of rivers but a “nonnatural” color such as red and purple usually causes the most concern (Carmen and Daniela 2012). Wastewater also leads to leakage in drains increasing their maintenance cost (Kant 2012). Other environmental issues of equal importance are air emission, notably volatile organic compounds (VOC)s, and excessive noise or odor as well as workspace safety.

Most processes performed in textile mills produce atmospheric emissions. Textile mills usually generate nitrogen and sulfur oxides from boilers. Other significant sources of air emissions in textile operations include resin finishing and drying

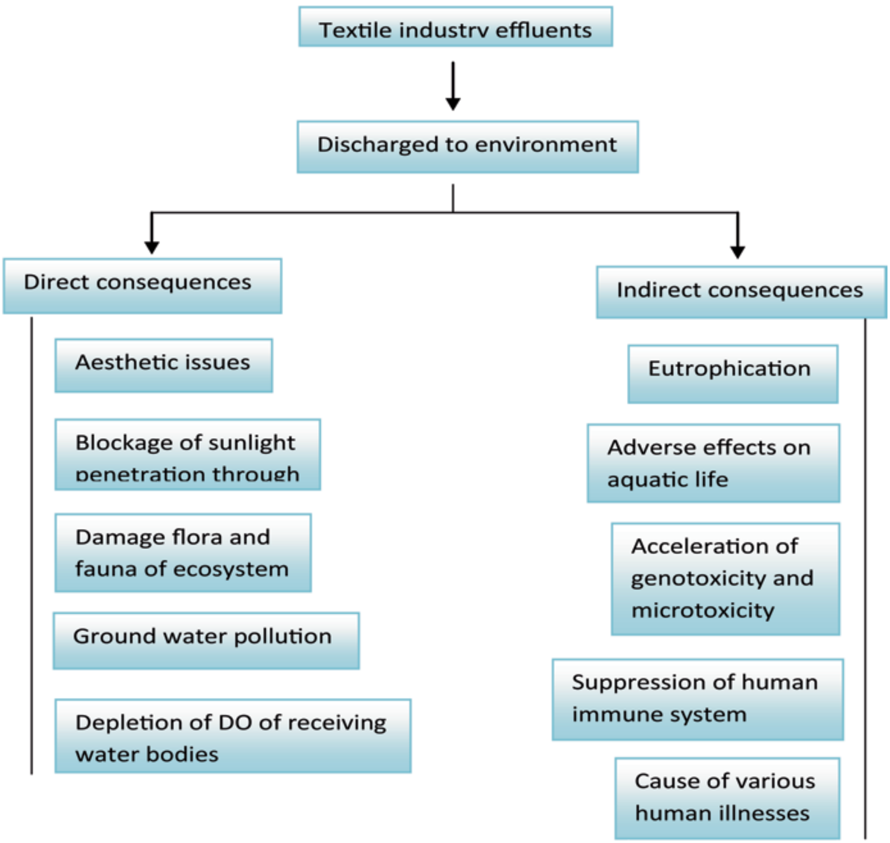


Fig. 4.2 Schematic representation of the effects of textile wastewater discharged into the environment

operations, printing, dyeing, fabric preparation, and wastewater treatment plants. Hydrocarbons are emitted from drying ovens and from mineral oils in high-temperature drying/curing. These processes can emit formaldehyde, acids, softeners, and other volatile compounds (Carmen and Daniela 2012).

4.5.2 Health Problems

The direct discharge of textile wastewater into water bodies like rivers, etc., pollutes the water and affects the flora and fauna (Shaikh 2009). Depending on exposure time and dye concentration, dyes can have acute and/or chronic effects on exposed organisms. Depletion of dissolved oxygen in water is the most serious effect of textile waste as dissolved oxygen is very essential for marine life. This also hinders the self-purification process of water.

The dyes used in textile industries are potential health hazards as they may be converted to toxic and/or carcinogenic products under anaerobic conditions

(Chung et al. 1992). Many dyes are toxic to fish and mammalian life; they inhibit growth of microorganisms and affect flora and fauna. Apart from this, several dyes and their decomposition derivatives have proved toxic to aquatic life (aquatic plants, microorganisms, fish, and mammals) (Kim et al. 2004; Ustun et al. 2007). They are also carcinogenic in nature and can cause intestinal cancer and cerebral abnormalities in the fetus (Doble and Kumar 2005). Textile dyes can cause allergies such as contact dermatitis and respiratory diseases, allergic reaction in the eyes, skin irritation, and irritation to mucous membrane and the upper respiratory tract. Reactive dyes form covalent bonds with cellulose, woolen, and polyamide (PA) fibers. It is assumed that, in the same way, reactive dyes can bind with $–NH_2$ and –SH groups of proteins in living organisms. Additionally, fairly intensive studies have inferred that such colored allergens may undergo chemical and biological assimilations, cause eutrophication, consume dissolved oxygen, prevent re-oxygenation in receiving streams, and have a tendency to sequester metal ions accelerating genotoxicity and microtoxicity (Walsh et al. 1980; Foo and Hameed 2010). A high potential health risk is caused by adsorption of azo dyes and their breakdown products (toxic amines) through the gastrointestinal tract, skin, lungs and also formation of hemoglobin adducts and disturbance of blood formation. Median lethal dose (LD50) values reported for aromatic azo dyes range between 100 and 2,000 mg/kg body weight (Börnick and Schmidt 2006). Several azo dyes cause damage to DNA that can lead to the genesis of malignant tumors. Electron-donating substituents in *ortho* and *para* position can increase the carcinogenic potential of these dyes. Some of the best-known azo dyes (e.g., Direct Black 38 azo dye, a precursor of benzidine; azodisalicylate, a precursor of 4-phenylenediamine) and their breakdown derivatives that induce cancer in humans and animals are benzidine and its derivatives and also a large number of anilines (e.g., 2-nitroaniline, 4-chloroaniline, 4,4'-dimethylendianiline, 4-phenylenediamine, etc.), nitrosamines, dimethylamines, etc. (Carmen and Daniela 2012). In addition to the environmental problem, the textile industry consumes large amounts of potable water. In many countries where potable water is scarce, this large water consumption has become intolerable and wastewater recycling has been recommended in order to decrease the water requirements.

Inhaling dust produced during cotton, flax, or hemp handling causes byssinosis, which is a respiratory syndrome. Today, byssinosis is among one of the most significant health problems in the entire textile industry. The noise level resulting from the machines used in the textile industry, especially from the dry processes, may violate the limit allowed by the law and cause hearing problems. The use of dyestuffs and pigments may cause a number of adverse effects to health. Health effects may be exerted directly at the site of application (affecting the workers) and later in the life cycle (affecting the consumers) (Shaikh 2009).

Because clothing comes into prolonged contact with skin, toxic chemicals are absorbed through the skin, especially when the human body is warm and skin pores have opened to permit perspiration. Once absorbed by humans, heavy metals tend to accumulate in the liver, kidney, bones, heart, and brain. The effects on health can be significant when high levels of accumulation are reached. The effect is particularly serious in children because toxic dye and/or heavy metal accumulation may negatively affect their growth and may be their life as well (Mirghani et al. 2008).

4.6 Conclusion

Pollution problems due to textile industry effluents have increased in recent years. The textile industry and its products give rise to a wide range of environmental and toxicological impacts. Without adequate treatment, textile dyes are stable and can remain in the environment for an extended period of time (Hao et al. 2000). Amendments and regulations in some countries have stated that azo-dyestuffs, which can release carcinogenic amines, should no longer be used in dyeing consumer goods (Mirghani et al. 2008).

Public perception of water quality is greatly influenced by the color. Therefore, the removal of color from wastewater is often more important than the removal of the soluble, colorless, organic substances. Removal of the dyes from the textile wastewater is often very costly, but a stringent environmental legislation has stimulated the textile sector to develop wastewater treatment plants. Dye removal from textile effluent is always connected with the decolorization treatment applied to textile wastewater in terms of respecting the local environmental quality requirements and standards (Carmen and Daniela 2012). The new environment regulations concerning textile products have banned the discharge of colored waste in natural water bodies. Therefore, an effective and economic treatment of effluents containing a diversity of textile dyes has become a necessity for clean production technology for textile industries.

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Chapter 5
Applications of *Bacillus thuringiensis* for Prevention of Environmental Deterioration

Showkat Ahmad Lone, Abdul Malik and Jasdeep Chatrath Padaria

Abstract The indiscriminate use of chemical insecticides for the control of insect pests over the years has led to serious environmental problems such as persistence of toxicity, which can in turn lead to the acquisition of resistance in target pests. These broad-spectrum insecticides, in addition to target pests, also kill non-target predators and parasites that otherwise check the pest populations. Furthermore, these pesticides keep on accumulating throughout aquatic and terrestrial food webs, creating ecological imbalances, and impairing human health.

Growing concerns regarding insect resistance, environmental degradation, and human health problems paved the way for the development of biological, target-specific, low-persistent pesticides with no or fewer long-term hazards. One of the most successful biological pesticides over the last century is *Bacillus thuringiensis*. *Bt* is a Gram-positive, spore-forming aerobic bacterium having the characteristic ability to produce proteinaceous insecticidal crystals during sporulation. These proteins, more popularly known as Cry and Cyt proteins, are toxic to certain groups of insect pests; the latter cause major losses to crops and many act as vectors of human and animal diseases. Owing to their specific mode of action, *Bt* products are unlikely to pose any hazard to humans or other vertebrates or to the great majority of nontarget invertebrates. Besides being effective against insect pests of agricultural

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and horticultural crops, *Bt* products are also safe for use in aquatic environments for the control of mosquitoes. The growing importance of bacterio-insecticides in insect control activities has encouraged many research programs aiming to discover new bacterial strains with improved insecticidal properties.

This chapter deals with the basic biology of *Bt* and the ways in which this entomopathogenic bacterium can be used for prevention of environmental deterioration and improvement of human health.

Keywords *Bacillus thuringiensis* · Crystalline proteins · Environmental deterioration · Human health

5.1 Introduction

As the world population is growing exponentially, there is an urgent need to devise multifaceted strategies to ensure food security for the next four decades (Godfray et al. 2010). One of the ways to achieve higher yields is to reduce the loss due to insect pests, which cause 14–25% annual loss of food grains (De Villiers and Hoisington 2011). Extensive use of chemical pesticides has helped in combating the problem of loss of food grains due to pest attack. However, over the past decades, there has been an increasing trend towards the use of environment-friendly biopesticides to reduce the crop yield losses and also to control vector-borne human diseases in a sustainable manner. Among the viable alternatives of chemical insecticides, *Bacillus thuringiensis* (*Bt*) has been one of the most successful bioinsecticides used for control of various agriculturally important pests and medically important insect vectors for more than four decades (Glare and Callaghan 1998). The toxicity of *Bt* is primarily due to its ability to produce crystalline (Cry and Cyt) proteins during sporulation, which are toxic to insect pests belonging to orders Lepidoptera, Diptera and Coleoptera (Feitelson et al. 1992). It is now a well-accepted fact that Cry proteins act by specifically binding to the receptors on the plasma membrane of the mid-gut epithelial cells of the susceptible insect host (Bravo et al. 2005). This property makes *Bt* an ecologically safer alternative to chemical insecticides (Glare and Callaghan 2000). The organism has also been used successfully to suppress the population levels of medically important dipteran pests like the blackfly that transmits onchocerciasis and the mosquito, which is a vector for diseases as malaria, dengue hemorrhagic fever, West Nile fever, and lymphatic filariasis (Becker 2000). *Bt*, during vegetative growth, secretes vegetative insecticidal proteins (Vips) which are also toxic to insect pests and in many cases act synergistically with the Cry proteins. Moreover, the difference in the mode of action of the two classes of proteins makes Vips good candidates for resistance management strategies (Rang et al. 2005). *Bt* also produces additional virulence factors like phospholipase C (Palvannan and Boopathy 2005; Martin et al. 2010), proteases (Hajaij-Ellouze et al. 2006; Brar et al. 2009; Infante et al. 2010), and hemolysins (Gominet et al. 2001; Nisnevitch et al. 2010). The virulence factors are controlled by the pleiotropic regulator PlcR and it has been demonstrated that the cytotoxicity of *Bt* is PlcR dependent (Ramarao and Lereclus 2006). These factors help in killing of the insect pests and help the bacterium to compete with other microbes. Certain *Bt* strains produce non-insecticidal crystals; these crystals were reported to be cytocidal against human cancer cells (Mizuki et al. 1999). These cytotoxic proteins are different in structure and function from Cry, Cyt, and Vips; they are neither insecticidal nor hemolytic and were designated as “parasporins” (PS; Mizuki et al. 2000). So far, six types of parasporins (PS1 to PS6) have been identified and classified by the Committee of Parasporin Classification and Nomenclature (http//parasporin.fich.pref.fukuoka.jp/index.htmal). Such a number of insecticidal, cytocidal, and nematicidal properties of *Bt* make it an ideal candidate for the eco-friendly control of insect pests of crops, vectors of human diseases, and nematode parasites and also for the treatment of cancer.

5.2 Chemical Control of Agricultural Insect Pests and Vectors of Human Diseases

Many insects belonging to different orders act as major pests of agricultural crops and as vectors of human and animal diseases. There are an estimated 67,000 pest species that damage agricultural crops, of which approximately 9,000 species are insects and mites (Ross and Lembi 1985). The extent of yield loss by insect pests in major crops is variable; it ranges from 52 % in wheat, 58 % in soybean, 59 % in maize, 74 % in potato, 83 % in rice to 84 % in cotton (Oerke et al. 1994). Apart from the direct loss mentioned, insect pests also cause indirect loss due to impaired quality of the produce and their role as vectors of various plant pathogens (Kumar et al. 2006a). In addition to agricultural crops, insects especially from the order Diptera act as vectors of human diseases (Table 5.1).

5.2.1 Benefits of Using Chemical Insecticides

The most common method for the control of insect pests is the use of chemical insecticides. Dichloro-diphenyl-trichloroethane (DDT), an organochlorine contact insecticide, was the first modern insecticide introduced for the protection of crops and forests and for controlling insect vectors of human diseases. It was effectively used to combat mosquitoes spreading malaria, typhus, and other insect-borne diseases. Chemical insecticides offer the following benefits.

5.2.1.1 Increase in Productivity

Use of chemical insecticides to kill larvae causing severe damage to vegetables and food-grain crops resulted in increase in agricultural productivity. In the Indian scenario, tremendous benefits have been derived from the use of pesticides in forestry, public health and in agriculture. Food-grain production increased from a mere

Table 5.1 Insect-borne diseases of humans with their zone of prevalence

Disease	Vector	Endemic zone
Malaria	Mosquitoes	Global tropical and subtropical areas
Yellow fever	Mosquitoes	Tropical areas of Africa and Central and South America
Dengue fever	Mosquitoes	Tropical Africa, South East Asia, South America, and the Pacific
Japanese B encephalitis	Mosquitoes	The Far East and South East Asia
West Nile virus	Mosquitoes	Africa, West Asia, the Middle East, and the USA
Filariasis	Mosquitoes, blackflies	Global tropical and subtropical areas
Tick-borne encephalitis	Ticks	Forested areas of central and eastern Europe, Scandinavia, and former USSR
Lyme disease	Ticks	Europe (inc. UK), USA, Australia, China and Japan
Leishmaniasis	Sandflies	Global tropical and subtropical areas including the Mediterranean
Sleeping sickness	Tsetse flies	East, West, and central southern Africa
Chagas disease	Assassin bugs	Tropical South and Central America
Typhus fever	Ticks and lice	Worldwide
Plague	Fleas	Worldwide

50 million t in 1948–1949 to 198 million t by the end of 1996–1997 on an estimated 169 million ha of permanently cropped land. This fourfold increase in production was possible due to the use of high-yield varieties of seeds, advanced irrigation technologies, and agricultural chemicals (Employment Information: Indian Labour Statistics 1994). Similarly, outputs and productivity have increased dramatically in most countries; for example, wheat yields in the UK and corn yields in the USA have increased manyfold due to the use of fertilizers, better varieties of seeds and use of machinery. Pesticides have been an integral part of this progress by reducing loss due to insect pests that can drastically reduce the amount of harvestable produce. Warren (1998) also drew attention to the spectacular increases in crop yields in the USA in the twentieth century. Webster et al. (1999) stated that "considerable economic losses" would take place without pesticide use and quantified the significant increases in yield and economic margin that result from pesticide use.

5.2.1.2 Vector Disease Control

Insect pests from the order Diptera are vectors of pathogens causing various human diseases like malaria, dengue, filaria, etc. (Table 5.1). These vector-borne diseases are best tackled by killing the vector insects, and chemical insecticides are sometimes the only practical way to control the insects that spread these deadly diseases. Among the various dipteran vectors, mosquitoes are the most important as they are vectors of many human diseases like malaria, dengue fever, filariasis, Japanese B encephalitis, West Nile virus, and yellow fever. Mosquitoes of the genera *Aedes*, *Anopheles, Culex, Psorophora*, and *Stegomyia* cause much human misery and have high societal costs associated with them. The conventional control of mosquitoes usually consisted of use of DDT, a broad-spectrum pesticide, residues of which persist throughout the food chain decades after its application. DDT, an organochlorine pesticide, has been banned in the USA since 1973, due to its high persistence, but it is still legally applied in many regions of the world where malaria is a menace. The dramatic results obtained by the use of DDT in terms of control of vectors led to the indiscriminate use of this insecticide and the introduction of other chemical insecticides.

5.3 Problems Associated with use of Chemical Insecticides

Chemical insecticides, though swift in action, lead to various environmental and health concerns, viz., contamination of water and food sources, land degradation, gene erosion, poisoning of nontarget beneficial insects, poisoning of other living organisms like fish and birds, and accumulation in various living organisms including humans through the food chain. The hazards associated with the use of pesticides can be summarized as follows.

5.3.1 Direct and Indirect Impact on Humans

The increased crop yield and amelioration of vector-borne diseases due to the use of chemical pesticides unfortunately also bring along serious health issues to humans and the environment. Pesticides affect almost all segments of the population, either directly or indirectly, including production workers, formulators, sprayers, mixers, loaders, and occupational farm workers. Accidental or intentional poisoning are the direct effects, while indirect effects are usually by environmental contamination through consumption of pesticide residues in food and drinking water. On long-term exposure, certain pesticides, termed endocrine disruptors, are known to cause immunosuppression, hormone disruption, diminished intelligence, reproductive abnormalities, and cancer (Brouwer et al. 1999; Crisp et al. 1998; Hurley et al. 1998). Although developed countries already have clear-cut guidelines in place to register pesticides and control their trade and use, such guidelines are not being applied in many of the developing countries. Regulations and legal frameworks on the production, trade, use, and storage of pesticides are already available from international bodies and conventions; these must be implemented at the global level.

5.3.2 Environmental Deterioration

Pesticides have the capacity to contaminate the soil, water bodies, and vegetation. In addition to killing insects or weeds, pesticides can be toxic to a host of other organisms including birds, fish, beneficial insects, and nontarget plants. Insecticides are generally the most acutely toxic class of pesticides, but herbicides can also pose risks to nontarget organisms. Excessive use of pesticides leads to surface and groundwater contamination through runoff from the treated plants and soil, reduction in soil fertility by causing decline in the number of beneficial microorganisms, and contamination of air, soil, and nontarget vegetation through aerosols. Apart from the above-mentioned ill effects of pesticides, their accumulation in the environment is the greatest threat to the biodiversity worldwide. Moreover, long-term persistence of toxicity in the environment steadily will lead to the development of resistance in the exposed insect pests.

5.4 Prevention of Environmental Deterioration: Role of *B. thuringiensis*

The ability of *Bt* to specifically control insect pests in the orders Coleoptera (beetles and weevils; López-Pazos et al. 2010; Sharma et al. 2010), Diptera (flies and mosquitoes; Pérez et al. 2007; Roh et al. 2010), Hymenoptera (bees and wasps; Garcia-Robles et al. 2001; Sharma et al. 2008), and Lepidoptera (butterflies and moths; Baig et al. 2010; Darsi et al. 2010) as well as noninsect species, such as nematodes (Cappello et al. 2006; Hu et al. 2010) and its cytocidal activity against human cancer cells (Mizuki et al. 1999) makes *Bt* a major biological control agent widely preferred to chemical insecticides and a source of anticancer proteins. The safety assessment studies of *Bt* toxins as sprays or transgenic crops to non-target organisms has proven *Bt* to be environment friendly without significant adverse effects (Kapur et al. 2010; Walter et al. 2010; Chen et al. 2011; Randhawa et al. 2011); however, a recent laboratory observation indicated that a commercial *Bt aizawai* strain led to the reduction in reproduction of bumblebee (*Bombus terrestris*) workers when applied at a concentration of 0.1 % through sugar water and pollen (Mommaerts et al. 2010). The reasons for increased popularity of *Bt* over chemical insecticides is due to the nonselective lethal effects of chemicals (Moser and Obrycki 2009; Kristoff et al. 2010; Shah and Iqbal 2010; Eriksson and Wiktelius 2011; Stevens et al. 2011) and the rapid development of resistance by insect pests to synthetic insecticides (Ahmad et al. 2008).

5.4.1 Brief History

The era of the insect pathogenic bacterium *Bt* started in the year 1901, when a Japanese scientist Shigetane Ishiwata isolated a bacterium during his study on bacterial disease of silkworms. This bacterium was responsible for the loss of large numbers of silkworms in Japan and the surrounding region. He named this bacterium *Bacillus sotto* causing "sotto disease" (sudden collapse disease; Aoki and Chegãsaki 1915). A decade later, in 1911, a German scientist Ernst Berliner isolated a similar bacterium from dead Mediterranean flour moths in a flourmill in "Thuringia" and published a description of the bacterium and its properties, naming it *Bt*. Berliner, during his study, observed inclusion bodies or "Restkoerper" alongside the endospore. The same inclusion bodies were observed by Mattes in 1972, but it took 25 more years to prove that these highly refractile bodies were responsible for the insecticidal activity of *B. thuringiensis* (Angus 1953). These inclusion bodies are now more popularly known as "parasporal crystals," a phrase coined by Christopher Hannay in 1953. Thomas Angus together with Philip Fitz-James and Hannay in 1955 discovered that the toxic parasporal crystals are composed of protein (Hannay and Fitz-James 1955). The first commercial *Bt*-based insecticide was produced in France in 1938 under trade name "sporine;" it was used primarily to control flour moths. The first *Bt*-based bioinsecticide was commercially manufactured in 1958 in USA and by 1961 the US Environmental Protection Agency started registering *Bt*-based bioinsecticides. *B. thuringiensis* var *israeliensis* was isolated in 1976 in Israel, and it was shown to be effective against dipteran larvae (blackflies and mosquitoes; Goldberg and Margalit 1977). Most *Bt* applications have been used as topical applications but *B. thuringiensis* var *israeliensis* has been applied to stagnant pools to prevent the spread of malaria (Margalith and Ben-Dov 2000; Fillinger et al. 2003). The genes coding for the crystalline proteins were first revealed in 1982 by Gonzalez et al. (1984). They also used a plasmid curing technique to prove that these genes were localized on plasmids that are transmissible. Schnepf and Whiteley were the first to clone and characterize crystalline protein gene coding for protein toxic to larvae of the tobacco hornworm from plasmid DNA of *Bt* subsp. *kurstaki* HD-1 (Schnepf and Whiteley 1981). This was followed by successive cloning of many other *cry* and *cyt* genes. The process of development of insect-resistant transgenic *Bt* crops started in 1996 and is expanding at a rapid pace around the world to date and thus proving to be quite efficient in reducing the use of chemical insecticides. In fact, more than 50 % of the cotton and 40 % of the corn planted in the USA are genetically engineered to produce *Bt* insecticidal toxins (Qaim and Zilberman 2003; Kleter 2007). This percentage is likely to increase in the years to come both in the developed and developing countries due to the enormous increase in global food demand.

5.4.2 Identification and Classification

Bt is an aerobic, soil-dwelling, motile, spore-forming, rod-shaped bacterium which gives positive reaction to Gram's stain. It has been isolated from various habitats including soil, insects, stored product dust, and deciduous and coniferous leaves (Bernhard et al. 1997; Chaufaux et al.1997; Martin and Travers 1989). Vegetative cells of *Bt* are large stout rods, straight or slightly curved, with rounded ends, usually found in pairs or short chains. It is grouped under *B. cereus* (BC) group of bacilli; it differs from the other group members (*B. cereus* (*Bc*), *B. anthracis* (*Ba*), *B. mycoides* (*Bm*), *B. pseudomycoides* (*Bpm*), and *B. weihenstephanensi* (*Bw*)) in its characteristic ability to synthesize proteinaceous insecticidal crystals during sporulation (Read et al. 2003; Rasko et al. 2005). The parasporal inclusions are formed by different insecticidal crystal proteins (ICPs). The crystals are of different shapes (bipyramidal, cuboidal, flat rhomboid, spherical, or composite with two crystal types), depending on their ICP composition. Partial correlation between crystal shape, ICP composition, and efficacy against target insects has been established. *Bt* has been classified primarily using serotyping on the basis of H- (flagellar) antigenic determinants (de Barjac 1981; de Barjac and Frachon 1990). To date, at least 69 different H-serotypes and 82 serological varieties (serovars) have been characterized (Lecadet et al 1999). H-serotyping, however, has limitations as it is not capable of distinguishing strains from same H-serotype or from the same serovar (Soufiane and Cote 2009). Due to the high economic and environmental value of *Bt,* several screening programs are being conducted worldwide to isolate novel *Bt* strains with unique insecticidal properties. As a result of extensive screening, numerous *Bt* strains with activity against lepidopteran, dipteran, coleopteran, hymenopteran, homopteran, and orthopteran insects as well as against nematodes, mites, and protozoa have been isolated from different regions. In order to manage the information generated by various screening programs regarding ecology, distribution, gene content, and host range of *Bt*, more robust tools for classification and grouping of *Bt* isolates/strains must be in place.

Sequencing of 16S and 23S ribosomal DNA (rDNA), indicated that species belonging to the BC group have a higher degree of sequence similarity (Ash and Collins 1992). Other molecular techniques such as multi-locus enzyme electrophoresis (Helgason et al. 1998), amplified fragment length polymorphism (AFLP) analysis (Ticknor et al. 2001), and multi-locus sequence typing (Helgason et al. 2004) have been helpful in resolving certain issues related to BC group classification. The higher degree of physiological and sequence similarity between *Bc* and *Bt* may be partly due to the higher frequency of genetic material exchange in their natural environments. It has been suggested that *Ba*, *Bc*, and *Bt* should be classified as one species (Helgason et al. 1998) or that *Ba* be considered in the lineage of *Bc* (Helgason et al. 2000). Pulsed-field gel electrophoresis (PFGE) and dendrographic studies showed that *Ba* isolates fall into the same cluster but are distinct from *Bc* and *Bt* (Zhong et al. 2007). Use of *gyr*B (a housekeeping gene encoding the β-subunit of DNA gyrase, topoisomerase type I) has proven very useful in distinguishing members of the BC group (Bavykin et al. 2004; Ko et al. 2004; La Duc et al. 2004; Park et al. 2007).

5.4.3 Bt Proteins and Their Diversity

The insecticidal properties of *Bt* are primarily due to the presence of crystalline toxin coding genes; these genes are located either on their plasmids or integrated in the bacterial chromosome. The expression of these gene products during sporulation leads to the formation of protein crystals; these crystals, once ingested by susceptible larva, kill them due to starvation. Different parasporal crystals are made either of single (Cry1Ac in the case of *Bt* subsp. *kurstaki* HD-73) or multiple (Cry1Aa, Cry1Ab, Cry1Ac, Cry2Aa, and Cry2Ab in the case of *Bt* subsp. *kurstaki* HD-1)

Cry proteins. The toxins were initially classified into four major groups primarily based on the host insects they attack (Hofte and Whiteley 1989). Group I toxins are toxic to lepidopterans, group II are toxic to lepidopterans and dipterans, group III are toxic to coleopterans, and group IV are toxic to dipterans. Two additional groups, group V and group VI, were added for nematode-active toxins (Feitelson et al. 1992). However, as the number of crystalline toxins increased due to various screening programs worldwide it became difficult to accommodate new toxins into the existing groups. Another nomenclature format based on amino acid sequence homology was proposed. In this nomenclature proposed by Crickmore et al. (1998), the *cry* genes are classified into 67 groups and subgroups and the Cry toxins are separated into six major classes according to their insect host specificities and include: Group 1, lepidopteran (Cry1, Cry9, and Cry15); group 2, lepidopteran and dipteran (Cry2); group 3, coleopteran (Cry3, Cry7, and Cry8); group 4, dipteran (Cry4, Cry10, Cry11, Cry16, Cry17, Cry19, and Cry20); group 5, lepidopteran and coleopteran (Cry1I); and group 6, nematodes (Cry6). A different group of crystalline protein genes has been identified as having cytolytic activity and is therefore termed Cyt toxins. These toxins are in the mass range of 25–28 kDa and are not related to Cry proteins as revealed by amino acid sequence homology analysis. The Cyt toxin proteins have been further grouped into three groups as Cyt1, Cyt2, and Cyt3 based on degree of amino acid homology. Certain strains of *Bt* have been found to harbor relatively newer class of proteins which are expressed during the vegetative stage of growth contrary to most Cry and Cyt proteins which are expressed during the sporulation phase. These insecticidal proteins expressed during the vegetative stage are known as vegetative insecticidal proteins (Vips). These proteins have been classified as Vip1 to Vip3 based on amino acid sequence homology. Compared to the previous classification method of Hofte and Whiteley, in the amino acid sequence homology method, the Roman numerals have been exchanged for Arabic numerals in the primary rank (e.g., Cry1Aa) to better accommodate the large number of expected new proteins but the "Cyt" nomenclature has been retained to designate crystal proteins showing cytolytic activity under in vitro conditions. The amino acid sequences of toxins were used to construct phylogenetic trees (Figs. 5.1a, b, and c). Vertical lines drawn through the trees define various nomenclature ranks and the name given to a particular toxin depends upon the location of the node where the toxin enters the tree relative to these vertical boundaries. A new toxin that joins the tree to the left of the leftmost boundary will be assigned a new primary rank (an Arabic number). A toxin that enters the tree between the left and central boundaries will be assigned a new secondary rank (an uppercase letter). It will have the same primary rank as the other toxins within that cluster. A toxin that enters the tree between the central and right boundaries will be assigned a new tertiary rank (a lowercase letter). Finally, a toxin that joins the tree to the right of the rightmost boundary will be assigned a new quaternary rank (another Arabic number). Toxins with identical sequences but isolated independently will receive separate quaternary ranks. By this method, each toxin will be assigned a unique name incorporating all four ranks. A completely novel toxin would currently be assigned the name Cry70Aa1.

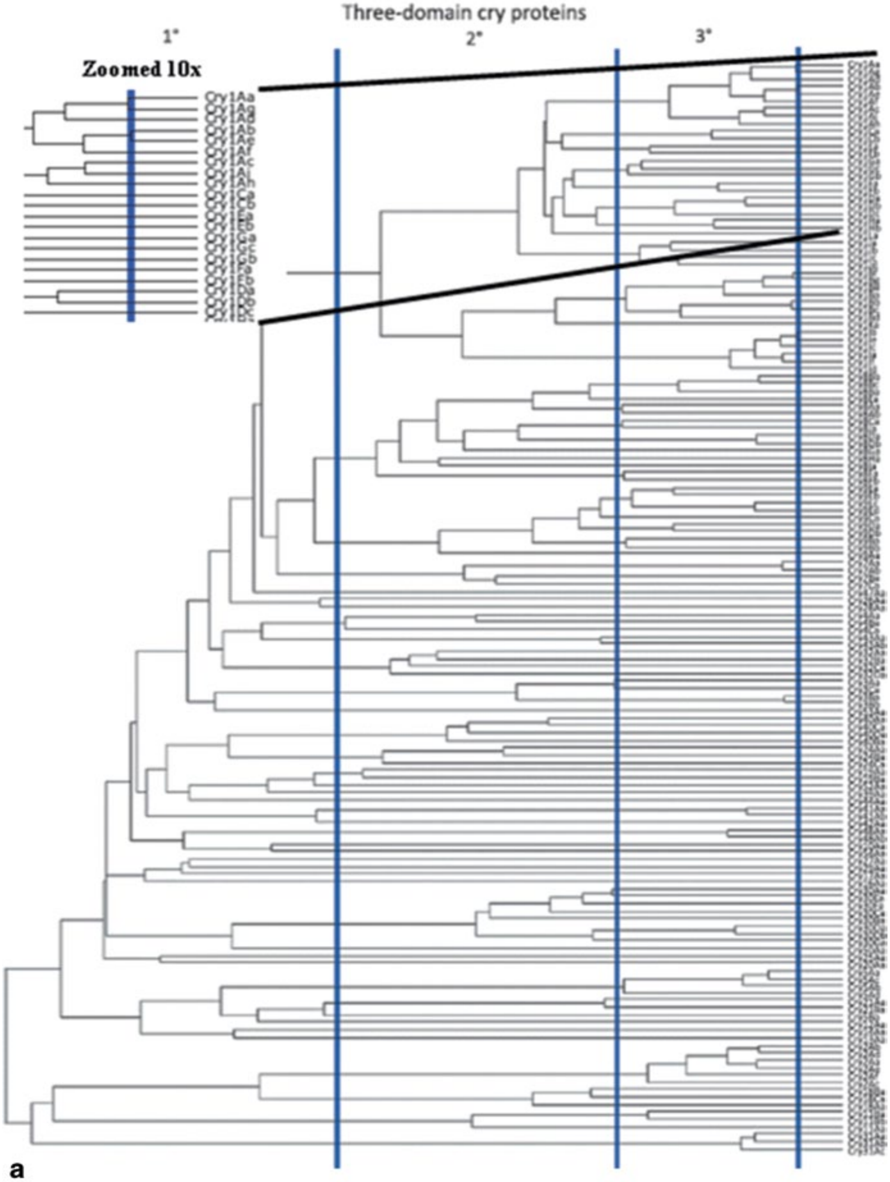

Fig. 5.1 Dendrograms showing diversity of, **a** three-domain Cry proteins, **b** related proteins (Cyt, Bin, and Mtx), **c** vegetative insecticidal proteins based on amino acid sequence identity. The *vertical bars* demarcate the four levels of nomenclature ranks. (Source: Crickmore et al., "*Bacillus thuringiensis* toxin nomenclature" (2013) http://www.lifesci.sussex.ac.uk/home/Neil_Crickmore/Bt/)

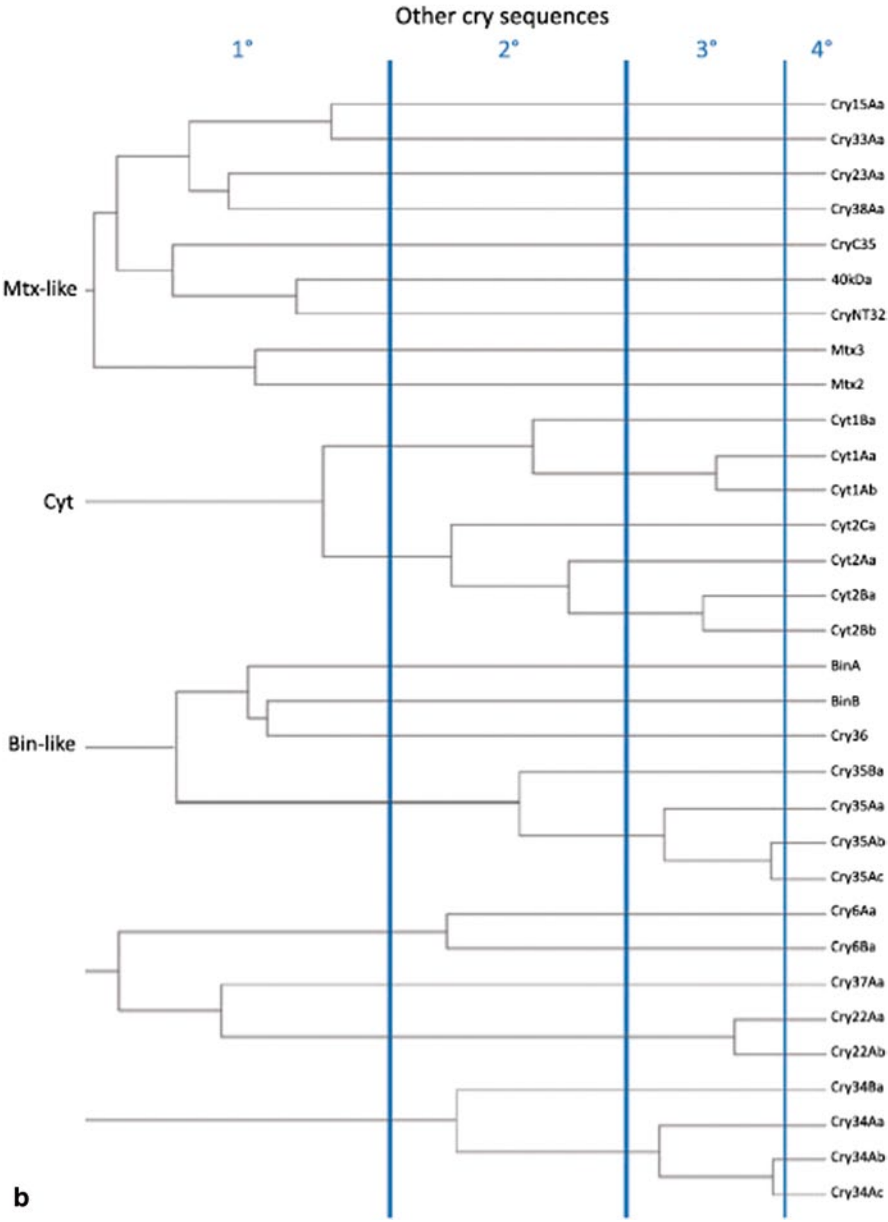

Fig. 5.1 (continued)

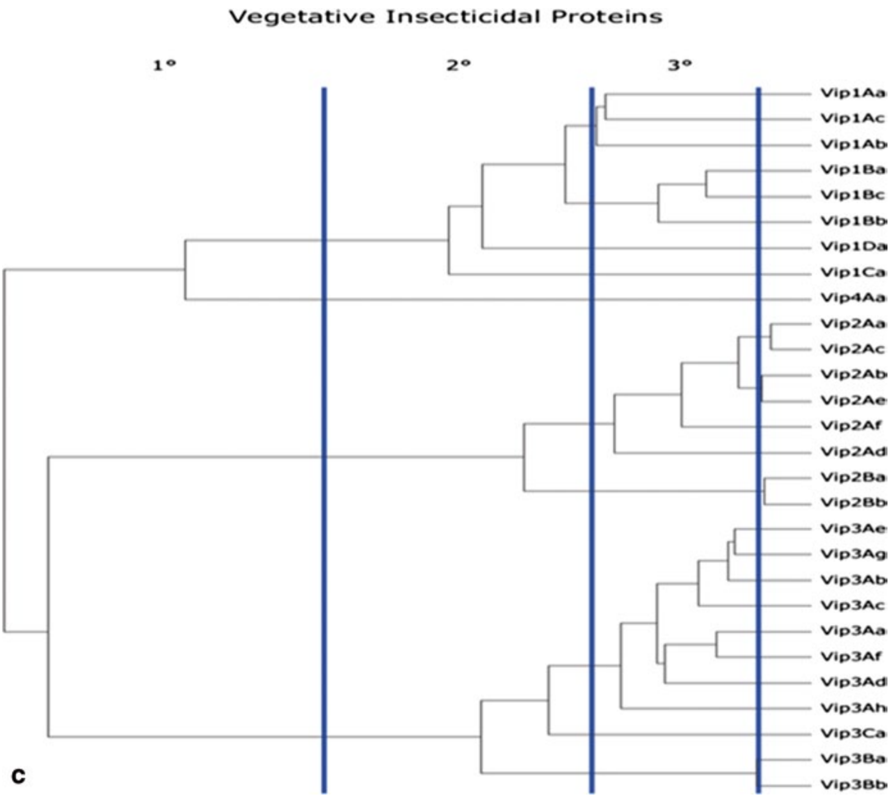

Fig. 5.1 (continued)

For the sake of convenience, however, it was proposed that the inclusion of the tertiary rank and quaternary rank 1 be optional, their use **be** dictated only by a need for clarity. This new toxin could therefore simply be referred to as Cry70A. With the addition of more toxins to the phylogenetic tree, these boundaries are likely to move or bend; currently, the boundaries from right to left represent 95, 78, and 45 % sequence identity (Crickmore et al. 1998).

5.4.4 Mode of Action of Crystalline Proteins

The *cry* genes code for proteins with a range of molecular masses from 50 to 140 kDa. The toxins are secreted as inactive protoxins, which upon ingestion by susceptible larvae are solubilized and digested proteolytically to release an active toxin. During protoxin activation, peptides are removed from both amino and carboxyl terminal ends of the protoxin. For the 130–140 kDa protoxin, the proteolytic activation of the carboxyl terminal results in an active toxin fragment of 60–70 kDa. The process of Cry toxin action is a multistage process, wherein the activated toxin initially binds to brush border epithelial cells of the mid gut. Once the activated

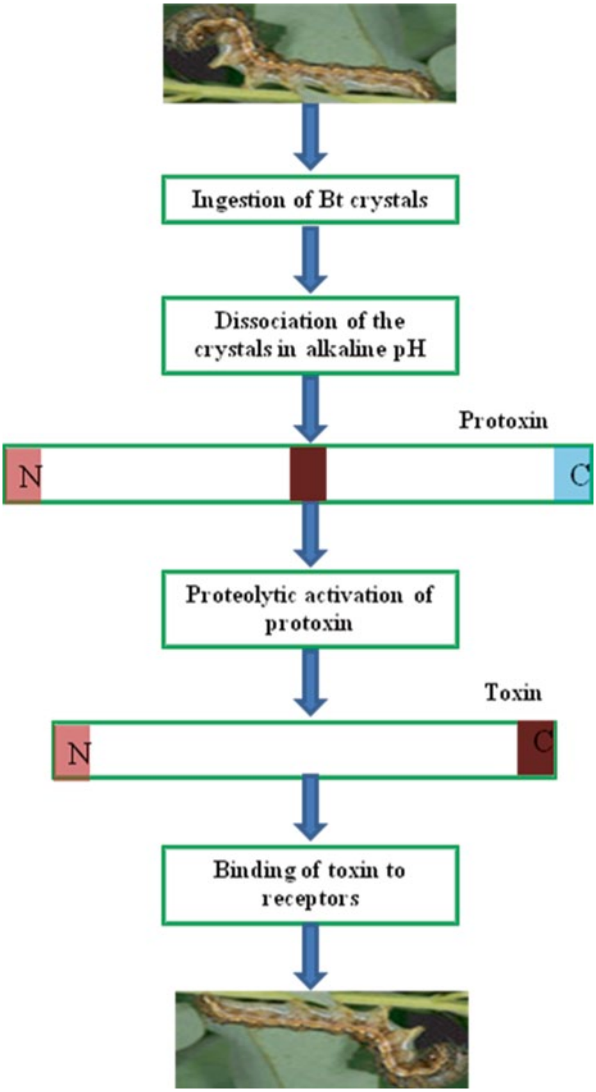

Fig. 5.2 Mechanism of action of *Bt* crystal protein. Once *Bt* parasporal crystals are ingested by an insect larva, the crystals are dissociated, followed by proteolytic activation of a protoxin and conversion to a toxin. The activated toxin binds to the receptor, initiating a cascade of signal transduction events that lead to eventual larval death. (Modified from Ibrahim et al. 2010)

toxin binds the receptor, there is some conformational change in the toxin structure allowing the toxin to enter into the membrane. This is followed by oligomerization of the toxin; the oligomerized toxin then forms a pore that leads to osmotic cell lysis and ultimately to larval death (Fig. 5.2). X-ray crystallographic studies of the tertiary structure of Cry toxins suggested that despite diversity in amino acid sequence, all Cry toxins share a similar tertiary structure as exemplified by six structures solved thus far (Cry1Aa, Cry2Aa, Cry3Aa, Cry3Bb, Cry4Aa, and Cry4Ba). The C-terminal of the toxin is involved in crystal formation but is not a part of the active toxin, as it is cleaved off in the insect gut (Fig. 5.2). The N-terminal portion is the toxin itself, and it contains three domains, domain I, domain II, and domain III.

Domain I consists of a bundle of seven α-helices connected by loops; the α-helical bundle has a central hydrophobic α-helix surrounded by six amphipathic α-helices. This domain is responsible for pore formation. Domain II consists of three anti-parallel β-sheets, each terminating with a loop and domain III is a β-sandwich. Both domains II and III confer receptor binding specificity, thus helping to define the host range (Boonserm et al. 2006). A current model suggests that domains II and III initially bind to primary receptors (cadherins) which cleave the toxin within domain I and induce oligomerization, which in turn promotes binding to high-affinity secondary receptors tethered to the membrane via C-terminal glycosylphosphatidylinositol anchors (Soberon et al. 2009). The requirement for oligomerization has recently been confirmed through the isolation of dominant-negative mutations of Cry1Ab (Rodriguez-Almazan et al. 2009). An alternative model (Zhang et al. 2006) suggests that initial binding triggers a Mg^{2+}-dependent signaling cascade that causes G-protein-dependent cyclic adenosine monophosphate (cAMP) accumulation and the activation of protein kinase A. Phylogenetic analysis has established that the diversity of the Cry family evolved by the independent evolution of the three domains and by swapping of domain III among toxins.

Cyt proteins, compared to Cry proteins, are less studied as they occur only in mosquitocodal strains of *Bt*. They are important in the toxicity of mosquitocidal strains because they act synergistically with mosquitocidal Cry proteins, such as Cry4Aa, Cry4Ba, and Cry11A, and thereby help in delaying the phenotypic expression of resistance to Cry proteins (Wu et al. 1994; Wirth et al. 1997; Wirth et al. 2005). Unlike Cry proteins, Cyt proteins do not require a protein receptor, and instead bind directly to the non-glycosylated lipid portion of the microvillar membrane. After binding to the membrane, they aggregate forming lipid faults that cause an osmotic imbalance resulting in cell lysis (Butko 2003).

5.5 *Bt* in Mosquito Control

Mosquitoes of the genera *Aedes*, *Anopheles, Culex, Psorophora*, and *Stegomyia* are vectors of many human diseases like malaria, dengue fever, filariasis, Japanese B encephalitis, West Nile virus, and yellow fever. These diseases cause human misery and take a heavy toll particularly in developing countries. Conventional mosquito control usually consisted of DDT, an organochlorine which is a highly toxic contact poison having long persistence in the environment. The World Health Organization (WHO) in the mid-1970s initiated a search for the development of new biological control agents; as the result of this initiative, a new mosquito pathogen was isolated from a stagnant pond located in the Negev Desert of Israel (Goldberg and Margalit 1977). The bacterium was later identified as *B. thuringiensis* and named *B. thuringiensis* var *israeliensis* (*Bti;* de Barjac 1978c). *Bti* is an aerobic spore-forming, Gram-positive, entomopathogenic bacterium specific to dipterans. At present, it is regarded as the most promising microbial control agent against mosquitoes and blackflies, which can be used alone, or as a component in integrated vector control programs. Like other *Bt* species, *Bti* also produces protein inclusions during

Table 5.2 List of some commercially available *Bt* -based biolarvicide formulations. (Source: Modified from Mittal 2003)

Products	Formulations
BMP-144–2X	AS
Moskiture	WP
Deltafix	G
Teknar HPD	(Liquid conc.)
VectoBac 12	AS
VectoBac	G
VectoBac	Tablets
Wockhardt	WP
Bacticide/Bactoculicide	WP

AS Aqueous suspension, *WP* Wettable powder, *G* Granules

sporulation; the parasporal crystal consists of a number of proteins ranging in size from 27 to 138 kDa. These proteins are secreted by the bacterium as protoxins; when ingested by susceptible larvae the protoxins are activated by solubilization in highly alkaline larval gut and converted to active toxins. The activated toxins primarily bind to the plasma membrane of the midgut epithelium; the binding leads to topological changes in the lipids leading to disruption of membrane integrity and cytolysis. Majority of studies revealed the safety of *Bti* to nontarget aquatic organisms, such as dragonflies, damsel flies, notonectid bugs, fish, frogs, and birds. The relative safety of *Bti* to the environment compared to chemical insecticides has resulted in its increased acceptability worldwide as various commercial products (Table 5.2) are in use in many countries. In 2005, *Bti*-based formulations were widely tested and used worldwide in mosquito control projects. They have been used in more than 25 countries.

5.6 Limitations of Using *Bt* Products

5.6.1 Threat of Development of Insect Resistance

The continuous use of *Bt* toxins for the control of insect pests is threatened by the development of resistance (Fabrick et al. 2009b; Pereira et al. 2008; Sayyed et al. 2004). There have been many cases where an insect population resistant to a particular toxin shows resistance to other toxins to which it has not previously been exposed, a term known as "cross-resistance" (Pereira et al. 2008; Sayyed et al. 2008; Gong et al. 2010; Xu et al. 2010). The insect pests become resistant to *Bt* toxins by various mechanisms like reduced binding of toxins to their specific receptors in the insect midgut, reduced solubilization of protoxin, changes in proteolytic protoxin processing, and toxin degradation or toxin precipitation by proteases (Bruce et al. 2007). The most studied mechanism of insect resistance is by "reduced binding of toxins to their specific receptors in insect midgut" which is characterized by recessive inheritance, reduced binding by at least one Cry1A toxin, and negligible cross-resistance to Cry1C (Tabashnik et al. 1998; Heckel et al. 2007). Alteration in the midgut protease profile of Cry1Ac-resistant *Helicoverpa armigera* resulted in the production of 95 and 68 kDa toxins instead of the active 65 kDa toxin produced by the midgut protease from a susceptible population (Rajagopal et al. 2009) suggesting a linkage between improper processing of *Bt* toxin and development of resistance. Apart from these mechanisms, there can be various other resistance mechanisms adopted by insect hosts to evade from the lethal effects of *Bt* toxins.

5.6.2 Narrow Spectrum of Activity

Although biopesticides containing *Bt* are environmentally safe, the problems of efficacy, reliability, spectrum of activity, speed of action, and cost of production (Regev et al. 1996; de Maagd et al. 2001; Kao et al. 2003; Shu et al. 2009) remain. *Bt* biopesticides are less persistent in the field as compared to chemical insecticides and are rapidly degraded by exposure to ultraviolet (UV) light (Pusztai et al. 1991). Consequently, the duration of pest control is often too short and its use on many crops is not cost-effective because too many applications are required (Cannon 1995). Moreover, only a small number of toxins (such as Cry1Ba) show activity against two to three insect orders (Zhong et al. 2000).

5.7 Strategies to Overcome threat of insect resistance development

5.7.1 Search for Bt Strains with Broader Host Range and Enhanced Activity

In order to overcome the threat posed by insect pests in terms of development of resistance against *Bt* products, efforts are being made to search for *Bt* strains expressing novel toxins with improved activity. At present, more than 600 insecticidal genes have been isolated and their sequences deposited at the *Bt* toxin nomenclature database (http://www. lifesci.sussex.ac.uk/home/Neil_Crickmore/Bt/). Of these, a large number have been found to be heterologously expressed and found to be either independently (Song et al. 2003; Gonzalez-Cabrera et al. 2006; Ibargutxi et al. 2008; Xue et al. 2008; Hu et al. 2010) or in combination (Sharma et al. 2010) toxic to specific insect species in one or more orders.

5.7.2 Gene stacking

Most of the *Bt* toxins are known have a narrow spectrum of action (Kao et al. 2003; Shu et al. 2009). However, when used in combination many prove to be potent and enhance the toxicity or help overcome resistance development, a strategy known as "gene stacking." The combinations used include: Cry with Cry (Jurat-Fuentes et al. 2003; Kaur 2006; Avisar et al. 2009) and the combination of Cry1Ac and Cry2Ab showed a synergistic effect to *H. armigera* (Ibargutxi et al. 2008); Cry with Cyt—expressed Cyt1Aa shows weak toxicity to mosquitoes on their own but shows synergistic activity when combined with other toxins like Cry4Ba and Cry11Aa (Fernandez-Luna et al. 2010); Cry with Chit—co-expression of chitinase, an enzyme that is known to disrupt chitin present in the peritrophic membrane in the midgut of insects, resulted in increased efficacy of Cry1Ac against *H. armigera* (Ding et al. 2008) and Cry1C against *Spodoptera littoralis* (Regev et al. 1996); and Cry with other compounds—gossypol, a toxic compound derived from the cotton plant has also been used in combination with Cry1Ac to enhance its efficacy against a resistant population of *H. zea* (Anilkumar et al. 2009).

5.8 Conclusion and Future Prospects

Chemical pesticides, though rapid in action, are very detrimental to the environment as most of them are persistent and keep on accumulating in the environment through the food chain. Pesticide residues are found in the soil and air, and in surface and groundwater across the countries, thereby affecting the quality of air we breathe and the food and water we consume. These pesticides not only affect human health but also kill many nontarget organisms ranging from beneficial soil microorganisms, to insects, plants, fish, and birds. *Bt*, an entomopathogenic soil bacterium, is more than a century-old bacterium discovered in "Thuringia" a federal state of Germany; the insecticidal properties of this bacterium are known since then. *Bt* is capable of producing crystalline protein (Cry and Cyt) toxins during sporulation that are specifically effective against insect pests in different orders. In addition to crystalline proteins, *Bt* also produces during its vegetative stage Vip; these proteins are also toxic to insect pests in different orders and act synergistically with crystalline proteins. It was only in 1938 that a commercial *Bt*-based insecticide was produced in France under the trade name "sporine." Since then, *Bt* and its products are in use for the control of various insect pests of crops and for the control of insect vectors transmitting human diseases. *Bt*-based products are comparatively safer, highly specific in action, safer to nontarget organisms including humans, and have relatively lower persistence in the environment. In addition to insecticidal proteins, many non-insecticidal *Bt* strains are known to produce a relatively new class of proteins called "parasporins," which are cytocidal proteins effective against human cancer cells. However, a few problems such as a narrow host range and threat of resistance development are also associated with the use of *Bt* technology. Searching for more efficient and novel strains harboring different insecticidal proteins can help in increasing the host range of *Bt* strains. The "gene-stacking" strategy using combinations of genes having different modes of action can certainly reduce the threat of resistance development. The insecticidal, cytocidal, and nematicidal properties of *Bt* make it an ideal candidate for the eco-friendly control of insect pests, vectors of human diseases, nematode parasites and also for the treatment of cancer. Further research needs to strengthen to develop strategies to fully utilize this gift of nature.

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Part II
Pollution and Health

Chapter 6
Insecticides: Impact on the Environment and Human Health

M. Shafiq Ansari, Maher Ahmed Moraiet and Salman Ahmad

Abstract Insecticides have saved millions of human and animal lives since the date of their synthesis and use. They have played an important role that brought revolution in the field of agriculture and human health on control of insect pests of crops and vector-borne diseases. More than 80,000 chemical substances are now commercially available in agriculture and industry. About 4.6 million t of pesticides are applied into the environment and insecticides accounted for the largest portion of total use in the world to increase the productivity of food and fibre as well as to prevent the incidence of vector-borne diseases.

Insects are the most successful group of animals existing in every segment of environment. They are polyphagous and migratory in nature, with high fecundity and short life span and diapausing (over-wintering) under adverse conditions. Food and fibre crops are damaged by more than 10,000 species of insects, with an estimated annual loss of 13.6 % globally. In human health, more than 3,100 species of mosquitoes, vector of malaria, kill more than 1–3 million people annually. Approximately 40 % of the world's population lives in areas at risk of malaria and every year about 500 million people become severely ill with malaria. Dengue, the most prevalent mosquito-borne viral disease, is estimated to cause 100 million infections each year, 250,000–500,000 of which are the cause of severe illness.

Despite their importance, insecticides also have negative impact, like toxic residues in food, water, air and soil, resurgence and resistance of insect pests, and effect on non-target organisms. More than 645 species of insects and mites have developed resistance to insecticides with 542 species of arthropods resistant to at least one compound. About 7,470 cases of resistance have been reported in insects to a particular insecticide; 16 species of arthropods accounted for 3,237 (43 %).

The effects of insecticides on human health are more risky because of their exposure either directly or indirectly; yearly, more than 26 million people suffer from pesticide poisoning with nearly 220,000 deaths. Hundreds of millions of people are

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exposed to pesticides every year, primarily through agriculture: Globally, 36 % of workers are employed in agriculture; this figure is rising to almost 50 % in South-east Asia and the Pacific and to 66 % in sub-Saharan Africa. However, with all their hazards, the production of insecticides is continuously increasing in the international trade. Global pesticide use reached record sales of US$ 40 billion in 2008.

We are continuously facing the challenges to decrease the incidence of insect pests and vectors to maintain a safe environment for future generations. Therefore, concerted global efforts shall be made to achieve this goal by safer alternatives.

Keywords Insecticides · Resistance · Pollution · Organophosphates · Pesticide residue · Resurgence

6.1 Development of Insecticides

Insect pests in agriculture and public health cause undesirable effects: negative impact on human activities and damage, spoilage, and losses of crop plants, infrastructure and the materials of everyday life. The losses may range from 10 to 40 % for all kind of food and fibre crops. Several insects are spreading human diseases such as malaria, river blindness, sleeping sickness and a range of serious fevers and illnesses. Mosquito, 'Public Enemy Number One', remains a major public health problem as vector of malaria, West Nile virus and yellow fever, filariasis, dengue fever and Japanese encephalitis. About 40 % of the world's population lives in areas at risk of malaria and 1–3 million deaths occurred annually, of which 90 % of cases are reported from sub-Saharan Africa (Snow et al. 2005). In Africa, malaria accounts for an estimated 25 % of all childhood mortality below age five, excluding neonatal mortality. Dengue, a mosquito-borne viral disease, is estimated to cause 50–100 million infections annually, 250,000–500,000 of which are the cause of severe sickness. The other serious vector-borne diseases are as follows: schistosomiasis, 200 million; lymphatic filariasis, more than 90 million; onchocerciasis, nearly 18 million; leishmaniasis, 12 million; dracunculiasis, 1 million; and African trypanosomiasis, 25,000 new cases are reported per year (WHO 2012).

Food and fibre crops are damaged by about 10,000 insect species with an estimated annual loss of 13.6 % globally, but the most damage to crops, whether in the field or stored, is caused by about 700 insect species. Thus, great efforts are required to figure out the problems caused by insects.

About 870 million people are still hungry and 8 million people died due to hunger and poverty from 2010 to 2012 (FAO 2012). The elemental sulphur was used as an insecticide by Sumerians in 4500 BC to protect their crops from insects. Body lice were controlled with mercury and arsenical compounds by the Chinese in 3200 BC. Nicotine sulphate extracted from tobacco leaves was used as an insecticide in the seventeenth century. Pyrethrum, derived from chrysanthemum and rotenone, from the roots of *Derris spp*. was used in the nineteenth century.

Synthetic organic insecticides were developed during World War II. Dichlorodiphenyltrichloroethane (DDT) and other chlorinated hydrocarbon insecticides were marketed between 1942 and 1950. However, DDT was first synthesized by Zeidler, a German chemist in 1874, but it was not used as an insecticide until 1939 when Dr. Paul Muller, who discovered the insecticidal property of DDT, was awarded the Nobel Prize in 1948. Rachel Carson, American biologist and editor, published *Silent Spring* in 1962, which says that the pesticides including DDT were toxic to human beings and wildlife and were contaminating the environment. As a result, the production and sale of DDT were banned in Sweden in 1970 and the USA in 1972 (Lear 2009), and, subsequently, banned from agricultural use worldwide under the Stockholm Convention, but its limited use in disease vector control continues to this day and remains controversial in many parts of this world. But it opened up a long line of new organic chemical insecticides that may be expected to change the agricultural systems.

In the late 1900s, the pyrethrum extracts containing pyrethrins were used as an insecticide. As a result of their thermal and photolability, analogues of pyrethroids were synthesized and were more potent and photo stable than natural pyrethrins (Housset and Dickmann 2009). By the 1980s, the neonicotinoid group of insecticides, chemically belonging to nicotine, had been introduced such as the neonicotinoid imidacloprid, which was used extensively in the world (Yamamoto 1999). Ryondine is an insecticidal component which was isolated from the roots and the stemwood of *Ryania speciosa* by Rogers et al. (1948) and its analogue was developed as rynaxypyr, causing paralysis and death of insect (Lahm et al. 2007).

The insecticide research and development process is a long journey that requires a multidisciplinary approach. Today, about 1,000 insecticides have been tested for their insecticidal properties and are available in the market.

6.2 Applications

Synthetic insecticides have played an important role in the management of insect pests in order to reduce the losses caused by them to meet the demands of increasing population. Generally, insecticides are often the only way to manage vectors. Organochlorines (OCs) had been used to control malaria, dengue fever and insect vectors in the 1950s. In 1955, World Health Organisation (WHO) released a programme to eliminate malaria worldwide, relying largely on DDT. It was primarily successful in the Caribbean, Taiwan, part of Northern Africa, the Balkans, etc. and played a minor role in North America and Europe. About seven million human lives have been saved by the control of insect-borne diseases, such as malaria, sleeping sickness, bubonic plague and typhus, with DDT and organophosphate (OP) compounds from 1945.

Today, about 1,000 pesticides are available in the market. For the global market of crop protection products, market analysts forecast revenues of more than US$ 52 billion in 2019 (Anonymous 2012b). Application of pesticides is increasing tremendously in recent years and about 5.2 billion pounds (of which 22 % used in USA) of pesticides were used with herbicides constituting 40 %, followed by insecticides (17 %) and fungicides (10 %) in 2006 and 2007 (Grube et al. 2011) where 70 % of pesticides were used in the developed countries. Globally, almost 85 % of the pesticides (estimated 2.9 million t) are used in the agriculture sector each year. Currently, there are more than 1,055 active ingredients recorded as pesticides to produce more than 20,000 agro-pesticides that are being marketed in the USA. However, 76 % of the pesticides are used as insecticide in India (Mathur 1999). The USA was the highest consumer of insecticides from 1990 to 2007, followed by China, Russia, Japan, Italy, Brazil, Turkey, India, Bangladesh and Vietnam.

6.3 Negative Impact of Insecticides on Agricultural Ecosystem and Environment

The environmental pollution caused by pesticides in Asia, Africa, Latin America, Middle East and Eastern Europe is now a serious concern (Zhang et al. 2011). The most important pollutants among the toxicants in India are OC and OP pesticides (Shafiani and Malik 2003). Even in earlier years, the residuals of DDT, lindane and dieldrin in fish, eggs and vegetables have been much beyond the safe range in India (Wu 1986). In India, the DDT content in humans was the highest ever in the world (Zhang et al. 2011).

Agricultural growth has taken place at various sectors in the twentieth century to fulfil the demand of food for the ever-increasing population. This target was achieved with increased application of agrochemicals, insecticides, fungicides, herbicides, etc., and chemical fertilizers that have resulted in loss of natural and semi-natural habitats and decreased habitat heterogeneity at agriculture ecosystem levels and the environment (Atreya et al. 2012). In fact, only 1 % of used insecticides reached their target pests and more than 99 % of them are disseminated in the environment (Zhang et al. 2011; Pimentel and Burgess 2012). Generally, 4.6 million t of pesticides are released into the environment annually (Zhang et al. 2011) and more than 500 insecticides are applied excessively, of which are OCs, while some of them containing mercury, arsenic and lead, which are highly poisonous and major contaminants of the environment (Zhang et al. 2011). Indiscriminate use of insecticides has created a fourfold problem through different trophic levels: health-related problems, environmental pollution, yield loss due to adverse effect on non-target resulting in insecticide-induced pest resurgence and financial burden to the poor farmers (Venkatesh et al. 2012). Insecticides are generally the most acutely toxic class of compounds, and they are lipophilic and degrade slowly in the environment.

6.3.1 Air

Generally, insecticides can contribute to air contamination. They are sprayed in the air as particles that could be drifted away by wind to other areas off target, potentially polluting the air (Fig. 6.1). They can volatilize or evaporate from contaminated non-

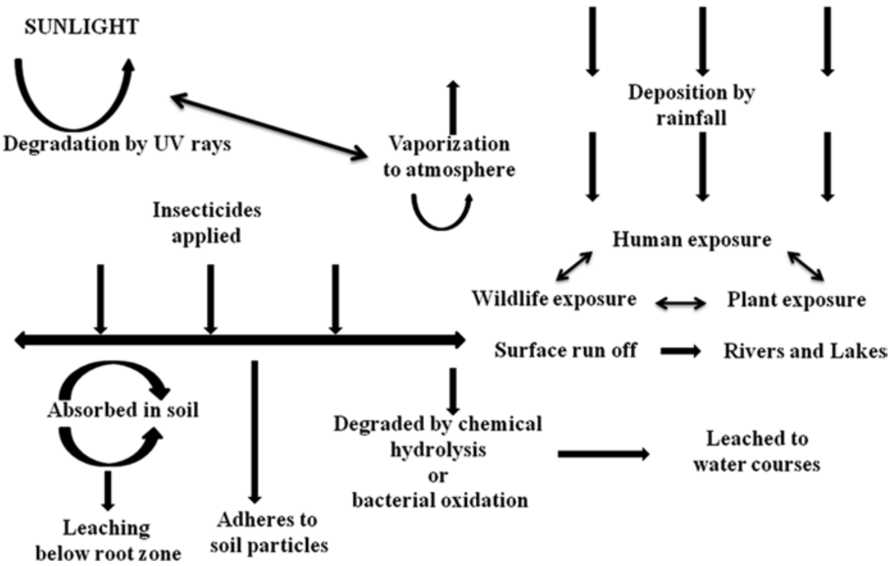

Fig. 6.1 Movement of insecticides into the environment

target. OCs were found at an altitude of 4,250 m on the snow of Nanjiabawa peak in Tibet (Shan 1997). DDT, lindane and aldrin residues were detected on the equator in India and to the high altitude of cold regions even in the Greenland ice sheet due to circulation of atmospheric and ocean currents and enrichment of biological pesticides (Zhang et al. 2011). Insecticides tend to volatilize at the time of application into atmosphere: affected by wind velocity, terrain/fetch, temperature, chemical properties, solubility, soil texture and type, molecular properties, concentration and vapour pressure (Kellogg et al. 2002). However, ground spraying of insecticide will produce less drift as compared to aerial spraying. Fumigants are also applied to field soil that can produce substances called volatile organic compounds, which react with other chemicals and form a contaminant called tropospheric ozone. Nearly 6 % of total insecticide application accounts for tropospheric ozone levels and is one of the reasons for global warming and the depletion of ozone layer.

6.3.2 Water

Insecticides are relevant stressor for various aquatic and terrestrial lives. They have been shown to cause potential negative effect on all groups of organisms in aquatic ecosystems: microorganisms (DeLorenzo et al. 2001), invertebrates (Castillo et al. 2006), plants (Frankart et al. 2003) and fish (Grande et al. 1994). The main route of movement of pesticides into water is through drift outside of areas off target when they are sprayed; they may percolate or leach through the soil, may be carried to the water as runoff or may be spilled, accidentally or through neglect (Fig. 6.1).

Insecticides may enter surface water and groundwater directly via spray drift or indirectly via surface run-off or drain flow from treated crops and soil. In UK, pesticide concentrations override those allowable for drinking water in some samples of river water and groundwater (Bingham 2007). The waterways are also polluted by insecticides: cypermethrin and chlorpyrifos mainly through spray drift rather more than drainage and surface run-off (Maltby and Hills 2008). Although pesticides had negative effects on aquatic organisms, such as reduced feeding rates, the changes were not seen in the population as a whole. Pesticide pollution is found in every stream and more than 90 % of water and fish in the USA (Gilliom et al. 2007). Pesticide residues have also been found in rain and groundwater (Kellogg et al. 2002), as well as in urban streams than in agricultural streams. Anjum and Malik (2013) reported the presence of lindane, α-endosulfan, β-endosulfan, chlorpyriphos, monocrotophos, dimethoate and malathion from the pesticide industrial wastewater samples from the Chinhat industrial area, Lucknow, India. Ansari and Malik (2009) showed the presence of certain OC (dichlorodiphenyldichloroethylene, DDE; DDT; Dieldrin; Aldrin and Endosulfan) and OP (Dimethoate, Malathion, Methlyparathion and Chlorpyrifos) pesticides in both the sampling sites of industrially polluted Ghaziabad, India, from January 2005 to June 2007. Rehana et al. (1996) indicated the presence of several pesticides such as DDT, α-BHC, aldrin, endrin and dieldrin at concentrations of 1.36, 1.38, 0.95, 0.61 and 0.41 ppb, respectively in the river Ganga at district Narora, India. The OP pesticides, such as dimethoate and methyl parathion, also appear to be present at concentrations of 0.20 and 0.41 ppb, respectively, obtained in water samples collected from the river Ganga at district Narora, India.

Insecticide concentrations in urban streams are generally exceed guidelines for protection of aquatic life. In India, 58 % of drinking water samples (ground water) obtained from several hand pumps and wells around Bhopal were found to be polluted with higher concentrations of OC insecticides that were more than the Environmental Protection Agency (EPA) standards (Kole and Bagchi 1995). Residues of DDT, hexachlorocyclohexane (HCH), dieldrin, endrin, etc. were detected in most of the water bodies in China also (Zhang et al. 2011). Several factors that affect pesticide's ability to pollute water consist of its water solubility, the distance from an application site to a body of water, weather, soil type, presence of a growing crop and the method used to apply the chemical.

6.3.3 Soil

Chemicals from agricultural field repeatedly penetrate the soil, subsoil and aquifer. This may happen either by normal management practices followed by the workers or by accident, and the resulting chemical residues in the soil create risks to the environment and ecosystem (Ali 2011). Pesticides are a common hazard around the world, as these chemicals are leaching into soils, groundwater and surface water and creating health concerns in many communities (Anjum et al. 2012). In India, alarming levels of pesticides have been reported in air, water, soil as well as in foods and biological materials (Nawab et al. 2003) and some common OC pesticides; DDT, dichlorodiphenyldichloroethane (DDD), DDE, HCH and Aldrin were found in the soil samples of Aligarh district, India. They have estimated c-HCH as 47.35 ppb whereas the concentrations of a-HCH, b-HCH, p,p′-DDE and o′,p′-DDT were 38.81, 1.79, 7.10 and 13.30 ppb, respectively, in the same soil. Soil contamination or soil pollution is caused by the presence of man-made chemicals or other alterations in the natural soil environment. It is typically caused by agricultural chemicals, industrial activity or improper disposal of waste. Most of the insecticides applied on the crops eventually end as accumulation in the soil. There are many ways in which an insecticide reaches the soil and aquatic ecosystem such as by direct application, spray drift, aerial spraying, atmospheric fallout, soil erosion and run-off from agricultural areas, discharge of industrial and domestic sewage, leaching, careless disposal of empty containers in the soil and equipment washing (Kaushik et al. 2010). The insecticides are more risky in soil as a result of their residues which may be comprised of many substances including any specified derivatives such as degradation products, metabolites and congeners that are considered to be of toxicological significance, such as OC insecticides, DDT, HCH, aldrin and dieldrin (Kalaikandhan et al. 2012), and their residues are still present. Insecticides not only contaminate the soils and water but also persist in the food and then enter the body system, blood and organs via food chain (Sheikh et al. 2011).

Pesticide leaching also occurs when pesticides are mixed with water and move through the soil, eventually contaminating groundwater as well as soil (Fig. 6.1). The amount of leaching is linked with a particular soil (like clay soil, sandy soil, alluvial soil) and characteristics of a pesticide and the degree of rainfall and irrigation. For example, both solarization and biosolarization enhanced the degradation rates of endosulfan, bifenthrin and tolclofos-methyl (Fenoll et al. 2011). The insecticidal application reduces the biodiversity of the soil. The microorganisms of soil are more spoiled by soil disturbance by application of chemicals than any other parameters. The communities of beneficial microorganisms in soil have declined due to overuse of pesticides, which has a negative impact on the available nitrogen, phosphorous and potassium (NPK) from soil (Sardar and Kole 2005). Insecticides may affect the population of invertebrates, which consist of the blooming of individual species of floodwater zooplankton and reducing populations of aquatic oligochaetes in soil. Many of the chemicals used in pesticides are continual soil pollutants, whose impact may continue for decades and adversely affect soil conservation.

The contaminated soil affects human health through direct contact with soil or via inhalation of soil pollutants which have been vaporized, while significantly greater hazards are posed by the penetration of soil contaminants into groundwater aquifers used for human consumption directly. The average consumption of insecticides in India is much lower than that of many other developed economies, but the problem of insecticide residues is very high (Abhilash and Singh 2009). Risks range from minimum to maximum, and there may be short- or long-term effects on human health and the most obvious is the possibility of xenobiotics that may enter the ground water through leaching from the surface soil and constitute a direct threat to human health (Philp 2013).

6.3.4 Non-Target Organisms

6.3.4.1 Aquatic Organisms

Insecticides are more toxic to aquatic life than herbicides and fungicides. Pesticide-polluted water is causing harmful effect on aquatic biota, such as fish and other kinds of organisms. Zooplankton, the major source of food for many young fish, could be killed by pesticides when they accumulate in bodies of water to dangerous levels (Anonymous 1999). Negative effects of chemical pollution on salamanders were likely a result of pesticide-induced reductions of food resources, as zooplankton abundance decreased by as much as 97 %, following carbaryl application (Metts et al. 2005). Some fish feed on the insects which may be killed by pesticides causing a fish migration to look for food and, thereby, exposing them to greater risks such as predators. A single application of malathion, carbaryl, chlorpyrifos, diazinon and endosulfan at 2–16 ppb as well as a mixture of insecticides with herbicides affect aquatic communities composed of zooplankton, phytoplankton, periphyton and larval amphibians such as gray tree frogs, *Hyla versicolor* and leopard frogs, *Rana pipiens* (Relyea 2009).

In North America and Europe, fish-eating water birds and marine mammals have been affected by OCs (Barron et al. 1995). Application of pesticides may be one of the reasons for reduction of amphibian population which has been happening all over the world, in the past decades. Aquatic mammals such as dolphins have the ability to accumulate increased concentrations of persistent organic pollutants as a result of their high trophic level in the food chain and relatively low activities of drug-metabolising enzymes (Tanabe et al. 1998) and are thereby vulnerable to toxic effects from contaminant exposures. Dolphins are more vulnerable to sources of pollution because of their close proximity to activities of humans in riverine and estuarine ecosystems. Decline of marine mammal populations is suspected to be a result of organochlorinated chemicals as well as degradation of their habitat (Borrell et al. 2001). DDT and polychlorinated biphenyls (PCBs) have negative effects on reproductive and immunological functions in captive or wild aquatic mammals (Colborn and Smolen 1996). Black sea dolphins accumulated different concentrations of OCs: PCBt, endrin, o,p DDT, β HCH and γ HCH and α HCH (Popa et al. 2008). Concentrations of OCs including lindane, heptachlor, aldrin, heptachlor-epoxide, endosulfan I, dieldrin and endrin were detected in the bodies of dolphins in the French Mediterranean (Wafo et al. 2012).

Globally, populations of amphibians are declining in agricultural ecosystems, which are characterized by pesticides (Brühl et al. 2013). Amphibians are more threatened than birds or mammals. Low concentrations of insecticides have indirect consequences on non-target members of the community across the multiple trophic levels, and the indirect insecticide-mediated effects are generalized across two geographically distinct amphibian assemblages (Hua and Relyea 2012). Tadpoles were killed and growth abnormalities were observed, when fields were sprayed with endosulfan. Tadpole mass was reduced to 20–35 % by the application of chlopyriphos for 4 days (Widder and Bidwell 2008).

Reduced cholinesterase (ChE) was monitored in 50 % of the population of *Hyla regilla* exposed to 190 ppb w/w of OP residue. In addition, up to 86 % of some populations had measurable endosulfan concentrations and 40 % had detectable 4,4′ dichlorodiphenyldichloroethylene, 4,4′-DDT and 2,4′-DDT residues (Sparling et al. 2001). Mortality of juvenile European common frogs, *Rana temporaria*, was 100 % after 1 h, and 40 % after 7 days at recommended level of registered insecticides under an agricultural overspray scenario (Brühl et al. 2013). Toxicity of chlorpyrifos, malathion and diazinon and their oxons can be harmful to the foothill yellow-legged frog, *R. boylii*, populations, and the corresponding oxons were 10–100 times more toxic than their parental forms (Sparling and Fellers 2007). Growth of African giant snails may be impaired by repeated application of endosulfan in cocoa plantations (Wandan et al. 2010).

6.3.4.2 Birds

Birds are killed regularly and frequently in insecticide-treated fields (Mineau 2005). It may be due to increasing application of systemic insecticides, notably neonicotinoids and fipronil in the past two decades (Mason et al. 2012), and also outbreaks of infectious diseases in bats and birds were negatively linked with toxic insecticides (Mineau et al. 2005). Pesticides kill about 72 million birds annually in the USA. In UK, more than 30 species have declined because of the agricultural practices (Donald et al. 2001). Populations of birds declined from 600 million to 300 million between 1980 and 2009 in farmlands of Britain and 116 species of birds are threatened in Europe (Anonymous 2012a). In India, the wild birds (resident and migratory birds) are exposed to great amounts of OC pesticides and their residues have been detected in whole-body homogenates (Tanabe et al. 1998).

Birds may be killed directly by some pesticides when they eat granular pesticides mistaking them to be grains of food. DDT and its metabolite, DDE, induced egg shell thinning especially in the European and North American bird populations (Vos et al. 2000). Sparrow hawks declined as a result of reduced eggshell thickness from application of OC insecticides in seed treatments during the 1950s and the 1960s (Bright et al. 2008).

Evidence of indirect effects of pesticides was thought to have resulted from reduction of plant and invertebrate species (insect food resources) on which the birds feed (Bright et al. 2008; Mineau and Whiteside 2013). Mortality of chick of grey partridge occurred because of the application of insecticides in soil (Bright et al. 2008). Indirect negative impact of insecticides was also observed on yellowhammer (Hart et al. 2006), corn bunting (Brickle et al. 2000) and songbirds (Mineau 2005; Mineau and Palmer 2013). Mortality rate of 3.0–16 songbirds/ha (17–91 million birds in total fields) occurred annually when cornfields were treated with granular carbofuran in Midwest USA. (Mineau 2005). A single corn kernel treated with a neonicotinoid can kill a songbird, and even a tiny grain of wheat or canola applied with neonicotinoid, imidacloprid can be toxic to a bird (Mineau and Palmer 2013).

Mortality in a colony of bats could be up to 95 % and about one million bats have died since 2006 in the USA. (Anonymous 2009). Decline of bat populations have also been linked to OC pesticide exposure in different parts of the world (Thies and Mc Bee 1994). High concentrations of *p,p′*–DDE have been detected in tissue of bats in Mexico and USA (Thies and Mc Bee 1994).

Biodiversity is greatly affected because of the delivery of ecosystem services (Hooper et al. 2005). Servicing by insecticides is commonly found to contaminate air, water, soil and non-target organisms as well as agriculture ecosystem. Non-target organisms include beneficial animals, birds, fish and other wildlife, beneficial insects, parasites, predators and pollinators and microorganisms and non-target plants.

6.3.4.3 Biological Control Agents

In an agricultural ecosystem, the services are considered most at risk from intensification of agricultural practices like biological pest control, crop pollination (Biesmeijer et al. 2006) and protection of soil fertility (Brussaard et al. 1997). Insecticides are directly or indirectly affecting the life history parameters or population dynamics of natural enemies. Indirect effects on natural enemies may have occurred via several mechanisms including killing of prey, consumption of contaminated floral parts and plant fluids and parts of prey either lethal or sub-lethal concentrations of the active ingredient, feeding upon the contaminated honeydew excreted by phloem-feeding insect prey and may also be associated with alterations in prey quality or induced changes in host plants which may reduce the attractiveness of plants to parasitoids (Elzen et al. 1989), thus impacting the foraging behaviour and searching efficiency of natural enemies (Elzen et al. 1989). Several studies have been conducted to determine the effect of insecticides on beneficial insect. In hot spots, a significant decline in population of birds, earthworms, natural predators, such as Coccinellids, *Chrysoperia carnea*, *Trichogramma* spp., *Apanteles* spp., spiders, black burni, Cheloanus, etc. (Palikhe 2007), has been seen. Insecticides have exhibited various degrees of toxicity to *Trichogramma* spp. (Zhao et al. 2012), predator of brown planthopper, *Nilaparvata lugens* (Preetha et al. 2010), *Cotesia plutellae*, endoparasitoid of *P. xylostella* (Haseeb et al. 2004), natural enemies of citrus scale pests, *Aphytis melinus* DeBach, *Coccophagus lycimnia* Walker, Leptomastix dactylopii Howard (Suma et al. 2009), *Aphytis melinus* Debach, *Eretmocerus eremicus* Rose and Zolnerowich, and *Encarsia formosa* (Gahan) and Mymaridae, *Gonatocerus ashmeadi* Girault that attack California red scale, *Aonidiella aurantii* (Maskell); sweetpotato whitefly, *Bemisia tabaci* (Gennadius) (both *E. eremicus* and *E. formosa*); and glassy-winged sharpshooter, *Homalodisca vitripennis* (Germar), respectively (Prabhaker et al. 2007), *Habrobracon hebetor* (Say), an ectoparasitoid of larval stage of lepidopterous pests (Rafiee-Dastjerdi et al. 2012), predatory lady bird beetle, Coccinellid spp. (Mollah et al. 2012) and the chrysopid, *Chrysoperla externa*—an important predator (Zotti et al. 2013). The insecticides, OPs, carbamates, pyrethroids, insect growth regulators (IGRs), neonicotine, phenylpyrazole and antibiotics showed negative effect against the adult parasitoid, *Anagrus nilaparvatae,* an egg parasitoid of the rice planthopper (Wang et al. 2008). OPs (chlorpyrifos, fenitrothion, phoxim, profenofos and triazophos) and carbamates (carbaryl, carbsulfan, isoprocarb, metolcarb and promecarb) exhibited the highest intrinsic toxicity to *Trichogramma japonicum*, an egg parasitoid of rice (Zhao et al. 2012).

6.3.4.4 Honeybees

The unintentional and the intentional exposure to insecticides can kill honeybees or any insect pollinators. Pesticide residuals have been detected in hive products, specifically beeswax (Johnson et al. 2010). Colony losses were especially severe from 1981 to 2005 with a drop from 4.2 to 2.4 million. Pesticide applications in the fields have eliminated nearly one fifth of honeybee's colonies and 15 % is harmed in the USA. More than 150 different agrochemicals have been detected in colony samples; most of them were insecticides and more concentrated in pollen than adult bees and occasionally honey, than in wax in the USA. (Mullin et al. 2010). Newer classes of insecticides have been detected in honey or pollen at ppb levels like phenylpyrazoles (fipronil) or neonicotinoides (imidacloprid) which significantly affected honeybee health (Desneux et al. 2007). In Europe, high losses of honeybee colonies were detected by the beekeepers when imidacloprid was applied on the crops (Rortais et al. 2005). Pesticides are the major problem for colony collapse disorder (CCD) and decline in the population of honeybees (Johnson et al. 2010). A total of 121 pesticides and metabolites with an average of 6.2 detections per sample were found in 887 heavy product samples (wax, pollen, bee and associated hive) from migratory and stationary beekeepers. Overall, pesticides in total wax and bee residues were pyrethroids and OPs, followed by fungicides, systemics, carbamates and herbicides, whereas in pollen samples, fungicides were found, followed by OPs, systemics, pyrethroids, carbamates and herbicides. Insecticides at lethal and/or sublethal doses affected adversely on immature and mature stages to reproductive stage of the queen bee (Desneux et al. 2007).

6.3.4.5 Other Animals

Contamination of animal food or water is the main pathway of poisoning of animals (Ledoux 2011). Persistent organic pollutants such as OC pesticides can be accumulated in livestock and domestic animals from contaminated food and water resources and/or from using pesticides on livestock area, treatment of cowshed, pigsties, sheepfold, etc. (Stefanelli et al. 2009) or on livestock pests (insects, ticks, mites, etc.). Poisoning in domestic animals and livestock was caused by carbamate insecticides with 50.3 %, rodenticides–anticoagulants 18.9 %, OP insecticides 5.1 %, rodenticides–non-anticoagulant 3.4 % and others 22.3 %, including molluscicides, herbicides, etc. Out of 225 animals, 123 animals were found positive for pesticide intoxication (Wang et al. 2007). OP insecticides and rodenticides were the most common causes of poisoning of livestock and accounted for one in 25 of all fatal poisonings between 1977 and 1980 (Quick 1982). The majority (60.1 %) of the intoxications in animals in the USA were caused by rodenticides and insecticides (38.6 and 21.6 %, respectively) and pesticides (66.6 %) (Brown and Patton 2012). Negative effect and detection of chlorpyrifos (Dursban) in animals, when fed to cows, were detected unchanged in the faeces, but changed in urine or milk (Anonymous 1984). Immunoglobulins and lymphocytes were decreased, while medulla and cortex were also depleted in chickens treated with imidacloprid (Kammon and Brar 2012). Terrestrial animals such as birds and small mammals may consume earthworms which are contaminated with pesticides (Yasmin and D'Souza 2010).

DDT residues were found in about 82 % of the 2,205 samples of bovine milk collected from 12 different states of India. About 37 % of the samples contained DDT residues above the tolerance limit of 0.05 mg/kg (whole milk basis). The highest level of DDT residues found was 2.2 mg/kg. The proportion of the samples with residues above the tolerance limit was lowest in Punjab (51 %), followed by Himachal Pradesh (56 %), Andhra Pradesh (57 %), Gujarat (70 %) and highest in Maharashtra (74 %). In the remaining states, this proportion was less than 10 %. Data on 186 samples of 20 commercial brands of infant formula showed the presence of residues of DDT and HCH isomers in about 70–94 % of the samples with their maximum level of 4.3 and 5.7 mg/kg (fat basis), respectively (Anonymous 1993).

The most commonly poisoned animals were dogs, particularly younger animals, as well as from exposure to insecticides and rodenticides in five European countries—Belgium, France, Greece, Italy and Spain in the last 10 years (Guitart et al. 2010). Most of the poisoning incidents were found in companion animals especially in dogs and cats because of insecticides while agrochemicals, heavy metals and toxic plants were the problems in farm animals in Belgium (Vandenbroucke 2010).

Physical endurance and working capacity of rats is reduced when exposed to chlorophos, diazinone and lindane (Georgiev et al. 1980). There are many health-related issues associated with HCH (Mehboob et al. 2013). Alpha, beta and gamma isomers of HCH act as depressants of nervous system and may cause cancer in mice (Nagata et al. 1996). Bensultap and fipronil insecticides can pass the blood–brain barrier in rats (Szegedi et al. 2005). Chlorpyrifos causes a significant ChE inhibition but does not exert overt toxicity and adversely affects the expression levels of critical genes involved in brain development during the early postnatal period in the rat (Betancourt et al. 2006). Pirimiphos-methyl (62.5 and 125 mg/kg) is detrimental to the reproductive potentials of male rats (Ngoula et al. 2007).

6.3.5 Insecticide Resistance

A significant progress has been made in controlling insect pests by means of insecticides. While insecticides have greatly improved the agricultural production and safety to human health worldwide, their utility, however, has been limited by the development of resistance in many major pests, including some that became pests only as a result of insecticide use. Continuous use of the insecticides may lead to the development of resistant populations of insect pests, and control failures were also observed in the field conditions (Avilla et al. 2010). The number of insect pests to be known as resistant to different insecticides is increasing with the time. In 1986, 260 insect species had been reported to develop resistance to various molecules of insecticides, but by 2009, 600 arthropod pests developed resistance to at least one insecticide or acaricide (Whalon et al. 2008). For example, the cotton bollworm, *Helicoverpa armigera*, has developed resistance to almost all the groups of insecticides all over the globe (Avilla et al. 2010; Yang et al. 2013). Fourteen populations of *H. armigera* from Northern China showed very strong resistance to fenvalerate (from 43- to 830-fold) when compared with the susceptible Specific Carbohydrate Diet (SCD) strain (Yang et al. 2013). High levels of pyrethroid resistance were recorded in intensive cotton- and pulse-growing regions of Central and Southern India where excessive application of insecticide is common (Armes et al. 1996). OP and pyrethroid resistance is reported in various African, Asian and Australian populations of *H. armigera*, with some reports indicating resistance factors exceeding a 100-fold for the OPs and a 1,000-fold for the pyrethroids. Srinivas et al. (2004) reported that *H. armigera* had developed high resistance to insecticides in the Gulbarga region of Karnataka, India. Highest seasonal average percentage survival of resistant strain was recorded by fenvalerate (65.0%), followed by cypermethrin (62.4%). Acetylcholinesterase (AChE) of resistant larvae was less sensitive to monocrotophos and methyl paraoxon. *H. armigera* has developed resistance to all the major insecticide classes and it has become increasingly difficult to control their population in India. Resistance to OP and carbamate insecticides has been reported in *H. armigera* and *Spodoptera litura* (Fabricius) in India (Kranthi et al. 2001). High resistance in *S. litura* against a wide variety of insecticides including OP (profenofos), carbamate, pyrethriods (deltamethrin) and some selected new chemistry insecticides (spinosad and indoxacarb) have been reported from South Asia (Ahmad et al. 2008; Saleem et al. 2008).

The insecticide resistance is primarily the result of the selection pressure exerted on sprayed populations, which increases the frequency of resistant individuals in the nature.

6.3.5.1 Knockdown Resistance (kdr)

The resistance developed in insects and other arthropods to DDT and pyrethroid insecticides results from reduced sensitivity of the nervous system caused by point mutations in the insect population's genetic make-up (Zhu et al. 2010). DDT and pyrethroids act fast on the central nervous system of the insects, leading to convulsions, paralysis and eventually death, an effect known as knockdown (Martins and Valle 2012). *kdr* occurs due to a point mutation in the voltage-gated sodium channel in the central nervous system, the target of pyrethroids and DDT action (Martins and Valle 2012).

6.3.5.2 Cross-Resistance

Cross-resistance enables the resistant species to survive exposure to related chemicals. For example, DDT-resistant houseflies are also resistant to methoxychlor. Cross-resistance was also found in *Leptinotarsa decemlineata* (Say) against neonicotinoid group of insecticides. Cross-resistance usually occurs from a common detoxification system or target site insensitivity (Metcalf 1994) or P450-monooxygenase detoxification mechanism in insects (Liu et al. 2010). The nicotinic acetylcholine receptors (nAChRs) in the insect central nervous system are the primary target for neonicotinoid insecticides, including imidacloprid.

6.3.5.3 Multiple Resistance

Multiple resistance is a far more serious type of resistance and extends to a variety of classes of insecticides with different modes of actions and dissimilar detoxification pathways. For example, knockdown resistance mechanism of houseflies showed reduced sensitivity of nerve axon to DDT as well as to completely unrelated pyrethroids. Multiple resistance is now present in at least 44 families of 10 insect orders. Multiple resistance to DDT and methoxychlor, lindane and cyclodienes, OPs and carbamates and pyrethroids is reported in *Musca domestica*; *Blattella germanica*; *Culex pipiens, Boophilus micropls; Tribolium castenium*; *Sitophilus granarius*; *Myzus persicae*; *Cacopsylla pyricola*; *Heliothis virescens*; *Plutella xylostella*; and *Spodoptera exigua* (Metcalf 1994).

6.3.5.4 Factors Responsible for Resistance

A number of factors are responsible for a susceptible pest population to evolve resistance against the toxicant. Firstly, most of the insects are capable of producing large number of offspring. The probability of random mutations is increased and it ensures the rapid build-up in numbers of resistant mutants once such mutations have occurred. Secondly, insects have been exposed to natural toxins for a long time before the onset of human civilization. For example, many plants produce phytotoxins to protect them from herbivores. As a result, co-evolution of herbivores and their host plants required development of the physiological capability to detoxify or tolerate the toxicants (Bishop and Grafius 1996). Insecticide resistance is characterized by quick evolution under strong selection of gene(s) that confers tolerance to insecticides. AChE has become insensitive, which has been associated as one of the mechanisms of resistance to organophosphorous and carbamate insecticides in *Bemisia tabaci* (Genn.) (Dittrich et al. 1990) and *H. virescens* (Brown and Bryson 1992). Similar insensitive AChE variants have now been detected in heterogeneous populations of many important insects such as *M. Domestica*, *Aphis gossypie* and several mosquito species. Overproduction of non-specific carboxylesterases as an evolutionary response to organophosphorus and carbamate selection pressure has been reported in mosquitoes, cattle ticks, aphids and cockroaches (Hemingway et al. 2004). A cytochrome P450 gene, *Cyp9m10*, is more than 200-fold over-expressed in a pyrethroid-resistant strain of *Culex quinquefasciatus* (Itokawa et al. 2011).

6.3.6 Insect Resurgence

Resurgence of insect pest occurs when the residual activity of the insecticide terminates and the pest population is able to rise more rapidly and natural enemies are absent or in low abundance. Insecticide-induced resurgence of insect pests has been reported a long time ago when chemicals were used as the principal tool for pest control. This can cause an increase in fecundity (physiological hormoligosis) or oviposition behaviour (behavioural hormoligosis) of the pest leading to a significant increase in its abundance. In 1947, the use of DDT sprays for citrus pest control was followed by dramatic resurgence of cotton cushiony scale, *Icerya purchasi* Maskell, which was under its best biological control by the introduction of predatory beetle, *Rodolia cardinalis* (Mulsant) (Metcalf 1994). Insecticide-stimulated pest reproduction is an important ecological mechanism of pest resurgence termed as insecticide hormoligosis. Insecticide hormoligosis was also known to occur in some insects and mites previously, which sometimes may result in resurgence of pests (Luckey 1968). Locust plagues may be caused by a mild stress which induces growth and reproduction inflicted by certain hormoligants (Luckey 1968). Fecundity of *P. xylostella* increased when larvae were exposed to fenvalerate at LC_{25} (Fujiwara et al. 2002). Spinosad has caused an enhanced fecundity of *Orious insidiosus* (Elzen 2001). Methyl parathion, quinalphos and deltamethrin enhance fecundity of *Sogatella furcifera* (Suri and Singh 2011), which leads to the resurgence of this pest in rice. Pest resurgence is mostly associated with indirect, secondary/minor pests for several reasons. Many factors are responsible for resurgence of the insect pests like reduced biological control, reduced competition, direct stimulation of pest to acute dose of insecticides and improved growth of crop. Studies of resurgent populations infrequently examine other mechanisms, although numerous alternative mechanisms, such as physiological enhancement of pest fecundity, reduction in herbivory, herbivore competition, changes in pest behaviour, altered host-plant nutrition or increased attractiveness, may also cause or enhance the probability of resurgence. Outbreaks of arthropod pests induced by pest control agents are end points triggered by complex interactions of environmental factors modulated vis-a-vis the external challenge are the major cause of resurgence (Cohen 2006) and might be correlated with the eradication of responsible competitors at a given ecological niche, as a sublethal level for one species might be toxic to another (Cohen 2006). The pyrethroid cypermethrin applied at low rates increased the fecundity and survival of immature stages of mite (Costa et al. 1988), suggesting that homeostatic modulations are involved.

6.4 Negative Impact on Human Health

Synthetic insecticides, introduced in the 1940s, a heterogeneous category of biologically active compounds, have become crucial, widely used weapons for pests control and infectious diseases (Bolognesi and Merlo 2011). In recent years, there has been an increasing concern that pesticides constitute a risk to the general population through residues in the food supply and through food chain (Margni et al. 2002) and cause potential effects on human health, wildlife and sensitive ecosystems (Ansari et al. 2013). Overzealous use of synthetic insecticides led to numerous problems unforeseen at the time of their introduction, like acute and chronic poisoning of handlers, farm workers and even consumers as the pesticides may enter food chain

(Fig. 6.2); destruction of water life, birds and other wildlife; interruption of natural biological control agents and pollinators; extensive contamination of groundwater, potentially threatening to human health by causing direct hazards to the users; and the development of resistance to pesticides in pest populations (Ansari et al. 2013), as well as occupational exposure to pesticides and adverse human health outcomes such as various cancers like leukaemia, lymphoma, liver, lung, brain, breast, prostate, kidney, pancreas, skin cancers, Parkinson's and other chronic diseases, and also potential adverse effects on mental health and reproduction (Bolognesi and Merlo 2011). In India, the first report of poisoning due to insecticide was reported from Kerala in 1958, where more than 100 people died after consuming wheat flour infected with parathion (Karunakaran 1958). The average daily intake of HCH and DDT by Indians was reported to be 115 and 48 mg per person, respectively, which was higher than those observed in most of the developed countries (Kannan et al. 1992). Pawar et al. (2006) have studied 200 patients with moderate organophosphorus poisoning (excluding severely ill patients) in Maharashtra, India. For human health, intake of food contaminated with insecticides results in the highest toxic exposure, about 10^3–10^5 times higher than that induced by drinking water or inhalation (Margni et al. 2002). Presence of DDT was found in milk to exceed the maximum residue limit fixed at 0.05 mg kg^{-1} in Punjab, India (Battu et al. 2005). The mean levels of total DDT and HCH in human blood were recorded as high as 743 μg L^{-1} and 627 μg L^{-1} for district Nagaon, while 417 μg L^{-1} and 348 μg L^{-1} for district Dibrugarh of North East India (Mishra et al. 2011). p,p′-DDT was the major component with the mean value of 6.125 mg/L, followed by p,p′-DDE, c-HCH, a-HCH and b-HCH, while in 2002, b-HCH and p,p′-DDE were comparable with mean values of 0.053 and 0.052 mg/L, respectively, followed by p,p′-DDT, a-HCH and p,p′-DDD in human blood during 1992 (Kaushik et al. 2012). The samples from human breast milk contained detectable residues of p,p′-DDT (urban mean 0.11 ± 0.18 mg kg^{-1}, rural mean 0.07 ± 0.03 mg kg^{-1}) and p,p′-DDE (urban mean 0.05 ± 0.04 mg kg^{-1}, rural mean 0.76 ± 1.46 mg kg^{-1}) (Burke et al. 2003). OC pesticides were detected in all pooled human milk samples typically with highest concentrations of p,p′-dichlorodiphenyldichloroethylene (p,p′-DDE) (median concentration 311 ± 174; 279 ng g^{-1} lipid), followed by β-hexachlorocyclohexane (β-HCH) (80 ± 173; 21 ng g^{-1} lipid). Other OCs consistently detected included dieldrin (16 ± 6; 17 ng g^{-1} lipid), hexachlorobenzene (HCB) (18 ± 16; 14 ng g^{-1} lipid), transnonachlor (11 ± 5; 9 ng g^{-1} lipid) and p,p′-dichlorodiphenyltrichloroethane (p,p′-DDT) (9 ± 6; 7 ng g^{-1} lipid) (Mueller et al. 2008). Rao et al. (2005) have recorded $>1{,}000$ pesticide poisoning cases occurring each year with hundreds of deaths in India. They have also reported 1,035 cases of poisoning; 653 patients were reported to have ingested organophosphorus pesticides, 213 had ingested OCs (one patient ingested OP and OC) and 170 had ingested other pesticides in 2002 in India. Insecticide residues are nearly everywhere, in soil, air, water and human adipose tissues and they are highly persistent non-degradable compounds, such as DDT, dieldin, endrin, benzene hexachloride (BHC) and heptachlor epoxide. The development of diseases in susceptible children may be more due to increased exposure through food and breast milk along with under developed detoxification pathways and long latency periods (Cohen 2006). It is estimated that 99 % of all deaths from

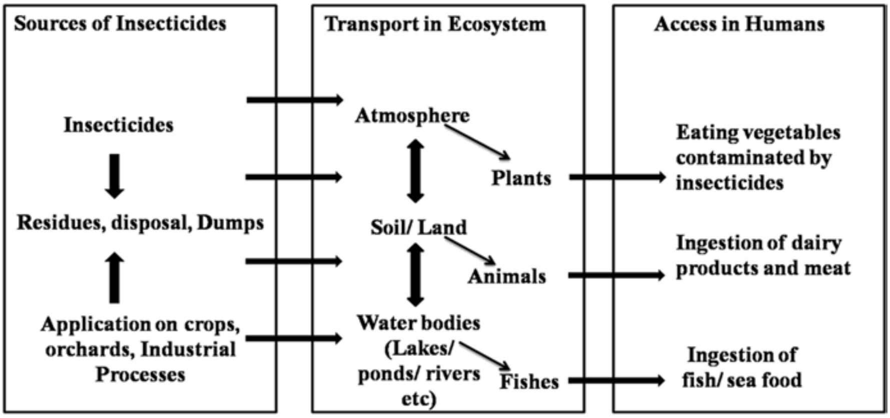

Fig. 6.2 Entry of insecticides into the human body

pesticide poisoning occur in developing countries (De Silva et al. 2006). The insecticides used in developing countries often consist of OCs (lindane and dieldrin), OPs (monocrotophos, parathion, methamidophos) and carbamates (carbofuran, thiodicarb, maneb; Wilson and Tisdell 2001).

The aerial spray of highly toxic insecticides has caused the poisoning of the people in that area contaminated by spray drift, and workers working in the orchards and vineyards have suffered a substantial number of incidents of parathion poisoning from the toxic residues from foliage and fruits (Metcalf 1994). Epidemics of poisoning by insecticides, especially through the accidental contamination of flour with parathion and endrin, have poisoned hundreds of people in India, Malaya, Arabia, Egypt, Columbia and Mexico. The Supreme Court of India, on 13 May 2011, ordered a country-wide ban on manufacture, sale and use of endosulfan citing its toxic effects on humans and environment. Endosulfan is readily absorbed by humans via the stomach, lungs and through the skin and causes acute and chronic toxicity. It has been demonstrated that much lower doses of toxicants may result in adverse health effects manifesting in functional and organic disorders in later stages of life if the exposure takes place during the early developmental phase.

6.5 Risk Assessments

The method used for evaluating the potential for health and ecological effects of an insecticide is known as risk assessment. Before allowing an insecticidal product to be sold in market, it is ensured that the insecticide will not pose any unreasonable risks to plants, wildlife, humans and the environment. Although pesticides are developed through very strict regulation processes to function with reasonable certainty and minimal impact on human health and the environment, serious concerns are raised about health risks resulting from occupational exposure and from residues in food and drinking water (Damalas and Eleftherohorinos 2011). The adverse effects of the insecticides on the water include soil and air contamination from percolating, surface run-off and drifting, as well as the detrimental effects on wild and water life, plants, and other non-target organisms, including humans depend on the toxicity of the insecticide, the measures taken during their applications, the dosage applied, the adsorption on soil colloids, the weather conditions prevailing after application and persistence of insecticide in the environment. Human population exposure to insecticides occurs mainly through eating food and drinking water polluted with insecticides, whereas significant exposure to the toxicant can also happen when residing near a workplace that makes use of pesticides or even when employees bring home-contaminated articles (Damalas and Eleftherohorinos 2011).

Apart from the difficulties in assessing risks of insecticide use on human health, the authorization for pesticide requires data of potentially negative effects of the active substances on human health. These data are usually obtained from several analyses focused on acute toxicity, sub-chronic or sub-acute toxicity, chronic toxicity, carcinogenicity, genotoxicity, teratogenicity, generation study and also irritancy trials using rat as a model mammal or in some cases dogs and rabbits. The risk assessment required acute toxicity test which considers the short-term effect of the single dose of insecticide; sub-lethal toxicity tests which assess the effects of intermediate repeated exposure of the insecticides or the long-term effect of an insecticide (Damalas and Eleftherohorinos 2011). The acute toxicity tests are involved in the calculation of lethal dose (LD_{50}), which is the insecticide dose that is required to kill half of the tested animals when entering the body by a particular route. In addition to this, the acute inhalation lethal concentration (LC_{50}), which is the insecticide concentration that is required to kill half of the exposed tested animal to an insecticide, can be calculated. Acute toxicity of an insecticide is referred to as the chemical's ability to cause injury to a person or animal from a single exposure, generally of short duration, whereas chronic toxicity of an insecticide is determined by subjecting test animals to long-term exposure to the active ingredient. The measurements of toxicity based on individuals, such as the LC_{50}, and effects on reproduction are used extensively in determining ecological risk (Stark et al. 2007). But only determination of LC_{50} and LD_{50} is not the only criteria for risk assessment of any insecticide (Stark et al. 2007; Ahmad et al. 2013). The use of demography incorporated with toxicants was proposed by Stark and Wennergren (1995) who put side by side the fitness parameters for unexposed populations with those exposed to various concentrations of an insecticide. It is the better way to understand the overall effect a toxicant might have on an exposed individual because it gives a complete portrait of life history of an insect (Stark et al. 2007; Ahmad et al. 2012; Ahmad and Ansari 2013; Ahmad et al. 2013).

6.6 Conclusion

Insecticides have been playing a significant role in the field of agriculture and human health but their debits have resulted in serious health implications to man, non-target organisms and the environment. They generally cause accidental environmental effects and are also toxic to the non-target organisms. Indiscriminate use of the insecticides has led to the development of insecticide resistance in the populations of insects and control failures are also constantly observed because of the pest resurgence. Environmental effects of insecticides are widely documented and their undesired residues are contaminating the air, soil, water bodies as well as causing deleterious effects on human health including neuromuscular dysfunctions and weakness. Recently, the residues of the insecticides are also detected in the human body at much higher levels. They get into aquatic ecosystems and affect many non-target organisms including fishes and birds due to biomagnifications through the food chain and food web. Therefore, sale and use of OC and cyclodiene insecticides should be banned so that their concentrations in the environment can be reduced below the tolerance level. Efforts should be made to increase the awareness among the farmers regarding the negative effects of insecticides on human beings and the environment. Biopesticides may be used as an alternative method to manage the insect pests, which are safer to the environment and non-target organisms.

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Chapter 7
Spread of Antibiotic Resistance in the Environment: Impact on Human Health

Melanie Broszat and Elisabeth Grohmann

Abstract Antibiotic-resistant pathogenic bacteria pose a high threat to human health, but the environmental reservoirs of resistance genes are poorly understood. The origins of antibiotic resistance in the environment are relevant to human health because of the increasing importance of zoonotic diseases as well as the requirement for predicting emerging resistant pathogens. Only little is known about the antibiotic resistomes of the great majority of environmental bacteria, although there have been calls for a greater understanding of the environmental reservoirs of antibiotic resistance. The data on antibiotic resistance before the antibiotic era and in soil show how far away we are from a complete picture about the ecology of antibiotic resistance genes (ARGs). Most of the natural antibiotic producers reside in soil, but soil is a particularly challenging habitat due to its chemical and physical heterogeneity. The prevalence and diversity of ARGs in the environment led to hypotheses about the native roles of resistance genes in natural microbial communities.

This chapter gives an overview on the occurrence of antibiotic resistance determinants in different environments, discusses the environmental sources, the functions and roles of resistance determinants in microbial ecology, and the ways by which those genes may be disseminated in response to human antibiotic use. It also describes molecular methodologies used to study antibiotic resistance dissemination in the environment and attempts to assess the risks associated with resistance spread in the environment for human health.

Keywords Antibiotic resistance · Antibiotic use · Horizontal gene transfer · Resistance monitoring · Human health

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7.1 Introduction

Antibiotics are probably the most successful family of drugs so far developed for improving human health. Besides this fundamental application, antimicrobials have also been used for preventing and treating animals and plants infections, as well as for promoting growth in animal farming (Martinez 2009; Cabello 2006; Singer et al. 2003; McManus et al. 2002; Smith et al. 2002). All these applications caused the release of large amounts of antibiotics in natural ecosystems. However, little is known on the overall effects of antibiotics on the population dynamics of the microbiosphere (Martinez 2009; Sarmah et al. 2006). Large amounts of the antibiotics administered for therapeutic reasons are only partially metabolized. They are discharged along with the excreta from humans and animals to sewage treatment plants and those used in animal husbandry are directly released without any treatment into the environment, particularly to waters or soils.

It is well accepted that antibiotics at therapeutic concentrations select for resistant microbes; however, there is only scarce information and in some cases, contradictory data are available on the effect of antibiotics at subtherapeutic concentrations or concentrations below the minimal inhibitory concentrations (MICs; Rodríguez-Rojas et al. 2013; Andersson and Hughes 2012; Hughes and Andersson 2012; Gullberg et al. 2011; Liu et al. 2011).

The debate on what was originally the major role of antibiotics in the environment is even more controversial: One well-accepted argument is that their role in nature is to inhibit microbial competitors. An alternative hypothesis states that antibiotics could be primarily signal molecules that shape the structure of microbial communities (Martinez 2009; Fajardo and Martinez 2008; Yim et al. 2007; Linares et al. 2006). Under this view, antimicrobials will have a hermetic effect, beneficial at low concentrations that are likely found in most natural ecosystems, and harmful at the high concentrations used for therapeutic reasons (Martinez 2009; Davies et al. 2006; Calabrese 2005).

For decades, the general opinion of medical doctors, clinicians, and scientists was that antibiotic resistance and the occurrence of the associated genetic determinants are a problem restricted to hospitals and health-care centers. Only recently it has been recognized that antibiotic-resistant microorganisms and the associated resistance determinants are ubiquitous and are also present in pristine environments which have never been in contact with antimicrobials (Allen et al. 2010), as evidenced clearly by the detection of antibiotic resistance determinants in soils conserved in a frozen state from the pre-antibiotic era (Knapp et al. 2011; Knapp et al. 2010).

Additionally, it has been stated that some genetic elements that serve to resist high concentrations of antimicrobials have distinct functional roles (e.g., cell homeostasis, signal trafficking, metabolic enzymes, etc.) in their original hosts (Martinez et al. 2009; Martinez 2009; Martinez et al. 2007). The strong increase of antimicrobial concentrations in natural ecosystems, as a consequence of human activities (human antibiotic therapy, farming), might have shifted the original functions of antimicrobials and resistance determinants to the threatening role they nowadays play in hospitals or farms (Martinez 2009, 2008). These changes might influence not just the selection of antibiotic-resistant bacteria, but also the structure of the natural bacterial populations and may as well change the physiology of bacteria (Martinez 2009).

The chapter will focus on the antibiotic resistance problem in the environment and the major sources of pollution by antibiotic resistance determinants and suggest ways to relieve the problem. Furthermore, we will give an overview on the major ways of antibiotic resistance spread in the environment and try to assess the risks associated with the occurrence and spread of resistance determinants for human health.

7.2 The Antibiotic Resistance Problem

7.2.1 State of the Art of the Problem

It is now well accepted that antibiotic resistance genes (ARGs) are found everywhere, in clinical settings, tertiary care centers, pets, wildlife, surface waters, and soils, basically in all locations which have been or are in contact with microbes. The major mechanisms conferring resistance to antibiotics are also known (Fig. 7.1). Concentrations of ARGs and the classes of antibiotics to which they confer resistance differ between sites. One thumb rule which holds true for most locations is: The closer the environment is to anthropogenic influence, the higher the incidence is of antibiotic-resistant bacteria and the prevalence of the respective ARGs. The major ways of antibiotic resistance spread in the environment are also known. However, their contribution in different habitats and between different microbes varies considerably and is still a cause for debates in the scientific community.

Ways to slow down the development of antibiotic resistance include: (i) prudent use of antibiotics in therapy (human and animals); (ii) worldwide ban of all antimicrobials which are generally used in human therapy from growth promotion in animal husbandry; (iii) strong worldwide reduction of the use of antibiotics in aquaculture and mariculture; (iv) separation and separated treatment of hospital waste and wastewater (ww) from sewage; (v) application of treated or at least partially treated ww for crop irrigation (never without any treatment); and (vi) application of advanced technologies for water purification for drinking water purposes.

The World Health Organization (WHO) and many national health authorities are now aware of the problem of the occurrence as well as of the dissemination of antibiotic resistance in the environment. However, to efficiently tackle the problem and to install countermeasures, systematic studies are required worldwide to assess the impact of ARGs in the environment on human health.

7.2.2 Relationship to Antibiotic Usage

Antibiotic utilization for clinical or farming purposes selects for resistant microorganisms (Martinez 2009; Livermore 2005; Teuber 2001). Thus, it can be predicted that residues from hospitals or farms contain both types of pollutants: antibiotics

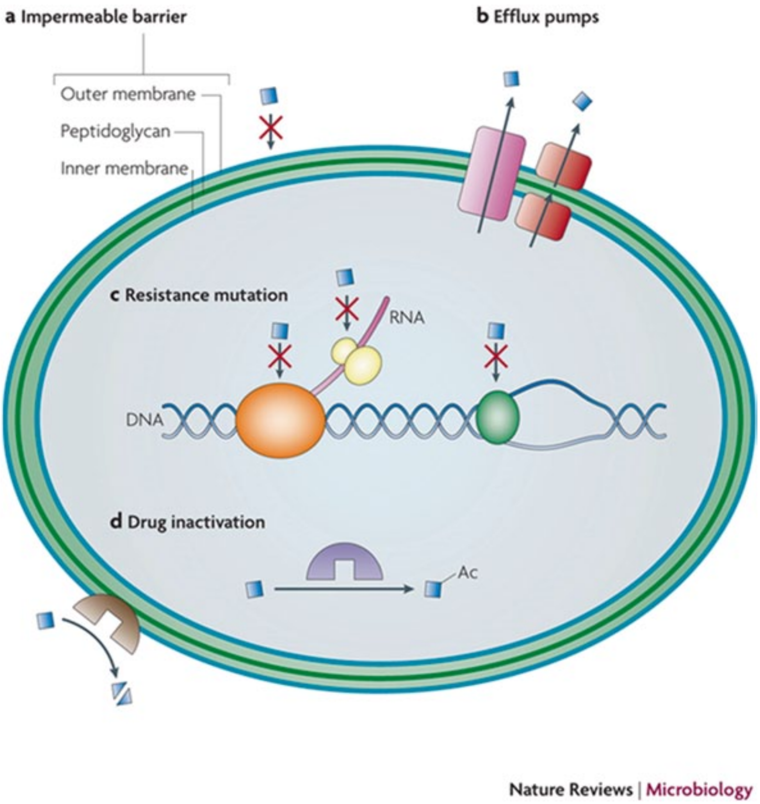

Fig. 7.1 Mechanisms of antibiotic resistance in a Gram-negative bacterium (adapted from Allen et al. 2010). **a** Impermeable barriers. Some bacteria are intrinsically resistant to certain antibiotics (*blue squares*) because they have an impermeable membrane or lack the target of the antibiotic. **b** Multidrug resistance efflux pumps. These pumps secrete antibiotics from the cell. Some transporters, such as those of the resistance–nodulation–cell division family (*pink*), can pump antibiotics directly outside the cell, whereas others, such as those of the major facilitator superfamily (*red*), secrete them into the periplasm. **c** Resistance mutations. These mutations modify the target protein, for example, by disabling the antibiotic-binding site but leaving the cellular functionality of the protein intact. Specific examples include mutations in the gyrase (*green*), which cause resistance to fluoroquinolones, in RNA polymerase subunit B (*orange*), which cause resistance to rifampicin, and in the 30S ribosomal subunit protein S12 (encoded by *rpsL*; *yellow*), which cause resistance to streptomycin. **d** Inactivation of the antibiotic. Inactivation can occur by covalent modification of the antibiotic, such as that catalyzed by acetyltransferases (*purple*) acting on aminoglycoside antibiotics, or by degradation of the antibiotic, such as that catalyzed by β-lactamases (*brown*) acting on β-lactam antibiotics. Ac, acetyl group

and ARGs. Nevertheless, the fate of both types of pollutants is most likely different. Several antibiotics are natural compounds that have been in contact with environmental bacteria for millions of years and are thus biodegradable; some can even serve as food resource for several microorganisms (Martinez 2009; Dantas et al. 2008). Synthetic antibiotics such as quinolones can be more refractory to biodegradation.

Recent work has shown that the binding of quinolones to soil and sediments delays their biodegradation (Martinez 2009). Nevertheless, ww treatment of quinolone-polluted waters efficiently removes these antibiotics through biodegradation and photodegradation (Sukul and Spiteller 2007). Consistent with these data, it has been demonstrated that most antibiotics are usually below detection limits in ground water samples, although they are more stable upon adsorption to sediments (Hirsch et al. 1999; Halling-Sorensen et al. 1998). Due to this fact, sediment samples from antibiotic-polluted environments contain higher antibiotic concentrations than water samples from the same site (Martinez 2009; Kim and Carlson 2007). The fact that antibiotics are degraded in natural ecosystems does not mean that they are not relevant pollutants, as the degradation process is slow at low temperatures in winter (Martinez 2009; Dolliver and Gupta 2008). Furthermore, some environments suffer a constant release of antibiotics (e.g., hospital effluents and farm residues); they are constantly polluted irrespective of antibiotic degradation. The consequence is that the organisms are continuously exposed to antibiotics at subtherapeutic concentrations (Martinez 2009; Lindberg et al. 2007). Since sub-inhibitory concentrations of antibiotics can trigger specific transcriptional responses in bacteria (summarized in Martinez 2009), the presence of antibiotics will necessarily modify the metabolic activity of the microorganisms present in these polluted environments. However, in any case, the fate of antibiotics in natural ecosystems is their degradation (Pei et al. 2006) in such a way that if the utilization of a given antibiotic is banned, it will sooner or later disappear as a pollutant from natural ecosystems.

In contrast, antibiotic resistance determinants present in gene transfer units on mobile genetic elements such as plasmids or integrative conjugative elements (ICEs) are auto-replicative elements that can be maintained in microbial populations unless they confer a fitness cost to the recipient bacteria (Martinez 2009). Some studies have clearly shown that reducing the antibiotic load in natural environments may reduce the amount of pollutant ARGs, e.g., it has been shown that sewage dilution in river waters reduced the number of plasmid-encoded ARGs in *Escherichia coli* (Martinez 2009; Gonzalo et al. 1989). In another well-known example, the ban of the utilization of some antibiotics in farming has significantly reduced antibiotic resistance in animals and its transfer to humans (Martinez 2009; Aarestrup et al. 2001). However, unfortunately the situation is not that simple. It has been observed that even though the incidence of antibiotic resistance declines, the decline is slow and part of the resistant population remains (Andersson 2003), a situation which is consistent with predictions based on mathematical models (Levin 2002). Furthermore, the presence of the same ARGs currently present in human pathogens has been reported in ecosystems without a history of antibiotic contamination (Pallecchi et al. 2008). These ecosystems include remote human and animal populations without known antibiotic exposure which can present a high prevalence of resistance despite not receiving any antibiotic (Bartoloni et al. 2009; Martinez 2009; Grenet et al. 2004; Gilliver et al. 1999). This indicates that ARGs can be resilient to elimination even in the absence of antibiotic selective pressure (Salyers and Amabile-Cuevas 1997). Several efficient mechanisms exist that allow the maintenance and the spread of ARGs in the environment. Thus, as opposed to antibiotic contaminations, pollution by antibiotic

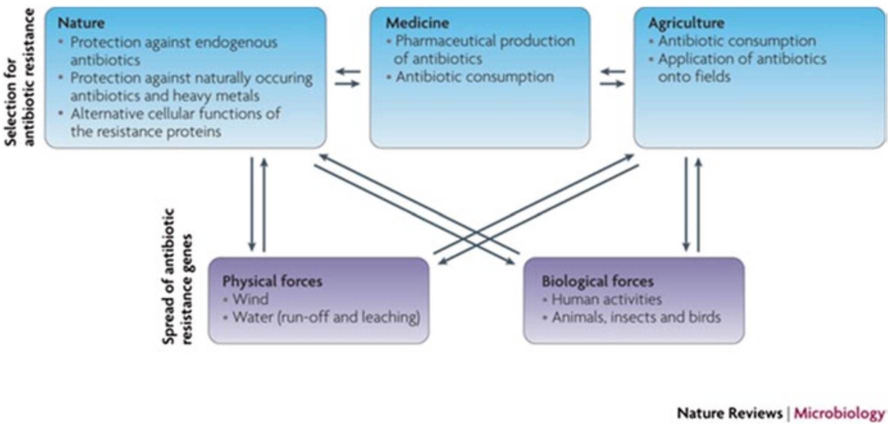

Fig. 7.2 Sources and movement of ARGs in the environment (adapted from Allen et al. 2010). ARGs exist naturally in the environment owing to a range of selective pressures in nature. Humans have applied additional selective pressure for ARGs because of the large quantities of antibiotics that we produce, consume, and apply in medicine and agriculture. Physical and biological forces also cause widespread dissemination of ARGs throughout many environments

resistance determinants will not necessarily disappear even if the release of ARGs in the environment is stopped (Martinez 2009). Sources and movement of ARGs in the environment are summarized in Fig. 7.2.

7.3 Environments of Particular Concern: Major Sources of Antibiotic Resistance Genes

We will focus here, by choice, on natural environments under anthropogenic influence and on anthropogenic environments excluding hospitals and health-care centers as a plethora of excellent articles are available on antibiotic resistances in hospitals and on their impact on human health (Arias and Murray 2012; Hollenbeck and Rice 2012; Yezli and Li 2012; Gould 2008; Witte et al. 2008; Koch et al. 2004; Klare et al. 2003). Additionally, we will consider the influence of the increased mobility of the human population on the spread of infectious diseases and resistant microbes. Wilson published an excellent review article on the traveler and emerging infections (Wilson 2003). The movement of populations shapes the patterns and distribution of infectious diseases globally. The consequences of travel are seen in the traveler and in places and populations visited and may persist long after travel. The traveler can be seen as an interactive biological unit who picks up processes, and carries and drops off microbial genetic material (Wilson 2003). Travelers can also be seen as couriers who inadvertently transfer pathogens and microbial genetic material to regions where researchers can perform detailed analyses that can help to map the location and movement of strains, genotypes, and resistance patterns. The connectedness and mobility in today's world facilitate the emergence of infectious diseases in humans and also in animals and plants. Population size and density favor spread of many infections. The rapid generation time of microbes and their adaptability to changes in the physico-chemical and immunological environment will pose continuing challenges to mankind (Wilson 2003).

Travelers regularly and effectively move antibiotic-resistant bacteria across borders (Wilson 2003; Okeke and Edelman 2001; Harnett et al. 1998; Slavin et al. 1996; Brown and Linham 1988). In 1987, Murray and co-workers examined fecal specimens from persons before, during, and after traveling to Mexico (Murray et al. 1990). They observed that resistance in *E. coli* increased to multiple antibiotics, including ampicillin, trimethoprim-sulfamethoxazole, sulfonamides, and chloramphenicol, in association with travel. This occurred even in persons who had taken no antibiotics. A multidrug-resistant methicillin-resistant *Staphylococcus aureus* (*S. aureus*; MRSA) clone is thought to have spread from Brazil to Portugal, presumably carried by one or more persons who were colonized or infected (Wilson 2003; Aires de Sousa et al. 1998). An ARG may emerge once on a single plasmid and subsequently be carried to multiple locations, where it may continue to spread, e.g., a gentamicin-resistance gene appears to have been spread on a conjugative plasmid (O′Brien et al. 1985). Highly resistant bacteria carried by travelers can also spread after the travelers had returned home, particularly in a clinical setting (Wilson 2003; M′Zali et al. 1997).

The industrialization of food animal production, specifically the widespread use of antimicrobials, not only increased pressure on microbial populations, but also changed the ecosystems in which antimicrobials and bacteria interact. Davis and colleagues defined industrial food animal production (IFAP) as an anthropogenic ecosystem (Davis et al. 2011).

7.3.1 Farms: Spread of Antibiotic Resistance Genes in the Food Chain

Today, the magnitude of human impacts on natural systems makes consideration of anthropogenic changes to ecosystems important. Agriculture is one such activity, because it inherently creates anthropogenic ecosystems (Jackson and Piper 1989), which are defined as collections of organisms and physical structures under human control and manipulation (Davis et al. 2011). The adoption of an industrialized model in modern food animal production (Martinez 2002) has been successful in increasing global food production, but it also has intensified its impact through the expansion of anthropogenic ecosystems (Tilman et al. 2002; Jackson and Piper 1989). Davis and coworkers argued that IFAP creates anthropogenic ecosystems wherein the use of antibiotics inevitably selects for antibiotic resistance in bacterial populations within animal hosts and the environment. Consequently, this alters microbial communities (microbiomes) and the collection of available mobile resistance determinants (resistome) dispersed into the surrounding ecosystems

(Davis et al. 2011; Wright 2007, 2010; Martinez 2009). Davis and colleagues have studied the role of anthropogenic ecosystems on the emergence of drug-resistant bacteria from agricultural environments on the example of US industrial poultry production. The anthropogenic ecosystems generated by IFAP practices have extensive direct impacts on the microbial ecology of poultry hosts and the environment, and probably have indirect impacts on consumers through poultry products (Davis et al. 2011). In nature, microorganisms are known to both produce and develop resistance to antimicrobials, resulting in a set of complex interactions now thought to contribute to the signaling and regulation in natural microbial ecosystems (Davis et al. 2011; Aminov 2009). However, the extent and magnitude of antimicrobial use in IFAP far exceed, in volume and impact, those of naturally occurring antimicrobials (Davis et al. 2011; Martinez 2009; Kumar 2005). The US **Food and Drug Administration** (FDA) reported that 13 million kg of antimicrobials were sold or distributed for use in food-producing animals during 2009 (FDA report 2010). Particularly, the practice of using nontherapeutic concentrations of broad-spectrum antimicrobials to feed (Baurhoo et al. 2009) creates an ideal environment for selecting individual bacterial cells or populations that have acquired resistance through mutations or horizontal gene transfer (HGT) (Love et al. 2011; Lees et al. 2006).

The process of natural selection by antimicrobial use in IFAP is reflected in observations of antimicrobial-resistant isolates from livestock, including poultry, shortly after the introduction of routine use of antimicrobials as feed additives in the 1950s and 1960s (Davis et al. 2011; De Soet 1974; Smith 1970; Starr and Reynolds 1951). As resistant populations replace susceptible populations at the community level, ARGs in one population/species are available to other populations/species through HGT. Consequently, the development of novel multidrug-resistant bacteria and/or multidrug resistance conferring Mobile Genetic Elements (MGEs) is enabled (Davis et al. 2011; Davies and Davies 2010; Wright 2007). M′ikanatha and colleagues typed *Salmonella* cultured from retail chicken purchased in Pennsylvania and compared the chicken isolates with human isolates. Applying molecular methods, an identical isolate was found in a retail chicken and in a patient (M′ikanatha et al. 2010).

Davis and colleagues focused their review on research along the pathways that connect the commercial poultry intestinal microbiome with microbiomes in surrounding environments. The impact of natural selection exerted by antimicrobial use within the intestine of individual poultry hosts can be further scaled up to the inter-microbiome and inter-ecosystem level (Fig. 7.3). Agricultural ecosystems interact with other ecosystems directly at both local and regional levels, and more broadly through global movement of dusts and water (Peterson et al. 2010), as well as economic trade in feeds, animals, and animal waste (Davis et al. 2011; Sapkota et al. 2007). Although the industrial poultry house often is assumed to be biocontained and biosecure, multiple pathways connect it with surrounding ecosystems (Silbergeld et al. 2008). These are ventilation systems required to keep crowded animals alive; movement of rodents (Henzler and Opitz 1992), wild birds (Leibler et al. 2009), and insects (Graham et al. 2009) in and out of confinement facilities; and transfer of wastes (Davis et al. 2011; Graham and Nachman 2010). These

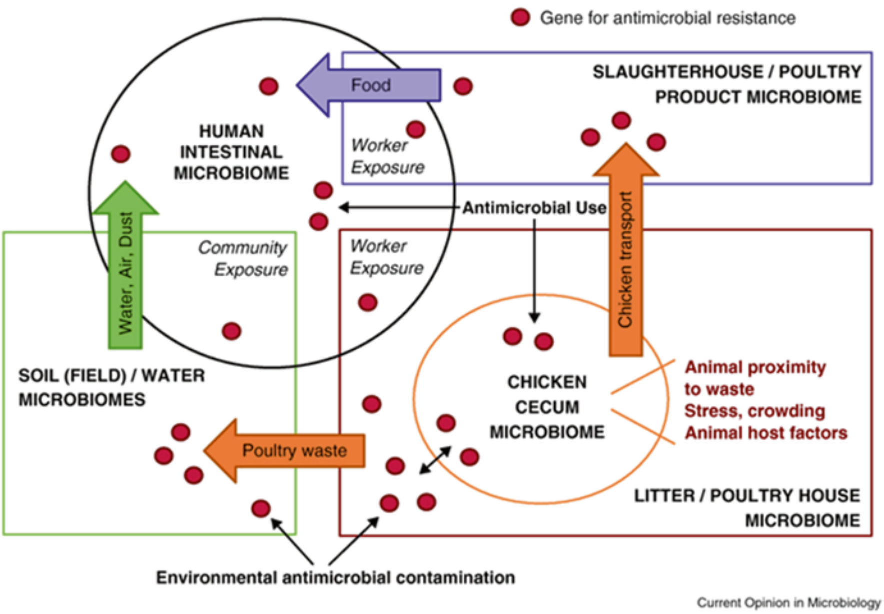

Fig. 7.3 Potential role of antimicrobial selective pressure in the environment (from Davis et al. 2011). Conceptual, potential role of selective pressure of antimicrobial use and other anthropogenic ecosystem alterations that impact microbiomes in the chicken cecum, poultry house environment, local soil and water environments, processing plant environment, and human intestine

conditions release viable bacteria and ARGs into surrounding environments, water systems, and wild animal reservoirs (Davis et al. 2011; Chee-Sanford et al. 2009; Baquero et al. 2008; Silbergeld et al. 2008).

Genetic analysis of the US commercial broiler cecum microbiome has shown that it contained a wide array of ARGs and genes enabling HGT (Davis et al. 2011; Qu et al. 2008). Recent Canadian studies also have found widespread prevalence of virulence and resistance genes from *Enterococcus* spp., *E. coli*, and *Clostridium perfringens* isolated from enteric samples from conventional broilers that were fed antimicrobials (Davis et al. 2011; Diarra et al. 2007, 2010; Bonnet et al. 2009). Furthermore, antimicrobial-treated broilers, compared to those not fed antimicrobials, were significantly associated with increases in the presence of ARGs and class 1 integron genes in cecal and environmental *E. coli* isolates (Davis et al. 2011; Diarra et al. 2007). Especially class 1 integrons are known to shuffle ARGs and are known to be able to promote transfer of ARGs among bacteria (Davies and Davies 2010; Diarra et al. 2007).

Much like the chicken cecum, poultry waste contains a significant number of resistance integrons, particularly within gram-positive bacteria (Diarra et al. 2007; Nandi et al. 2004). Some resistance patterns appear to persist in bacteria even after cessation of antimicrobial use, for example, fluoroquinolone resistance in *Campylobacter* (Price et al. 2007) and sulfonamide resistance in *E. coli* (Davis et al. 2011; Furtula et al. 2010).

Much of the impact of antimicrobial use on the environmental microbiome is exerted through poultry waste disposal. Application of litter onto open fields can impact the soil microbiome locally to regionally through run-off and air-borne drift. The USA has no regulatory requirements for treating animal wastes, leading to uncontrolled waste storage before land disposal (Davis et al. 2011; Graham and Nachman 2010). Simple storage methods do not affect prevalence of pathogens nor drug-resistant pathogens (Graham et al. 2009). Most of the antimicrobials in feeds pass largely unchanged through the broiler gut into the excreta (Kumar et al. 2005). Some antimicrobials, such as oxytetracycline and fluoroquinolone analogs, can persist in the soil environment with half-lives as long as 150–250 days with undiminished potency (Davis et al. 2011; Chee-Sanford et al. 2009; Kumar et al. 2005).

Spread of antimicrobial-resistant bacteria and resistance determinants represents the inter-ecosystem effects of antimicrobial usage in industrialized food animal production. Human links include vehicles, animal transport, and networks of social and commercial contact (Davis et al. 2011; Leibler et al. 2010; Rule et al. 2008). Cross-contamination of poultry during transport and at slaughter contributes to greater microbial diversity in retail chicken than in live birds (Hastings et al. 2011; Colles et al. 2010). Contamination during the harvest process can impact poultry house (Price et al. 2007) and slaughter workers (Mulders et al. 2010), as well as retail chicken consumers in the global market (Davis et al. 2011). Compelling evidence for the impact of antimicrobial use in industrialized food animal production comes from molecular analyses of bacteria in live poultry and/or on poultry products in conjunction with analysis of human isolates (Davis et al. 2011; McEwen et al. 2010; Denis et al. 2009; Gupta et al. 2004). Numerous studies demonstrated the presence of very similar or identical ARGs (Diarra et al. 2010; M′ikanatha et al. 2010; Simjee et al. 2007), identical strains of antimicrobial-resistant bacteria, such as MRSA (Smith and Pearson 2011; Bystroń et al. 2010), and related or identical resistance plasmids (McEwen et al. 2010) in humans and poultry (Davis et al. 2011).

Witte and coworkers performed an experiment with the antibiotic nurseothricin which is not used in humans; strains resistant to it were recovered from both animals and farm workers (Acar and Moulin 2006; Witte et al. 1984). More recent studies dealing with enterococci and Enterobacteriaceae confirmed transfer of resistant bacteria from animals to humans (Acar and Moulin 2006; Hershberger et al. 2005; Aarestrup and McNicholas 2002; Frey et al. 2000; Van den Bogaard et al. 1997).

7.3.2 Aquatic Environments

Basically, all aquatic environments can be considerably affected by pollution through antimicrobials, antimicrobial degradation products, by antimicrobial-resistant microbes and the genes conferring antimicrobial resistance. In the following section, aquatic environments especially affected by the occurrence of ARGs are discussed.

7.3.2.1 Aquaculture

Any agricultural or aquacultural farming operation that relies on the routine and regular use of antimicrobials to control losses is, on the long run, unsustainable. The continued usage of antimicrobials will lead to the emergence of resistance in the target bacteria. Thus, such a dependence on antimicrobials not only represents an unacceptable and imprudent use of these valuable agents, but it will almost certainly prove to be self-defeating (Smith 2008). In any population of farmed animals, maintaining appropriate living conditions, employing appropriate husbandry practices, and using vaccines, whenever available, against enzootic or frequently encountered infections are the primary and most effective methods by which losses due to infectious diseases can be limited (Smith 2008). However, the aim of all these prophylactic procedures is to limit the occurrence of infectious disease and it is unrealistic to expect them to entirely prevent any occurrence of these diseases (Smith 2008). Thus, the inevitability that disease emergencies will occur requires that we learn how to use antimicrobials in such a way so as to maximize their efficacy while minimizing the pressure for increased frequencies of resistant strains (Smith 2008).

Smith presented estimates of antimicrobial use in the aquaculture industries of different countries. The estimated antimicrobial use (g/t production) differs tremendously between the listed countries. Norway and Sweden apply 1 and 2 g/t production, whereas Greece and Canada apply 100 and 156 g/t production, respectively. At the end of the list are two countries applying enormous quantities, namely Chile (200 g) and Vietnam (700 g) per ton production (Smith 2008). There are three methods, medicated feed, bath, and injection, by which antimicrobials are routinely administered to aquatic animals. For the majority of farmed species, administration occurs via medicated feed.

In the following section, we will focus on the negative consequences of antimicrobial use in aquaculture as experienced in human and public health contexts. The most significant public health risks associated with increased frequencies of resistance due to the use of antimicrobial agents in aquaculture can be summarized by two major issues: (i) concerns associated with the selection of resistant variants of bacteria capable of inducing infections in humans that would require antimicrobial therapy and (ii) concerns associated with the movement of ARGs from bacteria in the aquatic environment to those in the terrestrial environment that are capable of infecting humans or other land-based animals (Smith 2008).

Selection for Resistance in Bacteria Associated with Human Disease

It has been assumed that the major risks associated with the use of antimicrobials in land-based agriculture are those leading to selective enrichment of resistant strains of zoonotic bacteria (Smith 2008; Helmuth and Hensel 2004). There is an ongoing debate on the size of this risk, with some arguing that it is relatively small (Wassenaar 2005; Bywater 2004) and others that it might be significant (Angulo et al. 2004). Bacteria capable of infecting humans are found much less frequently in aquaculture than in agriculture. Thus, the risks associated to the selection of resistant zoonotic bacteria by the use of antimicrobial agents will be significantly smaller in aquaculture than in agriculture (Smith 2008; Smith 2001).

The WHO/Food and Agriculture Organization (FAO)/World Organisation for Animal Health (OIE) expert working group (WHO 2013) identified two groups of bacteria that might be encountered in aquaculture and might also be capable of infecting humans, enteric pathogens such as *Salmonella*—due to contamination of aquaculture by human or animal wastes—and aquatic bacteria such as *Vibrio parahaemolyticus* and *V. cholerae* (Smith 2008).

Selection for Transmissible Resistance

The WHO/FAO/OIE expert group reached the following conclusion: "The greatest potential risk to public health associated with antimicrobial use in aquaculture is the development of a reservoir of transferable resistance genes in bacteria in aquatic environments from which such genes can be disseminated by HGT to other bacteria and ultimately reach human pathogens." There is a plethora of data available (recently reviewed by Sørum (2006)) demonstrating that ARGs capable of being transferred to terrestrial bacteria have been regularly detected in bacteria associated with disease of aquatic animals (Smith 2008). There are also ample data demonstrating that transmissible ARGs are present in the bacteria found in the vicinity of aquaculture operations (Smith 2008; Miranda et al. 2003; Schmidt et al. 2001; Rhodes et al. 2000). Surprisingly, there are only few papers that have convincingly linked the use of antimicrobials in aquaculture with an increase in the frequency of these transmissible genes. The available data support the hypothesis that a reservoir of transmissible ARGs will develop as a consequence of the use of antimicrobials in aquaculture. What is less certain is the size of this reservoir and its public health significance (Smith 2001, 2008).

Movement of Transmissible Resistances Between Terrestrial and Aquatic Microorganisms

Molecular studies have shown that the resistance genes in bacteria associated with aquaculture are significantly similar to those that have been found in terrestrial bacteria causing human and land-based animal disease (Smith 2008; Sørum 2006; Kim et al. 2004; Bolton et al. 1999). Confirmation that these genes can move between bacteria in these two environments has been provided through laboratory studies by Kruse and Sørum (1994) and Sandaa and Enger (1994), which have demonstrated that these genes can be transferred from aquatic to terrestrial bacteria with relatively high frequencies (Smith 2008).

The current monitoring and surveillance programs of the use of antimicrobials in aquaculture have to be considerably improved to be able to assess the impact of antimicrobial resistance as a consequence of antimicrobial use in aquaculture on human health. In addition, laboratory methods used to identify resistance and to quantify the frequencies of resistance that result from antimicrobial use in aquaculture have to be harmonized to enable comparison of results from different laboratories (Smith 2008).

7.3.2.2 Wastewater and Wastewater Treatment Systems

Urban wastewater treatment plants (UWTPs) are among the main sources for the release of antibiotics into the environment. The occurrence of antibiotics may promote the selection of ARGs and antibiotic-resistant bacteria, which shade health risks to humans and animals (Rizzo et al. 2013). Rizzo and colleagues reviewed the fate of antibiotic-resistant bacteria and ARGs in UWTPs, focusing on the different processes typically included in UWTPs, e.g., mechanical, biological, physical, chemical, and physical–chemical processes, which may affect the fate of antibiotics, antibiotic resistant bacteria, and ARGs in different ways and consequently the development and spread of resistance into the environment (Rizzo et al. 2013).

Over the past years, a renewed interest on the antibiotic resistance phenotypes in UWTPs was obvious in the scientific literature (Rizzo et al. 2013; Manaia et al. 2012; Kümmerer 2009; Baquero et al. 2008). Human and animal commensal bacteria and other of environmental origin have been the major focus of the studies on antibiotic resistance in ww. Due to their close contact with humans and the easiness to isolate and identify, the fecal indicators, coliforms and enterococci, have been the most studied groups (Rizzo et al. 2013; Araùjo et al. 2010; Sabate et al. 2008; Boczek et al. 2007; Ferreira da Silva et al. 2007; Martins da Costa et al. 2006; Reinthaler et al. 2003). To establish a relationship between the most severe cases reported in clinical settings and environment, a search for the last-generation antibiotic resistance determinants has also been reported in UWTP studies (Rizzo et al. 2013; Czekalski et al. 2012; Figueira et al. 2011a, b; Araùjo et al. 2010; Parsley et al. 2010; Szczepanowski et al. 2009; Gajan et al. 2008). In particular, the presence of MRSA, vancomycin resistant *Enterococcus* spp. (VRE), and gram-negative bacteria producing extended spectrum beta-lactamases (ESBL) has been studied.

Although the occurrence of antibiotic-resistant superbugs in the effluents may be an issue of particular concern, the numbers of common bacteria harboring ARGs that are continuously discharged in receiving waters are impressive (Galvin et al. 2010; Łuczkiewicz et al. 2010; Ferreira da Silva et al. 2007; Martins da Costa et al. 2006). The final effluent of UWTPs can discharge approximately 10^9–10^{12} colony forming units (CFU) per day, per inhabitant equivalent; among these, at least 10^7–10^{10} could have any kind of acquired antibiotic resistance (Rizzo et al. 2013; Novo and Manaia 2010). Moreover, these estimates only include the culturable fraction of the bacterial population, and might only represent 1 % of the total. Indeed, the numerous unculturable bacteria dwelling in ww and related systems (sludge, biofilms) can host an immense number of ARGs (Rizzo et al. 2013; Szczepanowski et al. 2009). Szczepanowski and coworkers found, in a study performed with ww samples in Germany, 140 different clinically relevant ARGs, encoding resistance to the different classes of antibiotics (aminoglycosides, β-lactams, chloramphenicol, fluoroquinolones, macrolides, rifampicin, tetracycline, trimethoprim, and sulfonamides, as well as efflux pumps) (Rizzo et al. 2013; Szczepanowski et al. 2009). The majority of the studies have focused on the selection and relative prevalence of antibiotic resistant bacteria and ARG transfer in UWTPs irrespective of the biological process, technology, and operating conditions. Only a few studies investigated the effects of the operating parameters (Kim et al. 2007a, b, c) and different ww treatment technologies (summarized in Rizzo et al. 2013; Munir et al. 2011; Mezrioui and Baleux 1994) on the occurrence and release of ARGs and antibiotic-resistant bacteria.

The *E. coli* strains isolated from the effluent of an aerobic lagoon showed higher antibiotic resistance (35 %) than those isolated from domestic sewage (23 %). In the activated sludge, the percentage of antibiotic resistant strains (resistance to at least one antibiotic) showed seasonal changes in the inflow and outflow ww samples. The increase of the percentage of antibiotic-resistant strains of *E. coli* in the effluent of the aerobic lagoon was probably related to the selection of antibiotic-resistant strains by this treatment (Rizzo et al. 2013). Furthermore, survival experiments comparing *E. coli* strains resistant to seven antibiotics and *E. coli* strains susceptible to 15 tested antibiotics demonstrated that resistant bacteria had higher survival rates than susceptible ones in ww treated in lagoons (Rizzo et al. 2013).

Advanced treatments aim at improving the quality of the secondary effluent of ww treatment plants before disposal or reuse. Sand filtration, adsorption membranes, and advanced oxidation processes are among the most applied and studied advanced treatment technologies. In contrast to a myriad of studies available on the effect of advanced processes on bacteria inactivation, only very few studies exist regarding the effect on antibiotic resistance (summarized in Rizzo et al. 2013). Öncü and colleagues compared ozonation and TiO_2 heterogeneous photocatalysis with conventional chlorination in terms of effects on DNA structure and integrity (Öncü et al. 2011). In contrast to chlorine, which did not affect plasmid DNA structure at the studied doses, ozone and photocatalytic treatment resulted in conformational changes and the damage increased with increasing oxidant doses (Rizzo et al. 2013; Öncü et al. 2011). This finding is of particular interest taking into consideration that most of the ARGs are encoded on plasmids and the most applied disinfection process in ww treatment is chlorination, but ultraviolet (UV) radiation also finds extended applications.

In a recent study, the inactivation of tetracycline-resistant *E. coli* and antibiotic-sensitive *E. coli* by UV irradiation was investigated to assess their tolerance to UV light (Huang et al. 2013). The authors did not find any difference in the inactivation of tetracycline-resistant and antibiotic-sensitive *E. coli* after disinfection treatment. The general lack of data concerning the effect of UV-dependent DNA damage on antibiotic resistance makes this topic worthy of investigation (Rizzo et al. 2013). Iwane and colleagues found out that chlorination treatment did not significantly affect the percentage of resistance in *E. coli*, randomly isolated from ww samples, to one or more antibiotics (from 14.7 to 14.0 %) or specifically to ampicillin (constant at 7.3 %) and tetracycline (from 8.0 to 6.7 %) (Rizzo et al. 2013; Iwane et al. 2001). Munir and coworkers investigated the effect of five different UWTPs located in Michigan, USA on the occurrence and release of ARGs and antibiotic-resistant bacteria into the environment. They observed that disinfection by chlorination and UV radiation processes did not significantly reduce ARGs and antibiotic-resistant bacteria (Rizzo et al. 2013; Munir et al. 2011). In summary, in light of the available data, the effect of chlorine on bacterial DNA may be achieved only for high disinfectant dose compared to those typically used in ww disinfection (Rizzo et al. 2013; Dodd 2012).

7.3.2.3 Other Water Environments

Zhang and coworkers recently published an excellent review on antibiotic resistance in water environments (Zhang et al. 2009). As a result of extensive use of human and veterinary antibiotics, hospital ww and livestock manure are considered as the major sources of environmental ARGs. ARGs can enter into aquatic environments by the direct discharging of untreated ww or into sewage treatment plants through ww collection systems and subsequently into the environments with effluents and discharged sludge (Zhang et al. 2009; Auerbach et al. 2007). ARGs are transferred into soils by amending farm land with animal manure and processed biosludge from sewage treatment plants and subsequently can leach to groundwater or be carried by runoff and erosion to surface waters (Yang and Carlson 2003). Surface water and shallow groundwater are commonly used as sources of drinking water; thus, ARGs can go through drinking water treatment facilities and enter into the water distribution system (Schwarz et al. 2003).

Untreated Sewage

During the past years, various bacterial species isolated from untreated sewage were found to contain a variety of ARGs encoding resistance to aminoglycosides, β-lactam antibiotics, trimethoprim, tetracyclines, and vancomycin (reviewed in Zhang et al. 2009). Sewage receives the bacteria previously exposed to antibiotics from private households and hospitals and is considered as a hotspot for ARGs. ARGs enter sewage treatment plants with sewage water, and most of them cannot be effectively removed with traditional treatment processes before being released into the environment (Zhang et al. 2009; Auerbach et al. 2007; Volkmann et al. 2004). In addition, environmental conditions of activated sludge or biofilms facilitate horizontal transfer of the ARGs from one host to another because of the nutritional richness and high bacterial density and diversity (Zhang et al. 2009; Schlueter et al. 2007; Tennstedt et al. 2003).

Sewage Treatment Plant Activated Sludge and Biofilms

Several previous studies have shown that sewage treatment plants serve as important reservoirs for various ARGs (Zhang et al. 2009; Schlueter et al. 2007; Tennstedt et al. 2003; Smalla and Sobecky 2002). Sewage treatment plants receive the antibiotic-resistant bacteria with the inflow sewage water originating from hospitals, private households, industry, and agriculture. So, they play important roles in recombination, exchange, and spread of environmental ARGs (Zhang et al. 2009; Szczepanowski et al. 2004). Sewage treatment plants are known as important interfaces between different water bodies, such as hospital ww, domestic ww, surface water, and groundwater; therefore, they may facilitate gene exchange and spread between these environments (Zhang et al. 2009; Schlueter et al. 2007). It is also well known that the presence of antibiotics in sewage selects for the maintenance of ARGs conferring resistance in activated sludge (Kümmerer 2003). Many ARGs, such as *vanA* and *vanB*, are not effectively removed by activated sludge process commonly used in sewage treatment plants, as the genes are being found in both influent and effluent water (Zhang et al. 2009; Caplin et al. 2008; Iversen et al. 2002). ARGs enter into other water bodies with effluent water and can be transferred horizontally to the indigenous bacteria in these water environments (Schwartz et al. 2003).

Natural Water

Different ARGs have been found in bacterial isolates or microbial communities in natural waters which were not or only slightly polluted (Zhang et al. 2009; Mohapatra et al. 2008; Rahman et al. 2008; Jacobs and Chenia 2007). ARGs in surface water and soils can leach to groundwater close to agriculture areas of animal production or aquaculture. Tetracycline resistance genes encoding both ribosomal protection proteins and efflux pumps have been detected in the groundwater as far as 250 m downstream from waste lagoons of swine farms (summarized in Zhang et al. 2009). Besides, in fresh waters, some ARGs conferring resistance to aminoglycosides (Heuer et al. 2002) and chloramphenicol (Dang et al. 2008) have also been detected in marine waters with no evidence for pollution (Zhang et al. 2009).

Sediments

It is evident that ARGs in sediments are acquired from water environments or generated and/or spread due to selection by the antibiotics present in the sediments. Sediments of aquaculture farms are important antibiotic resistance reservoirs where various antimicrobials and ARGs are concentrated (Zhang et al. 2009; Agersø and Petersen 2007; Dalsgaard et al. 2000). Marine sediments were shown to contain many different tetracycline resistance genes (Rahman et al. 2008). Nonaka and colleagues found that the numbers of oxytetracycline-resistant bacteria increased in sediments around a marine aquaculture site after oxytetracycline therapy, the *tet*M resistance gene was detected in different genera of gram-positive and gram-negative bacteria in the sediments of this marine environment (Zhang et al. 2009; Nonaka et al. 2007).

In rivers running through pristine, urban, and agriculturally impacted areas, ARG detection frequency correlated with the degree of pollution by antibiotic compounds (Zhang et al. 2009; Pei et al. 2006; Yang and Carlson 2003).

Drinking Water

Prevalence and resistance patterns of various microbial genera from drinking water distribution systems have been recently reported (Zhang et al. 2009; Ram et al. 2008; Koksal et al. 2007). Multiple antibiotic-resistant *E. coli* strains isolated from drinking water were found to carry ARGs conferring resistance to aminoglycosides, β-lactams, tetracyclines, and trimethoprim-sulfamethoxazole (Alpay-Karaoglu et al. 2007; Cernat et al. 2007), as well as class 1 integrons which are known as ARG shuffling units (summarized in Zhang et al. 2009; Ozgumus et al. 2007).

To investigate possible ARG transfer from ww and surface water to the drinking water distribution network, Schwartz and colleagues and Obst and colleagues analyzed biofilms in hospital and municipal ww, as well as drinking water from river bank filtrate. They found *vanA* and *ampC* conferring resistance to vancomycin and ampicillin resistance, respectively, both in ww and drinking water biofilms (Zhang et al. 2009; Obst et al. 2006; Schwartz et al. 2003).

7.3.3 Soils Impacted by Wastewater Irrigation

Sewage treatment plant effluent and sludge application to agricultural fields are recognized as important sources of ARGs to surface waters and soils and subsequently into groundwater (Rizzo et al. 2013; Yang and Carlson 2003).

Dalkmann and coworkers investigated the effect of ww irrigation on the occurrence of antibiotics or their degradation products as well as on the prevalence of the corresponding ARGs in soils from the Mezquital Valley in Mexico, which have been irrigated with untreated ww for distinct periods of time (Dalkmann et al. 2012). Long-term irrigation of soils with untreated ww led to an accumulation of antibiotics (e.g., sulfamethoxazole) and the regular input of ww increased the concentrations of *sul1* and *sul2* resistance genes in irrigated soils relative to soils under rain-fed agriculture.

7.4 Mechanisms of Spread and Maintenance of ARGs

There exist three major mechanisms of HGT within and among bacterial populations; all three of them contribute significantly to the horizontal dissemination and persistence of ARGs in the environment.

7.4.1 Conjugative Transfer

The conjugative plasmid systems are the largest and most widely distributed subfamily of type IV secretion systems, with systems described for most species of the *Bacteria* and some members of the *Archaea* (Alvarez-Martinez and Christie 2009). The overall process of conjugative DNA transfer can be dissected into three biochemical reactions: DNA substrate processing, substrate recruitment, and translocation (Alvarez-Martinez and Christie 2009; Christie et al. 2005; Schröder and Lanka 2005; Ding et al. 2003; Pansegrau and Lanka 1996). In the DNA processing reaction, DNA transfer and replication (Dtr) proteins initiate processing by binding a cognate origin of transfer (*oriT*) sequence on the conjugative element. The Dtr proteins include a relaxase and accessory factors (for some plasmid systems, such as the broad-host-range plasmid pIP501, no accessory factors have been found so far (Kurenbach et al. 2006; Kopec et al. 2005)) and when bound to *oriT*, the resulting DNA–protein complex is termed the relaxosome (Alvarez-Martinez and Christie 2009). Accompanying the nicking reaction, the relaxase remains bound to the 5'-end of the transferred plasmid strand (T strand). The bound relaxase, probably together with other relaxosome components, mediates recognition of the DNA substrate by a cognate T4SS. The relaxase guides the T strand through the translocation channel. In the recipient cell, the relaxase catalyzes the re-circularization of the T strand and may also be involved in second strand synthesis or recombination into the chromosome (Alvarez-Martinez and Christie 2009; César et al. 2006; Draper et al. 2005). The self-transmissible plasmids are only one of the two major subgroups of conjugative elements. The second group of conjugative elements, originally denominated "conjugative transposons" and more recently termed Integrating Conjugative Elements (ICEs), is also present in many bacterial and archaeal species (Alvarez-Martinez and Christie 2009; Juhas et al. 2008, 2007; Burrus and Waldor 2004; Burrus et al. 2002). These elements are excised from the chromosome through the action of a recombinase/excisionase complex and followed by the formation of a circular intermediate. Then, the circularized intermediate is processed at *oriT* in the same way as described for conjugative plasmids. In the recipient cell, ICEs reintegrate into the chromosome by homologous recombination or through the action of an integrase encoded by the ICE itself (Alvarez-Martinez and Christie 2009). Conjugative plasmids and ICEs are recruited to the transfer machinery through interactions between the relaxosome and a highly conserved adenosine triphosphatase (ATPase) termed the type IV coupling protein. This protein interacts with the translocation channel, which consists of the mating pair formation proteins (Alvarez-Martinez and Christie 2009; Schröder and Lanka 2005; Christie 2004). In gram-negative bacteria, the mating pair formation proteins build the secretion channel as well as a pilus or other surface filaments to achieve attachment to target cells (Alvarez-Martinez and Christie 2009; Christie and Cascales 2005; Lawley et al. 2003). In gram-positive bacteria, surface adhesins rather than conjugative pili mediate attachment (Alvarez-Martinez and Christie 2009; Grohmann et al. 2003); for the majority of gram-positive bacteria, the origin and nature of the surface adhesins or other surface located factors involved in attachment and/or recognition of the recipient cell have not been elucidated so far.

7.4.2 Transformation

DNA transformation is based on the uptake of free DNA from the environment and, therefore, does not rely on MGEs; it is only encoded by the acceptor bacterium. Natural competence is the developmental state of the bacterium in which it is capable of taking up external DNA and of recombining this DNA into the chromosome, thereby undergoing natural transformation (Seitz and Blokesch 2013). A wide variety of bacterial species can develop natural competence and consequently take up external DNA (for recent reviews, see Chen and Dubnau 2004; Lorenz and Wackernagel 1994). The principal steps to take up the external DNA include:

(i) binding of double stranded (ds) DNA outside the cell to a (pseudo-) pilus structure elaborated by the acceptor cell; (ii) extension and retraction of the pilus, driven by ATP-dependent motor proteins, that mediate the uptake of the ds DNA through the secretin pore spanning the outer membrane of the acceptor cell; (iii) binding of the ds DNA by the DNA-binding protein ComEA, which takes place in the periplasmic space; (iv) transport across the inner membrane by ComEC concomitantly with the degradation of one DNA strand by a so far unidentified nuclease; (v) single stranded (ss) DNA reaches the cytoplasm and is immediately protected against degradation by DNA processing protein A (DprA) and a single strand binding protein; and (vi) DprA recruits RecA, which catalyzes homologous recombination within the genomic DNA of the acceptor cell (Seitz and Blokesch 2013).

7.4.3 Transduction

Transduction is the process in which bacterial DNA gets erroneously packaged into the heads of bacteriophages. When the phage infects another bacterial cell, the packaged DNA is incorporated into the new host's genome (Roberts and Mullany 2010).

Bacteriophages are highly specific to their bacterial hosts, able to infect even after significant periods of hiatus, and reproduce rapidly when their ecosystem allows to. The viral genome is stored encapsulated in the protein "head" until the virion attaches itself to a bacterial host cell for genome insertion (Brabban et al. 2005). This attachment process is highly specific involving the precise recognition of cell surface components, such as proteins and lipopolysaccharide elements, by specialized bacteriophage recognition structures. When the viral genome has been introduced into the host, the lifecycles of the lytic and temperate bacteriophages diverge determined by both the bacteriophage's biology and the cellular environment. Lytic bacteriophages only reproduce via a lytic lifecycle, whereas temperate bacteriophages can either reproduce lytically or enter lysogeny. Therefore, bacteriophages are historically classified based on their lifecycle (lytic vs. temperate), although finer subdivisions are based on their morphological characteristics (tailless vs. tailed), nature of the genome (e.g., DNA vs. RNA, single-stranded vs. double-stranded), and other factors (Brabban et al. 2005). Nowadays, it has become more common to classify bacteriophages at a molecular level through the comparison of specific genes with the well-characterized T-4-like bacteriophages (Tétart et al. 2001).

7.5 Monitoring of Occurrence of Antimicrobial Resistance and Spread

Based upon the knowledge that ARGs are widespread in aquatic and terrestrial environments, there is a need for the development and application of molecular methods to investigate the occurrence, spread, and fate of ARGs in the environment.

So far, the methods used for detection, typing, and characterization of ARGs have covered, but have not been limited to specific and multiplex polymerase chain reaction (PCR), real-time PCR, DNA sequencing, and hybridization-based techniques, including microarray (Zhang et al. 2009).

7.5.1 DNA Hybridization

Molecular hybridization has been used to detect the presence/absence of specific ARGs for more than 30 years (Zhang et al. 2009; Mendez et al. 1980). Many improvements have been made on molecular hybridization, in particular in probe design and synthesis, so that the technique, especially Southern blot, is still often applied to distinguish different ARGs of one group (e.g., *tet* genes) from each other (Levy et al. 1999; Robert and Kenny 1986) or to prove the presence of specific ARGs in certain environments (Zhang et al. 2009; Malik et al. 2008; Agerso and Petersen 2007).

With a number of non-radiolabeled systems commercially available, radioactive labeling of probes is no longer a reasonable option. As an important non-radiolabeled method, fluorescence in situ hybridization (FISH) has been successfully established and implemented for clinical detection of antimicrobial resistance. The application of the FISH technique has been described for the rapid identification of macrolide resistances due to ribosomal mutations (Rüssmann et al. 2001). Werner and coworkers have performed a study to assess the reliability of FISH for clinical detection of linezolid-resistant enterococci. They report that FISH, along with DNA probes containing locked nucleic acids with point mutation, demonstrated 100% sensitivity for the detection of phenotypic linezolid resistance and even allowed detection of a single mutated 23S rRNA gene allele in phenotypically linezolid-susceptible enterococci (Werner et al. 2007). Although FISH has been often applied for clinical detection of antibiotic resistance, only few reports so far exist about its use in the identification of bacteria harboring ARGs in environmental samples (Zhang et al. 2009).

7.5.2 PCR (Simple and Multiplex PCR)

PCR assays have been widely applied in both pure cultures and environmental samples for the detection of ARGs encoding resistances to aminoglycosides (Mohapatra et al. 2008; Taviani et al. 2008), chloramphenicol (Dang et al. 2008), β-lactams (Taviani et al. 2008), macrolides (Chen et al. 2007; Patterson et al. 2007), sulfonamides (Agerso and Petersen 2007), tetracycline (Jacobs and Chenia 2007), vancomycin (Caplin et al. 2008), and other antibiotics as summarized in Zhang et al. (2009). Environmental target DNA or RNA at low concentrations can be amplified and detected by PCR. However, false-positive results sometimes occur in the PCR assays. These false-positive results can be avoided by application of a second method, namely Southern hybridization of PCR products labeled and used as DNA probes on plasmid or genomic DNA samples from strains putatively harboring antibiotic resistance target genes (Zhang et al. 2009; Akinbowale et al. 2007; Ahmed et al. 2006). In addition, DNA sequencing is another common method to verify the PCR products of different ARGs (Thompson et al. 2007). To save time and effort, multiplex PCR methods have been developed and often used for simultaneous detection of various environmental ARGs (summarized in Zhang et al. 2009). With various primer pairs in the same PCR system, multiplex PCR can amplify the DNA fragments of several ARGs at the same time (Gilbride et al. 2006). However, the method also has its drawbacks due to compromise conditions applied to simultaneously amplify different ARGs. This can include inhibition of the amplification of some genes and/or generation of false-positive results. Therefore, the cycling and reaction conditions of multiplex PCRs have to be carefully adjusted prior to the application on complex environmental samples. Despite these drawbacks, multiplex PCR is still considered a rapid and convenient method for the detection of multiple ARGs in isolated bacteria or environmental DNA (Zhang et al. 2009; Agersø et al. 2007; Gilbride et al. 2006).

7.5.3 Quantitative PCR

The quantitative real-time PCR (qPCR) is usually used to quantify target DNA on basis of the principle that the initial target gene concentration can be estimated by determining the number of amplification cycles to obtain a PCR product concentration above a certain defined threshold. Among the fluorescent reagents developed for qPCR, SYBR Green is the most common method used for the amplification of ARGs (summarized in Zhang et al. 2009). Recently, the technique has been frequently used to quantify ARGs in environmental samples, including *tet* genes in beef cattle farms (Yu et al. 2005), groundwater (Mackie et al. 2006), river sediments (Pei et al. 2006), sewage treatment plants (Auerbach et al. 2007), *sul* genes in river sediments (Pei et al. 2006), *npt* genes in river water (Zhu 2007) and *qnr* genes in water and soil samples (Dalkmann et al. 2012; Siebe et al., unpublished data).

TaqMan probe has also been applied to quantify *tetO*, *tetW*, and *tetQ* (Smith et al. 2004), *vanA*, *mecA* and *ampC* genes (Volkmann et al. 2004) in ww and *sul* genes in ww-irrigated soils and water samples (Siebe et al., unpublished data; Dalkmann et al. 2012).

qPCR is not only used for the quantitative analysis of the distribution of ARGs in the environment, but also often applied to study the effects of environmental factors or treatment processes on removal of ARGs (Zhang et al. 2009), such as *tet* genes (Auerbach et al. 2007; Mackie et al. 2006), *sul* genes (Pei et al. 2006), and *erm* genes (Chen et al. 2007). Through qPCR, Mackie and coworkers found that the detection frequency of *tetM*, *O*, *Q*, and *W* genes was much higher in wells located closer to and down gradient from swine lagoons than in wells more distant from the lagoons (Mackie et al. 2006). Also by qPCR, Chen and colleagues observed that the abundance of *erm* genes in composted swine manure samples was significantly lower than those in swine manure, indicating that manure storage probably decreases the persistence of environmental ARGs (Zhang et al. 2009; Chen et al. 2007).

7.5.4 DNA Microarray

The DNA microarray technique is a genomic analysis technique with high throughput, high speed, and high dedicacy. For detection of antibiotic resistances, DNA microarrays can provide detailed, clinically relevant information on the isolates by detecting the presence or absence of a large number of ARGs simultaneously in a single assay (Zhang et al. 2009; Gilbride et al. 2006). Microarrays allow detection of antibiotic resistance determinants within several hours and can be used as a timesaving, convenient method supporting conventional resistance detection assays (Antwerpen et al. 2007). Although microarrays have been successfully applied to assess the antibiotic resistances of clinical samples, only few reports exist applying this technique to detect ARGs in environmental samples (Zhang et al. 2009). The first factor hampering its application in environmental samples is the low detection limit of the method, but microarray coupled with PCR can enhance the detection limit for environmental ARGs (Gilbride et al. 2006). Patterson and coworkers designed a microarray system based on PCR amplification of 23 different *tet* genes and ten different *erm* genes to screen environmental samples for the presence of these ARGs (Patterson et al. 2007) and found that *tetW*, *O*, and *Q* were the most abundant ARGs found in swine fecal samples, and *ermV* and *ermE* were the most frequent ones detected in farm and garden soil samples (Zhang et al. 2009; Patterson et al. 2007). Another reason for the poor application of microarray in most environmental samples is the complexity of the samples and the required pretreatment. The presence of contaminants, such as humic substances and humic acids in environmental samples, inhibits DNA extraction and/or target gene amplification, therefore, a complicated pretreatment of environmental samples is necessary and crucial to get satisfactory detection results (Zhang et al. 2009; Call 2005). However, the microarray technique can provide a detailed description of bacterial antibiotic resistance and can reveal global changes in the expression of ARGs in response to environmental changes (Gilbride et al. 2006; Call et al. 2003). The information on gene expression levels can provide insights into the mechanisms of antibiotic resistance and into general responses of ARGs to environmental changes (Zhang et al. 2009).

7.5.5 Biosensors

The development of biosensors and their application for the detection of antimicrobials in environmental samples have made fundamental progress in the past years. Reder-Christ and Bendas recently summarized the applications of biosensors in the field of antibiotic research in an interesting review (Reder-Christ and Bendas 2011). In general, there are two main principles for the recognition of antimicrobials by biosensor systems. The first one comprises the widespread use of immobilized RNA or DNA aptamers as recognition elements (so-called aptasensors) (Rowe et al. 2010; Zhang et al. 2010; de-los-Santos-Alvarez et al. 2009; Kim et al. 2009). Their sensitivity is comparable to that of antibodies. The second principle of antibacterial recognition for bio-sensing is given by antibody-mediated binding processes. Those immunosensors have been widely used for antibacterial detection (summarized in Reder-Christ and Bendas 2011; Cha et al. 2011; Dong et al. 2009; Giroud et al. 2009; Rebe Raz et al. 2008; Ionescu et al. 2007; Ferguson et al. 2002). It is possible either to immobilize antimicrobial-specific antibodies at the sensor surface to directly detect the binding of the antimicrobial or to invert the assay and detect the binding of antibody-spiked samples onto immobilized antimicrobials in terms of a competitive assay (Reder-Christ and Bendas 2011). In summary, biosensors are comparable to conventional methods with respect to sensitivity and specificity of antimicrobial detection and thus fulfill international regulatory requirements. As biosensors represent fast, simple, and cost-efficient methods that can be used without additional sample preparation, they offer large advantages compared to conventional analytical techniques and will, therefore, hold great promises for a wide application in the near future (Reder-Christ and Bendas 2011).

7.6 Risk Assessment of Antibiotic Resistance Spread

Several reviews with the intention to assess the impact of the occurrence and spread of clinically relevant bacteria and/or ARGs in the environment on human health have been published recently. Most of them deal with ww habitats (Varela and Manaia 2013), ww treatment plants (Rizzo et al. 2013), and aquaculture (Smith 2008). Bacteria in ww habitats play a plethora of different roles; the beneficial ones include their participation in the waste degradation processes (those will not be reviewed here) and the harmful ones with potential impact on human health include the carriage and potential spread of virulence genes and ARGs.

Several chemical contaminants present in the ww (heavy metals, disinfectants and antibiotics) may select for these bacteria and/or their genes (Varela and Manaia 2013). Worldwide studies showed that treated ww can contain antibiotic-resistant bacteria or genes encoding virulence or antimicrobial resistance, demonstrating that treatment processes may fail to eliminate efficiently these bio-pollutants. The contamination of the surrounding environment, such as rivers and lakes receiving ww treatment plant effluents, has also been documented in several studies (summarized in Varela and Manaia 2013). The current state of the art suggests that still only part of the antibiotic resistance and virulence potential in ww is known, as well as only some of the factors that trigger their maintenance and spread in the environment (Varela and Manaia 2013). Although there is much uncertainty concerning the transmission of ARGs or virulence genes from ww bacteria to human commensal and pathogenic bacteria, the current knowledge recommends the application of the precautionary principle regarding the discharge and particularly the reuse of ww. Varela and Manaia recommended going one step further in relation to the current recommendations (APHA 1995; Council Directive 91/271/EEC 1991). They urgently recommended the regular detection and quantification of ARGs or virulence genes, as well as the presence of heavy metals or antimicrobial residues in ww-impacted areas. Furthermore, the assessment of negative impacts due to long-term exposures to the discharge of treated ww should be a priority (Varela and Manaia 2013). The accumulation of apparently very small concentrations of harmful bacteria, genetic determinants encoding for ARGs or virulence genes or micropollutants may generate measurable and relevant effects after some years as demonstrated by Dalkmann et al. (2012) and Aleem et al. (2003). It is also important to consider that risk assessments carried out in one world region cannot be simply used or transposed to regions with distinct geological and climate conditions, since it cannot be taken for granted that conditions such as temperature, precipitation, insolation, or properties of the soil will not interfere with the accumulation of potential hazardous pollutants discharged by ww treatment plants (Varela and Manaia 2013).

Recently Rizzo and colleagues published a comprehensive review on UWTPs as hotspots for antibiotic-resistant bacteria and ARG spread into the environment (Rizzo et al. 2013). They concluded that in spite of intense efforts made over the past years to find solutions to control antibiotic resistance spread in the environment, there are still important gaps to fill in. In particular, it is important to: (i) improve risk assessment studies to allow accurate estimates about the maximum abundance of antibiotic resistant bacteria in UWTP effluents that would not pose risks for human and environmental health and (ii) elucidate the factors and mechanisms that drive maintenance and selection of antibiotic resistance in ww habitats (Rizzo et al. 2013). The final objective should be to implement ww treatment technologies that are able to assure the production of UWTP effluents with an acceptable level of antibiotic resistant bacteria (Rizzo et al. 2013). In the opinion of Rizzo and colleagues, one of the most important questions to address to advance towards ww treatment plants generating effluents with an acceptable level of bio-pollutants would be the setup of a public database with information on ww habitats such as: (i) antibiotic resistant bacteria and their phylogenetic lineages; (ii) ARG and respective nucleotide sequences and genetic environment as well as (iii) sampled sites and their major characteristics. Such a public database would represent a valuable tool to a better understanding of antibiotic resistance ecology and control measures (Rizzo et al. 2013).

Recently, Smith published an interesting review on antimicrobial resistance in aquaculture. Appropriate antimicrobial therapy represents one of the most effective management responses to emergencies associated with infectious disease epizootics. The use of these agents, however, has the potential to increase the frequencies of bacterial resistance and this would result in a negative impact on the subsequent use of these antimicrobials to control infectious disease in aquaculture. It is also possible that the enrichment of resistant bacteria or ARGs could negatively influence the use of antimicrobials to control diseases in humans and other land-based animals (Smith 2008). Attempts to apply formal risk analysis to this problem have failed due to the extreme diversity of aquaculture and the general shortage of relevant data. Smith argued that not only do we lack relevant data to perform this exercise but we also lack validated methods to collect those data in the first place (Smith 2008). Due to the lack of any significant risk assessment, current attempts at risk management are focused on the development of lists of critically important antimicrobials for the various users of these agents. Smith argued that studies of gene ecology and models of gene flow in the environment are urgently needed if we should be able to evaluate this risk management approach, to predict its consequences or to generate more appropriate strategies (Smith 2008).

The two most valuable outcomes that can be expected from any risk assessment are the definition of rational, evidence-based risk mitigation strategies and the identification of the future requirements for additional research (Smith 2008). A risk assessment should enable the identification of key areas where intervention could minimize the risk. The identification of these key areas would consequently allow the development of effective risk mitigation strategies. To the extent that risk analysis can provide some estimate on the size or significance of a risk, it will also provide us the basis for a cost–benefit analysis of any intervention (Smith 2008). Smith concluded that we urgently need to develop evidence-based management strategies that will enable us to minimize the impact of bacterial resistance, selected by the aquacultural use of antimicrobials, both on the control of diseases encountered in aquaculture itself and in those encountered in humans and land-based agriculture (Smith 2008).

7.7 Conclusions and Perspectives

Bacteria resistant to antimicrobials are widespread. Humans, animals, and environmental habitats are all reservoirs where bacterial communities live that contain bacteria that are susceptible to antimicrobials and others that are resistant (Acar and Moulin 2006). Farm ecosystems offer a particular environment in which resistant bacteria and ARGs can emerge, amplify, and spread. Dissemination can occur via the food chain and via several other pathways, such as sewage and manuring of agricultural fields. Ecological, epidemiological, molecular, and mathematical approaches are currently used to study the origin and expansion of the antimicrobial resistance problem and its relationship to antibiotic usage (Acar and Moulin 2006). Prudent and responsible use of antibiotics is an essential part of an ethical approach to improving animal health, food safety, and consequently human health (Acar and Moulin 2006). The responsible use of antibiotics during research is vital, but to fully contribute to the containment of antimicrobial resistance, prudent and responsible use must also be part of good management practices at all levels of farm life (land-based and aquaculture) and human antibiotic therapy.

ARGs can flow among different biological units of different hierarchical levels, such as integrons, transposons, plasmids, clones, species, or genetic exchange communities (Baquero 2012). Baquero argued that metagenomics would be the best-suited tool to explore the presence of ARGs in all these biological and evolutionary units, and to identify possible "high risk associations." He is in favor of a multilayered metagenomic epidemiology approach which can help to understand and eventually predict and apply intervention strategies aiming to limit antibiotic resistance (Baquero 2012).

Another valuable approach would be the more frequent application of biosensors particularly destined to detect and quantify antibiotics and their degradation products in environmental samples (summarized in Reder-Christ and Bendas 2011).

The combination of both, sensitive and quantitative detection of antibiotic resistance determinants as well as of the corresponding antibiotics, would present a valuable innovative approach whose data could feed the modeling approaches that are urgently required to predict the spread of ARGs in certain habitats sufficiently well in advance to act and implement countermeasures.

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Chapter 8
Persistent Organic Chemicals of Emerging Environmental Concern

Luciana Pereira

Abstract The use of chemicals and chemical derivatives in agriculture and industry has contributed to their accumulation and persistence in the environment. Persistent organic pollutants (POPs) are among the environmental pollutants of most concern since, when improperly handled and disposed, they can persist in the environment, bioaccumulate through the food web, and may create serious public health and environmental problems. Development of an effective degradation process has become an area of intense research. The physical/chemical methods employed, such as volatilization, evaporation, photooxidation, adsorption, or hydrolysis, are not always effective, are very expensive, and, sometimes, lead to generation/disposal of other contaminants. Biodegradation is one of the major mechanisms by which organic contaminants are transformed, immobilized, or mineralized in the environment. A clear understanding of the major processes that affect the interactions between organic contaminants, microorganisms, and environmental matrix is, thus, important for determining persistence of the compounds, for predicting in situ transformation rates, and for developing site remediation. Information on their risks and impact and occurrence in the different environmental matrices is also important, in order to attenuate their impact and apply the appropriate remediation process. This chapter provides information on the fate of pesticides and polycyclic aromatic hydrocarbons (PAHs), their impact, bioavailability, and biodegradation.

Keywords Persistent organic compounds · Pesticides · Polycyclic aromatic hydrocarbons · Environmental and health impact · Bioremediation

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8.1 Introduction

Over the last several decades, the term xenobiotic has been related to environmental impact, since environmental xenobiotics are understood as substances foreign to a biological system, which did not exist in nature before their synthesis by humans. It can also cover substances which are present in much higher concentrations than are usual (El-Moneim and Afify 2010). In this context, persistent organic pollutants (POP) are persistent xenobiotics, either by broad use or by improper disposal or other unintentional releases, such as dioxins and polychlorinated biphenyls, petroleum hydrocarbons, solvents, plastics, and pesticides. They are often classified as based on the fact that they exhibited one or more of the following properties: environmental persistence and bioaccumulation, toxicity and potential risks to the human food chain, or endocrine disruption. The persistence and bioaccumulation of POP is related to the fact that they are not commonly produced by nature and, therefore, are extremely resistant to biodegradation by native flora (Rochkind-Dubinsky et al. 1987; Seo et al. 2009) compared with the naturally occurring organic compounds that are readily degraded upon introduction into the environment. The recalcitrant nature of those compounds is also related to their lack in permease needed for the transport into microbial cell, their large molecular nature making them difficult to enter microbial cell, and their highly stability and insolubility in water. However, also compounds that easily biodegrade can be classified as persistent pollutants due to their continuous release to the environment. For example, pesticide use must ensure public safety and environmental protection with regard to both the chemical itself and their potentially harmful metabolites. These recalcitrant compounds are highly toxic in nature and can affect the microbiology of aquatic and terrestrial ecosystems. They may also be hazards and carcinogenic to humans when directly or indirectly exposed, especially if they enter in the food chains. POPs include compounds such as pharmaceuticals, aromatic amines, pesticides, solvents, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs; Clarke and Smith 2011). Concern over the contamination of groundwater resources combined with the realization that engineered cleanup of contaminated sites is limited by technological and monetary constraints has led to an interest in remediation by natural attenuation (National Research Council 1994). Some microorganisms have been seen as capable of interacting chemically and physically with many hazardous chemicals, leading to structural changes or complete breaking down of the target molecule decreasing their toxicity partially or totally (Raymond et al. 2001; Wirén-Lehr et al. 2002). Some others are continually evolving new metabolism in response to the continuous exposure of a new industrial chemical introduced into the environment, developing the ability to degrade them as a result of mutations (Copley 2009; Jennifer and Wackett 2001). Mutations resulted in modification of a microbial gene so that the active site of enzymes is modified to show increased affinity to the pollutant. Certain mutations also resulted in developing a new enzymatic pathway for xenobiotic degradation. Enzymatic degradation occurs on certain groups present in the compound that are susceptible to enzymatic attack. For example, the bonds like ester, amide, or ether, present in the compounds, are first attacked leading to breaking down of compounds. In some cases, the aliphatic chains and, in aromatic compounds, the aromatic components may be targeted. Enzymes like oxygenases have been found to be more involved in biodegradation of xenobiotics. Often, it is seen that the xenobiotics do not act as a source of energy to microbes and, to be degraded, the presence of a suitable substrate to induce its breakdown is required. In another process, the xenobiotics serve as substrates and are acted upon to release energy. Therefore, biodegradation is one of the major mechanisms by which organic contaminants are transformed, immobilized, or mineralized in the environment. A clear understanding of the major roles that affect the interactions between hydrophobic organic contaminants, microorganisms, and environmental matrix is, thus, important for determining persistence of the compounds, for predicting in situ transformation rates, and for developing site remediation programs. Use of mixed population of microbes usually yields better results as different microbes attack different parts through different mechanisms, ensuring the effective breakdown, or act at different phases of biodegradation. Biodegradation of an organic chemical in natural systems may be classified as primary (alteration of molecular integrity), ultimate (complete mineralization; i.e., conversion to inorganic compounds), or acceptable (toxicity ameliorated). According to Alexander (1999), the first explanation is the most common one and is based on the fact that many enzymes act on structurally related substrates. Three types of bioremediation are predominant: natural attenuation, biostimulation, and bioaugmentation (Alexander 1999) The simplest method of bioremediation to implement is natural attenuation, where contaminated sites are only monitored for contaminant concentration to evaluate that natural processes of contaminant degradation are active and self-effective. Biostimulation is the process of providing bacterial communities with a favorable environment in which they can effectively degrade contaminants.

The intent of this chapter is to present a broad and updated overview of pesticides and PAHs, the main sources and structures, environmental impacts and risks, and their biodegradation in marine, freshwater, and soil ecosystems. The ability of indigenous microorganisms to naturally transform organic contaminants to less or nontoxic products, mitigating or eliminating contamination from the environment, and the isolation of many strains to develop efficient biotechnological approaches of local decontamination are emphasized.

8.2 Pesticides

8.2.1 Main Sources and Structure of Pesticides

Pesticide means any substance or mixture of substances intended for preventing, destroying, or controlling any pest, and pesticides are named according to the application which they are proposed for: insecticides (insects), miticides (mites), nematicides (nematodes), fungicides (fungi), bactericides (bacteria), herbicides (weeds and other plants), and rodenticides (rodents), etc. (Arias-Estévez et al. 2008; Gravilescu 2005). The term pesticide was often used in the USA in the 1950s–1960s and was adopted in 1972 by the Federal Insecticide Fungicide and Rodenticide Act (FIFRA), replacing the term economic poison (Amaro 2008). Also, in European countries, the designations *pesticide* and *plant protection* products were taken in the 1950s, in the course of Phytopharmacy ISA in 1955 and 1956 (Amaro 2008).

The use of pesticides has a long data, for example, Greek and Roman civilizations used sulfur dust to control insects. In the nineteenth century, Paris green and kerosene were commonly used to combat against potato beetle. Until World War II, used-up products were of organometallic or inorganic nature. Since World War II, plant breeding, land improvement, and the use of organic fertilizers and pesticides have risen due to increasing primary production (Carlier et al. 2010). The development of organic pesticides, such as dichlorodiphenyltrichloroethane (DDT), has also controlled some pests namely typhoid fever and malaria in Europe and the USA, but many were banned due to severe environmental effects. Though organic compounds are still in use, currently, the research of new pesticides less harmful to the environment, modeled from natural pesticides, such as pyrethroid (synthetic compounds similar to pyrethrins) and natural insecticides, synthesized by plants, has been proposed. There are many different pesticide products available, containing almost a 1,000 types of active ingredients, making it difficult to deduct their full range of environmental impacts. Many pesticide compounds are hydrophobic or moderately hydrophobic with a complex chemical composition that is very different from hydrocarbons and their derivatives. The main classes of pesticides consist of organochlorines (e.g., DDT, atrazine, diuron, alachlor, metolachlor, mecocrop), organophosphates (OPs; e.g., diazinon, malathion, parathion), carbamates (e.g., carbofuran, aldicarb, carbaryl), and pyrethroids (e.g., fenpropathrin, deltamethrin, cypermethrin; Diez 2010; Laabs et al. 2002; Singh and Walker 2006). Figure 8.1 shows the chemical structure of some typical pesticides.

Worldwide, each year about 3 million tons of pesticides are used, formulated from about 1,600 different chemicals (Horrigan et al. 2002). Some common household chemicals are also technically pesticides, for instance, bug repellents, household disinfectants, and pool chemicals. Consequently, pesticides are present not only in rural areas, but also in urban areas. Pesticide residues and their transformation products are frequently found in groundwater and surface water. Therefore, they constitute a class of compounds of high concern at local, regional, national, and global scales (Lewis et al. 1988; Planas et al. 1997; Fatoki and Awofolu 2005; Westbom et al. 2008). Pesticide residues in soil, ground, and superficial water of different countries have been identified and evaluated (Table 8.1).

Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine] is one of the most found pesticides in rivers, streams, and groundwater and is an environmentally prevalent s-triazine-ring herbicide through its global use to control, by photosystem II inhibition, pre- and postemergence broadleaf and grassy weeds in major crops such as maize, sorghum, and sugarcane (US Environmental Protection Agency (EPA) 2001; Cox 2001; Ribeiro et al. 2005). 2,4-Dichlorophenoxyacetic acid

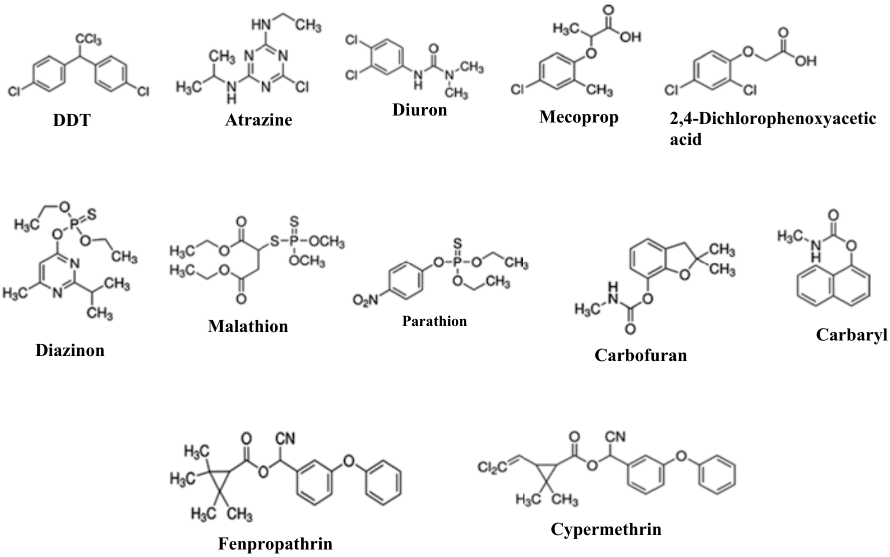


Fig. 8.1 Molecular structures of some typical organochlorines, organophosphates (OPs), carbamates, and pyrethroids pesticides

(2,4-D) is also one of the most widely used herbicides throughout the world (Boivin et al. 2005; Mangat and Elefsiniotis 1999). 2,4-D belongs to a group of chemicals known as phenoxyalkanoic herbicide, which are potentially toxic to humans. The herbicide is widely used to control broad leaf weeds and grasses in crops, and has been frequently detected in groundwater supplies in Europe and North America (Boivin et al. 2005). 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) also belongs to the phenoxyalkanoic herbicides and is a component of Agent Orange, that was widely used as a defoliant.

8.2.2 Risks and Impact of Pesticides

Pesticides have become widely accepted as an integral part of modern farming for the control of insects, weeds, and crop diseases. The first preoccupations about their use were limited to the acute oral, dermal, and inhalation toxicity, and eye and skin irritation. Ecotoxicological nature was restricted to birds, fish, bees, and other beneficial organisms. It is currently evident, however, that their broad-spectrum insecticidal activity, long persistence in the environment, and tendency to bioaccumulate along food chains have caused significant environmental problems, which are forcing many farmers and agricultural policy makers to rethink the way in which pesticides are used in modern food production processes (Amaro 2008). The effective persistence of pesticides in soil varies from a week to several years depending upon structure and properties of the pesticide and availability of moisture and nutrients in

Table 8.1 Pesticides identification and evaluation in different countries and sources, in chronologic order

Country	Detected pesticides	Contaminated source	References
Portugal	Lindane, atrazine, simazine, dimethoate, metribuzin, endosulfan, prometryn, metolachlor	Groundwater	Barceló (1991)
Canada	Alachlor, metalachlor, atrazine, metribuzin, cianazina	Superficial	Goss et al. (1998)
Netherlands	Atrazine, simazine, dieldrin, propazine, lindane (α+β-HCH)	Groundwater	Maanen et al. (2001)
Brazil	Alachlor, atrazine, chlorothalonil, endosulfan, simazine, metribuzin, monocrotofos, malathion, chlorpyrifos, metribuzin, etc.	Superficial, river, lakes	Laabs et al. (2002)
Caribbean island of Martinique	Chlordecone, aldicarb sulfoxide, aldicarb sufone, ametryn, simazine	Rivers and their coastal plumes	Bocquené and Franco (2005)
Greece	Lindane (γ-BHC), chlorpyrifos, propachlor	Groundwater	Karasali et al. (2002)
Portugal	Quinalphos Paraquat	Groundwater	Teixeira et al. (2004)
England	Lindane, heptachlor, Aldrin, γ-Chlordane, endosufan, dieldrin, endrin, 2,4′-DDT, etc.	Superficial	Fatoki and Awofolu (2005)
South Africa	Lindane (α+β-HCH), heptachlor, aldrin, γ-Chlordane, endosufan, dieldrin, endrin, 2,4′-DDT, etc.	Superficial	Fatoki and Awofolu (2005)
Caribbean island of Martinique	Chlordecone	Marine organisms	Coat et al. (2006)
Hungary	Acetochlor, atrazine, carbofuran, diazinon, fenoxycarb, metribuzin, phorate, prometryn, terbutryn, trifluralin	Superficial	Maloschik et al. (2007)
USA	27 pesticides (data from 10 years of study)	Groundwater streams	Gilliom (2007)
Netherlands	27 different pesticides	Groundwater	Schipper et al. (2008)
Spain	Atrazine, desethylatrazine, simazine, desethylsimazine, metolachlor, desethylterbuthylazine, terbuthylazine, metalaxyl	Superficial groundwater	Hildebrandt et al. (2008)
China	Organochlorine pesticides	Surface soil	Jiang et al. (2009)
Iran	Diazinon	Rice paddies	Arjmandi et al. (2010)

soil (Gravilescu 2005). For instance, the highly toxic phosphates do not persist for more than 3 months while chlorinated hydrocarbon insecticides are known to persist many years. Organochlorine insecticides, for example, could still be detectable in surface waters 20 years after their use had been banned (Jiang et al. 2009; Mehmood et al. 1996; Li et al. 2008; Shegunova et al. 2007). For example, the half-life of

DDT is 2–15 years and 4 years for chlordane. Therefore, DDT fungicide has been banned for use in agriculture as well as in public health department. Once a persistent pesticide has entered the food chain, it can undergo "biomagnification," i.e., accumulation in the body tissues of organisms, where it may reach concentrations many times higher than in the surrounding environment (Brewer 1979). In many circumstances, pesticide contamination of soil and water resources is more likely to result from point sources (farms where pesticides are handled) than from diffuse sources subsequent to the application to crops in the field. However, pesticides can migrate through soil, groundwater, and air, drifting on to neighbor property, posing serious environmental and human health risks miles away from the treated fields (Park et al. 2002; Rudel et al. 2003). Extensive quantities of pesticides in soil have a direct effect on soil microbiological aspects, which in turn influence plant growth. Continued application of large quantities of pesticides may cause an adverse effect on soil fertility and crop productivity; inhibition of N_2-fixing soil microorganisms, suppression of nitrifying bacteria, and consequent alterations in nitrogen balance of the soil; inhibition of cellulolytic and phosphate solubilizing soil microorganisms; interference with ammonification in soil; adverse effect on mycorrhizal symbioses in plants and nodulation in legumes; and alterations in the rhizosphere microflora, both quantitatively and qualitatively.

The toxic effects produced by pesticides are largely determined by the biological activity of their chemical ingredients and the magnitude of dose received by the organism. Definitely, extremely small percentages of the pesticide applied in the field, less than 0.1 % in many cases, actually reaches the target pest, the rest enters the environment gratuitously, contaminating soil, water, and air, as well as pollinators, several soil-dwelling insects and microbes, birds, and finally, animals in the food chain (Pimentel 1995). 2,4-D is quite susceptible to bacterial degradation and generally does not persist for long in the environment except under adverse conditions, such as low soil pH and low temperature which increase its longevity in soil. On the other hand, 2,4,5-T is relatively more resistant to microbial degradation and tends to persist in the environment. It has been blamed for serious illnesses in many veterans of the Vietnam War, where they were exposed to Agent Orange. 2,4-D and 2,4,5-T were also reported to be mutagenic agents. Furthermore, during the manufacture of 2,4,5-T, contamination with low levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) occurred which is very toxic to humans.

National governments introduced residue limits and guideline levels for pesticide residues in water when policies were implemented to minimize the contamination of groundwater and surface water. However, even now residues of pesticides used in agriculture can be detected in aquatic environments, nutrients from fertilizers, or sediments from soil erosion (Carlier et al. 2010). Organochlorine pesticides are generally banned in most industrialized countries although they are still used in developing countries. For example, the USA prohibited the use of DDT in 1972, but continued to export over 18 million kg annually to developing countries for many years (Lear 1997). The book *Silent Spring* written in 1962 by Rachel Carson (Carson et al. 2002) facilitated the ban of the DDT in 1972 in the USA. The scientist wrote down her observations of nature and pointed out the sudden dying of birds caused by indiscriminate spraying of pesticides including DDT. This book became a landmark on the use of pesticides, stimulating public concern on their impact on health and the environment.

Even though the use of chlordecone has been prohibited since 1993, it was detected in 2002 at nearly all of the monitored sites of the coastline of the Caribbean island of Martinique by Bocquené and Franco (2005). Metabolites of aldicarb (a carbamate nematicide), and two triazines herbicides (ametryn and simazine), were also identified. The concentrations of carbamates and triazines detected in the water and sediment samples from Martinique are comparable to those reported for mainland France. The high levels of chlordecone detected are of particular concern since it is a carcinogenic and bioaccumulating pesticide with a strong endocrine disruption potential. High levels of chlordecone were also detectable in a number of aquatic species of Martinique (up to 386 μg kg^{-1} chlordecone in locally consumed tilapia) by Coat et al. (2006). Measured values were impressively high compared to those reported for other regions around the world. Although atrazine has been banned or concentration limits regulated in several countries, higher concentrations of it, as well of their biodegradation products, have been still obtained in surface waters (Parra et al. 2004; Protzman et al. 1999; Ralebits et al. 2002). In lakes and groundwater, atrazine and its breakdown products can persist for decades (Cox 2001). Comparing the acute toxicity of 40 herbicides exerting nine different modes of action on the green alga, Ma et al. (2006) found that photosynthesis was the most sensitive process, and atrazine was among the most toxic herbicides tested. Atrazine has also been suggested to be a potential disruptor of normal sexual development in male frogs (Hayes et al. 2002, 2003; Murphy et al. 2006) as well as to alter some aspects of the immune response (Christin et al. 2003, 2004). Triazinic compounds, such as atrazine, simazine, propazine, and similarly their metabolites, namely 2-hydroxyatrazine, diaminochlorotriazine, deethylatrazine, and deisopropylatrazine, were shown to induce mammary gland tumors in Sprague-Dawley female rats (Stevens et al. 1994). Atrazine is also classified as a possible human carcinogen (Dunkelberg et al. 1994; Loprieno et al. 1980; Ribas et al. 1995; Van Leeuwen et al. 1999). The International Agency for Research on Cancer (IARC 1983) has included atrazine in the group 2B carcinogen. The maximum contaminant level (MCL) for atrazine in drinking water established by the USEPA (1990) is 3.0 μg L^{-1}. The urine samples collected between 2002 and 2006 from pregnant women (before the 19th week of gestation) showed the presence of atrazine residues (Chevrier et al. 2011). The authors suggest that environmental atrazine exposure may impair fetal growth. They also measured urinary concentrations of other triazine metabolites and found higher detection frequencies and levels for most of them than for atrazine or atrazine mercapturate.

The chlorobenzene, hexachlorobenzene (HCB), extensively used as a fungicide, is known as being a hepatic carcinogen (Mehmood et al. 1996). Pentachlorophenol (PCP), a metabolite of HCB and pentachlorobenzene (PCB), is also an environmental contaminant and carcinogen which is widely used as preservative in leather, canvas, and timber (Butte 1987). In humans, the toxicity and carcinogenicity of HCB, PCB, and PCP have been long observed (Carthew and Smith 1994; Choudhury et al.

1986; Handa et al. 1983). The nematocide 1,2-dibromo 3-chloro propane1, being relatively mobile in soils with high groundwater recharge rates and fairly persistent, has been classified as a carcinogenic and as a cause of sterility in human males (Babich et al. 1981). Most synthetic OP compounds, such as parathion and methyl parathion, are highly toxic and are powerful inhibitors of acetylcholine esterase, a vital enzyme involved in neurotransmission, in the form of acetylcholine substitutes (Bakry et al. 1988; Costa et al. 2008; Bjørling-Poulsen et al. 2008). OPs may also cause delayed neurotoxic effects which are not due to acetylcholine esterase inhibition via phosphorylation. The risk of physiological damage in nontarget organisms caused by these pesticides is extremely high since acetylcholine esterase is present in all vertebrates, including humans (Yang et al. 2007). Once 80 % of the enzyme is inactivated, usually within 4 days of exposure, potentially lethal symptoms can be observed, including neck muscle weakness, diarrhea, and respiratory depression (Grimsley et al. 1997). On the other hand, the new fungicide ametoctradin, which was evaluated by the Joint Food and Agriculture Organization (FAO)/World Health Organization (WHO) Meeting on Pesticide Residues (JMPR) for the first time in 2012, causes no or minimal effects at limited doses in the extensive suite of repeated-dose mammalian toxicity.

The Thematic Strategy on the sustainable use of pesticides was adopted in 2006 by the European Commission (EU), together with a proposal for a Framework Directive on the sustainable use of pesticides. It aims to fill the current legislative gap regarding the use phase of pesticides at the EU level through setting minimum rules for their use in order to reduce risks to human health and to the environment.

The fate of pesticides will be further discussed in the succeeding chapters: the environment and human health impact of insecticides in Chap. 8 (Insecticides: Impact on the Environment and Human Health, M. Shafiq Ansari, Maher Ahmed Moraiet and Salman Ahmad, India) and organochlorine pesticide residues in foodstuffs in Chap. 13 (Organochlorine Pesticide Residues in Foodstuffs, Fish, Wildlife and Human Tissues from India: Historical Trend and Contamination Status, V. Dhananjayan, B. Ravichandran, India.).

8.2.3 Biodegradation of Pesticides

Different pesticides have been shown to promote or inhibit the growth of certain soil microorganisms in either aerobic or anaerobic conditions (Lo 2010). Definitely, microbes have a great effect on the persistence of most pesticides in soil (Krutz et al. 2010; Surekha et al. 2008). Though pesticides in soil and water can be degraded by biotic and abiotic pathways, microbial degradation is the principle mechanism which prevents the accumulation of these chemicals in the environment (Briceño et al. 2007; Krutz et al. 2010). Among the microbial communities, bacteria, and fungi are the main transformers and pesticide degraders (Diez 2010; Sene et al. 2010). Table 8.2 summarizes various publications on microbial degradation of different pesticides. Atrazine, previously considered to be nonmetabolizable by the majority of soil bacteria due to its moderate water solubility (33 mg L^{-1} at 20 °C)

Table 8.2 Pesticides biodegradation by different microbial strains

Pesticide	Microorganisms and enzymes	Main results	References
Atrazine	A mixed enrichment culture of microorganisms	Mineralization initiated with formation of the metabolite hydroxyatrazine; after 145 days, soil extractable hydroxyatrazine declined to zero and no metabolites were recovered	Assaf and Turco (1994)
Atrazine Alachlor	Microbial consortium isolated from contaminated soils	Consortium exhibited a unique degradation pattern being alachlor degradation dependent on atrazine degradation; the average half-life ($t_{1/2}$) was 7.5 days for atrazine and 11 days for alachlor; five strains were identified: *Alcaligenes xylosoxydans* sp., *Alcaligenes xylosoxydans* sp., *Pseudomonas putida*, *Pseudomonas marginalis* *Providencia rustigianii*	Chirnside et al. (2007)
Atrazine Alachlor	Extracellular fungal enzyme solution derived from the white-rot fungus, *Phanerochaete chrysosporium*	32 % of atrazine and 54 % of alachlor biodegradation at the rate of 0.0882 d^{-1} and 0.2504 d^{-1}, respectively; the half-life ($t_{1/2}$) was 8 days for atrazine and 3 days for alachlor	Chirnside et al. (2011)
Atrazine 2,4-Dichlorophenoxyacetic acid	*Hymenoscyphus enicae* 1318 *Oidiodendron griseum* *Gautieria crispa* 4936 *Gautieria othii* 6362 *Radiigera atrogleba* 9470 *Rhizopogon vinicolor* 7534 *Phanerochaete chrysosporium* 1767 *Sclerogaster pacificus* 9011 *Trappea darkeni* 8077	Biodegradation dependent on the fungus and the herbicide, but not correlated to fungal ecotype; *P. chrysosporium* had the highest level of 2,4-D mineralization and degradation under all nitrogen conditions; *H. enicae* and *O. griseum* were the best at degrading atrazine	Donnelly et al. (1993)
Atrazine	Mixed bacterial consortium	Sodium citrate and sucrose lead to highest atrazine biodegradation rate (87.22 %); atrazine biodegradation rate decreased more quickly by the addition of urea (26.76 %) compared to ammonium nitrate; pH of 7.0 was the optimum for atrazine biodegradation	Dehghani et al. (2013)
Atrazine	*Pseudomonas* sp. isolated from a herbicide spill site	*Pseudomonas* sp. strain ADP metabolized atrazine as its sole nitrogen source; nongrowing suspended cells also metabolized atrazine; atrazine was metabolized to hydroxyatrazine, polar metabolites, and carbon dioxide	Mandelbaum et al. (1995)

Table 8.2 (continued)

Pesticide	Microorganisms and enzymes	Main results	References
Atrazine	Soil microorganisms in the rhizosphere of *Zea mays* L. and in the bulk soil	Lower mineralization potential in bulk than in planted soil; atrazine mineralization was transiently stimulated by atrazine application, being no longer effective after 2 months of cultivation	Marchand et al. (2002)
Atrazine	*Agrobacterium radiobacter* strain J14a	Dealkylation, dehalogenation, and mineralization of the s-triazine ring when the molecule was used as a nitrogen source	Struthers et al. (1998)
Atrazine and other triazine	*Acinetobacter* sp.	Atrazine was utilized as a carbon and not as a nitrogen source; *Acinetobacter* sp. was also active on other triazine pesticides: simazine, terbutryn, cyanazine, and prometon	Singh et al. (2004)
Atrazine	Native fungal strain, identified as *Penicillium* sp.	Atrazine was degraded at a faster rate in inoculated mineral salt medium (MSM) than noninoculated MSM; within 20 days; cell-free extract of fungal mycelium degraded about 50 % of the atrazine in 96 h; four atrazine metabolites were isolated and characterized: hydroxyatrazine, 2-hydroxy-4-ethylamino-5-isopropylamino-1,3,5-triazine, 2-hydroxy-4-ethylamino-5-amino-1,3,5-triazine, 2-chloro-4,5-diamino-1,3,5-triazine, 2-chloro-4-ethyleneamino-5-(1-methyl ethyleneamino-1,3,5-triazine	Singh et al. (2008)
Atrazine	*Nocardioides* sp. strains isolated from four farms in central Canada	S-triazine degradation by whole cells or cell extracts occurs via sequential hydrolytic reactions converting atrazine to hydroxyatrazine and then to the end product N-ethylammelide. Isopropylamine, the putative product of the second hydrolytic reaction, supported growth as the sole carbon and nitrogen source; a novel s-triazine hydrolase, capable of degrading a range of s-triazine herbicides, was isolated and purified	Topp (2000a)
Atrazine	*Pseudoaminobacter* sp.	A number of chloro-substituted s-triazine herbicides were degraded, but methylthio-substituted s-triazine herbicides were not degraded; atrazine degradation occurred via a series of hydrolytic reactions initiated by dechlorination and followed by dealkylation	Topp (2000b)

Table 8.2 (continued)

Pesticide	Microorganisms and enzymes	Main results	References
Atrazine	*Pseudomonas* sp. strain ADP *Pseudaminobacter* sp., and a *Nocardioides* sp.	Bacteria hydrolytically dechlorinate atrazine, and degrade it in pure culture with comparable specific activities. The *Pseudaminobacter* and *Nocardioides* can utilize atrazine as the sole carbon and nitrogen source, whereas the *Pseudomonas* can utilize the compound only as a nitrogen source. The *Pseudomonas* and *Pseudaminobacter* mineralize the compound; the end product of atrazine metabolism by the Nocardioides is N-ethylammelide	Topp (2001)
2,4-Dichlorophenoxyacetic acid	Sequencing batch reactors	All reactors achieved practically complete removal; rates were affected by the type of supplemental substrate used (phenol or dextrose), being significantly lower (30–50 %) in the case of dextrose	Mangat and Elefsiniotis (1999)
Mecoprop	Consortium of three bacteria isolated from soil: *Alcaligenes denitrificans*, *Pseudomonas glycinea*, and *Pseudomonas marginalis*	Culture exclusively degraded the (R)-(+)-isomer of the herbicide while the (S)-(−)-enantiomer remained unaffected; single members of the consortium were able to degrade mecoprop as pure only after prolonged incubation	Tett et al. (1994)
Methyl parathion	Gram-negative strain, *Serratia* sp. DS001	Methyl parathion was used as the sole carbon and energy source; p-nitrophenol and dimethylthiophosphoric acid were found to be the major degradation products	Pakala et al. (2006)
Parathion	*Bacillus* sp. *Pseudomonas* sp.	Degradation of parathion past the p-nitrophenol stage to the end product, nitrite: *Bacillus* sp. readily liberated nitrite from the hydrolysis product, p-nitrophenol, but not from intact parathion; *Pseudomonas* sp. hydrolyzed parathion and then released nitrite from p-nitrophenol	Siddaramappa et al. (1973)
Methyl parathion Parathion	*Bacillus* sp. DM-1	Using either growing cells or a cell-free extract, parathion and methyl parathion were transformed to amino derivatives by nitro group reduction; nitroreductase activity was NAD(P)H dependent, O_2 insensitive and exhibited the substrate specificity for parathion and methyl parathion; decrease on the toxicity of pesticides	Yang et al. (2007)
Tetrachlorvinphos	*Stenotrophomonas malthophilia, Proteus vulgaris, Vibrio metschinkouii, Serratia ficaria, Serratia* spp. and *Yersinia enterocolitica*	Microorganisms use the pesticide as a source of carbon and energy, leading to its hydrolysis through a nucleophilic attack; Products: 1-(2,3,4) trichlorophenylethanone and phthalate	Ortiz-Hernández and Sánches-Salinas (2010)

Table 8.2 (continued)

Pesticide	Microorganisms and enzymes	Main results	References
Metalaxyl Triazine Atrazine Terbuthylazine Phenylurea Diuron	Nine species of basidiomycete white-rot fungus	White-rot fungi have the capacity to degrade contrasting groups of pesticide and at a different extent; the mechanisms involved are not proposed, but were found as not being related to ligninolytic potential	Bending et al. (2002)
Tetrachlorvinphos (TCV)	Consortium of: *Stenotrophomonas malthophilia,* *Proteus vulgaris,* *Vibrio metschinkouii,* *Serratia ficaria,* *Serratia* spp. *Yersinia enterocolitica*	Consortium was able to grow in mineral medium containing TCV as the only carbon source; however, only one pure strain was able to remove TCV in mineral medium, while all of them removed it in rich medium; Metabolites identified: 1-(2,3,4) trichlorophenylethanone 1-(2,4,5) trichlorophenylethanone and phthalate	Ortiz-Hernández and Sánches-Salinas (2010)

and low soil sorption partition coefficient (Kd of 3.7 L kg^{-1}), has been the most studied pesticide. During the first 35 years of its use, bacterial atrazine catabolism was proposed to occur largely via N-dealkylation reactions, resulting in the accumulation of aminotriazine compounds (Behki and Kahn 1986; Cook 1987). Later on, some reports have demonstrated the ability of some soil microorganisms to degrade atrazine to CO_2 and ammonia formation (Kolic et al. 2007; Martinez et al. 2001; Rousseaux et al. 2003; Singh et al. 2004a; Vargha et al. 2005). Several researchers have reported the enrichment and isolation of microorganisms from compromised sites in different geographical regions which are able to dealkylate atrazine in a carbon-limited medium, to mineralize and use atrazine as a sole carbon and energy source, to utilize the heterocyclic nitrogen and, in the presence of supplemental carbon, mineralize atrazine and its metabolites as a source of nitrogen (De Souza et al. 1998; Mandelbaum et al. 1995; Topp et al. 2000a, b, Vargha et al. 2005). One factor that has been shown to induce or to accelerate the microbial degradation of pesticides in soil is the successive application of the same pesticide or another pesticide with a similar chemical structure in the same area (Arbeli and Fuentes 2007; Assaf and Turco 1994; Krutz et al. 2008; Tyler et al. 2013). This phenomenon is known as microbial adaptation. In fact, repeated application of pesticides in the same field for a certain number of years may lead to development of an active microbial population in soil with the ability to degrade determined compounds which may reduce the effectiveness of subsequent pesticide applications (IAEA—International Atomic Energy Agency 2001). Arbeli and Fuentes (2007) listed some of the herbicides known to undergo acceleration of biodegradation. Those sites are, therefore, the most appropriate ecological niches to find and isolate strains capable of degrading pesticides (García et al. 2008; Horne et al. 2002; Ortiz-Hernández et al. 2001; Ortiz-Hernández and Sánches-Salinas 2010; Ralebits et al. 2002). In this way, isolation of microorganisms present in contaminated soils with the capacity

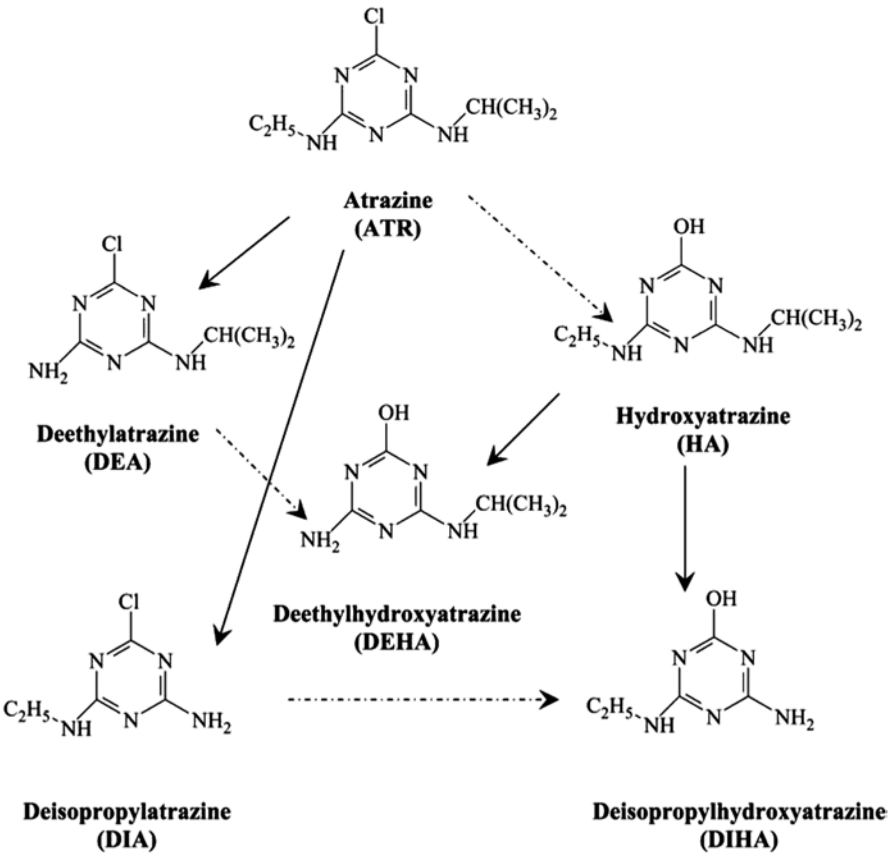


Fig. 8.2 Atrazine degradation through a hydrolytic dechlorination, catalyzed by the enzyme atrazine chlorohydrolase (AtzA), yielding hydroxyatrazine. (Lin et al. 2010)

to degrade them has been done, as well as their application for soil and wastewater treatment containing related compounds (Grundmann et al. 2007; Dehghani et al. 2007, 2013; Rousseaux et al. 2001; Sørensen et al. 2001). Moreover, transferring those isolated microorganisms or simply spots of contaminated soils to other soils has also been shown as a good approach of decontamination (Dehghani et al. 2013; Grundmann et al. 2007). Dehghani et al. (2013) concluded that bioaugmentation of soil with a mixed bacterial consortium may enhance the rate of atrazine degradation in a highly polluted soil.

Hydrolysis has been reported as the most significant step in pesticide detoxification, since it makes compounds more vulnerable to further biodegradation and complete mineralization by the same or other microorganisms' consortium (Ortiz-Hernández et al. 2003; Krutz et al. 2010). Souza et al. (1998) have elucidated the biodegradation of atrazine by a *Pseudomonas* sp. strain. Degradation of atrazine generally initiates through a hydrolytic dechlorination, catalyzed by the enzyme atrazine chlorohydrolase (AtzA), encoded by the *atzA* gene, yielding hydroxyatrazine (Fig. 8.2). The following steps are two hydrolytic deamination reactions catalyzed by hydroxy-atrazine ethylamino-hydrolase (AtzB) yield N-isopropylammelide and, as the last step, N-isopropylammelide isopropyl-amino-hydrolase (AtzC), encoded by the genes *atzB* (trzB) and atzC (*trzC*), convert it to cyanuric acid that is then completely mineralized to CO_2 and NH_3 by other three hydrolases. Three new catabolic genes, *atzD*, *atzE*, and *atzF*, which participate in atrazine catabolism, were later identified by Martinez et al. (2001). Crude extracts from *Escherichia coli* expressing AtzD hydrolyzed cyanuric acid to biuret. *E. coli* strains bearing *atzE* and *atzF* were shown to encode a biuret hydrolase and allophanate hydrolase, respectively. The ability to degrade atrazine by using the products of *atzABCDEF* is not an exclusivity of the *Pseudomonas* sp. Indeed, *atzABC* genes were widespread, having been detected in Canada, the USA, France, Croatia, and China, and were also highly conserved (>97% similarity) indicating their recent dispersion within soil microflora (De Souza 1998; Rousseaux et al. 2001; Devers et al. 2004). Krutz et al. (2010) review on the bacterial genes *atzABCDEF* and trzNDF and the corresponding enzymes AtzABCDEF and TrzNDF responsible for rapid s-triazine mineralization in soil. The substrate specificity of enzymes initiating the metabolism of atrazine and analogous compounds was studied by Seffernick and Wackett (2001). The authors have firstly tested a purified AtzA from *Pseudomonas* sp. strain ADP on atrazine analogs and, secondly, on different synthesized s-triazine and pyrimidine compounds not commercially available. Purified AtzA from *Pseudomonas* sp. strain ADP catalyzed the hydrolysis of an atrazine analog that was substituted at the chlorine substituent by fluorine, but not the hydrolysis of atrazine analogs containing the pseudohalide azido, methoxy, and cyano groups or thiomethyl and amino groups. All atrazine analogs, with a chlorine substituent at carbon 2 and N-alkyl groups, underwent dechlorination by AtzA. The enzyme AtzA catalyzed hydrolytic dechlorination when one nitrogen substituent was alkylated and the other was a free amino group. However, when both amino groups were unalkylated, no reaction occurred. Subsequently, in vitro enzymatic cell extracts prepared from other atrazine-degrading bacteria were investigated for their ability to degrade the atrazine analogs and the degradation was compared to degradation by AtzA from *Pseudomonas* sp. strain ADP. *Pseudomonas* sp. were also proposed to hydrolyze parathion to yield p-nitrophenol and diethyl thiophosphate (Singh and Walker 2006). Furthermore, those microorganisms can degrade p-nitrophenol to p-benzoquinone by using monooxygenase. Additional degradation of p-benzoquinone produces unidentified intermediates that can enter the tricarboxylic acid (TCA) cycle; therefore, parathion can act as a source of carbon and nitrogen for *Pseudomonas* sp. (Singh and Walker 2006). *Pseudomonas stutzeri* is able to degrade parathion co-metabolically to diethyl thiophosphate and p-nitrophenol but it cannot use p-nitrophenol as a source of energy (Kanekar et al. 2004). Interestingly, *Pseudomonas aeruginosa* can use p-nitrophenol resulting from the biodegradation of parathion by *P. stutzeri* as a source of carbon and energy (Kanekar et al. 2004). Previously, other authors have isolated two bacteria, *Bacillus* sp. and *Pseudomonas* sp., from parathion-amended flooded alluvial soil which exhibited parathion-hydrolyzing ability (Siddaramappa et al. 1973).

Bacillus sp. readily liberated nitrite from the hydrolysis product, p-nitrophenol, but not from intact parathion. Pakala et al. (2006) have isolated a soil bacterium, the gram-negative strain *Serratia* sp. DS001, capable of utilizing methyl parathion as the sole carbon and energy source. The authors have identified the key enzyme involved, namely parathion hydrolase. The parathion hydrolase encoded by the highly conserved organophosphate degradation (*opd*) gene, localized either on dissimilar indigenous plasmids or on the chromosome (Pakala et al. 2006; Singh and Walker 2006; Zhang et al. 2005). The enzyme hydrolyzes the characteristic tri-ester bond found in a variety of OP pesticides, p-nitrophenol being one of the major hydrolytic products generated. Although in most of the studies on microbial degradation of parathion and methyl parathion, the first reaction was hydrolysis of the phosphotriester bond, there have been reports of different degradation pathways. A soil bacterium, *Bacillus* sp. DM-1, able to transform parathion and methyl parathion to amino derivatives by reducing the nitro group, was identified by Yang et al. (2007). Pesticide transformation by a cell-free extract was specifically inhibited by three nitroreductase inhibitors, indicating the presence of nitroreductase activity. The nitroreductase activity was nicotinamide adenine dinucleotide phosphate (NAD(P)H) dependent, O_2 insensitive, and exhibited the substrate specificity for parathion and methyl parathion. Reductive transformation significantly decreased the toxicity of pesticides. Microbial degradation of parathion was shown to occur through the following three pathways (Karpouzas and Singh 2006; Fig. 8.3): (1) formation of p-nitrophenol via hydrolysis of the phosphotriester bond, (2) reduction of the nitro group forming the amino parathion and further hydrolysis to yield p-aminophenol, and (3) conversion of parathion to paraoxon before hydrolysis of the phosphotriester bond. Monocrotophos, alachlor, and 4-chlorophenol have also been degraded by soil microorganisms (Bhadbhade et al. 2002; Strong et al. 2002; Westerberg et al. 2000). 2,4-D, one of the most used herbicides, though being considered a possibly carcinogenic to humans and an endocrine disruptor, is classified as a “moderately hazardous” pesticide when its acute toxicity is concerned. This is related to its high biodegradability which leads it to not persist for long in the environment except under adverse conditions, such as low soil pH and low temperature, which increase its longevity in soil. Boivin et al. (2005) have studied the fate of 2,4-D in three soils. The compound was found to be readily mineralized by microorganisms and, while this herbicide is one of the most mobile pesticides, the rapid mineralization (50% of the applied dose in 10 days) diminishes some of its potentially adverse effects on the environment.

Pesticide biodegradation by fungi has also been recognized. Fungi generally biotransform pesticides and other xenobiotics by introducing minor structural changes to the molecule, rendering it nontoxic. In the soil, the so-biotransformed pesticide is susceptible to further degradation by bacteria (Gianfreda and Rao 2004). The potential of the white-rot fungi to perform in situ bioremediation has been attributed to their ability to degrade a variety of xenobiotic chemicals via free radical mechanism mediated by extracellular peroxidases (Reddy 1995). The extracellular white-rot fungi peroxidase enzymes are nonspecific (Evans et al. 1991) and have been implicated in the degradation by of a variety of contrasting aromatic xenobiotics, including

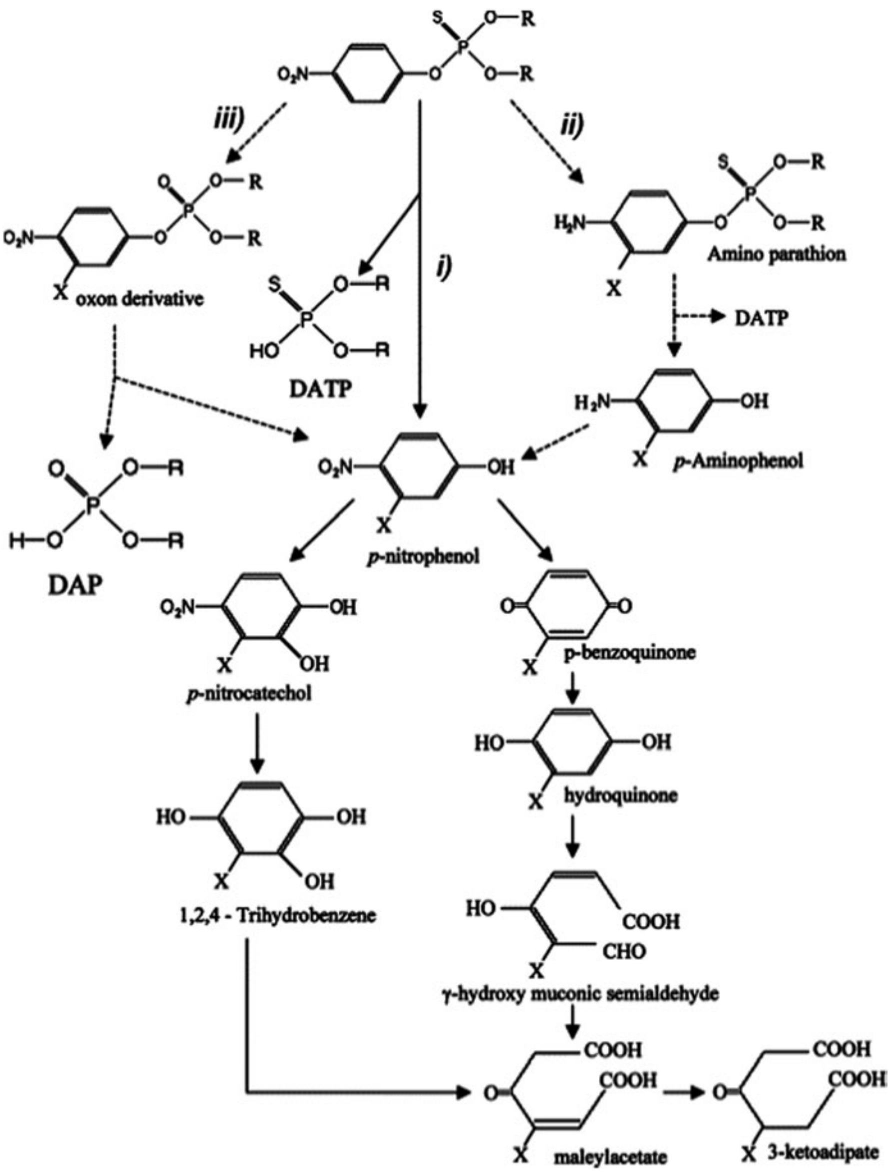


Fig. 8.3 Proposed pathways (*i*, *ii*, *iii*) of microbial parathion degradation. (Karpouzas and Singh 2006)

chlorophenols, dyes, and also pesticides (Pointing 2001; Bending et al. 2002; Tortella et al. 2008; Rubilar et al. 2008). For example, degradation of the aromatic herbicides 2,4-D and atrazine in vitro, under various physiological conditions, by nine fungi was studied by Donnelly et al. (1993). The fungi include two ericoid mycorrhizal fungi (*Hymenoscyphus enicae* 1318 and *Oidiodendron griseum*), two mat-forming ectomycorrhizal fungi (*Gautieria crispa* 4936 and *Gautieria othii* 6362), one ectomycorrhizal fungus associated with decomposing wood (*Radiigera atrogleba* 9470), one general ectomycorrhizal fungus (7534), and three nonmycorrhizal fungi (*P. chrysosporium* 1767, *Sclerogaster pacificus* 9011, and *Trappea darkeni* 8077), and one actinomycete. The data showed that both the mycorrhizal and nonmycorrhizal fungi were capable of degrading the two aromatic herbicides, *P. chrysosponum* being the best 2,4-D-degrading microorganism, with most of the substrate being mineralized instead of being incorporated into the tissue. However, *P. chrysosponum* was not able to mineralize atrazine. The ericoid mycorrhizal fungi were the best cultures at degrading atrazine. Extensive mineralization of 2,4-D and 2,4,5-T by *P. chrysosporium* has been demonstrated in liquid media (Yadav and Reddy 1992, 1993). Degradation of the two pesticides was found not to be related to the activity of peroxidases (lignin peroxidase, LiP and manganese peroxidase, MnP). These authors have also observed that ring-labeled 2,4-D is mineralized faster in nutrient-rich (nonligninolytic) media and that 2,4,5-T and 2,4-D were simultaneously mineralized at a higher rate when presented as a mixture. Reddy et al. (1995) reconfirmed that ligninolytic peroxidases were not encharged of the initial cleavage reaction of 2,4-D and 2,4,5-T. However, they showed that ligninolytic peroxidases of *P. chrysosporium* and *Dichomitus squalens* were involved in the degradation of chlorinated phenolic intermediates of 2,4-D and 2,4,5-T. These results were based on the increased degradation by *D. squalens* in a medium containing Mn^{2+}, an MnP inducer, and on increased degradation by *P. chrysosporium* in a nitrogen-limited medium (in which production of both LiP and MnP are induced). Degradation of 2,4-D by *D. squalens* occurs by an initial ether cleavage resulting in the formation of 2,4-dichlorophenol and acetate. The chlorophenol intermediate underwent subsequent oxidative dechlorination to a benzoquinone intermediate, followed by mineralization to CO_2 (Reddy et al. 1995; Fig. 8.4). More recently, studies on various pesticides biodegradation by different white-rot fungi led to the conclusion that those white-rot fungi have the capacity to degrade contrasting groups of pesticides, although the mechanisms involved were not clearly related to ligninolytic activity (Bending et al. 2002). Sanino et al. (1999) could degrade 60% of 2,4-dichlorophenol by a purified laccase, produced by white-rot fungus. *Phanerochaete chrysosporium* and *Pleurotus pulmonarius* are other lignocellulolytic fungi that have been found to degrade atrazine in liquid culture, producing mainly the N-dealkylated metabolites deethylatrazine, deisopropylatrazine, and deethyldeisopropylatrazine and the hydroxypropyl metabolite hydroxyisopropylatrazine (Entry et al. 1996; Masaphy et al. 1997). The degradation of pesticides was also observed in other fungi such as *Aspergillus* sp. (Bhalerao and Puranik 2007, 2009; Kaufman and Blake 1970, 1973; Pinto et al. 2012; Qing et al. 2003), *Rhizopus* sp. (Gonçalves et al. 2013; Harish et al. 2013; Kaufman and Blake 1970), *Fusarium* sp. (Kaufman and Blake 1970, 1973; Pinto et al. 2012), *Penicillium* sp. (Gonçalves et al. 2013; Kaufman and Blake 1970, 1973; Liu et al. 2004; Pinto et al. 2012; Singh et al. 2008), and *Trichoderma* sp. (Harish et al. 2013; Kaufman and Blake 1970, 1973; Patil et al. 1970; Ortega et al. 2011). Phytoremediation of pesticides is also reported; for example, Singh et al. (2004b) have studied the ability of the rhizosphere of four plant species, rye grass (*Lolium perenne*), tall fescue (*Festuca arundinacae*), Pennisetum (*Pennisetum clandestinum*),

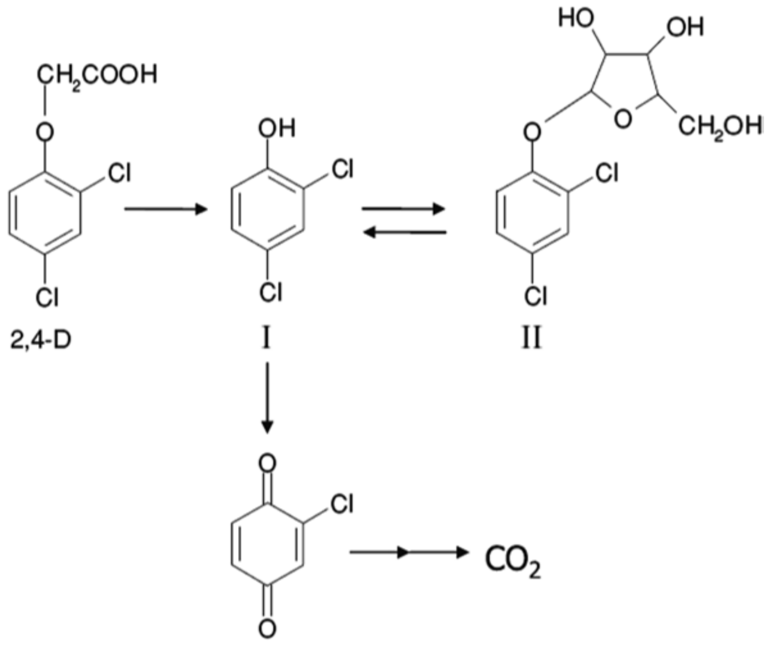


Fig. 8.4 Degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) by *D. squalens* by an initial ether cleavage resulting in the formation of 2,4-dichlorophenol and acetate. The chlorophenol intermediate undergoes subsequent oxidative dechlorination to a benzoquinone intermediate, followed by mineralization to CO_2. (Reddy 1995)

and a spring onion (*Allium* sp.), to promote the degradation of charcoal-fixed atrazine and simazine in cement blocks of a long-term contaminated soil. Only *P. clandestinum* was able to survive in herbicide-contaminated soil, degrading both atrazine and simazine, while other plants died within few days after germination/transplanting.

The use of acclimated microbial cultures to degrade pesticides is definitely a promising approach; however, there are some limitations: Strains selected in laboratory conditions might be stressed when reintroduced into the soil, due to extreme physicochemical conditions of soils and competition with autochthonous microorganisms, which can destroy or harm the inoculum and limit its degradative capacity. Environmental conditions, soil pH and water content, agricultural management, and the amount and mixture of pesticides added are some important factors for pesticides microbial degradation (Arias-Estévez et al. 2008). Hiltbold and Buchanan (1977) estimated that atrazine persistence increased from 9 to 29 days with each unit increase in pH, depending on soil. They also reported that atrazine degraded more rapidly in acid soils compared with basic soils, but that microbes played a greater role in degradation as pH increased. Adsorption and desorption of pesticides on soils are the main phenomena that regulate their transport, transformation, and biological effects in soil environments (Guo et al. 2000; Kah and Brown 2007a, b;

Moorman et al. 2001). Sorbed chemicals are generally assumed to be less accessible to microorganisms, which preferentially or exclusively utilize chemicals in solution, as the degradation rate may be limited by desorption or dissolution rate of the molecule and not by the metabolic rate of microorganisms (Alexander 1999). The adsorption and mobility of organic pesticides in soils depend on extrinsic parameters such as soil characteristics (organic carbon content; inorganic constituents such as clay, oxides and hydroxides of iron and aluminum content; water content; pH; temperature; and soil depth) and intrinsic parameters (ionic or neutral character of the molecule, water solubility, and polarity) (Chung 2000; Kah and Brown 2006; Gravilescu 2005; Li et al. 2003; Liu et al. 2008; Mermoud et al. 2008; Si et al. 2009; Wauchope et al. 2002; Weber et al. 2004).

8.3 Polycyclic Aromatic Hydrocarbons

8.3.1 Main Sources and Structure of PAH

Hydrocarbons are compounds that consist of exclusively carbon and hydrogen (Wilkes and Schwarzbauer 2010). Due to the lack of functional groups, those chemicals are largely apolar and exhibit low chemical reactivity at room temperature. They are commonly classified according to their bonding features into four groups: the aliphatic alkanes, alkenes, and alkynes, and the aromatic hydrocarbons. They can further be arranged as straight chain, branched chain, or mono or polycyclic. PAHs, also known as polynuclear aromatic hydrocarbons, include a large and diverse group that contain two or more fused aromatic rings in linear, angular, or cluster arrangements (Kanaly and Harayama 2000). The position at which aromatic rings are fused to another, as well as number, chemistry, and position of substituents on the basic ring system, also differ. PAHs can be divided into two groups based on their physical, chemical, and biological characteristics: the lower molecular weight (LMW) PAHs (2- to 3-ring group of PAHs such as naphthalenes, fluorenes, phenanthrenes, and anthracenes) and the high molecular weight (HMW) PAHs (4 to 7 ring, from chrysenes to coronenes; Fig. 8.5). Naphthalene ($C_{10}H_8$, MW of 128.16 g mol^{-1}), formed from two benzene rings fused together, has the lowest molecular weight of all PAHs. Nitrogen, sulfur, and oxygen atoms may readily substitute in the benzene rings to form heterocyclic aromatic compounds, which are commonly grouped with the PAHs. Furthermore, PAHs substituted with alkyl groups are normally found together with the PAHs in the environment. Chemical reactivity, aqueous solubility, and volatility of PAHs decrease with increasing ring number and, consequently, with molecular weight (Semple et al. 2003). For instance, PAH resistance to oxidation, reduction, and vaporization increases with increasing molecular weight, whereas the aqueous solubility of these compounds decreases. As a result, PAHs differ in their behavior and distribution in the environment, and, hence, in their environmental fate. In general, PAHs are relatively stable and recalcitrant and can, therefore, accumulate to substantial levels in the environ-

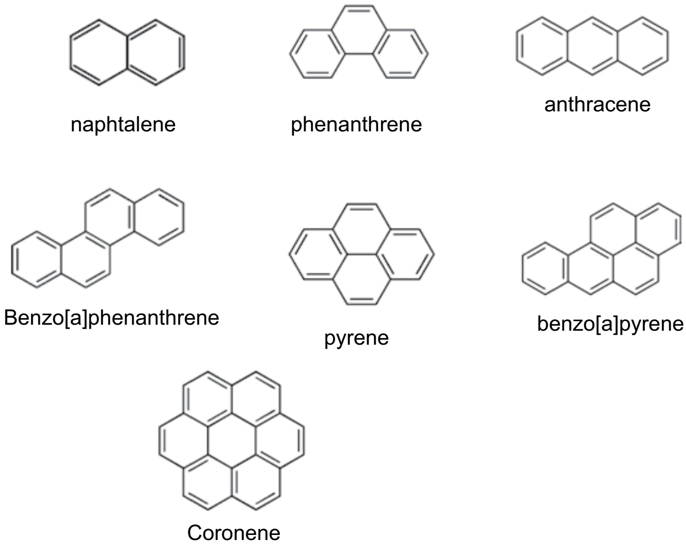


Fig. 8.5 Molecular structures of some typical low-molecular-weight (naphthalene, phenanthrene, and anthracene) and the high-molecular-weight (Benzo[a]phenanthrene, pyrene, benzo[a]pyrene, and coronene) polycyclic aromatic hydrocarbons (PAHs)

ment. Consequently, anthropogenic and natural sources of PAHs in combination with global transport phenomena result in their worldwide distribution. Some fractions of PAHs float on water and form surface films, others sink to the sediments, some move into soil then groundwater, some are broken down by bacteria, some evaporate or photodegrade, and others stay in soil for a long time. Thus, PAHs have been detected in a wide range of soils and sediments, including some ancient sediments (e.g., Capotori et al. 2004; Fernandez et al. 1992; Muniz et al. 2004), in fresh and wastewaters (e.g., Cooney 1984), and in the atmosphere (e.g., Morville et al. 2011; Velasco et al. 2004; Yu et al. 2009). Table 8.3 provides other published results of PAH's evaluation in different sites and countries. There are typically three main sources of PAHs (Neff et al. 2005): petrogenic, pyrogenic, and biogenic. Petrogenic PAHs arise from petroleum and petroleum-derived products, petroleum refining and transport activities being the major contributors to localized loadings of PAHs into the environment. Such loadings may occur through discharge of industrial effluents and through accidental release of raw and refined products (Jiménez et al. 2006, 2007; Venosa et al. 2010). Pyrogenic PAHs are comprised of predominantly unsubstituted PAHs and result from combustion processes such as urban runoff and chemical industries and can be considered as a major source in urban atmosphere (Lim et al. 1999; Marr et al. 1999; Morville et al. 2011). Tobacco cigarette smoking is also a significant source of PAH exposure (Gündel et al. 1996; Velasco et al. 2004). Biogenic PAHs have a natural origin in coal deposits, from natural aromatics such as terpenes, sterols, and quinones from plants, which volatilize and can become condensed, can also result during thermal geologic reactions associated with fossil

Table 8.3 PAHs identification and evaluation in different countries and sources, in chronologic order

Country	Detected PAHs	Contaminated source	References
Porto Rico	Petroleum hydrocarbons by the petroleum spills occurred in 1962 and in 1977	Intertidal sediments contaminated	Corredor and Morell (1990)
British Columbia	Aluminum smelter-derived PAHs	Marine sediments	Simpson et al. (1998)
Texas	Total PAHs	Atmosphere	Park et al. (2002)
Spain	16 PAHs	24 soil and 12 wild chard samples from urban/residential zones	Nadal et al. (2004)
Uruguay	20 PAHs	Soil sediments	Muniz et al. (2004)
Mexico	Total PAHs	Environments polluted mostly by cigarette smoke (indoor) and diesel engines in (outdoor)	Velasco et al. (2004)
Japan	Pyrene Fluoranthene Benzo[g, h,i]perylene, Benzo[k]fluoranthene Chrysene Benzo[b]fluoranthene Benzo[a]pyrene	Deposited road particles collected from 13 heavily traveled roadways in an urban area	Lee et al. (2005)
Spain	PAHs from Prestige oil spill	Seawater and mussel (*Mytilus galloprovincialis*) tissues	Laffon et al. (2006)
Vietnam	47 PAHs	Particulate matter and the gaseous phase at ten roadside sites contaminated mainly by motorcycles without catalytic converters	Kishida et al. (2008)
China	Total PAHs	Atmosphere	Yu et al. (2009)
China	Naphthalene Acenaphthene Phenanthrene Chrysene Perylene	Dissolved particulate phase of precipitation	Deyin et al. (2009)
France (urban, suburban, and rural areas)	17 PAHs Most abundant were naphthalene, phenanthrene, and acenaphtene	Atmosphere	Morville et al. (2011)

fuel and mineral production, and during burning of vegetation in forest and bush fires (Juhasz and Naidu 2000; Tyson 1995). PAHs are mostly used as intermediaries in pharmaceutical, photographic, and chemical industries. Naphthalenes are also used in the production of fungicides, insecticides, moth repellents, and surfactants.

8.3.2 Risks and Impact of PAH

PAHs are ubiquitous contaminants of great concern due to their distributions in the environment and possible exposure to humans, in particular the High Molecular Weight (HMW) ones as they are recalcitrant. Release of hydrocarbons into the environment whether accidentally or due to human activities is a main cause of water and soil pollution (Holliger et al. 1997). A wide range of PAH-induced ecotoxicological effects are observed in a diverse fraction of biota, including microorganisms, terrestrial plants, aquatic biota, amphibians, reptiles, birds, and terrestrial mammals. Effects have been documented on survival, growth, metabolism, and tumor formation, i.e., acute toxicity, developmental and reproductive toxicity, cytotoxicity, genotoxicity, and carcinogenicity. However, the primary focus of the toxicological research on PAHs has been on genotoxicity and carcinogenicity. PAHs can decimate marine populations, once they are toxic and persistent. Soluble fractions can kill plankton communities at low concentrations and many organisms have been physically smothered. Soil contamination with PAHs can cause extensive damage of the local system since accumulation of pollutants in animals and plant tissue may cause death or mutations (Alvarez and Vogel 1991). Some PAHs are considered to be possible or probable human carcinogens (Menzie et al. 1992). PAH compounds, as being lipid soluble, can quickly be absorbed by the mammals whose metabolism generates products with mutagenic and carcinogenic properties (Netto et al. 2000). Eighteen unsubstituted PAHs (acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[e]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene, coronene, dibenz(a, h)anthracene, fluoranthene, fluorine, indeno(1,2,3-cd)pyrene, phenanthrene, and pyrene) considered as possible or probable human carcinogens are listed by the USEPA as priority pollutants (Yan et al 2009; Luch 2005). One of the most common ways PAHs can enter the body is through breathing contaminated air. Exposure to PAHs can also occur through eating food grown in contaminated soil, or by eating meat or other grilled food, by drinking water contaminated with PAHs, by skin contacts with PAH-contaminated soil, or through products like heavy oils, coal tar, roofing tar, or creosote. Once in the body, PAHs can spread and target fat tissues, such as kidneys and liver. Several PAHs have been shown to damage DNA and cause mutations, which in some cases may result in cancer. The PAHs require metabolic activation and conversion to display their genotoxic and carcinogenic properties. This happens as the PAHs are metabolized in higher organisms. For example, the compound benzo[a]pyrene (b[a]p), found in coal tar, in automobile exhaust fumes, and in cigarette smoke, is one of the most carcinogenic PAHs (Nisbet and LaGoy 1992; Lee and Shim 2007). The initial step in the metabolism of b[a]p involves the multifunctional P-450 enzyme system forming benzo[a]pyrene-7,8-oxide through the addition of one atom of oxygen across a double bond. The epoxide is short-lived and may rearrange spontaneously to the phenol compound 7-hydroxybenzo[a]pyrene or undergo hydrolysis to dihydrodiol (Fig. 8.6). These products may then be conjugated with glutathione, glucuronic acid, or sulfuric acid, to form products that

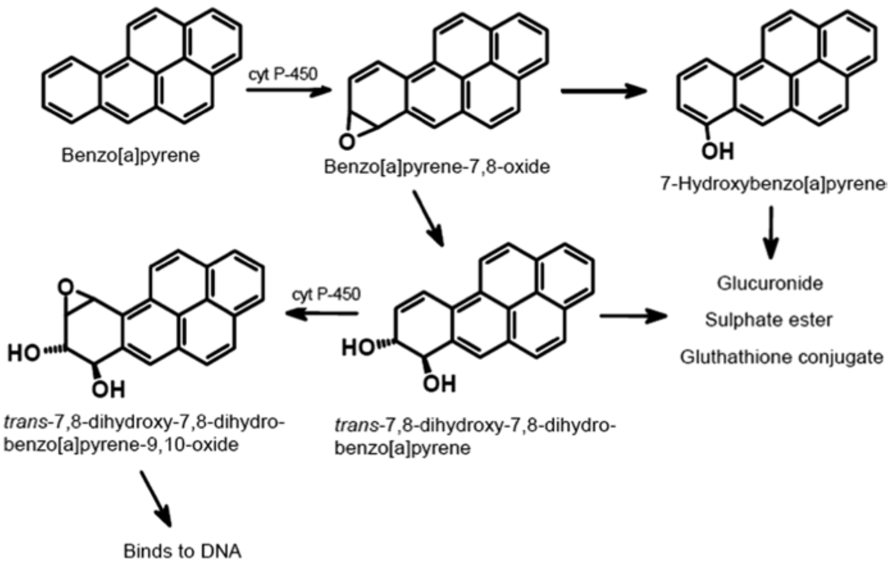


Fig. 8.6 Methabolic activation of benzo[a]pyrene. (IARC 1983)

can be excreted by the organism (detoxification). However, the dihydrodiol may also act as a substrate for cytochrome P-450 once again, to form new dihydrodiol epoxide, trans-7,8-dihydroxy-7,8-dihydrobenzo[a]pyrene-9,10-oxide, which react with proteins, RNA, and DNA, thus causing mutations and possibly cancer (IARC 1983). A similar pathway occurs with other PAHs. However, for the unsubstituted PAHs, it is not the original compound that reacts with DNA.

Neff et al. (2005) listed the acute and chronic toxicity of different PAHs frequently found in crude and refined petroleum.

The toxicity of PAHs is structure dependent. Isomers (PAHs with the same formula and number of rings) can vary from being nontoxic to extremely toxic. In addition to increases in environmental persistence with increasing PAH molecule size, evidences also suggest that in some cases, PAH genotoxicity also increases with size, up to at least four or five fused benzene rings (Cerniglia 1992). Structure–activity relationships become even more complex when substitution of the molecular structure occurs. For example, although benz[a]anthracene is a fairly weak carcinogen, 7,12-dimethylbenz[a]anthracene is a very potent carcinogen (Coombs et al. 1974). Furthermore, some environmental transformation products of PAHs may react directly with DNA, causing mutations and possibly cancer, without the need for metabolic activation.

8.3.3 Biodegradation of PAH

As abiotic factors do not contribute significantly to the elimination of PAHs with more than three rings from soil (Cerniglia 1993), much effort has been expended in examining the contribution of microorganisms to degrade PAHs. Among the hydrocarbons, PAHs are generally more difficult to biodegrade (Huesemann 1995). LMW PAHs are readily degraded, but HMW ones are more persistent, in part because of their low bioavailability, low water solubility, and their strong adsorption onto the soil organic matter (Atlas and Bragg 2009; Launen et al. 1995). HMW PAHs can, therefore, remain in the soil for many centuries, posing a long-term threat to the environment, while LMW PAHs are partly lost through degradation processes, volatilization, and leaching (Blumer 1976). In a bioremediation attempt, the problem of low water solubility and soil adsorption that limit PAH availability to microorganisms can be diminished by the use of surfactants or by stimulating in situ production of biosurfactants, after addition of an oxidant such as O_2 or H_2O_2 (Garon et al. 2002; Nazina et al. 2008). These molecules solubilize PAHs, increasing their concentrations in the aqueous phase, and consequently enhancing their degradation. The effect of sorption generally increases as the number of benzene rings in the PAH molecule increases, since this implies higher lipophilicity (Blumer 2003). The relationship between PAH environmental persistence and increasing numbers of benzene rings is consistent with the results of various studies correlating environmental biodegradation rates and PAH molecular size (Bossert and Bartha 1986; Couling et al. 2010; Heitkamp and Cerniglia 1987). For example, Shuttleworth and Cerniglia (1995) reported that the half-lives in soil and sediment of the three-ring phenanthrene molecule may range from 16 to 126 days, while for the five-ring molecule benzo[a]pyrene they may range from 229 to >1,400 days. The difficulty of PAH biodegradation is also related to the lack of any functional groups (Schink 1985, 1988). Aerobic organisms can introduce functionality into unsubstituted hydrocarbons by inserting elemental oxygen with oxygenases. These enzymes activate the oxygen by partially reducing it, allowing the incorporation of a hydroxyl group. Anaerobes have a much more difficult task, as they must introduce functional groups with H_2O, HCO_3, or organic acids. The steric hindrance, due to branching of molecules, has also been proven to be difficult for degradation processes. However, the capabilities of anaerobic and aerobic microorganisms to degrade those compounds previously considered to be recalcitrant have long been documented (Atlas 1981, 1984; Cerniglia 1992; Gibson and Subramanian 1984; Leahy and Colwell 1990; Schneider et al. 1996; Widdel and Rabus 2001; Zobell 1946). Table 8.4 provides other recent reports on PAHs' biodegradation by different microorganisms and the main results achieved. Polyaromatic hydrocarbon degradation in soils and sediments is complex, in part due to the fact that these environments typically contain a variety of different PAH degrading microorganisms with different metabolic pathways and substrate ranges (Grossman et al. 1999; Seo et al. 2009; Zhang et al. 2006). PAH-contaminated soils also frequently contain mixtures of PAHs and, as a result, the degradation of one type of PAH may affect the degrada-

Table 8.4 Polycyclic aromatic hydrocarbons biodegradation by different microbial strains

PAH	Microorganisms and enzymes	Main results	References
Naphthalene Phenanthrene Anthracene	Thirteen deuteromycete ligninolytic fungal strains	Degradation varied with the strain and the ligninolytic enzymes present in the culture supernatants; highest degradation of naphthalene (69 %) was related to Mn-peroxidase activity; the greatest degradation of phenanthrene (12 %) was observed with strain containing Mn-peroxidase and laccase activities; anthracene degradation (65 %) was related with Mn-peroxidase	Clemente et al. (2001)
Anthracene Phenanthrene Pyrene Diesel fuel	Maize plant inoculated with bacteria *Azospirillum* spp. and *Pseudomonas stutzeri*	PAHs were more degraded in plants inoculated with bacteria; *Azospirillum* spp. and *Pseudomonas stutzeri* populate the root area and the interior of grass roots, fixing nitrogen and using aromatic hydrocarbons as the only source of carbon and energy	Gałązka et al. (2010)
15 PAHs	Meadow fescue plant inoculated with bacteria *Azospirillum* spp. and *Pseudomonas stutzeri*	PAHs were better degraded in plants inoculated with bacteria; *Azospirillum* spp. and *Pseudomonas stutzeri* populate the root area and the interior of grass roots, fixing nitrogen and using aromatic hydrocarbons as the only source of carbon and energy	Gałązka et al. (2012)
Petroleum PAHs	Bacterial community of a land treatment unit	Major portion of petroleum degradation is carried out by a few species represented by *Flavobacterium*, *Pseudomonas*, and *Azoarcus* 2 phylotypes; specific phylotypes of bacteria were associated with the different phases of petroleum degradation	Kaplan and Kitts (2004)
Diesel fuel	Ten bacterial strains isolated from an oil refinery field in Iran	B*acillus cereus* or *B. thuringiensis* (>98 % similarity) were isolated and characterized as a commercial diesel degrading (85.20 % diesel fuel degradation within 15 days)	Kebria et al. (2009)
Naphthalene Phenanthrene Chrysene Perylene Naphthol[2,3-a] pyrene Decacyclene	Seven soil fungi	Transformation of high- and low-molecular-weight PAHs under microaerobic and very low oxygen conditions	Silva et al. (2009a)

Table 8.4 (continued)

PAH	Microorganisms and enzymes	Main results	References
Naphthalene Phenanthrene Anthracene Pyrene Benz[a]anthracene Benz[a]pyrene	Individual fungi Bacterial and a fungal consortia	During the 1st week, low-molecular-weight PAHs (naphthalene, phenanthrene and anthracene) were degraded rapidly both in the native microbiota and in bioaugmented microcosms; phenanthrene was the best degraded; high-molecular-weight PAHs (benz[a]anthracene and benz[a]pyrene) removal proceeds slower and at less extent, being improved by bioaugmentation; pyrene removal ran rapidly in the first week followed by a shift to a slower rate of removal in the subsequent weeks; PAHs were used as carbon and energy sources by microcosms microbial communities	Silva et al. (2009b)
16 PAHs	21 filamentous fungi isolated from the soil	Greatest degradation was obtained with *Coniothyrium* sp. (26.5 %) and *Fusarium* sp. (27.5 %) inoculums; the highest percentage of degradation was obtained for benzo(a)pyrene	Potin et al. (2004)
Crude oil PAHs	*Pseudomonas aeruginosa* CH23, *Bacillus licheniformis* MTCC 2465 *Acinetobacter calcoaceticus* MTCC 2409	Microorganisms were able to utilize hydrocarbons as the sole carbon source both as a single and mixed culture; higher degradation was observed when they are used as a mixed culture; *Pseudomonas aeruginosa* CH23 showed maximum efficiency of biodegradation	Afuwale and Modi (2012)
Anthracene Phenanthrene Pyrene	Microbial consortium (five bacteria: *Mycobacterium fortuitum*, *Bacillus cereus*, *Microbacterium* sp., *Gordonia polyisoprenivorans*, *Microbacteriaceae bacterium*); naphthalene-utilizing bacterium; fungus identified as *Fusarium oxysporum*	The microbial consortium degraded PAHs almost completely, in 70 days; bacterial and fungal isolates from the consortium, when inoculated separately to the soil, were less effective in anthracene mineralization compared to the consortium	Jacques et al. (2008)
Pyrene	10 Micromycetes isolated from PAHs-contaminated sediment	Zygomycetes appeared as one of the most efficient taxonomic groups on pyrene degradation	Ravelet et al. (2000)

Table 8.4 (continued)

PAH	Microorganisms and enzymes	Main results	References
Anthracene Fluoranthene	40 fungal species (24 genera) isolated from an experimental constructed wetland for wastewater treatment	Fluoranthene was degraded efficiently by 33 species while only 2 species were able to remove anthracene over 70 %; not previously reported species capable of degrading the compounds were revealed: *Absidia cylindrospora*, *Cladosporium sphaerospermum*, and *Ulocladium chartarum*; degradative ability of fungi was not related to their extracellular phenoloxidases activity	Giraud et al. (2001)
PAHs from a water-flooded thermophilic oil reservoir	Indigenous microbial communities from a water-flooded thermophilic oil reservoir	Methanogenic biodegradation; degree of degradation strongly varied between different parts of the reservoir	Jiménez et al. (2012)
Phenanthrene Pyrene	*Aspergillus niger*, isolated from hydrocarbon-contaminated soil	Metabolites identified: 1-methoxyphenanthrene, 1-methoxypyrene, 1- and 2-phenanthrol and 1-pyrenol	Sack et al. (1997)
PAH	Associated microbes from abattoir wastes in the Niger Delta, Nigeria	Both mixed cultures of bacteria and fungi can biodegrade polycyclic aromatic hydrocarbons; higher degradation of low-molecular-weight than of the high-molecular-weight PAHs	Ogbonna et al. (2012)
Naphthalene Phenanthrene	Sulfidogenic consortia	Complete loss of naphthalene and phenanthrene was observed after 150 days of incubation; upon refeeding, naphthalene and phenanthrene were utilized within 14 days; carboxylation may be the initial key reaction for the anaerobic metabolism of compounds	Zhang and Young (1997)

tion of other PAHs. The metabolic cooperation by several microorganisms may result in enhanced PAH utilization, since metabolic intermediates produced by some organisms may serve as substrates for the growth of others (Afuwale and Modi 2012). For example, LMW PAHs may affect the biodegradation of HMW PAHs, and vice versa, via cometabolism, induction of enzyme activities by degradation intermediates, or via competitive inhibition, or even toxicity (Cerniglia 1993; Dean-Ross et al. 2002; Van Herwijnen et al. 2003). Microorganisms capable of growing and degrading the complex mixtures of hydrocarbons from aquifers, soil, freshwater and marine environments contaminated by crude oil have been characterized (Adebusoye et al. 2007; Bekins et al. 2002; Conney 1984; Das and Mukherjee 2007; Floodgate 1984; Jacques et al. 2008; Kebria et al. 2009; Potin et al. 2004; Ravelet et al. 2000). This is very important for the natural attenuation of PAH-contaminated sites. Figure 8.7 shows different possibilities of hydrocarbon utilization in the

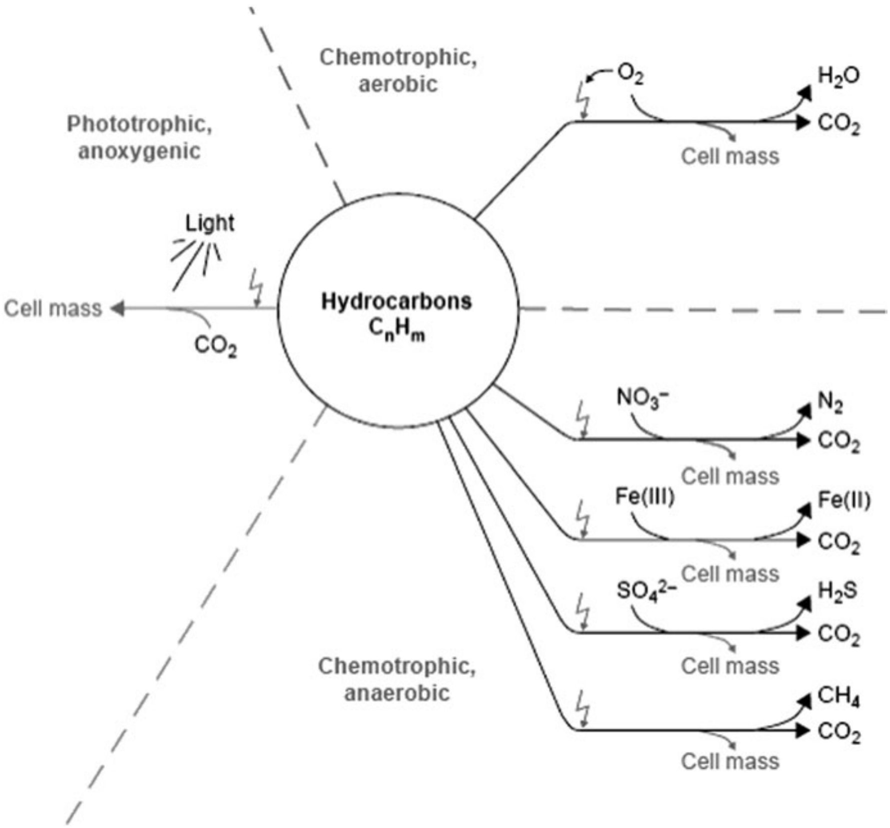


Fig. 8.7 Possibilities of hydrocarbon utilization in the environment under diverse conditions: aerobic and anaerobic chemotrophic, and phototrophic anoxygenic degradation. (Widel and Rabus 2001)

environment, under diverse conditions: aerobic and anaerobic chemotrophic and phototrophic anoxygenic (Widdel and Rabus 2001). Under chemotrophic conditions, part of hydrocarbons is used in catabolism and the rest is assimilated into cell mass. Under aerobic conditions, oxygen is required as an electron acceptor but also serves as a co-substrate for oxygenase enzymes that are known to initiate PAH metabolism under aerobic conditions (Hurst et al. 1996; Meléndez-Estrada et al. 2006; Venosa et al. 2010). Under anaerobic conditions, other electron acceptor compounds such as NO_3^-, Fe(III), and SO_4^{2-} are used. The hydrocarbons found in the environment are degraded primarily by bacteria and fungi, and the extent of biodegradation depends on the conditions of the ecosystem, of the local environment, and of seasonal and climatic conditions (Leahy and Colwell 1990; Morville et al. 2011). PAH-degrading bacteria generally use PAHs as a carbon and energy source while fungi metabolize the PAHs to more water-soluble compounds, thereby facilitating their subsequent excretion. Bacteria and fungi have, therefore, different metabolic pathways (Fig. 8.8; Cerniglia 1992). The main PAH's degrading fungi found in the

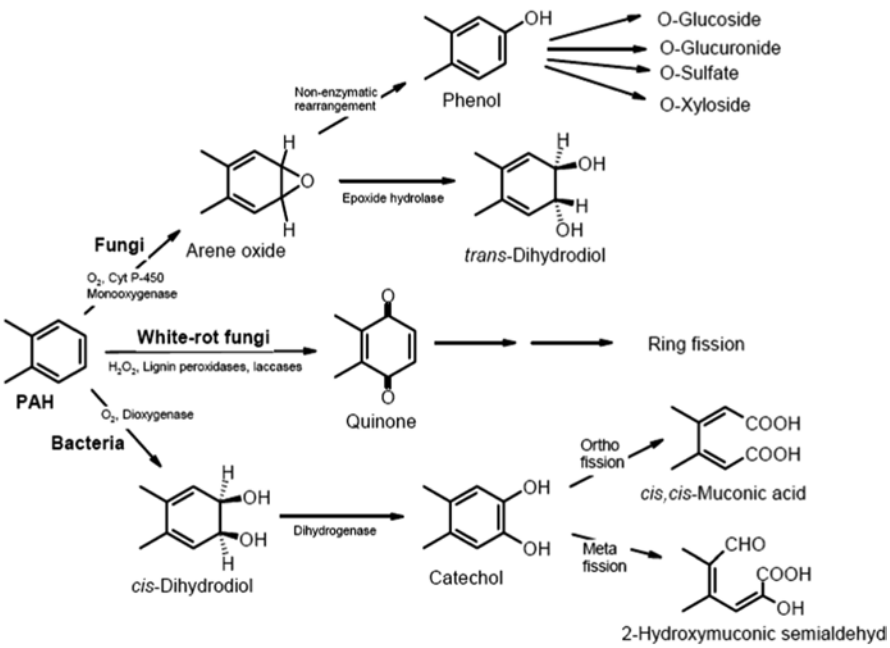
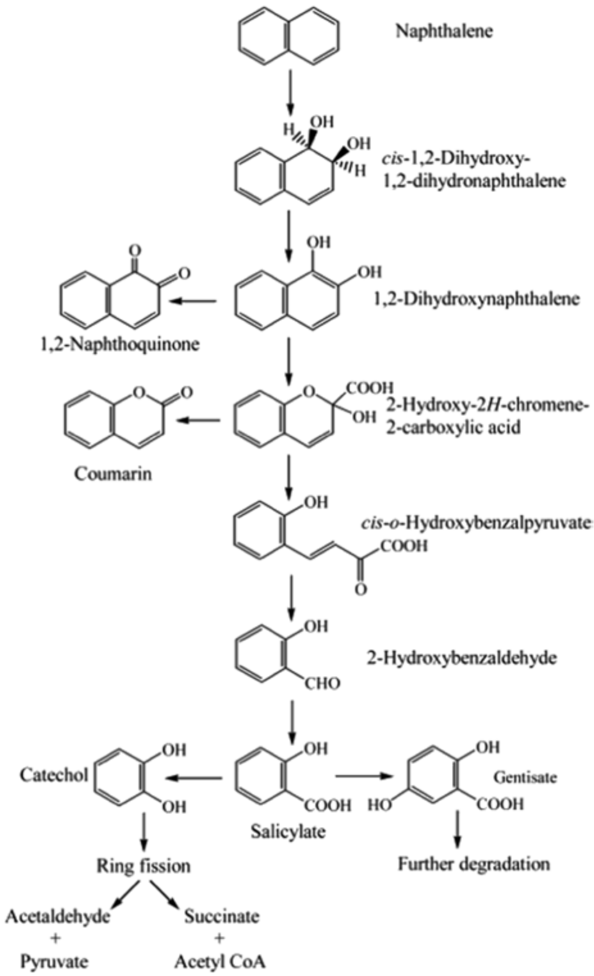


Fig. 8.8 General pathways for bacterial and fungi degradation of PAHs. (Cerniglia 1992)

literature are the species of *Penicillium* sp. and *Aspergillus* sp. (Cortes-Espinosa et al. 2006; Leitão 2009; Okoro 2008; Ravelet et al. 2000; Sack et al. 1997; Saraswathy and Hallberg 2005; Silva et al. 2009a). However, other microorganisms such as *Phanerochaete chrysosporium*, *Cunninghamella* sp., *Coniothyrium* sp., and *Fusarium* sp., have also shown their ability to degrade them (Cerniglia 1993; Launen et al. 1995; Potin et al. 2004; Sutherland 1992). Many times each species is responsible for degrading a single component of the oil. At the same time, the efficiency of degradation of a different compound may vary with the microorganism (Gao et al. 2001). In most of the bioremediation cases, the use of a single consortium or mixed consortia to improve the efficiency of biodegradation is necessary (Afuwale and Modi 2012; Jacques et al. 2008; Zanaroli et al. 2010). The use of microorganism consortia obtained from rich sources of microbes (e.g., sludges, composts, manure), polluted with hydrocarbons, would provide bioremediation enhancements more robust and reproducible than those achieved with specialized pure cultures or tailored combinations (cocultures) of them, together with none or minor risks of soil loading with unrelated or pathogenic allochthonous microorganisms.

PAH degradation by filamentous fungi is mediated by either extracellular ligninolytic enzymes (Cerniglia and Sutherland 2001, 2010; Lamar 1992) or intracellular cytochrome P450 monooxygenases (Cerniglia and Sutherland 2001, 2010; Van den Brink et al. 1998). Metabolism of PAHs by involving cytochrome P450 monooxygenase enzyme systems is quite similar to the transformation pathways found in

Fig. 8.9 Proposed aerobic catabolic pathways of naphthalene by bacteria. (Seo et al. 2009)



humans and other mammals, as described previously for b[a]p. The first steps of PAH oxidation result in the formation of monophenols, diphenols, dihydrodiols, and quinones (Cerniglia 1992; Launen et al. 1995). In a second step, water-soluble conjugates such as sulfates and O-methyl conjugates, which are detoxification products, can be formed (Wunder et al. 1997). However, both pathways yield PAH quinones as major oxidation products (Field et al. 1992; Launen et al. 1995). These metabolites have higher water solubility and reactivity than the parent PAH (Launen et al. 1999). White-rot fungi have also been reported as PAHs biodegraders (Anderson and Henrysson 1996; April et al. 2000; Boyle et al. 1998; Clemente et al. 2001; Field et al. 1992). This activity is due to the lignin-degrading systems of these fungi, which are composed of enzymes such as LiP (EC 1.11.1.7), MnP (EC 1.11.1.7), and laccase (EC 1.10.3.2; Augustin and Muncnerova 1994; Barr and Aust 1994; Eibes et al. 2006; Hammel 1995). Some yeasts also confirmed their efficiency for

PAH biodegradation (Mollea et al. 2005; Silva et al. 2009). Examples comprise the strains *Candida lipolytica*, *Rhodotorula mucilaginosa*, *Geotrichum* sp., and *Trichosporon mucoides* isolated from contaminated water noted to degrade petroleum compounds (Bogusławska-Was and Dąbrowski 2001). Bacterial biotransformation of PAHs has also been well documented. Naphthalene, being the simplest and the most soluble PAH, is often used as a model compound to investigate the ability of bacteria to degrade and to understand and predict degradation pathways of other PAHs. The review of Seo et al. (2009) illustrates the proposed bacterial degradation pathways for naphthalene (Fig. 8.9) and also fluorene, phenanthrene, fluoranthene, pyrene, and b[a]p. Degradation of naphthalene starts through the naphthalene dioxygenase attack on the aromatic ring to form *cis*-(1,2)-dihydroxy-1,2-dihydronaphthalene. This is subsequently dehydrogenated to 1,2-dihydroxynaphthalene by a *cis*-dihydrodiol dehydrogenase, which is then metabolized to salicylate via 2-hydroxy-2H-chromene-2-carboxylic acid, *cis*-o-hydroxybenzalpyruvate, and 2-hydroxy-benzaldehyde. 1,2-dihydroxynaphthalene can also be nonenzymatically oxidized to 1,2-naphthaquinone. Salicylate is typically decarboxylated to catechol, which is further metabolized by ring fission in meta- and ortho-pathways.

The fact that oxygen is not available in all environments where PAHs occur, leads to the possibility of anoxic biodegradation. In fact, the concentration of oxygen gas in soil is generally thought to be one of the limiting factors in the aerobic PAH degradation. Oxygen concentration varies according to soil depth and its availability depends on the amounts of substrate available and the type of soil. Similarly, deeper aquifers have low nitrate and oxygen availability. As a result, in those environments, degradation by aerobic or facultative anaerobic organisms is limited. Polycyclic aromatic hydrocarbon mineralization under anaerobic conditions has been observed under denitrifying (Ambrosoli et al. 2005; McNally et al. 1998; Rockne et al. 2000; Venosa et al. 2010), sulfate reducing (Bedessem et al. 1997; Coates et al. 1996; Galushko et al. 1999; Meckenstock et al. 2000; Musat et al. 2009; Zhang and Young 1997), and manganese-reducing conditions (Langenhoff et al. 1996; Canfield et al. 1993). Zhang and Young (1997) have proposed that carboxylation may be the initial key reaction for the anaerobic metabolism of PAH compounds. They have studied degradation of naphthalene and phenanthrene by a sulfidogenic consortium, which was able to totally degrade the compounds. According to the reaction intermediates identified, 2-naphthoic acid and phenanthrene carboxylic acid, the authors have proposed that carboxylation may be the initial key reaction for the anaerobic metabolism of compounds under sulfate-reducing conditions (Fig. 8.10). Methanogenic degradation, on the other hand, does not require external electron acceptors. Bekins et al. (2002) have explored how the aquifer conditions control the redox succession from iron reduction to methanogenesis. The authors have documented that microbial numbers increase in locations with direct access to contaminants and surface nutrient supplies, such as nitrogen and phosphorus, which are limited in contaminated aquifers. They showed that the succession of microbial physiological types in a crude oil-contaminated aquifer is controlled primarily by the hydrocarbon flux: (1) Methanogenic activity appears first in areas with high carbon flux rates either by advection or by dissolution from the nonaque-

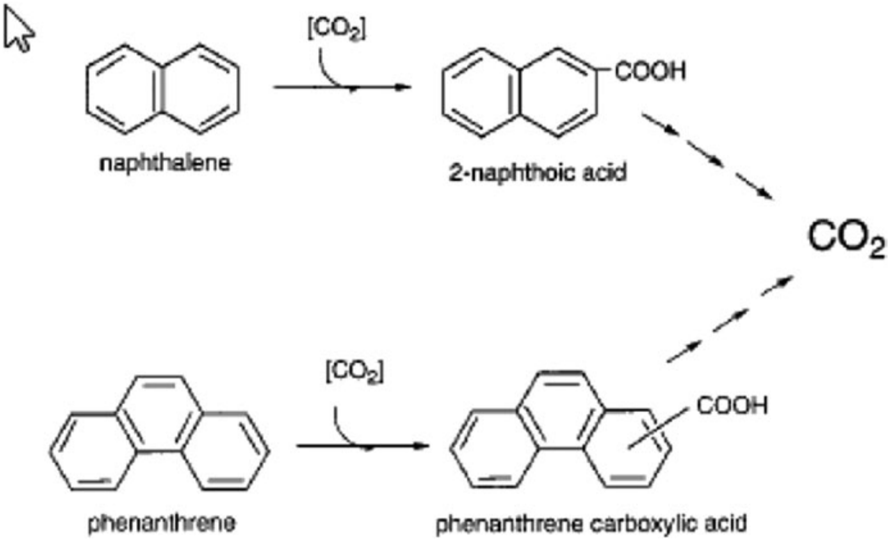


Fig. 8.10 Proposed pathways for the anaerobic metabolism of naphthalene and phenanthrene in the sulfidogenic enrichments. (Zhang and Young 1997)

ous oil and (2) low carbon flux areas at the edges of the plume or in low permeability zones remain iron reducing for longer.

A number of other limiting factors have been recognized to affect the biodegradation of PAHs (Das and Chandran 2011; Rogers et al. 1993; Shuttleworth and Cerniglia 1995). Among physical factors, temperature plays an important task in biodegradation of hydrocarbons by directly affecting the chemistry of the pollutants as well as affecting the physiology and diversity of the microbial flora. Although hydrocarbon biodegradation can occur over a wide range of temperatures, the rate of biodegradation generally decreases with the decreasing temperature. This is related to the fact that at low temperatures, the viscosity of the oil increases, while the volatility of the toxic LMW hydrocarbons is reduced, delaying the beginning of biodegradation (Atlas 1975). Temperature also affects the solubility of hydrocarbons (Leahy and Colwell 1990; Whitehouse 1984). For example, petroleum released to the sea in tropical environments generally suffers rapid degradation due to higher temperatures (Corredor and Morell 1990). The effect of soil pH on degradation of PAHs (phenanthrene, anthracene, fluoranthene, and pyrene), with a view to manipulating soil pH to enhance the bioremediation of PAHs, was studied by Pawar (2012). The author observed that pH 7.5 was most suitable for the PAH's degradation. A degradation of 50% occurred in soil at pH 7.5 in 7 days, while at pH 5.0 and 6.5 it took 21 days. The greatest rates of degradation were associated with the prevalent bacterial population under basic conditions, whereas fungal populations are widespread at acidic and alkaline soil pH. Soil enzyme activities in general were also greater at pH 7.5. Nutrients such as nitrogen, phosphorus, and, in some cases, iron are also very important for successful biodegradation of hydrocarbons (Bragg

Table 8.5 Bioremediation agents according to the National Oil and Hazardous Substances Pollution Contingency Plan (NCP) product schedule

Product name	Product type	Manufacturer
BET BIOPETRO	Microbial culture	BioEnviro Tech, Tomball, TX, USA
MICRO-BLAZE		Verde Environmental, Inc., Houston, TX, USA
OPPENHEIMER FORMULA		Oppenheimer Biotechnology, Inc., Austin, TX, USA
PRISTINE SEA II		Marine Systems, Baton Rouge, LA, USA
STEP ONE		B & S Research, Inc., Embarrass, MN, USA
SYSTEM E. T. 20		Quantum Environmental Technologies, Inc. (QET), La Jolla, CA, USA
WMI-2000		WMI International, Inc., Houston, TX, USA
BILGEPRO	Nutrient additive	International Environmental Products, LLC, Conshohocken, PA, USA
INIPOL EAP 22		Societe, CECA S.A., France
LAND and SEA RESTORATION		Land and Sea Restoration LLC, San Antonio, TX, USA
VB591™WATER VB997™SOIL BINUTRIX		BioNutra Tech, Inc., Houston, TX, USA
OIL SPILL EATER II	Nutrient additive/ enzymatic additive	Oil Spill Eater International, Corporation Dallas, TX, USA

For other categories of remediation products, namely dispersants, surface washing, and miscellaneous oil spill control agents, see http://www.epa.gov/osweroe1/content/ncp/categories.htm

et al. 1994; Leahy and Colwell 1990). Thus, PAH biodegradation can be enhanced by the addition of nitrogenous and phosphorus-containing fertilizers (Bragg et al. 1994; Jiménez et al. 2007; Venosa et al. 2010). For example, biodegradation of the Prestige fuel oil spill on a beach on the Cantabrian coast (north Spain) was enhanced in the presence of the oleophilic fertilizer S200 (Díez et al. 2005; Jiménez et al. 2007).

Plants are also capable, through the root system, of absorbing various organic compounds depending on their relative lipophilicity. Phytoremediation of PAHs is also reported (e.g., Cerniglia 1992; Gałązka et al. 2012). Compounds uptaken by the plant may accumulate in the root or become permanently built into its structure, for example, lignin, which is an example of pollution phytostabilization (Domingues-Rosado and Pichtel 2004; Khoramnejadian et al 2013; Parrish et al. 2005). However, a significant part of the absorbed organic compound undergoes only translocation along the vascular bundles of the plant and is released through transpiration by the leaves. This process decreases pollution concentration in the soil but it is not advantageous to the environment because it causes atmosphere pollution. Some microorganisms that live inside root, stem, and leaf tissues of plants can alleviate the problem by using those accumulated compounds. Examples of such microorganisms are strains of *Azospirillum* spp. and *Pseudomonas stutzeri* (Gałązka et al. 2010). Recent studies on the possibility of using the plant *Zea mays* L. (commonly named maize) in the purification of soils polluted with crude oil derivatives have been published (Huang and Wei 2004; Liste and Felgentreu 2006; Marchenko et al. 2001; Muratova et al. 2003; Parrish et al. 2005). Maize, thanks to a well-developed and dense root system, may be a proper habitat to inoculate endophytic bacteria capable of using PAHs as the only source of carbon and energy.

The National Oil and Hazardous Substances Pollution Contingency Plan (NCP), governs the use of dispersants and other chemical and biological agents that may be used in responding to oil spills. EPA has scheduled those compounds, known as the NCP product schedule (USEPA 2007), which include bioremediation agents, dispersants, surface collecting agents, surface washing agents, and miscellaneous oil spill control agents. Table 8.5 gives some of the bioremediation agents.

8.4 Conclusions and Future Perspectives

Concerns on the use of xenobiotic compounds and on their fate and environmental persistency has increased in the past few years. As a result, the ideal industry is that which manufactures an important product with minimum use of resources, at low cost and minimum or no pollution. This is a difficult task, once chemical reactions generate side products which usually become dispensable and constitute pollutants. Because of this, and in order to reduce costs, an intelligent way should be the recycling of those side products into the production, either in the same process or to make a new valuable product. Likewise, bioremediation of xenobiotic compounds to avoid their discharge into environmental resources and, complementarily, to produce valuable compounds seems to be an intelligent strategy. Researchers, especially in the pollution prevention and remediation field, are more stimulated with regard to those approaches. Bioprocesses appear as a candidate to replace the chemical ones. This is possible because microorganisms have enzyme systems to degrade and utilize different compounds as a source of carbon and energy. Based on the matters discussed in this chapter, it may be concluded that microbial degradation can be considered as a key component in the cleanup strategy for persistent organic compounds such as the pesticides and PAHs. Risk assessment of POPs also requires information on the toxicological and ecotoxicological properties of these compounds as well as on their levels in environment. As a consequence, more restrictions in the use of chemical products have been imposed at national and international levels.

The world practice of using agrochemicals for long periods, in an indiscriminate and abusive way, has been a concern of the authorities involved in public health and sustainability of the natural resources, as a consequence of environmental contamination. Herbicide bioremediation has been researched extensively although new microbial consortia with high specific growth rates and high substrate concentrations toleration may still be isolated and/or modified by engineering molecular tools. Identification of intermediates and final products and their environmental fate in order to establish the biodegradation pathways is the key for the implementation of effective bioremediation processes. Sustainable agriculture is a recent direction, developed over the last 20 years. Organic farming and integrated production are two methods of sustainable agriculture with the aim to preserve ecosystems, biodiversity, soil fertility, and cycle nutrients, as well as being technically appropriate, economically viable, and socially acceptable. Instead of using toxic compounds to control a pest, the new biotechnological approaches to integrated pest management include the use of a variety of biological control agents such as bacteria, algae, fungi, viruses, protozoa, and plants, but also modified chemicals such as pheromones and kairomones. The level of efficacy that is required in a trial of such products may be similar to that expected from a synthetic chemical pesticide.

Microbial degradation of PAHs has also been a challenge to solve an enormous problem, especially that of the crude oil spills, pressed by their ubiquitous distribution and their harmful effects on human health. LMW PAHs are usually easier to degrade and less persistent in the environment, contrarily to the HMW ones, generally highly persistent due to their physical and chemical properties. However, knowledge regarding biodegradation of HMW PAHs has been advanced in the past decade. A number of HMW PAH-degrading strains have been isolated and characterized, although a better understanding of the mechanism of biodegradation is indispensable, which depends on various factors such as the indigenous microorganisms to transform or mineralize the organic contaminants and also contaminated source constituents.

Advances in various science fields, namely molecular biology, microbial techniques, chemical techniques, and engineering, are aiding in the extraction, detection, and identification of xenobiotics and also of degrading organisms, enzymes identification, and degradation pathways. This has been extremely helpful for predicting the environmental fate of those compounds and contributes to the advances in bioremediation strategies.

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Chapter 9
Application of Microorganisms in Bioremediation of Environment from Heavy Metals

Katarzyna Hrynkiewicz and Christel Baum

Abstract Heavy metals are important environmental pollutants which belong to the group of non-biodegradable and persistent compounds deposited in plant tissue (e.g. vegetables) which are then consumed by animals and humans. Increased pollution of natural environment with heavy metals, particularly in areas with anthropogenic pressure, also contributes to disorders in the natural balance of microbial populations. Molecular analysis carried out during the past decades revealed that density and diversity of microorganisms significantly correlated with increased contamination of the environment with heavy metals. As a result, a selective promotion of metal-tolerant genera of microorganisms was observed. In general, microorganisms are organisms with relatively high tolerance of unfavourable conditions, and these properties evolved over millions of years. In this chapter, a variety of mechanisms responsible for adaptation of microorganisms to high heavy metal concentrations, e.g. metal sorption, uptake and accumulation, extracellular precipitation and enzymatic oxidation or reduction, will be reported. Moreover, molecular mechanisms responsible for their metal tolerance will be described. The efficiency of accumulation of heavy metals in the microbial cells will be discussed and presented in photos from a reflection electron microscope (REM). The capacities of microorganisms for metal accumulation can be exploited to remove, concentrate and recover metals from polluted sites. This provides the basis for biotechnological solutions for the remediation of contaminated environments. Bioremediation has been regarded as an environment-friendly, inexpensive and efficient means of environmental restoration. Since microorganisms constitute a key factor of this technology, knowledge of the nature and molecular mechanisms of their tolerance of increased heavy metal concentrations is essential.

Keywords Pesticides · Environmental and health impact · Bioremediation

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9.1 Environmental Pollution with Heavy Metals and its Influence on the Living Biota: Actual Status and Perspectives

Metals most frequently found at polluted sites are divided into two categories: cationic metals (metallic elements whose forms in soil are positively charged cations) and element compounds (elements whose forms in soil are combined with oxygen and are negatively charged). The most common problem-causing cationic metals are mercury, cadmium, lead, nickel, copper, zinc and chromium, whereas the most common anionic element is arsenic (Olaniran et al. 2013). Analysis of the negative effects of metal toxicity on the environment is complicated since heavy metals may be present in a variety of chemical and physical forms, namely, soil-adsorbed species, soluble complexed species and ionic solutes. Moreover, the effect of environmental conditions such as pH, redox potential of the water phase as well as soil properties, including ion exchange capacity, clay type and content and organic matter content, on the physical and chemical states of the metals can cause further impediments (Olaniran et al. 2013).

The actual status of environmental heavy metal pollution in urban soils, road dusts and in agricultural soils in China was reviewed by Wei and Yang (2010). They revealed the highest heavy metal concentrations (mainly Cr, Ni, Cu, Pb, Zn and Cd) in urban road dusts and identified the traffic and industrial emissions as the major source of this pollution. About 65 % of all tested cities in China had high to extremely high levels of contamination. Compared with this, agricultural soils were mainly uncontaminated or slightly contaminated with Cr, Cu, Pb, Zn and Ni. Some agricultural soils were considerably contaminated by Cd and Hg. Worldwide, the main sources of heavy metal pollution in agricultural soils are fertilisation (especially Cd from phosphorus fertilisers) and pesticide applications (especially Cu from fungicides; e.g. Aikpokpodion et al. 2010). Since some heavy metals are characterized by great solubility in water, they can be easily absorbed by the living organisms and are found to be accumulated in humans at the end of the food chain (Charrier et al. 2010). Especially Cd and Zn are known to have high soil-to-plant transfer factors (Olayinka et al. 2011) and can be easily transferred into food products for this reason. Cadmium is, together with Pb and Hg, associated with the main threats to human health from heavy metals (Järup 2003).

Remediation of polluted sites can be done on- or off-site. Appropriate remediation strategies for these sites were reviewed by Peng et al. (2009). Bioremediation, in particular, offers valuable strategies for an ecological and economical advantageous on-site remediation. At present, bioremediation of heavy metal-polluted soils, water and sediments is often based on plant uptake during phytoremediation (Peng et al. 2009). However, microbial promotion can significantly increase the efficiency of phytoextraction of metals (e.g. Hrynkiewicz and Baum 2013, Zimmer et al. 2009).

Since microbes can promote plant growth in heavy metal-polluted areas in various ways (actively or passively), they should be analysed both in relation to particular taxonomic groups and as a result of different rhizosphere soil conditions including organic matter, pH, temperature, nutrients and pollutants level (Glick 2003; Bais et al. 2006). Among the rhizosphere microorganisms involved in plant interactions with metal-contaminated soil milieu, deserving special attention are plant growth-promoting bacteria (PGPB) and plant growth-promoting fungi (PGPF)—the plant-associated bacteria/fungi which migrate from the bulk soil to the rhizosphere of living plants and colonize the rhizosphere and roots of plants (Hrynkiewicz et al. 2009, 2012; Elsharkawy et al. 2012). Microorganisms colonizing the internal tissues of plants without causing symptomatic infections or negative effects on their host have been defined as endophytes (Schulz and Boyle 2006). In general, the beneficial effects of endophytes are greater than those of many rhizobacteria (Pillay and Nowak 1997) and might be aggravated when the plant is growing under either biotic or abiotic stress conditions (Hardoim et al. 2008). Endophytic microorganisms may be potential resources of highly efficient biosorbents for heavy metal biosorption since they have the advantage of being relatively protected from the competitive, high-stress environment of the soil (Sturz and Nowak 2000; Xiao et al. 2010).

Direct microbial strategies, besides the promotion of phytoremediation, in remediation of contaminated soils can include the use and stimulation of indigenous microbial populations, bioaugmentation (the addition of adapted or designed inoculants) or addition of genetically modified microorganisms. Particularly, the combination of genetic engineering of bacterial catalysts with judicious eco-engineering of the polluted sites was supposed to be especially important in future bioremediation strategies (Valls and Lorenzo 2002).

9.2 Resistance of Microorganisms to Heavy Metals: Mechanisms of Action

In general, metals and metalloids can be categorized as being essential and non-essential to biological life. Some metals, such as calcium, chromium, cobalt, copper, iron, magnesium, manganese, nickel, potassium, sodium and zinc, play an integral role in the life processes of microorganisms and serve as micronutrients which are used for redox processes, stabilization of molecules through electrostatic interactions, as components of various enzymes and for regulation of osmotic pressure (Bruins et al. 2000; Hussein and Joo 2013; Olaniran et al. 2013). Many other metals (e.g. silver, aluminium, cadmium, gold, lead and mercury) have no biological role and are non-essential and potentially toxic to microorganisms (Hussein and Joo 2013; Olaniran et al. 2013). However, all metals according to their concentration have toxicity with respect to living organisms. The minimal inhibitory concentrations of heavy metal/s for *Escherichia coli* are reported in Table 9.1.

Some cations of heavy metals (e.g. Hg^{2+}, Cd^{2+} and Ag^{2+}) can bind to sulfhydryl (–SH) groups of enzymes essential for microbial metabolism and inhibit the activity of sensitive enzymes. Moreover, many divalent heavy metal cations (e.g. Mn^{2+}, Fe^{2+},

Table 9.1 Minimal inhibitory concentrations (MIC) of heavy metals for *Escherichia coli* (Nies 1999)

MIC (mM)	Heavy metals
0.01	Hg^{2+}
0.02	Ag^{2+}, Au^{3+}
0.2	CrO_4^{2-}, Pd^{2+}
0.5	Pt^{4+}, Cd^{2+}
1.0	Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}
2.0	Tl^{+}, UO_2^{2-}, La^{3+}, Y^{3+}, Sc^{3+}, Ru^{3+}, Al^{3+}
5.0	Pb^{2+}, Ir^{3+}, Os^{3+}, Sb^{3+}, Sn^{2+}, In^{3+}, Rh^{2+}, Ga^{3+}, Cr^{3+}, V^{3+}, Ti^{3+}, Be^{2+}
10.0	Cr^{2+}
20.0	Mn^{2+}

MIC minimal inhibitory concentrations

Co^{2+}, Ni^{2+}, $Cu^{2+}$and Zn^{2+}) are structurally very similar. To differentiate structurally similar metal ions, microorganisms have evolved two types of uptake mechanisms: fast—unspecific, constitutively expressed and driven by the chemiosmotic gradient across the cytoplasmic membrane of bacteria—and inducible (slower)—with high substrate specificity, with the use of ATP hydrolysis as the energy source and applicable by the cell in times of starvation or a special metabolic situation (Bruins et al. 2000; Nies 1999; Olaniran et al. 2013). Regardless of specific microbial uptake systems, high concentrations of non-essential metals can be transported into the cells by a constitutively expressed unspecific system and (similarly as non-essential metals) damage cell membranes, alter enzyme specificity, disrupt cellular functions, damage the structure of DNA and impose oxidative stress on microorganisms (Bruins et al. 2000; Kachur et al. 1998; Nies 1999). Since metal ions (unlike other toxic pollutants) cannot be degraded or modified (Orhan and Buyukgungor 1993), some microorganisms develop metal ion homeostasis factors and metal-resistance determinants (Bruins et al. 2000; Nies 1999; Ji et al. 1995). One (or more) from the following six metal-resistance mechanisms allow microorganisms to function in metal-contaminated environments: (1) exclusion by permeability barrier, (2 and 3) intra- and extracellular sequestration, (4) active transport efflux pumps, (5) enzymatic detoxification and (6) reduction in the sensitivity of cellular targets to metal ions (Bruins et al. 2000; Nies 1999; Ji et al. 1995; Carine et al. 2009; Rensing et al. 2009; Silver and Misra 1988; Olaniran et al. 2013).

High concentrations of heavy metals reduce biomass of sensitive soil microorganisms and can lead to changes in their structure, diversity and enzymatic activities (Hartmann et al. 2005; Frey et al. 2006; Lazzaro et al. 2006). Several results revealed decreased bacterial and fungal diversity in heavy metal-polluted soils (e.g. Brandt et al. 2006; Hu et al. 2007, Del Val et al. 1999; Li et al. 2012). Metal-sensitive microbial populations are reduced or disappear, and are replaced by other indigenous populations, which can better tolerate and adapt to high concentrations of heavy metals in the environment (Lazzaro et al. 2008). Changes in bacterial and fungal diversity of heavy metal-polluted soils can be useful for environmental monitoring (Turnau et al. 2006; Demoilng and Baath 2008). The diversity of microbial population at metal-polluted sites has been investigated already by several scientists using culture-dependent and molecular techniques. Microorganisms naturally inhabiting metal-polluted soils can belong to gram-positive bacteria such as *Bacillus* and *Arthrobacter* and gram-negative bacteria such as *Pseudomonas* and *Burkholderia* (Kozdrój and van Elsas 2001; Ellis et al. 2003; Héry et al. 2003; Hrynkiewicz et al. 2012). However, in the group of *Proteobacteria*, bacteria with high tolerance as well as those very sensitive to increased heavy metal concentrations can be present (Tsai et al. 2005). Mechanisms of adaptation of microorganisms are correlated with the time of their exposure to increased heavy metal concentrations. In short term, naturally inhibiting microbial populations can survive the pollution, and in long term, the surviving microorganisms may adapt to unfavourable conditions using phenotypic or genetically based adaptation mechanisms (Lazzaro et al. 2008). To date, several genes coding metal resistance of bacteria have been discovered; however, a detailed understanding of the key indigenous organisms able to tolerate heavy metal pollution is still lacking (Naz et al. 2005; Lazzaro et al. 2008). Tolerance mechanisms are often plasmid encoded, but, in some instances, the genes are found on the chromosome, suggesting an important evolutionary pressure to keep these genes, e.g. mercury (Hg^{2+}) resistance in *Bacillus*, cadmium (Cd^{2+}) efflux in *Bacillus* and arsenic efflux in *E. coli* (Carlin et al. 1995; Shrivastava et al. 2003).

The potential of selected microorganisms to survive and grow in soils with high concentrations of heavy metals may be a useful feature for risk assessment and bioremediation of polluted sites (Lazzaro et al. 2008). The application of microorganisms to extract or immobilize heavy metal contaminants is considered as a biotechnological approach to clean up polluted environments (Cristiani et al. 2012). Microorganisms can improve phytoextraction by altering the solubility, availability and transport of heavy metals and nutrients by reducing soil pH, release of chelators, P solubilization, or redox changes (Ma et al. 2011). Among different metabolites produced by microorganisms, siderophores may play a very important role in metal mobilization and accumulation (Rajkumar et al. 2010). These microbial compounds may be synthesised by both mycorrhizal fungi and rhizosphere bacteria. Siderophores solubilize unavailable forms of heavy metal-bearing Fe but form complexes with bivalent heavy metal ions that can be assimilated by root-mediated processes (Braud et al. 2009).

9.3 Microorganisms as Biosorbents of Heavy Metals

Since degradation and metabolism of heavy metals are not possible, microorganisms have evolved coping strategies to either transform the element to a less-harmful form or bind the metal intra- or extracellularly, thereby, preventing any harmful interactions in the host cell (Monachese et al. 2012). Moreover, they are able to actively transport the metal out of the cell cytosol (White and Gadd 1998).

Bacterial strains can be specific to accumulate one or several heavy metals (Mejare and Bulow 2001). They can bind high levels of heavy metals according to a variety of mechanisms: accumulate metals by either a metabolism-independent (passive) or a metabolism-dependent (active) process and can remove heavy metals through bioaccumulation or biosorption (Cristani et al. 2012). In the bioaccumulation process, metals are transported from the outside of the microbial cell through the cellular membrane into the cell cytoplasm, where the metal is sequestered (Cristani et al. 2012). Metals adsorption is determined by the sorptivity of the cell envelope and influenced by differences in the cell wall construction of gram-positive and gram-negative bacteria (Jiang et al. 2004; Cristani et al. 2012). The factors responsible for metal adsorption of bacterial cells include the presence of phosphoryl groups, lipopolysaccharides, carboxylic groups and teichoic and teichuronic acids (parameters characteristic for specific groups of bacteria) as well as toxicity, composition and total content of metals in the environment (Haferburg and Kothe 2007; Cristiani et al. 2012).

The metal-accumulating capacity of microorganisms can be exploited to remove, concentrate and recover heavy metals from mine tailings and industrial effluents (Malekzadeh et al. 2002). Several reports of aerobic bacteria accumulating metals like Ag, Co, Cd, Cu, Cr and Ni are available (e.g. Adarsh et al. 2007; Karelová et al. 2011).

A multi-metal-resistant endophytic bacterial strain *Bacillus* sp. L14 (EB L14) was isolated from the cadmium hyperaccumulator *Solanum nigrum* L (Guo et al. 2010). The hormesis of EB L14 was observed in the presence of divalent heavy metals (Cu, Cd and Pb) at a relatively lower concentration (10 mg/L). This observation was the effect of abnormal activities of increased ATPase which provided energy to help EB L14 reduce the toxicity of heavy metals by exporting the cations. It was revealed that within a 24-h incubation period, EB L14 can specifically take up about 76, 80, and 21 % of Cd, Pb and Cu from a pre-given solution, respectively (Guo et al. 2010). Subcellular fractionation studies revealed that almost 81 and 76 % of the Cd and Pb taken up by the cells are found in the membrane fraction, whereas the presence of Cd and Pb in the cytoplasm is only about 5 and 7 %, and on the cell wall is 14 and 16 % of the total uptake, respectively (Guo et al. 2010).

Opposite results were obtained in our laboratory during observation of rhizosphere bacteria *Pseudomonas* sp. (Fig. 9.1). Microscopic analysis revealed the highest concentrations of Cd in external components (capsule) and cell walls of the bacterial cells, cultivated in the presence of Cd ions (not published data). The internal spaces of bacterial cells possessed lower concentrations of Cd.

The results shown in Fig. 9.1 were similar to other reports (Bai et al. 2008; Kumar and Upreti1 2000) in which bacterial cell walls were always responsible for almost all heavy metal uptakes. These kinds of uptakes seem to depend on the intrinsic surface properties of the cells wall which involves the contribution of diffusion, sorption, chelation, complexation or micro-precipitation mechanisms (Guo et al. 2010).

Bacteria can interact with a range of toxic metals through differences between the net negative charge of bacteria and the cationic charge of many metals. It is

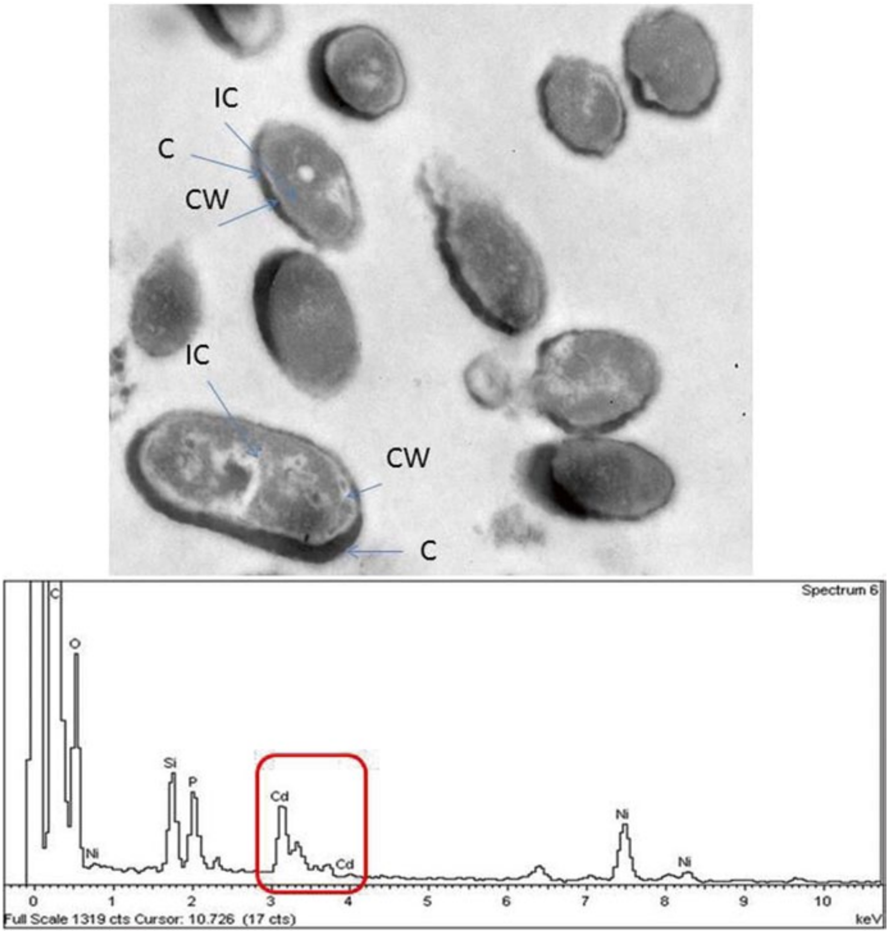

Fig. 9.1 Spatial distribution of Cd in bacterial cells (*Pseudomonas* sp.). Qualitative and quantitative analyses of the elemental composition and location of Cd in bacterial cells of *Pseudomonas* sp. Analyses were performed using a JEM 1400 electron microscope (JEOL Co., Japan 2008) equipped with an X-ray microanalyser (EDS INCA Energy TEM, Oxford Instruments) and tomography system as well as a charge-coupled device (CCD) camera MORADA (SiS-Olympus). *CW* cell wall, *IC* inside the cell, *C* capsule

known that nucleation sites on the bacterial cell surface have the ability to bind metals of opposite charge (Monachese et al. 2012). However, analysis of potentiometric titration showed that changes in the pH of the environment can alter the cell surface charge and affect the ability of bacterial species to bind metal in solution (Fein et al. 2001). Fein and co-workers proposed (2010) that a neutral pH 7 has the optimum binding potential of heavy metal cations, since at this pH, reactive functional groups are not ionized. However, this is not valid for all bacterial species or all interactions with metals, since in many environments (e.g. acid mine tailings), bacterial species exist with the ability to not only survive in extreme pH conditions but also cope with high metal concentrations that are toxic to humans and the majority of other species. It means that unique microbes have the ability to cope with metals through a variety of mechanisms but most notably through the precipitation of metal particles and active efflux (Monachese et al. 2012). The potential of specific/selected microorganisms to survive and grow in extreme heavy metal-polluted soils may be a useful feature for risk assessment and bioremediation of polluted sites (Lazzaro et al. 2008).

9.4 Microbial Technologies of Remediation

The potentials of microbes in metal remediation were reviewed by Rajendran et al. (2003). Microbial metal bioremediation can be an efficient strategy due to its low cost, high efficiency and eco-friendly nature. Microbes can effectively sequester heavy metals. They can partly tolerate high heavy metal concentrations and can develop high heavy metal-binding capacity. They can produce heavy metal-binding proteins in response to toxic heavy metal concentrations. Microbial bioimmobilization of metals in terrestrial and aquatic environments is promoted by the high surface to volume ratio of microorganisms. Furthermore, metal-related reactions catalysed by bacteria allow altering the physicochemical conditions in polluted substrates (Valls and Lorenzo 2002).

Microorganisms can be used as biosurfactants in metal-contaminated soils. The biosurfactant technology can be an effective and non-destructive method for bioremediation of soils polluted with Cd and Pb (Das et al. 2009). The efficiency of bacterial extraction of metals from polluted wastewater using metal-resistant bacteria was tested for strains of *Pseudomonas aeruginosa* by Nezhad et al. (2010). In this investigation, the strains were subjected to mutation to increase the inhibitory concentration of Cd for their growth. Nezhad et al. (2010) concluded from their results that the biomass of *P. aeruginosa* strains can be used for bioremediation of Cd-polluted industrial waste.

9.5 Engineering of Microorganisms in Remediation of Heavy Metals

The use of autochthonic microorganisms found in the environment, e.g. soil and water, pioneered the field of bioremediation and is still a main object of further improvements of this technology. However, the use of genetically engineered microorganisms (GEM) can significantly increase capabilities of bacteria to degrade environmental toxins and bind heavy metals (Monachese et al. 2012). Sayler and Ripp (2000) designed the *Pseudomonas fluorescens* strain KH44 which was able to sense toxic polycyclic aromatic hydrocarbons and degrade them. Application of GEM to increase heavy metal remediation in contaminated sites was based on the transformation and expression of metallothionein by bacterial cells. Valls et al. (1998) successfully engineered metallothionein to be expressed on the surface of *E. coli* as an attempt to increase metal-binding sites, leading to increased Cd accumulation.

Recombinant bacterial sensors (biosensors) have been constructed and used for the determination of a broad range of toxic parameters, including, e.g. heavy metal pollutants. In the main mechanism of action, the toxic compound crosses the cell wall and cell membrane and then triggers a sensing element (in most cases, a promoter linked to a reporter gene), leading to the production of easily measurable reporter proteins. The most commonly used reporter proteins for optical detection in microbial systems are green fluorescent protein for fluorescence and bacterial luciferase for luminescence. For the construction of metal-sensing strains, the operons for metal resistance that some naturally occurring bacteria possess are often used as promoters (Woutersen et al. 2011). Biosensors based on luminescent bacteria provide a rapid, easily measurable response in the presence of relevant toxic (mixtures of) compounds and may be valuable tools for monitoring the chemical quality and safety of soil and drinking water. The genes used most often for construction of recombinant bacterial strains are luciferase genes *lux* (Woutersen et al. 2011). Bacterial biosensors with *lux* genes can detect contaminations ranging from milligrams per litre to micrograms per litre. The sensitivity of *lux* strains can be enhanced by various molecular manipulations; however, most reported detection thresholds are still too high to detect levels of individual contaminants. Bacterial *lux* strains sensing specific toxic effects may also respond to mixtures of contaminants and, thus, could be used as a sensor for the sum effect (Woutersen et al. 2011).

Ivask et al. (2002) constructed recombinant luminescent bacterial sensors for the determination of the bioavailable fraction of cadmium, zinc, mercury, and chromium in soil. The sensors carried the firefly luciferase gene as a reporter under the control of zinc-, chromate- and mercury-inducible units. The specificity of the above sensors was determined by using different heavy metal compounds. They have revealed that the zinc and mercury sensors were not completely specific to the target metals. The zinc sensor was co-inducible with cadmium and mercury and the mercury sensor with cadmium. The chromate sensor was inducible not only by chromate but also with Cr^{3+}. In another experiment (Rasmussen et al. 2000), the *mer–lux* gene fusion in *E. coli* was applied for the estimation of the bioavailable fraction of mercury in soil. The *mer*-promoter was activated when Hg^{2+}, present in the cytoplasm of the biosensor bacterium, binds to *merR*, resulting in transcription of the *lux* genes and subsequent light emission. The luminescence-based bacterial sensor strains *P. fluorescens* OS8 (pTPT11) for mercury detection and *P. fluorescens* OS8 (pTPT31) for arsenite detection were used in testing their application in detecting heavy metals in soil extracts (Petanen and Romantschuk 2002). The sensor strain with pTPT31 appeared to have a useful detection range similar to that of chemical methods.

Strict regulatory guidelines of the Environmental Protection Agency make the use of GEM difficult, and a better understanding of how these microbes work and their safety and environmental containment is needed before they are used for bioremediation (Monachese et al. 2012).

In the end, it is worth mentioning that many plants have been genetically modified with microbial catabolic genes and specific transporters for increased remedial activities (Abhilash et al. 2012). For example, poplar plants carrying g-glutamylcysteine synthetase from *E. coli* accumulate higher concentrations of cadmium and copper (Bittsanszky et al. 2005).

9.6 Potentials and Limitations of Microbial Bioremediation of Heavy Metals

The food and water we consume are often contaminated with a range of heavy metals (e.g. lead and cadmium) that are associated with numerous diseases. The ability to prevent and manage this problem is still a subject of much debate, with many technologies being ineffective and others too expensive for practical large-scale use, especially for developing nations where major pollution occurs (Monachese et al. 2013).

Microbial-assisted phytoremediation is a reliable and dependable process. Microorganisms, especially rhizosphere and endophytic, can accelerate phytoremediation in metal-contaminated soils, e.g. by promoting plant growth/health and increasing the bioavailability of metals by plants. However, there are still many areas of poor understanding or lack of information. First of all, basic molecular mechanisms of microbial-assisted phytoremediation have to be still elucidated in order to speed up this process and to optimize the rate of mobilization/absorption/accumulation of pollutants by microorganisms. Many functional properties (e.g. adapting strategies, production of various metabolites, metal-resistant, biosorption as well as mobilization/immobilization mechanisms) of bacterial isolates, the factors required by bacteria to colonize the rhizosphere and/or interior tissues of the plant, promote plant growth, and metal uptake should be identified (Ma et al. 2011). The other problem is related with colonization and survival of microbial inoculums at natural sites and under different environmental conditions (Hrynkiewicz and Baum 2013). Moreover, implementation of microbial-assisted phytoremediation in the field level needs intensive future research on understanding the diversity and ecology of plant-associated microorganisms in multiple-metal-contaminated soils. Explanation of the role of naturally adapted indigenous microbes that have been cultured and enriched in the laboratory in the phytoremediation potential of various plants in multiple-metal-contaminated soils can also improve this technology (Ma et al. 2011).

New insight into ability of microorganisms to bind metals suggests that species such as *Lactobacillus*, present in the human mouth, gut and vagina and in fermented foods, have the ability to bind and detoxify pollutants. The gut microbiota have key roles in regulating digestion by providing enzymes required for metabolic breakdown by processing and metabolizing compounds as they enter the host through normal diet. However, so far we do not know what effect the gut microbiota may have on binding and sequestering metals, thus imparting protection to the host.

This is why understanding of detoxification mechanisms of lactobacilli and how, in the future, humans and animals might benefit from these organisms in remediating environmental contamination of food is, so far, a big challenge (Monachese et al. 2013).

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Chapter 10
Organochlorine Pesticide Residues in Foodstuffs, Fish, Wildlife, and Human Tissues from India: Historical Trend and Contamination Status

V. Dhananjayan and B. Ravichandran

Abstract Ever since people started utilizing natural resources, environmental quality started to deteriorate. Deterioration of the quality of these resources affects human health and well-being and therefore becomes a threat to human security. Organochlorine pesticides (OCPs) are ubiquitous environmental contaminants relevant due to their high toxicity and potential carcinogenicity. These contaminants are considered to be hazardous to aquatic organisms, fish, birds, and humans. Varying levels of these pesticides have been reported in different segments of the ecosystem including humans. Health damage to fish and wildlife has prompted concern about the health effects of these contaminants on humans. It has been found that a greater amount of total intake of these contaminants in human beings is through consumption of contaminated food. A number of abnormalities seen in the reproductive system of various wildlife species can be correlated with similar abnormalities on the rise in the human population. Exposure to these pollutants also suppresses the immune system, thereby increasing the risk of acquiring several diseases. Temporal trends examined by comparing the results of previous studies on OCP levels in the Indian environment revealed a decline in the trend of dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs) in some parts of the natural environment. In contrast, very high concentrations were detected in biotic samples. Continuous monitoring and epidemiological studies of OCP levels in humans are warranted. In this chapter, we outline the environmental and human health problems associated with pesticide contamination. To our knowledge, this is the first report to present the residue levels of persistent OCPs in fish, wildlife, and human tissues from India.

Keywords Organochlorine pesticides · Exposure · Effects · Fish · Wildlife · Human

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10.1 Introduction

The application of pesticides to agriculture has greatly improved the food production worldwide. India is the second largest producer of vegetables after China and accounts for 13.4 % of world production. Surveys carried out by institutions spread throughout the country indicate that 50–70 % of vegetables are contaminated with insecticide residues. India has a wide variety of climate and soils on which a range of vegetable crops can be grown (Karanth 1982). During the last three decades, considerable emphasis has been laid on production of crops in India and vegetable exports have been stepped up. However, increased use of chemical pesticides has resulted in contamination of the environment and also caused many associated long-term effects on human health (Bhanti and Taneja 2007). The presence of pesticide residues in food commodities has always been a matter of serious concern. The problem is especially serious when these commodities are consumed (Solecki et al. 2005). Pesticides have been associated with a wide spectrum of human health hazards, ranging from short-term impacts such as headaches and nausea to chronic impacts like cancer, reproductive harm, and endocrine disruption (Berrada et al. 2010). The heavy use of pesticides may result in environmental problems like disturbance of natural balance, widespread pest resistance and environmental pollution, hazards to non-target organisms, wildlife, and humans.

India is among the largest agricultural societies in the world as the agricultural sector provides livelihood to the majority of its 1 billion people. Modern agriculture uses inputs such as chemical fertilizers, pesticides, seeds of high-yielding varieties, and mechanization that resulted in increased yields ushering an era of green revolution in the country. Synthetic pesticides are one of the major agro inputs that significantly contributed to the agricultural production in the country. Pesticides may have helped in enhancing agricultural production, but at the same time these chemicals have caused adverse effects (Shetty and Sabitha 2009).

Organochlorine pesticides (OCPs) are an important potential component of chemical pollutants used extensively for agriculture and public purposes in India as these are comparatively cheap and effective. These persistent organic compounds such as hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) are the predominant chemical contaminants found in various environmental matrices in India. Our biggest concern is that these molecules are stable in the environment. It is suspected that most of water bodies and soils are contaminated with these chemicals or with their degradation products (Krisahnamurthy 1984). HCH, aldrin, dieldrin, and heptachlor are banned in India. However, gamma-HCH (lindane) and DDT have restricted use and are allowed for termite control and public health purposes, respectively. Greater concentrations of organochlorine (OC) residues in human breast milk and adipose tissues (Kutz et al. 1991) collected from various developing countries indicated increased exposure of humans in these regions to OC insecticides. In more developed nations, foodstuffs are monitored through periodical surveys to assess human exposure and to maintain public health standards (Hotchkiss 1992; Krieger et al. 1992; Yess et al. 1993). However, comprehensive nationwide residue monitoring studies are prohibitively expensive and are yet to be implemented in many developing nations. Despite the continuing use of OCs, little information is available on their levels in foodstuffs in India.

An international convention aiming to restrict persistent organic pollutants (POPs) was formally adopted in May 2001, and global actions to reduce and eliminate release of the pollutants have been recommended. The OCPs form part of the "dirty dozen" and have already had a strong impact on wildlife and human beings (Choi et al. 2001). Chlorinated pesticides have shown to give rise to estrogen-dependent reproductive effects in several avian species (Fry 1995); further, DDT and its metabolites have also been shown to cause obstruction of Ca^{2+} metabolism in birds (Lundholm 1994). However, for the clarification of the toxic effects of OCs, basic information such as the distribution of OCs among organ (or tissue) is essential.

There are 234 pesticides registered in India. Out of these, 4 are WHO Class Ia pesticides, 15 are WHO Class Ib pesticides, and 76 are WHO Class II pesticides, together constituting 40 % of the registered pesticides in India. In terms of consumption, too, the greatest volumes consumed are of these poisons. India is the fourth largest pesticide producer in the world after the USA, Japan, and China. During 2003–2004, the domestic production of pesticides was approximately 85,000 t, and about 60,000 t was used annually (Anonymous 2005) against 182.5 million ha of land where 70 % accounts for DDTs, HCHs, and organophosphate pesticides (Bhattacharyya et al. 2009; Nirula and Upadhyay 2010). The domestic consumption of pesticides in agriculture is comparatively low (0.5 kg/ha; only 3.75 % of global consumption) against 12.0, 7.0, 6.6, and 3.0 kg/ha in Japan, USA, Korea, and Germany, respectively (Chauhan and Singhal 2006). Our objective in this chapter is to provide a comprehensive account of the distribution of OCPs in foodstuffs, fish, wildlife, and human tissues from India: historical trend and contamination status and their environmental sources, their movement through the food chain, and possible ecotoxicological risk of health in biota including humans.

10.2 Historical Trend and Contamination Status

The birth of modern pesticide era was hailed as a major breakthrough for mankind. The persistent pesticides belonging to the group of OC compounds were potent weapons against vectors of diseases, pests of crops, forests, and rangeland. Originally, certain pesticides like DDT and HCH were imported in the formulated form for mosquito control; however, slowly India started using these pesticides for agricultural purposes as well. The large-scale manufacture and distribution of OCPs did not take place until after the accidental discovery of DDT as an insecticide by Muller in 1946. Later, while several countries banned DDT, India stopped its use in agriculture in 1989. However, DDT is still being manufactured and used for malaria control. Pesticide demand is close to 90,000 t per annum. Insecticides

(73 %) dominate the market, followed by herbicides (14 %) and fungicides (11 %). Cotton, rice, and wheat growers account for almost 70 % of pesticide consumption, and the states consuming more are Andhra Pradesh, Punjab, Karnataka, and Gujarat. Presently, 44 types of pesticides are manufactured in India. DDT, benzene hexachloride (BHC), malathion, and carbofuran are commonly used. About 83,000 t of pesticides are used in the agricultural sector annually (Menon 2003). About 144 pesticide molecules are registered in India and 65 technical-grade pesticides are manufactured indigenously (The Pesticides Scenario 2000).

In India, in 1960, about 600 t of DDT was used in agriculture and 21,000 t for public health. As against this for public health in 1980, DDT used was 15,500 t and 9,100 t of DDT was used for 1983–1984. With increased use of the chemicals world over, negative environmental effects began to be noticed. These included toxicity in non-target organisms, bioaccumulation, long-term environmental persistence, and persistence in target pests. Since its introduction in Indian agriculture, about 575,000 t of BHC have been used—500,000 t in agriculture and 75,000 t in the public health sector to date. The current annual consumption of HCH is nearly 30,000 t in agriculture and 6,000 t in public health. It forms 60 % of the total insecticides consumed in the agriculture sector (Gupta 1986). Effects of pesticide use on ecosystems in India have scarcely been investigated.

Though complete ban on DDTs was imposed in many developed nations, in India it was banned only for agricultural use, but it is still used for malaria control, and HCH also is not completely banned (still used for agriculture). About 31 banned or restricted pesticides in other countries are still in use in India and about 350,000 t since 1985 and 7,000 t in 2001–2002 of DDT were used (http://www.cseindia.org/2002). Earlier studies in Indian marine environment showed that polychlorinated biphenyls (PCBs) and OCP residues are comparable with those found in other developing countries, but suggested an increase in the future due to the continuing usage of OCPs in agriculture and vector control measures. HCH and DDT were introduced in 1948 and 1949, respectively, for agricultural and public health purposes. Their cumulative consumption until 1995 was estimated to be 500,000 t for DDT and 1 million t for HCH. The values suggest that India has been the major consumer of HCH in the world (Kannan et al. 1995). Until 1992, these two insecticides accounted for two-thirds of the total consumption of pesticides in the country (Kannan et al. 1992a).

In global comparison, HCH levels in India are 1–2 orders of magnitude higher than those in countries like Cambodia (Kunisue et al. 2004b), Philippines (Kunisue et al. 2002), Vietnam (Minh et al. 2004), and Indonesia (Sudaryanto et al. 2006), but relatively lower than those in China (Kunisue et al., 2004a) and Hong Kong (Wong et al. 2002). The levels reported in Chennai by Subramanian et al. (2007) were among the highest found so far. It is also worthy to note that high levels of HCHs were also found in various environmental and biotic samples from India (Senthilkumar et al. 2001; Kunisue et al. 2003; Ramu et al. 2007) suggesting that India acts as a major source for HCHs which can also contribute to pollution by these compounds (Table 10.1).

Table 10.1 Top ten countries with highest technical HCH use (Li et al. 1999)

Number	Country	Total usage (kt)
1	China	4,464
2	India	1,057
3	Soviet Union (Erstwhile)	693
4	France	520
5	Egypt	479
6	Japan	400
7	USA	343
8	Germany East	142
9	Spain	133
10	Mexico	132

10.3 OCPs in Foodstuffs

Many surveys invariably indicated the predominance of DDT and HCH in Indian foodstuffs. Residues of chlorinated pesticide (OCP) in food have given rise to major concerns. This has reflected in the large number of reports in the literature on this subject. Moreover, the chronic effects of such exposure levels from food intake are mostly unknown but there is growing evidence of carcinogenicity and genotoxicity as well as endocrine disruption capacity (Miller and Sharpe 1998) being attributed to the ingestion of or exposure to pesticides. Despite the fact that the use of certain OCPs in agriculture is prohibited in many countries, these compounds have been detected in the environment worldwide due to their persistent nature (Rejendran and Subramanian 1999).

The long persistence of some agrochemicals in the environment sets in a series of undesirable effects through contamination of food and feed. Food contamination surveys have been conducted in this country since the late 1960s, when the Insecticide Act was enacted in 1968. Nevertheless, most of these studies have been conducted by certain institutions with a limited number of market samples. Report on comprehensive nationwide monitoring has not as yet been performed. The results of some of the earlier surveys have been reviewed by Kalra and Chawla (1981). Bioaccumulation of pesticides and biomagnification processes have become the weak links in the food chain. Among the pesticides that have acquired notoriety, DDT and HCH are particularly important. Although now partially banned, they are still very much in use because of their wide spectrum of activity and ready availability at low cost (Krisahnamurthy 1984; Aslam et al., 2013). During the last few decades, widespread contamination and toxic effects of organic chemicals have become a serious environmental problem. These chemicals enter the soil by direct treatment or being washed off from the plant surface during rainfall. Their physicochemical characteristics, which include hydrophobicity and resistance to degradation, cause these chemicals to accumulate in soils and sediments (Hong et al. 2008; Hu et al. 2010). Soil and sediments can act as contributors of organic pollutants to the atmosphere, especially of semi-volatile compound in warm climates. The fate of pesticides in soils with different cropping land use has been extensively studied worldwide including India (Viet et al. 2000; Oldal et al. 2006; Senthil Kumar et al. 2009).

10.3.1 Vegetables

Pesticides are widely used to ensure high crop yields. Indian diet contains vegetables as important component in food, because majority of Indians are vegetarian and per capita consumption of vegetables is approximately 135 g/day. Therefore, information on pesticide residues in vegetables is very important for human health. Bankar et al. (2012) investigated pesticide residues in market foods in Uttar Pradesh, India. About 58.33 % of the samples were free from residues, 28.33 % of samples contained pesticide residues at or below maximum residue limit (MRL), and 13.33 % of samples contained pesticide residues above MRL. Brinjal was the most positive followed by cabbage, tomato, and lady's finger. A study conducted by Mukherjee et al. (2011) in West Bengal, India, to access the level of OCPs residues in vegetables revealed that the concentration of total OCPs (ΣOCPs) ranged between <0.01 and 65.07 μg/kg with an average of 9.67 ± 2.34 μg/kg (wet wt.). The concentration of total DDTs (ΣDDTs), total HCHs (ΣHCHs), aldrin, dieldrin, and heptachlor was 3.49 ± 0.93 μg/kg, 2.07 ± 0.53 μg/kg, 1.32 ± 0.65 μg/kg, 1.36 ± 1.18 μg/kg, and 1.80 ± 0.4 μg/kg (wet wt.), respectively.

Bakore et al. (2002) conducted a study during 1993–1996 to investigate the magnitude of contamination of OC insecticides in vegetables which were brought for sale to the consumers in the local markets of Jaipur City, Rajasthan, India. Samples of vegetables (potato, tomato, cabbage, cauliflower, spinach, and okra) collected at the beginning, middle, and end of the seasons with respect to different vegetables and OC levels were assessed. Most of the collected samples were found to be contaminated with residues of DDT and its metabolites (dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE) isomers of HCH (alpha, beta, and gamma-HCH), heptachlor, heptachlor epoxide, and aldrin. Some of the detected insecticides exceeded the limit of tolerance prescribed by World Health Organization (WHO)/Food and Agriculture Organization (FAO). Kumari et al. (2002) monitored pesticide contamination among market samples (60) of six seasonal vegetables during 1996–1997. The estimation of insecticide residues representing four major chemical groups, i.e., OC, organophosphorous, synthetic pyrethroid (SP), and carbamate, was done. The tested samples showed 100 % contamination with low but measurable amounts of residues. Among the four chemical groups, the organophosphates were dominant followed by OCs, SPs, and carbamates. About 23 % of the samples showed contamination with organophosphorous compounds above their respective MRL values. More extensive studies covering different regions of Haryana state are suggested to get a clear idea of the magnitude of vegetable contamination with pesticide residues.

Kumari et al. (2004) analyzed 84 farm gate samples of seasonal vegetables for pesticide residues. About 26 % samples contained residues above MRL values. The contamination was mainly with organophosphates followed by SPs and OCs. The residues of HCH, DDT, and endosulfan were found in all the samples but did not exceed the tolerance limit. Bhanti and Taneja (2005) analyzed the summer and winter vegetable samples during 2002–2003 for pesticide residue estimation. The contamination levels of winter vegetables (average concentration of 4.57, 6.80, and

5.47 ppb, respectively, for lindane, endosulfan, and DDT) were found to be slightly higher than those of the summer vegetables (average concentration of 4.47, 3.14, and 2.82 ppb, respectively, for lindane, endosulfan, and DDT). The concentrations of these OCPs in summer and winter vegetables were well below the established tolerances but continuous consumption of such vegetables even with moderate contamination level can accumulate in the receptor's body and may lead to chronic effects that could be fatal.

Bhanti and Taneja (2005) assessed the pesticide contamination in vegetables grown in different seasons (summer, rainy, and winter). Data obtained were then used for estimating the potential health risk associated with the exposure to these pesticides. The pesticide residue detected in vegetables of different seasons shows that the winter vegetables are the most contaminated followed by summer and rainy vegetables. The concentrations of the various pesticides were well below the established tolerances but continuous consumption of such vegetables even with moderate contamination level can accumulate in the receptor's body and may prove fatal for human population in the long term. The analysis of health risk estimates indicated that chlorpyrifos and malathion did not pose a direct hazard; however, exposure to methyl parathion has been found to pose some risk to human health.

A recent study by Kumar et al. (2010) investigated the OCP residues in five varieties of vegetable samples collected from different markets in Uttar Pradesh. Vegetables tested in this study do not contain any quantities of pesticide residues hazardous to humans. Kumar et al. (2012) analyzed pesticides, namely, aldrin, dieldrin, heptachlor, and lindane in selected root and leaf vegetables collected from Kolkata. The concentration of total OCPs ranged between <0.01 and 6.00 ng/g, with an average of 2.16 ± 0.21 ng/g (wet wt.). The concentration of individual aldrin, dieldrin, heptachlor, and lindane was 0.48 ± 0.06 ng/g, 0.13 ± 0.02 ng/g, 1.03 ± 0.11 ng/g, and 0.52 ± 0.06 ng/g (wet wt.), respectively. The selected vegetables had residue levels much below the recommended MRLs set by the European Commission and the Indian Government (Tables 10.2 and 10.3).

Kumar et al. (2011) have conducted a study to assess the levels of OCPs (DDTs, HCHs, and endosulfan) in vegetables from Kolkata, India. The total concentration of OCPs ranged between 0.29 and 106.65 $\mu g\ kg^{-1}$ (wet wt.). The results indicated that all the vegetable samples had some levels of one or more OCPs. The mean concentration of DDT, HCH, and endosulfan was 6.63 ± 1.17 $\mu g\ kg^{-1}$ (wet wt.), 4.29 ± 1.47 $\mu g\ kg^{-1}$ (wet wt.), and 1.34 ± 0.99 $\mu g\ kg^{-1}$ (wet wt.), respectively. The ratio of α-HCH to γ-HCH isomers (α/γ-HCH ratio) ranged from 0.03 to 5.69, which reflects the use of lindane as well as technical formulation of the HCH. The ratios of (DDE + DDD)/ΣDDT and DDT/DDE were 0.52 and 1.21, respectively, which indicate that these vegetables were contaminated with fresh input as well as biotransformation of DDTs. Residue levels of HCH, DDT, and endosulfan in vegetables from Kolkata market were below the MRLs set by the European Commission and the Indian Government indicating minimal risk to the consumers.

Srivastava et al. (2011) conducted a study on 20 vegetables to analyze 48 pesticides including 13 OCs, 17 organophosphates (OPs), 10 SPs, and 8 herbicides (H). A total number of 60 samples, each in triplicates, were analyzed using a quick, easy,

Table 10.2 MRLs (European Commission 2006) for OCPs in the selected fruits and vegetables

Commodity	MRLs (mg/kg)						
Fruits	Gamma-HCH	Methoxychlor	Aldrin	Dieldrin	Endrin	*p, p'*-DDE	DDT
Papaya	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Water melon	0.01	0.01	0.03	0.03	0.01	0.05	0.05
Banana	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Mango	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Pear	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Pineapple	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Vegetables							
Tomato	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Lettuce	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Cabbage	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Carrot	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Onion	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Cucumber	0.01	0.01	0.02	0.02	0.01	0.05	0.05

Table 10.3 MRLs for pesticides in vegetables

OCP compounds (ng/g)					
MRLs	Aldrin	Dieldrin	Heptachlor	Lindane	References
Europe	10	10	10	50	European Commission 2008
India	100	100	50	1,000	FSSAI 2011

FSSAI Food Safety Standards Authority of India

cheap, effective, rugged, and safe method. About 23 pesticides were detected from total 48 analyzed pesticides in the samples with the range of 0.005–12.35 mg/kg. The detected pesticides were above MRL (PFA 1954). However, in other vegetables the level of pesticide residues was either below detection limit (BDL) or MRL.

Kumari et al. (2012) monitored 80 winter vegetable samples during 1997–1998 for pesticidal contamination. All the tested samples were contaminated with pesticide residues with measurable amounts. Among the four major chemical groups, residue levels of organophosphorous insecticides were the highest followed by bicarbamates, SPs, and OCs. About 32% of the samples showed contamination with organophosphorous and carbamate insecticides above their respective MRL values. These studies suggested that more extensive monitoring studies covering all vegetable crops from different agro-climatic regions of the state be carried out to know the exact level of pesticidal contamination, which may serve as a basis for future policy on chemical use.

10.3.2 Tea

Tea is a perennial plantation crop grown under monoculture providing favorable conditions for a variety of pests. The concept of pest control has undergone a considerable change over the past few decades. In recent years, there has been a greater dependence on the use of pesticides (7.35–16.75 kg/ha) with little importance laid on other safe control methods for the management of tea pests. Due to this practice, the tea pests showed a higher tolerance/resistance status due to formation of greater amount of esterases, glutathione S-transferase, and acetylcholinesterase. Thus, over-reliance on pesticides ends up with pesticide residue in made tea (DDT—10.4–47.1 %; endosulfan—41.1–98.0 %; dicofol—0.0–82.4 %; ethion—0.0–36.2 %; cypermethrin—6.0–45.1 %). The growing concern about the pesticide residue in made tea, its toxicity hazards to consumers, the spiraling cost of pesticides, and their application have necessitated a suitable planning which will ensure a safe, economic, as well as effective pest management in tea. At present, it is a global concern to minimize chemical residue in tea and the European Union and German law imposed stringent measures for the application of chemicals in tea and fixed MRL values at ≤0.1 mg/kg for the most commonly used pesticides, which is not met in the real practice and has been a major constraint to tea-exporting countries like India. In order to regulate the situation of the Indian market at a global level, central insecticide board and prevention of food adulteration regulation committee have reviewed the MRL position for tea and has recommended 10 insecticides, 5 acaricides, 9 herbicides, and 5 fungicides for use in tea and issued the tea distribution and export control order in 2005 which will help the country to limit the presence of undesirable substances in tea (Gurusubramanian et al. 2008).

Bishnu et al. (2009) quantified the residues of organophosphorus (e.g., ethion and chlorpyrifos), OC (e.g., heptachlor, dicofol, endosulfan), and SP (e.g., cypermethrin and deltamethrin) pesticides in made tea, fresh tea leaves, soils, and water bodies from selected tea gardens in the Dooars and hill regions of West Bengal, India, during April and November, 2006. The organophosphorus (OP) pesticide residues were detected in 100 % substrate samples of made tea, fresh tea leaves, and soil in the Dooars region. In the hill region, 20–40 % of the substrate samples contained residues of organophosphorus (OP) pesticides. The OC pesticide residues were detected in 33–100 % of the substrate samples, excluding the water bodies in the Dooars region and 0–40 % in the hill region. The estimated mean totals of studied pesticides were higher in fresh tea leaves than in made tea and soils. The SP pesticide residues could not be detected in the soils of both the regions and in the water bodies of the Dooars. Sixteen percent and 20 % of the made tea samples exceeded the MRL level of chlorpyrifos in Dooars and hill regions, respectively. Based on the study, it was revealed that the residues of banned items like heptachlor and chlorpyrifos in made tea may pose health hazards to the consumers.

10.3.3 Dry Fruits

The use of pesticides on cash crops and exportable food commodities had always been a serious concern. Fruits form one of the important constituents of human diet, in that they give one-third of the requirement of calories, vitamins, and minerals. Kumari et al. (2005) have reported the pesticide residues in butter (45) and ghee (55) samples collected from rural and urban areas of cotton growing belt of

Haryana. Butter samples were comparatively more contaminated (97 %) than ghee (94 %), showing more contamination with OC insecticides from urban samples. About 11 % samples of butter showed endosulfan residues above MRL value and 2 % samples had residues of SPs and organophosphates each above their respective MRL values. In ghee, residues of HCH and DDT both and of endosulfan exceeded the MRL values in 5 and 20 % samples, respectively. Among organophosphates, only chlorpyriphos was detected with 9 % samples showing its residue above MRL value. Irrespective of contamination levels, residues above the MRL values were more in ghee. More extensive study covering other agricultural regions/zones has been suggested to know the overall scenario of contamination of milk products. Pandey et al. (2010) have carried out a study to determine the OCP residues in commonly used dry fruits like cashew nut, walnut, coconut, chilgoza, *chironji, makhana,* resins, apricot, almonds, date palm, and pistachio nut collected from local markets of Lucknow, India. The results indicate the presence of very low levels of HCH (0.007–1.328 mg kg^{-1}), DDT (BDL–0.140 mg kg^{-1}), and endosulfan (BDL–0.091 mg kg^{-1}). There are no MRL values established for nuts in the country.

10.3.4 Diet

Battu et al. (2005) analyzed 46 samples each of vegetarian and nonvegetarian total diet consumed from March 1999 to December 2002 by male subjects in the age group of 19–24 years to assess their risk through dietary intake with respect to pesticide residues. The results revealed low dietary intake of levels of DDT which were almost comparable to levels reported in developed countries. The results are indicative of contamination of total diet with pesticide residues despite a ban on the use of DDT and restricted use of lindane in agriculture only. Predominance of lindane residues indicates that liquid milk was a main contributory source as it constitutes almost 21 % of the total diet consumed per day. Concerted efforts by regulatory authorities and emphasis on judicious use of agrochemicals in pest control are required to decrease the burden of these chemicals in food stuffs to levels safe for dietary intake.

10.3.5 Bovine Milk and Dairy Products

In a multicentric study that assessed the pesticide residues in selected food commodities collected from different states of our country, *p, p′*-DDE was found in 82 % of the study samples of bovine milk collected from 12 states (Toteja 1993). Pandit et al. (2002) monitored the milk and dairy product samples of various brands from different cities in Maharashtra, India, to determine the presence of OCP residues contamination. Trace levels of DDT and HCH were detected in the samples. Total HCH levels in milk and milk product samples were lower than total DDT levels, which could be attributed to earlier extensive antimalaria sanitary activities.

Butter had higher levels of DDT than cheese and milk powder. All levels of OCP residues in milk and milk products were well below the maximum permissible limits given by the FAO/WHO.

The risk posed by the presence of OCPs in milk and milk products was estimated for the population. Pandit and Sahu (2002) determined the levels of OCPs in milk and milk products in and around Mumbai City. A total of 520 samples were used to determine the mean daily consumption of milk and milk products by different age groups and these data were used to evaluate the daily exposure to the public. Non-cancer effects were evaluated by comparing the predicted exposure distributions to the published guidance values. For chemicals identified as potential human carcinogens, cancer risk was evaluated using standard methodology. The majority of the chlorinated pesticides identified in the milk and milk product samples studied were found to be at levels which do not pose unacceptable risks to the public, with the exception of HCH. The cancer risk estimated for this chemical slightly exceeds the US Environmental Protection Agency (EPA) guidance value.

Indian Council of Medical Research (2001) has reported DDT residues in 82 % of the 2,205 samples of bovine milk collected from 12 states. About 37 % of the samples contained DDT residues above the tolerance limit of 0.05 mg/kg (whole milk basis). The highest level of DDT residues found was 2.2 mg/kg. The proportion of the samples with residues above the tolerance limit was maximum in Maharashtra (74 %) followed by Gujarat (70 %), Andhra Pradesh (57 %), Himachal Pradesh (56 %), and Punjab (51 %). In the remaining states, this proportion was less than 10 %. Data on 186 samples of 20 commercial brands of infants' formulae showed the presence of residues of DDT and HCH isomers in about 70 % and 94 % of the samples with their maximum level of 4.3 and 5.7 mg/kg (fat basis), respectively.

John et al. (2001) conducted a survey during 1993–1996 to investigate the magnitude of contamination of bovine milk with OCP residues from Jaipur City, Rajasthan, India. Milk samples, i.e., dairy (toned and whole) and buffalo milk, were collected seasonally, and pesticide residues were assessed. The results indicate that all the milk samples were contaminated with DDT and its metabolites, and isomers of HCH, heptachlor, and its epoxide, and aldrin. Seasonal variations of these pesticide residue levels were also observed in all the milk samples. Samples collected during winter season were found to contain higher residue levels as compared to other seasons.

Monitoring of bovine milk of different places in Bundelkhand region of India was carried out by Nag and Raikwar (2008) to evaluate the status of OCP residues. Out of a total of 325 samples, 206 (63.38 %) were contaminated with residues of different OCPs. The average concentration of total HCH was 0.162 mg/kg. Among the different HCH isomers, the frequency of occurrence of α-isomer was the highest followed by δ, γ, and β. Endosulfan (α, β, and sulfate) was detected in 89 samples with a mean concentration of 0.0492 mg/kg, while total DDT comprising DDT, DDE, and DDD was present in 114 samples having a mean concentration of 0.1724 mg/kg.

One hundred forty-seven samples of bovine milk were collected from 14 districts of Haryana, India, during December 1998 to February 1999 and analyzed for the presence of OCP residues. ΣHCH, ΣDDT, Σendosulfan, and aldrin were detected in 100, 97, 43, and 12 % samples and with mean values of 0.0292, 0.0367, 0.0022, and 0.0036 μg/ml, respectively. Eight percent samples exceeded the MRL of 0.10 mg/kg as recommended by WHO for ΣHCH, 4 % samples of 0.05 mg/kg for α-HCH, 5 % samples of 0.01 mg/kg for γ-HCH, 26 % samples of 0.02 mg/kg for β-HCH as recommended by PFAA, and 24 % samples of 0.05 mg/kg as recommended by FAO for ΣDDT. Concentrations of β-HCH and *p, p′*-DDE were more as compared to other isomers and metabolites of HCH and DDT (Sharma et al. 1999).

10.3.6 Fish

Singh and Singh (2008) investigated the ΣHCH and ΣDDT, aldrin, endosulfan, and chlorpyrifos in liver, brain, and ovary, gonadosomatic index (GSI), and plasma levels of testosterone (T) and estradiol-17β (E2) during breeding season of captured catfishes and carps from the unpolluted ponds of Gujartal, Jaunpur (reference site) and polluted rivers Gomti, Jaunpur and Ganga, Varanasi. Results have indicated that catfishes have higher bioaccumulation of pesticides than the carps: it was beyond the permissible limits for ΣHCH, whereas for ΣDDT only in catfishes of polluted rivers. The GSI and plasma levels of T and E2 were lowered in the fishes captured from the polluted rivers. It was concluded that the fishes of Gomti and Ganga reflect the degree of pesticide pollution present in those water bodies.

Muralidharan et al. (2009) determined the OCP residues in ten species of fishes caught at Cochin and Rameshwaram coast and sold in Coimbatore, Tamil Nadu, India. Species were selected on the basis of their regular availability throughout the year and commercial value. A total of 389 fishes were analyzed for OC residues and their suitability for human consumption was evaluated. Results show varying levels of residues of HCH, DDT, heptachlor epoxide, endosulfan, and dieldrin. About 22 % of the fishes exceeded the MRLs of total HCH prescribed by FAO/WHO for fish products. The calculated dietary intake of total HCH through consumption of *Carangoides malabaricus, Chlorophthalmus agassizi,* and *Sardinella longiceps* exceeded the maximum acceptable daily intake (ADI) limits prescribed for human consumption. The present study recommends continuous monitoring of environmental contaminants in marine fishes to assess the possible impact on human health.

Dhananjayan and Muralidharan (2010b) assessed the contamination status of inland wetlands of India, through evaluating the OCP residues in fishes collected from different inland wetlands in Karnataka, India and their suitability for human consumption. Among the OCPs tested, isomers of HCH were the most frequently detected with β- and γ-HCH as the main pollutants. Average concentration of ΣHCH and ΣDDT ranged from 2.1 to 51.7 lg/kg and BDL to 12.3 lg/kg, respectively. Other OCPs such as heptachlor epoxide, dieldrin, and endosulfan were found at lower levels. OCPs detected in the present study were well below the tolerance limits recommended for fishes. The calculated daily dietary intake of OCPs in all the species examined was lower than the maximum ADI limits prescribed for human consumption (Table 10.4).

Table 10.4 Comparison of calculated dietary intake concentration of OCPs with the ADI stipulated by various statutory agencies

OCPs	The average calculated dietary intake concentration through consumption of fishes (μg/person/day consumption; Dhananjayan and Muralidharan 2010b)	Allowable limits by various statutory agencies (μg/person/day)
ΣHCH	0.61	18[a]
HE	0.21	–
ΣEndosulfan	0.15	450[b]
Dieldrin	0.13	6[a]
ΣDDT	0.27	300[b]

[a] Health Canada (1996)

[b] IARC (International Agency for Research on Cancer 1989)

Dhananjayan et al. (2012a) evaluated the OCP residues in the inland wetland fishes of Gujarat, India and their suitability for human consumption. Among the various OCPs analyzed, γ-HCH and β-HCH were detected in 70–80 % of samples. *p, p′*-DDE, the metabolite of DDT, was detected in higher load. DDT and HCH detected in the present study were well below the tolerance limits recommended for fishes. The calculated daily dietary intake of OCPs in all the species examined was lower than the maximum ADI limits prescribed for human consumption. Further studies on continuous monitoring of OCPs and dietary intake are warranted to characterize the residue accumulation and to facilitate the early identification of risks due to fish consumption.

10.3.7 Birds and Wildlife

The OCs due to their persistent nature remain stored in the body fat of birds and largely disturb calcium metabolism and thereby induce eggshell thinning over a period of time eventually leading to population decline (Tanabe et al. 1998). The effects of pesticide on wildlife, especially raptors, waterfowl, and fish-eating birds have been extensively studied around the world (Stickel et al. 1969; Fleming et al. 1984). Although food abundance and quality greatly impact reproductive effort and success in many predatory birds (Korpinaki and Norrdahl 1991; Rohner 1996), there has been increasing concern about the potential deleterious effects of OC and other pesticides on the population of many species of birds (Gard et al. 1995; Block et al. 1995). Although reduction of the food supply, disruption of delicate predator–prey relationship, alteration of habitat, and a variety of similar changes could all affect the distribution and abundance of wildlife, the role of pesticide cannot be ruled out.

The pesticide exposure pattern of birds in India presents a varied picture compared to their counterparts in Europe and America. Due to the human and environmental risks associated with the use of such pesticides, they have been banned in several countries but are still used in India and their presence was reported in various studies (Mathew 1993; Saiyed et al. 1999; Kannan et al. 1997). A large number of studies have focused on the accumulation of pesticides in various species of flora and fauna around the world (Minh et al. 2002). There is little information available on the presence of few OCP residues in the tissues of a few species of birds and the higher accumulation of OC in resident and migratory birds from South India (Tanabe et al. 1998). Reports also show that the decline in the population of many species of birds was mainly due to the application of aldrin and monocrotophos in agricultural fields. Declining population of birds breeding at regular sites and infrequent sightings or total absence of insectivorous birds, such as drongos and bee-eaters in the agricultural fields in various parts of India are being reported.

Declining breeding population of Sarus Crane (*Grus antigone*) (Vijayan 1991; Muralidharan 1993; Pain et al. 2004) in Keoladeo National Park, Bharatpur, the reports on the unsuccessful breeding of Himalayan Grey-headed Fishing Eagle, *Ichthyophaga nana,* at Corbett National Park in Uttarakhand (Naoroji 1997), the higher accumulation of OC in resident and migratory birds from South India (Tanabe et al. 1998), fast-disappearing common bird "House Sparrow" in India (Vijayan 2003), and accumulation of various concentration of OCPs in tissues of vultures (Muralidharan et al. 2008) give credence to the concern of ornithologists. In the case of Sarus Crane in Bharatpur, it was inferred that the decline in population was mainly due to application of aldrin in the agricultural fields around the park; 18 Sarus Cranes were found dead inside the park within a span of 3 years due to aldrin (Muralidharan 1993). Even after the ban on aldrin, death of 15 Sarus Cranes due to monocrotophos poisoning was reported (Pain et al. 2004). Unfortunately, mortality of Sarus Crane has become rather frequent. Although such definite information is not available for many species of birds in India, study conducted elsewhere gives definite proof for the deleterious effects of pesticides on avifauna and the ecosystem.

In India, although we keep guessing that pesticide could be the reason for the decreasing population trend in many insectivorous and piscivorous birds, nothing has been proved till date (Muralidharan 2002). Except a very few studies on the problems of pesticide contamination in Indian wildlife and birds, especially resident birds (Muralidharan 1993; Tanabe et al. 1998; Senthil Kumar et al. 1999; Muralidharan et al. 2008), not much of research has been carried out to bring out the exact picture of pesticide contamination in a specific region

10.3.8 Impact of Pesticides on Birds in India

In India, unfortunately systematic monitoring has never been done to evaluate the level of residues and their biological effects. Limited surveys were carried out by various authors that have been mainly confined to very small number of individuals to a particular place and period. The results of scattered studies in the Indian environment are reviewed and discussed as follows: HCH and DDT residues of the internal body organs, depot fat, and blood plasma of a few species of Indian wild birds from Lucknow were estimated by Kaphalia et al. (1981). High levels of DDT were detected in depot fat of crow, kite, and vulture (50.8, 67.0, and 95.3 ppm, respectively) Total HCH detected in depot fat of crow was 29.7 ppm; lesser amounts were found in vulture, kite, and cattle egret, respectively. A single specimen of pigeon ovary examined contained 1.21 ppm total HCH and 0.31 lindane. Kaphalia et al. (1981) reported that within the same food habit group, smaller individuals are likely to ingest larger amounts of pesticide residues. Studies also clearly indicate that, HCH levels in liver, lung, and kidney were generally high in pigeon and crows and in the breast muscles and spleen of vulture. More lindane and total HCH was found in tissues of vulture compared with other species. Avian species, thus, reflect biological magnification of HCH and DDT residues, presumably due to their food habits.

A study by Misra (1989) in monitoring and surveillance of pesticide pollution of Mahala water reservoir with reference to its avifauna reported relatively high levels of total OCP residues in Flamingo and Red-wattled Lapwing brain, as compared with other tissues. Flamingo contained 7.39 µg/g beta HCH and 7.46 µg/g *p, p′*-DDE in brain while Red-wattled Lapwing had 3.45 µg/g alfa HCH, 5.82 µg/g gamma-HCH, and 3.66 µg/g aldrin in brain. Large Pied Wagtail had 5.42 µg/g *p, p′*-DDE in the brains which is much higher than the concentrations present in other species of birds studied. Total DDT residue concentrations were 2.0, 5.42, and 6.34 µg/g in brain of Black-winged Stilt, Large Pied Wagtail, and Flamingo, respectively. In other tissues, total residues of DDT generally occurred in the following order: Large Pied Wagtail > Flamingo > Black-winged Stilt > Indian Sandgrouse > Red-wattled Lapwing. Snipe had no detectable total DDT residues. Total DDT detected was 3.73, 10.53, 0.56, 0.15, and 5.05 µg/g in liver of Black-winged Stilt, Large Pied Wagtail, Indian Sandgrouse, Red-wattled Lapwing, and Flamingo, respectively (Misra 1989).

Misra (1989) found high correlations of OCPs between breast muscle and body tissue when the data from all the individual birds were combined and subjected to a correlation test. The total OC residue levels in brain, alimentary canal, kidney, liver, and ovary correlate at the 0.01 significant levels. Brain, alimentary canal, and kidney rank 1, of which alimentary canal and kidney have the highest correlation (Misra 1989). Muralidharan et al. (1992) conducted a study on OC residues in the eggs of selected colonial water birds breeding at Keoladeo National Park, Bharatpur, India. The study recorded higher concentration of dieldrin in eggs of Large Cormorant (1.54 ppm), Indian Shag (2.94 ppm), Darter (1.52 ppm), Grey Heron (5.95 ppm), Cattle Egret (2.52 ppm), Painted Stork (5.78 ppm), and Spoon Bill (1.3 ppm). As the concentration in all the eggs was higher than 1 ppm, it was suggested that the concentration would have been associated with reproductive impairment (Stickel 1973).

The breeding population of Sarus Crane in Keoladeo National Park in Rajasthan has come down to six pairs as against 27 pairs in 1973 (Walkinshaw 1973). As diagnostic and circumstantial evidence prove the cause of death of 18 Sarus Crane between 1987–1988 and 1989–1990 to be aldrin poisoning (Muralidharan 1993), the reason for the decline in the breeding population becomes obvious. Brain tissue of Sarus Cranes, Collared Doves, and Blue Rock Pigeons collected from Keoladeo National Park, Bharatpur, showed an average of 19.33, 15.19, and 20.42 ppm of dieldrin, respectively. Dieldrin in other tissues ranged from 0.78 to 92.26 ppm in Sarus Cranes, 3.44 to 66.17 ppm in Collared Doves, and 16.92 to 20.99 ppm in Blue Rock Pigeons. Very high residues of aldrin in the gastrointestinal tract (89.75 ppm) and dieldrin at much higher quantities in the brain than the lethal level (4–5 ppm) clearly indicate that dieldrin after being metabolized from aldrin was responsible for the death of many Sarus Cranes in Bharatpur (Muralidharan 1993). Himalayan Grey-headed Fishing Eagle *I. nana* an endangered species has been breeding unsuccessfully for the last 5 years in Corbett National Park in Uttarakhand. Detection of high levels of DDT, HCH, dieldrin, endosulfan, and heptachlor in the unhatched egg (Rishad 1995) makes the reason all the more strong. Unsuccessful breeding of Himalayan Grey-headed Fishing Eagle at Corbett National Park in Uttarakhand was also reported by Naoroji (1997).

Higher accumulation of OC in resident and migratory birds from South India was documented by Tanabe et al. (1998), and Senthilkumar et al. (1999, 2001) measured levels of pesticides, dioxins, and PCBs in a few species of birds. Tanabe et al. (1998) suggest that generally the OC contamination levels in individual species of birds may vary with feeding habits and the residue pattern of OC in most species of resident birds analyzed followed the order of HCHs > DDTs > PCBs. The concentrations of HCHs in resident birds of South India were in the range of 14–8,800 ng/g followed by DDTs ranging in concentrations from 0.3 to 3,600 ng/g. Global comparison of OC concentrations indicated that resident birds in India had the highest residues of HCHs and moderate to high residues of DDTs.

Among the various OC residues analyzed in the tissue of six species of birds collected from Nilgiri District, Tamil Nadu, high levels of endosulfan residues were detected in the tissues of Large Cormorant with values of 10.9, 126.8, 112.88, 217.2, and 233 ppm in brain liver, kidney, muscle, and food content, respectively (Muralidharan and Murugavel 2001). While Muralidharan (1993) attributed the mortality of 18 Sarus Cranes and a few granivorous birds in Keoladeo National Park, Bharatpur to aldrin, Muralidharan et al. (2008) reported the levels of persistent OCP residues in tissues of White-backed Vulture from different locations in India. The levels of DDT, HCH, dieldrin, and endosulfan residues among other OCs have been detected in the tissues and eggs; none of them was indicative of either food chain buildup or poisoning leading to population decline.

Muralidharan et al. (2008) determined OCP residues in tissues of five Indian White-backed Vultures and two of their eggs collected from different locations in India. All the samples had varying levels of residues. *p, p′*-DDE ranged between 0.002 μg/g in muscle of vulture from Mudumali and 7.30 μg/g in liver of vulture from Delhi. Relatively higher levels of *p, p′*-DDT and its metabolites were documented in the bird from Delhi than other places. Dieldrin was 0.003 and 0.015 μg/g, while *p, p′*-DDE was 2.46 and 3.26 μg/g in eggs 1 and 2, respectively. Dieldrin appeared to be lower than the threshold level of 0.5 μg/g. *p, p′*-DDE exceeded the levels reported to have created toxic effects in eggs of other wild birds. Although varying levels of DDT, HCH, dieldrin, heptachlor epoxide, and endosulfan residues were detected in the vulture tissues, they do not appear to be responsible for the present status of population in India.

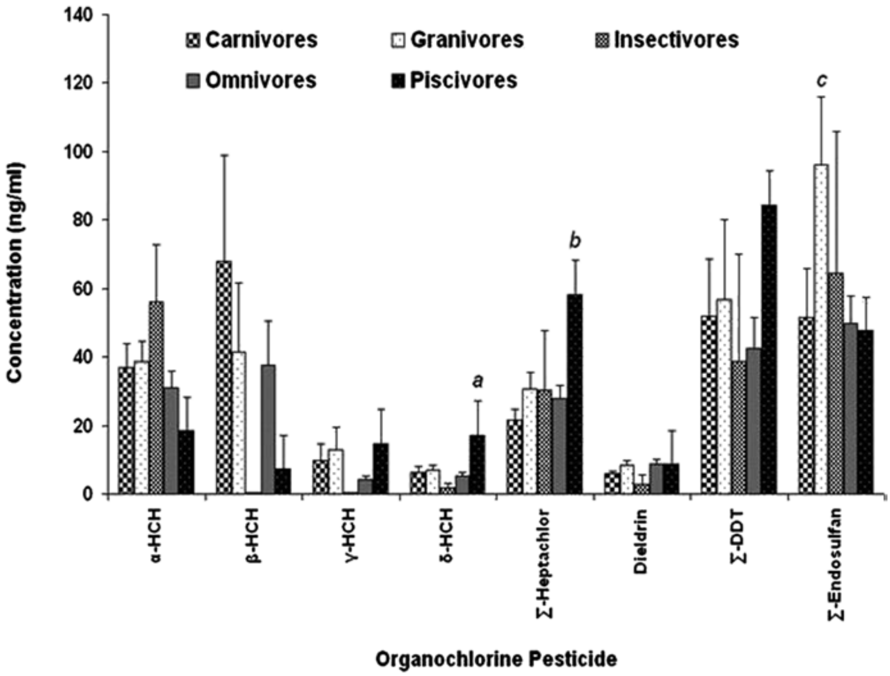

Fig. 10.1 Distribution pattern of OCP residues (mean ± standard error, ng/ml) in plasma of birds according to their feeding habits. $a = P < 0.05$ vs carnivores, granivores, omnivores, and insectivores; $b = P < 0.05$ vs carnivores, granivores, omnivores, and insectivores; $c = P < 0.05$ vs omnivores. (Source: Dhananjayan and Muralidharan et al. 2010a)

Dhananjayan and Muralidharan (2010a) reported the concentrations of OCPs in blood plasma of 13 species of birds collected from Ahmedabad, India. Among the various OCPs determined, HCHs and their isomers had higher contribution to the total OCPs. Concentration of HCHs varied from 11.4 ng/mL in White Ibis (*Threskiornis melanocephalus*) to 286 ng/mL in Sarus Crane (*Grus antigone*) , while DDT ranged between 19 ng/mL in Black Ibis (*Pseudibis papillosa*) and 147 ng/mL in Painted Stork (*Mycteria leucocephala*). *p, p′*-DDE was accounted for more than 50 % of total DDT in many of the samples analyzed. However, a *p, p′*-DDT to *p, p′*-DDE ratio higher than 1 obtained for many species of birds indicates the recent use of DDT in this study region. The concentrations of cyclodiene insecticides, heptachlor epoxide, dieldrin, and total endosulfan ranged from 15.8 to 296.2 ng/mL, BDL to 15, and 41.1–153.2 ng/mL, respectively. The pattern of total OCP load generally occurred in the following order: granivores\insectivores\omnivores\ piscivores\carnivores. Although the OC residues detected in blood plasma of birds are not indicative of toxicity, the presence of residues in birds over the years 2005–2007 indicates continued exposure to OC compounds (Fig. 10.1; Table 10.5).

Dhananjayan et al. (2011b) determined the presence of persistent OCPs and PCBs in blood plasma of White-backed Vulture (*Gyps bengalensis*), Egyptian

Table 10.5 OCP residues (ng/ml) in plasma of birds in India

Region	Species	Year	Tissue	*N*	*p, p'*-DDE	dieldrin	Source
India	House Crow	1980	Plasma	3	35 (20–40)	–	Kaphalia et al. 1981
India	Pariah Kite	1980	Plasma	3	100 (43–190)	–	Kaphalia et al. 1981
India	White-backed Vulture	1980	Plasma	3	183 (106–250)	–	Kaphalia et al. 1981
India	Cattle Egret	1980	Plasma	3	29 (26–30)	–	Kaphalia et al. 1981
India	Blue Rock Pigeon	1980	Plasma	3	4 (3–10)	–	Kaphalia et al. 1981
India	House Crow	2005–2007	Plasma	3	34.2 (4.6–51)	4.1 (2.9–6.3)	Dhananjayan and Muralidharan 2010
India	Pariah Kite	2005–2007	Plasma	51	15.3 (<1–137)	9.1 (<1–68.5)	Dhananjayan and Muralidharan 2010
India	Cattle Egret	2005–2007	Plasma	3	38.6 (6.5–101)	3 (<1–7.9)	Dhananjayan and Muralidharan 2010
India	Blue Rock Pigeon	2005–2007	Plasma	34	13 (<1–101)	7.8 (<1–37.7)	Dhananjayan and Muralidharan 2010

Vulture (*Neophron percnopterus*), and Griffon Vulture (*Gyps fulvus*) collected from Ahmedabad, India. All the samples had varying levels of OCPs and PCBs. The mean concentration of HCHs, DDTs, and PCBs among plasma ranged from 43.7 to 136, 8.8 to 64.8, and 226 to 585 ng/ml, respectively. Among the various OCPs analyzed, *p, p'*-DDE was detected most frequently. The concentrations of cyclodiene insecticides detected were lower than the other OC residues. The levels of pesticides measured in plasma samples of three species of vulture were comparable to the results documented for a number of avian species and were lower than those reported to have deleterious effects on survival or reproduction of birds. Although no threat is posed by any of the OCPs detected, continuous monitoring of breeding colonies is recommended. This study is also the first account of a comprehensive analysis of toxicants present in blood plasma of vulture species in India. The values reported in this study can serve as guidelines for future research in general as well as control values during the analysis of samples obtained from birds in the event of suspected OC poisoning (Table 10.6).

Dhananjayan et al. (2011c) reported the information on the current status of contamination by OCPs in eggs and tissues of House Sparrow, *Passer domesticus*, in Tamil Nadu, India. The mean concentration of ΣHCH and ΣDDT in eggs ranged from 0.01 to 1.81 μg/g and 0.02 to 1.29 μg/g, respectively. Concentration of

Table 10.6 Organochlorine chemical residues (ng/ml) in blood plasma of three species of vultures from India. (Source: Dhananjayan et al. 2011b)

	Egyptian vulture (n=6)				Griffon vulture (n=8)				White-backed vulture (n=17)			
	Mean	Min	Max	%	Mean	Min	Max	%	Mean	Min	Max	%
α-HCH	3.67	BDL	9.07	50	38.1	BDL	75.6	38	41.7	BDL	115	56
β-HCH	41.4	BDL	79.1	67	5.9	BDL	11.3	63	83.0[a]	BDL	661	69
γ-HCH	32.1	BDL	127	33	BDL	BDL	BDL	0	6.51	BDL	60.6	50
δ-HCH	BDL	BDL	BDL	0	BDL	BDL	BDL	0	5.62	BDL	16.7	44
ΣHCH	76.56	BDL	215	83	43.7	BDL	86.9	75	136[a]	BDL	770	94
HE	14.4	BDL	17. 9	50	12.9	BDL	14.4	50	23.87	BDL	73.4	75
Dieldrin	4.8	BDL	7.26	33	5.65	BDL	6.34	25	6.51	BDL	15.7	50
p, p′-DDE	8.75	BDL	25.6	83	16.2	BDL	26.5	75	16.28	BDL	39.5	94
p, p′-DDD	6.78	BDL	9.37	33	19.9	BDL	39.3	63	17.58	BDL	163	44
p, p′-DDT	5.42	BDL	8.24	67	3.45	BDL	8.62	38	31.56[a]	BDL	261	63
ΣDDT	8.75	BDL	25.6	83	35.9	26.5	45.2	100	64.83	BDL	455	88
α-Endosulfan	21.21	BDL	25.8	33	BDL	BDL	BDL	0	BDL	BDL	BDL	0
β-Endosulfan	BDL	BDL	BDL	0	27.3	BDL	54	25	8.54	BDL	28	56
Endosulfan sulfate	5.16	BDL	10.1	50	25.8	BDL	39	63	23.31	BDL	76.1	63
ΣEndosulfan	26.24	BDL	33.1	67	52.8	BDL	93	75	31.69	BDL	104	69
ΣPCBs	225.5	186	275	100	253	164.5	342	100	585	109	3,776	100

p, p′-DDE ranged from BDL to 0.64 µg/g, representing more than 60 % of the PDDTs. About 28 % of samples had *p, p′*-DDE levels above the critical concentration associated with reproductive impairment. However, the mean concentrations of cyclodiene insecticides were less than 0.5 µg/g.

A review by Dhananjayan et al. (2011a) explained the exposure and effects of orgnochlorine pesticides in birds in India. Although we have information on the levels of persistent environmental contaminants in many species of birds in India, due to lack of adequate data, we are unable to make any direct correlation with the reported population decline. Of all the birds, levels of DDT, HCH, and dieldrin recorded in some of the species were indicative of poisoning. Although varying levels of many persistent pesticides have been documented, the levels were not indicative of either food chain buildup or poisoning. However, the residue levels recorded were higher than the concentration reported in some other parts of the world. Further, even though very high levels of lead, indicative of poisoning, was observed, it cannot account for the massive reduction that the species has witnessed. However, such levels have to be viewed with concern.

Dhananjayan (2012a) reported that the OCPs and PCBs are responsible for the mortality of waterbirds in Nalaban bird sanctuary in Chilika Lake. One or more residues were detected in all the tissues of birds analyzed. Concentrations of HCHs, DDTs, and PCBs ranged from BDL to 811 ng/g, BDL to 1,987 ng/g, and BDL to 1,027 ng/g, respectively. PCBs levels were less than the food and drug administration's (FDA's) action limits. However, the need for additional research is heightened when considering that some of the birds are classified as a globally protected species by the international bodies.

Dhananjayan (2012b) assessed the persistent OCPs in various tissues of House Sparrow, *Passer domesticus,* from Tamil Nadu, India, between 2001 and 2006. The major compounds quantified in eggs, liver, brain, and muscle tissues are HCH, *p, p′*-DDE, dieldrin, and heptachlor epoxide. The mean concentrations of total polychlorinated biphenyls (ΣPCBs), ΣHCH, and ΣDDT in eggs are 0.94 ± 0.66 μg/g and 0.35 ± 0.26 μg/g on wet wt. basis. Concentrations of *p, p′*-DDE, a metabolite of *p, p′*-DDT, contributed 77 % to the total DDT. Twenty-eight percent of egg samples exceeded the *p, p′*-DDE concentration which was proposed as critical levels for birds.

Dhananjayan (2013) assessed the presence of OCPs in liver tissues of 16 species of birds collected from Ahmedabad, India, during 2005–2007. The higher concentrations of total OCPs were detected in livers of Shikra (*Accipiter badius;* 3.43 ± 0.99 μg/g wet wt.) and the lower levels in White Ibis (*Pseudibis papillosa;* 0.02 ± 0.01 μg/g wet wt.). Concentrations of DDT and its metabolites, HCH and isomers, dieldrin, and heptachlor epoxide were lower than the concentrations reported for various species of birds in India. Accumulation pattern of OCPs in birds was, in general, in the order HCH > DDT > heptachlor epoxide > dieldrin.

10.3.9 Human Blood

OC insecticide residues, especially DDT and HCH, have been detected in man and his environment. High levels of DDT and HCH have been reported in human blood, fat, and milk samples in India (Chatterjee et al. 1980). OCPs reported in the blood samples of human are listed in Table 10.7. Analysis of human exposure to selected OC compounds shows that the residue levels of *p, p′*-DDE and BHC were found to be persistent and higher in the human milk samples (Slorach and Vaz 1983), until the ban imposed on their use in the 1960s (ICMR 2001). High concentrations of both BHC and DDE were observed in the serum samples of the people who had direct exposure to the pesticides, namely agriculturalists and public health workers with few exceptions. The pesticide residue concentration in serum ranges from 0.006 to 0.130 ppm for BHC and from 0.002 to 0.033 ppm for DDE. This study reveals the presence of banned pesticides in human serum (Subramaniam and Solomon 2006).

Mathur et al. (2008) assessed the influence of OCPs upon the occurrence of reproductive tract cancers in women from Jaipur, India. Blood samples were collected from 150 women. In that group, 100 women suffered from reproductive tract cancers like cervical, uterine, vaginal, and ovarian cancers, while the rest did not suffer from cancers or any other major disease and were treated as control group. The pesticides detected were BHC and its isomers, dieldrin, heptachlor, and DDT and its metabolites. The data obtained indicate that the OCP residue levels were significantly higher in all the cancer patients as compared with the control group.

Pathak et al. (2008) analyzed the levels of OCP residues in maternal and cord blood samples of normal healthy women with full-term pregnancy to gain insight

Table 10.7 OCP residues (μg/L) in human blood reported in India

Location	α-HCH	β-HCH	γ-HCH	ΣHCH	*p, p′*-DDE	*p, p′*-DDD	*p, p′*-DDT	ΣDDT	**Source**
Lucknow	–	–	–	75	–	–	–	28	Kaphalia and Seth (1983)
Delhi	–	–	–	490	–	–	–	710	Ramachandra et al. (1984)
Delhi	–	–	–	–	–	–	–	301	Saxena et al. (1987)
Ahmedabad (rural)	–	–	–	148	37.2	1.33	8.83	47.7	Bhatnagar et al. (1992)
Ahmedabad	4.49	35.1	1.69	41.2	20.9	2.03	9.28	32.6[a]	Bhatnagar et al. (2004)
Punjab	–	–	–	57	–	–	–	65.2	Mathur et al. (2005)
Madurai	–	–	–	6.0–61	–	–	–	8.0–26	Subramaniam and Solomon (2006)
Bangalore (rural)	3.54	9.55	10.2	26.7[b]	5.67	3.01	3.81	10.6	Dhananjayan et al. (2012c)

[a] Total DDT (*p, p′*-DDE, *p, p′*-DDD, *p, p′*-DDT, *o, p′*-DDT) in serum
[b] ΣHCH (α-HCH, β-HCH, γ-HCH, δ-HCH)
– not available

into the current status of pesticide burden in newborns in North India. HCH contributed the maximum towards the total OC residues present in maternal and cord blood followed by endosulfan, *p, p′*-DDE, and *p, p′*-DDT being the least. This is also the first report indicating endosulfan levels in this population. These data indicate a transfer rate of 60–70 % of these pesticides from mothers to newborns, and this high rate of transfer of pesticides is of great concern as it may adversely affect the growth and development of newborn.

Dhananjayan et al. (2012c) described exposure level of OCPs among workers occupationally engaged in agriculture and sheep wool-associated jobs in rural neighborhood of Bangalore City, India. Thirty participants were interviewed and informed consent was obtained before blood sample collection. The maximum concentrations of OCP were detected in blood samples of agriculture workers rather than sheep wool workers. Among the metabolites of HCH and DDT, lindane (γ-HCH) and *p, p′*-DDE contributed the most to the total OCPs. There were no differences in pesticide residues found between sex and work groups.

10.3.10 Breast Milk

Bioaccumulation of OCs has been linked to effects such as endocrine disruption because of their capability of altering hormonal balance (Kelce et al. 1997; Beard et al. 2000). Furthermore, exposure to OCs has also been associated with an increased risk of breast and prostate cancer, endometriosis, cryptorchidism, and hypospadias (Birnbaum 1994; Hosie et al. 2000). Particularly, infants are extremely vulnerable to pre- and postnatal exposure to OCs, resulting in a wide range of adverse health effects including possible long-term impacts on intellectual function (Jacobson and Jacobson 1996; Eskenazi et al. 2006) and delayed effects on central nervous system functioning (Ribas-Fito et al. 2003; Beard 2006). Human breast milk was used as one of the best indicators of long-term exposure of OCs because it is easy to obtain, can be collected non-invasively, and indicates the contaminant levels in maternal fat (Tanabe and Subramanian 2006). In addition, breast milk monitoring provides a means of estimating intake of OCs by breast-fed infants. Previous studies reported the existence of high levels of certain OCs, particularly HCHs and DDTs in human breast milk from southern India (Tanabe et al. 1990; Subramanian et al. 2007; Kunisue et al. 2002; Minh et al. 2003; Tanabe and Kunisue 2007).

Blood and milk samples were collected from lactating women who were divided into four groups on the basis of different living standards, viz., residence area, dietary habits, working conditions, and addiction to tobacco. The level of total OCPs in blood ranged from 3.319 to 6.253 mg/L, while in milk samples it ranged from 3.209 to 4.608 mg/L. The results are in concurrence with the reports from other countries (Kumar et al. 2006). Aulakh et al. (2007) have reported the occurrence of DDT and HCH insecticide residues in human biopsy adipose tissues in Punjab, India.

Generally, levels of DDTs in India were lower than those observed previously, indicating that the concentration of DDTs has been declining in the Indian environment. For example, DDTs in human breast milk from New Delhi collected in 1989 by Nair and Pillai (1992) were 3,700 ng/g lipid wt. and have declined in 2006 by 1,500 ng/g lipid wt. (Devanathan et al. 2009); the DDT levels in Mumbai have declined from 8,000 ng/g lipid wt. in 1984 (Ramakrishnan et al. 1985) to 450 ng/g lipid wt. in 2006 (Devanathan et al. 2009), and in Kolkata there was a decline from 4,800 ng/g lipid wt. in 1984 (Ramakrishnan et al. 1985) to 1,100 ng/g lipid wt. in 2006 (Devanathan et al. 2009) (Table 10.8). However, increase in DDT concentrations was observed in Chennai from 760 ng/g lipid wt. in 1988 (Tanabe et al. 1990) to 1,200 ng/g lipid wt. in 2003 (Subramanian et al. 2007). Past and ongoing usage of DDT for controlling vector-borne diseases and/or continuing intake of contaminated foods may be a plausible reason for such an increasing trend. The general declining trends confirm the positive effects of governmental and voluntary restrictions and prohibitions on the usage of DDT and other measures taken to minimize the pollution. Although the results show declining trends, worldwide comparison indicates that India is still at the top of DDT contamination levels. In general, levels of DDTs in India resemble those of other developing countries like Indonesia (Sudaryanto et al. 2006), Malaysia (Sudaryanto et al. 2005), and Cambodia (Kunisue et al.

Table 10.8 Concentrations of OCs (ng/g lipid wt.) in human breast milk from major cities in India

Compound	New Delhi[a] (n=21)		Mumbai[a] (n=26)		Kolkata[a] (n=17)		Chennai[b] (n=12)	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Lipid (%)	0.73–4.5	2.1	0.76–4.5	2.4	0.90–6.8	2.6	0.72–3.3	1.8
p, p′-DDE	68–10,000	1,200	39–1,300	380	110–2,300	920	640–2,800	1,100
p, p′-DDD	<0.026–230	24	1.2–25	7.3	3.0–31	15	2.2–17	8.0
p, p′-DDT	2.0–1,900	210	1.7–330	68	1.2–680	200	41–140	94
ΣDDTs	140–12,000	1,500	47–1,500	450	240–2,800	1,100	750–2,900	1,200
α-HCH	<0.21–22	4.6	0.59–19	4.7	3.2–34	9.1	2.5–15	7.9
β-HCH	4.2–1,600	240	6.1–1,200	210	61–1,900	680	1,700–8,700	4,500
γ-HCH	<0.20–1,700	82	<0.20–3.2	1.1	<0.20–7.6	2.0	0.30–10	1.9
ΣHCHs	6.3–1,800	340	12–1,200	220	74–1,900	670	1,700–8,700	4,500

n number of individuals
[a] Devanathan et al. (2009), [b] Subramanian et al. (2007)

2004b), but relatively lower than those of China (Kunisue et al. 2004a), Hong Kong (Wong et al. 2002), and Vietnam (Minh et al. 2004). The levels were one order of magnitude higher than the industrialized nations such as Japan (Kunisue et al. 2006), UK (Harris et al. 1999), Sweden (Nore'n and Meironyte 2000), Germany (Schoula et al. 1996), and Canada (Newsome and Ryan 1999). The elevated levels of DDTs in developing countries in the tropical region, including India, may be because considerable portions of DDT are still applied for malaria control and sanitary purposes. This contamination pattern implies that developing countries in the tropical region play a major role as a source of DDTs.

Among the DDTs, *p, p′*-DDE was the main compound found in many of the recent studies, accounting for more than 75% of the total DDTs concentrations, suggesting wide usage in the past and long-term accumulation of DDTs in humans. Due to various biological processes, metabolism of DDTs may occur throughout the food chain and, therefore, it can be suggested that the presence of *p, p′*-DDE in human tissues is derived not only from direct ingestion of *p, p′*-DDT but also from the ingestion of *p, p′*-DDE previously degraded in the environment. However, *p, p′*-DDT contributed to 15–20% of the total DDT concentrations in milk which also could be due to fresh exposure to DDT. The proportion of *p, p′*-DDT reported in the recent studies was relatively higher than other studies in developing countries such as Indonesia (Sudaryanto et al. 2006); 5–6% in China (Kunisue et al. 2004a); 8% in Phnom Penh, Cambodia (Kunisue et al. 2004b); and 8–12% in Vietnam (Minh et al. 2004). These results could be interpreted as an evidence for continuous fresh exposure to DDT in India, maybe from the malaria eradication program.

Although the usage of technical HCHs in India has been banned since 1997 for agriculture, the government still allows using HCHs for public health purposes and on certain crops (Li 1999). Furthermore, the government is also encouraging the replacement of technical HCHs with lindane (Gupta 2004). Relatively higher concentrations of HCHs were reported in human milk from Kolkata (670 ng/g lipid wt.) than in those from New Delhi and Mumbai (340 and 220 ng/g lipid wt., respectively) (Devanathan et al. 2009). These findings clearly show that the usage pattern of pesticides and exposure levels are different among the regions in India. As observed for DDTs, HCHs also show declining trends in New Delhi from 13,000 ng/g lipid wt. in 1997 (Banerjee et al. 1997) to 340 ng/g lipid wt. in 2006 (Devanathan et al. 2009), coinciding with the restrictions and prohibition on HCH usage in India. However, in Chennai, situated in the southern part of India, an increasing trend of HCH use was observed between 1988 (2,900 ng/g lipid wt; Tanabe et al. 1990) and 2003 (4,500 ng/g lipid wt.; Subramanian et al. 2007) which may be due to precarious use of HCHs and/or consumption of HCH-contaminated food.

Among HCH isomers, β-HCH was the predominant isomer contributing 80–96 % of the total HCH. β-HCH is the most persistent and bioaccumulative form and is eliminated slowly from the body. In addition, the ratio between different HCH isomers changes from lower tropic level in food chains to human milk, resulting in the more persistent β-HCH being predominant in human milk (Solomon and Weiss 2002). Interestingly, in all cities in India, α-HCH was higher in multipara mothers than in primipara, which also could be interpreted as an evidence for continuous intake of technical HCH. In general, γ-isomer in the present study accounted for lesser contribution to total HCHs. Generally, it was known that the levels of OCs in human breast milk were positively correlated with the age of mothers (Bates et al. 1994; Albers et al. 1996).

DDTs and HCHs were the most prevalent of OCs in human breast milk from India, HCHs being more predominant in southern part and DDT in other parts of India (northern, western, and eastern). Differences in accumulation patterns of OCs indicate region-specific usage of chemicals in India. Except in Chennai, levels of DDTs and HCHs in the present study were lower when compared to previous observations, indicating the effects of bans and restrictions imposed. No significant correlation was observed between concentrations of OCs in human breast milk and age of mothers and there was no difference in the concentrations between primipara and multipara mothers. The estimated infant daily intake of OCs shows that the intake of HCHs through lactation exceeded the TDI, which is of concern to infant health. Comprehensive studies on the OCs contamination in India are, therefore, necessary to understand the source and evaluation of possible long-term impacts of OCs (Devanathan et al. 2009). HCH isomers, endosulfan, malathion, chlorpyrifos, and methyl parathion were monitored in human milk samples from Bhopal, Madhya Pradesh. The endosulfan concentrations were highest and exceeded the HCH, chlorpyrifos, and malathion concentrations by 3.5-, 1.5-, and 8.4-fold, respectively. Through breast milk, infants consumed 8.6 times more endosulfan and 4.1 times more malathion than the average daily intake levels recommended by the WHO (Sanghi et al. 2003).

10.3.11 Biochemical Changes in Humans

Although 80 % of pesticides produced annually in the world are used in developed countries, less than half of all the pesticide-induced deaths occur in these countries. A higher proportion of pesticide poisonings and deaths occur in developing countries where there are inadequate occupational safety standards, ineffective protective clothing and washing facilities, insufficient enforcement, poor labeling of pesticides, illiteracy, and insufficient knowledge of pesticide hazards (Pimental and Greine 1996). Because farmers and farm workers directly handle 70–80% of the pesticides they use, they are at the greatest risk of exposure (McDuffie 1994). Most people do not realize that they are being poisoned by the pesticides, because many symptoms of pesticide poisoning are similar to other health problems, for example, skin rashes and dizziness. Apparently, therefore, a large number of acute pesticide poisonings each year go undiagnosed and unreported. Due to heavy pesticide exposure, various chronic effects such as brain and nervous system damage, cancer, birth defects, miscarriages, and still births have been reported. Few surveillance studies have been conducted in India on high-risk population groups involved in the spraying of pesticides in field conditions (Rupa et al. 1991; Gupta et al. 1995; Srivastava et al. 1995; Chaudhuri 2000).

The biochemical effects produced by certain pesticides can be enzyme induction or enzyme inhibition. The effect of pesticides may be detected by ensuring biochemical changes even before adverse clinical health effects can occur. Organophosphorus and carbamate pesticides are inhibitors of cholinesterase. Altered liver enzyme activities have been reported among pesticide workers exposed to organophosphorus pesticide alone or in combination with OC or other pesticides. More recently, various studies from several parts of the world revealed the toxic effects of pesticides on human beings especially by elucidating free radical mechanism, which can be confirmed by the direct measurement of lipid peroxidation by-products such as malondialdehyde (Ko et al. 1997). There has been no study so far on the biochemical aspects of environmental health with special reference to grape cultivation from developing countries.

Dhananjayan et al. (2012b) estimated the cholinesterase activity in blood samples of agricultural workers engaged in vegetables and grape cultivation. The results showed a marked inhibition in acetylcholinesterase (AChE) and butyrylcholinesterase (BChE) activity among agricultural workers (exposed subjects) compared to control subject. There was a statistically significant reduction in enzyme activity in both AChE (14 %) and BChE (56 %) among exposed groups (Patil et al. 2003). A total of 85 healthy male pesticide sprayers in grape garden exposed to different classes of pesticides for 3–10 years were compared with 75 controls matched for age with respect to serum cholinesterase, serum total protein, albumin, aspartate aminotransferase (AST), alanine transaminase (ALT), and hematological parameters such as Hb, Hct, red blood cell (RBC), and serum lipid peroxidation. Serum lipid peroxidation was estimated in the form of thiobarbituric acid reactive substances (TBARSs) produced. A significant decrease was observed in serum cholinesterase, serum total proteins, albumin, and hematological parameters, viz., Hb, Hct, and RBC. A significant increase in lipid peroxidation, AST, and ALT was observed in the exposed group when compared with control. These results suggest that the long-term exposure of various pesticides on sprayers of grape garden affects liver and heme biosynthesis and decreases serum cholinesterase.

Singh and Kaur (2012) presented a study that had been carried out to examine the acute symptoms of pesticide spraying in the farm workers of three villages in

Talwandi Sabo block of Bathinda district of Punjab, a cotton-growing area with high usage of pesticides. This is an exploratory health study recorded face-to-face with pretested questionnaire. A total of 108 male sprayers from villages of Bangi Nihal Singh (34), Jajjal (39), and Mahi Nangal (35) were field interviewed about the immediate impact of pesticides during spraying season from September to October 2003. Majority of the sprayers complained of having nausea, itchiness of the eyes, pain while urinating, discolored nails, nails dropping off, swollen fingers, sleeplessness, headache, excessive sweating, and skin rashes. Immediate attention should be given to the implementation of proper awareness programs for pesticide workers. Also, practices like integrated pest management, organic farming, biopesticides, and crop diversification should be promoted.

The analysis of OCPs using confirmatory techniques, e.g., GC–MS or GC–MS/MS, gives unambiguous results and is, therefore, extremely important for such monitoring studies as has been reviewed in the chapter (Selvi et al. 2012; Maurya et al. 2013).

10.4 Conclusion and Recommendation

OC insecticides are still used for agriculture and public health purposes raising a major concern on their residual concentrations in the environment. In developing countries, OCs are preferred since they are cheap and more effective. Nevertheless, only a minor fraction of applied OCPs reaches the target species. The excess pesticide moves through the environment, potentially contaminating soil, water, and all other biotic matrices. In India, agricultural fields are generally located in plains, highlands, and valleys; rivers and streams carry pesticide residues into estuaries and into the ocean contaminating the sediments which act as a sink to most OC residues in aquatic environments. OCP residues detected in foodstuffs, fishes, birds, and humans reflect the usage of various types of OCs in this country. Although *p, p′*-DDT had been banned in 1997 following the Stockholm Convention on POPs, the presence of DDT in environmental matrices was reported in many studies. In several cases, the DDT levels exceeded the recommended levels in comparison with the sediment quality guidelines and could, thus, cause acute biological impairments. Contributions of DDT metabolites vary in different Indian regions predominated by *p, p′*-DDT and *p, p′*-DDD. HCH and DDT residues in fish in India were lower than those in the temperate countries indicating a lower accumulation in tropical fish, which might be related to rapid volatilization of this insecticide in the tropical environment.

This review of data on the environmental fate and effects of OCPs in India suggests a causal relationship between the application of pesticides for public health purposes and agriculture use. The comparison of concentrations reported in various research studies with reference values from various national and international standard documents leads to the assumption that the presence of these OCPs has created serious detrimental effects on fish, wildlife, humans, and the environment.

However, the long-term effects of pesticide were reported for various biological systems. Most of the data suggest that DDTs and HCHs were the most prevalent OCs within different compartments of the ecosystem, HCHs being more predominant in the southern part and DDT in other parts of India. Because of their high biological activity and, in some cases, of their persistence in the environment, the use of pesticides may cause undesired effects on human health and the environment. In view of their potential toxic and persistent nature, there is a pressing need for their control and monitoring in the environment. As far as wildlife refuges are concerned, the literature is negligible. In India, unfortunately, no historical data on the levels of OCPs are available in many species of wildlife. It is needless to say that each and every organism in the ecosystem will get affected by persistent OCPs.

At present, POPs are banned in most of the countries. Trade in these substances is also restricted. However, some stock of these compounds is still available in the market. Some developing countries allow some use of these compounds for public health purposes, while their use in developed countries for any purpose is banned. Rotation of pesticides used and integrated pest management practices have been recommended as possible solutions to this problem. The level of education in developing countries is low. The challenge for the future is to generate resources for education and research. Disposal of pesticides requires heavy investment that is beyond the financial resources available to most developing countries. The challenge here is first to develop human capacity in waste management and research in order to install facilities for POP disposal. The need of the hour, therefore, is regular monitoring attempts at pesticide residue evaluation in order to give a baseline for further studies in these disciplines. Hence, comprehensive studies on the OCs contamination in India are, therefore, necessary to understand the source and evaluation of possible long-term impacts of OCs.

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Chapter 11
Management of Municipal Solid Waste Landfill Leachate: A Global Environmental Issue

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Abstract Landfills are one of the most historical and ordinary methods of waste disposal and still remain in many parts of the world. Landfill leachate from open dumpsites has become a crucial environmental issue. Still, the predominant waste disposal method in many developing countries is open dumping, which leads to the generation of significant amounts of leachate mostly to nearby water bodies. Landfill leachate treatment is not an easy task, specifically because of its uniqueness depending on climate, culture, age of the dumpsite, and waste characteristics. Acetogenic leachate characteristics are extremely variable and difficult to predict. However, landfill leachate in the methanogenic phase possesses quite stable characteristics. Herein, we report qualitative and quantitative data on landfill leachate from different parts of the world and discuss the best management practices. In addition, we provide a case study on assessing the physiochemical characteristics of landfill leachate generated from a municipal solid waste dumpsite in Sri Lanka. Overall, landfill leachate poses a risk to the environment and effective leachate management is vital to avoid environmental deterioration.

Keywords Municipal solid waste · Methanogen · Acetogen · Organic carbon · Nitrate · Phosphate

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11.1 Introduction

11.1.1 Municipal Solid Waste

Municipal solid waste (MSW), commonly known as trash or garbage, not only contains household or domestic waste but can also contain commercial and industrial waste with the exception of industrial hazardous waste that is collected through community sanitation services. Industrial hazardous waste (e.g., radioactive and pharmaceutical waste) is excluded from municipal waste because it is typically treated separately based on environmental regulations. In many countries, MSW is generated by three main sources: (1) domestic solid waste (from households and public areas, including waste collected from residential buildings, litter bins, streets, marine areas, and country parks); (2) commercial solid waste (from shops, restaurants, hotels, offices, and markets in private housing estates); and (3) industrial solid waste (industries, but does not include construction and demolition waste, chemical waste, or other special waste). MSW can further be grouped into five different categories (Fig. 11.1) and various techniques have been developed and practiced for MSW management worldwide, such as incineration, anaerobic reactors, and gasification (Kılıç, et al. 2007). However, MSW finally ends up in landfills in most cases.

11.1.2 MSW Landfilling

Although there are a number of different ways to dispose of MSW, the first and most well-known method is landfilling. Landfills are discrete, specially created, and excavated areas, so MSW can be put in these areas with little or no harm to the natural environment through pollution. Table 11.1 shows the general characteristics and the major differences in the main land disposal facilities (Training Module 2005). A number of significant characteristics are given in detail in the following:

1. *Open dumps* are particularly practiced in the developing countries. An open dumpsite is a land disposal site where solid wastes are disposed of in a manner that does not protect the environment, is susceptible to open burning, and is exposed to the elements to spread disease vectors (Joseph et al. 2002). Any available vacant area with government ownership is the basic consideration for an open dumpsite and no environmental guidelines are considered. Open dumps are unplanned heaps of uncovered wastes, often burned (many open dumps operators set fire to the MSW at the dumpsite to reduce the waste and increase disposal area at the site) and surrounded by pools of stagnated polluted water, rat, and fly infestations with domestic animals roaming freely and families of scavengers picking through the wastes (Fig. 11.2). Open dumpsites are swamp/marshy lands or low-lying areas where the MSW is being used for reclamation. This type of landfill requires the least development and operational costs and is prevalent in

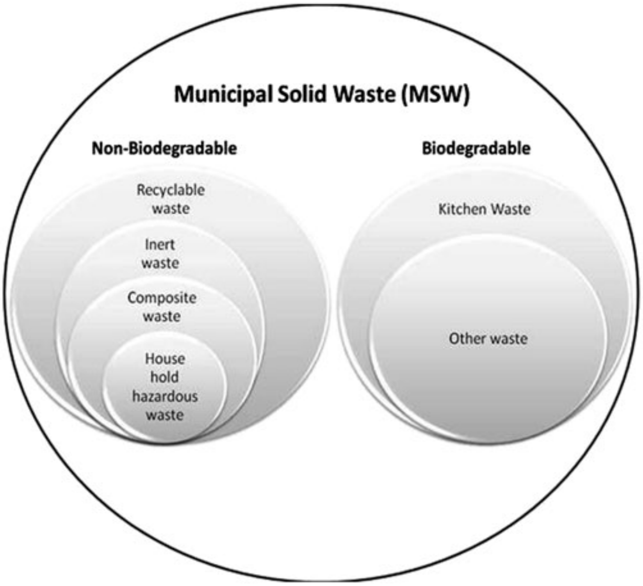

Fig. 11.1 Five different types of MSW in the environment

developing countries, in particular, where sanitary and engineered landfills are now a public health and environmental concern.

2. *Controlled dumps* are the first level of improvement from open dumps (Joseph et al. 2005). Controlled dumpsites are designed to eliminate problems associated with open MSW dumpsites through operational and management aspects rather than high-cost engineering applications. Hydrogeologic conditions are considered for site selection. In addition, several steps are considered compared to open dumping. For example, disposal only occurs at designated areas with planned capacity and where leachate/landfill gas is partially managed. Moreover, drainage and surface water control along the periphery of the site and covering the waste are implemented regularly in controlled dumps to prevent leachate- and landfill gas-related pollution. However, the practice of controlled dumping should be adopted in accordance with other modern waste management strategies.
3. *Engineered landfills* protect the environment and prevent pollutants from entering the soil and possibly polluting ground water in one of two ways. An engineered landfill uses clay or polythene liners High-density polyethylene (HDPE) liners and landfill covers to obstruct pollutants from leaving the landfill (Hartz and Ham 1983). This may reduce the risk of environmental pollution through groundwater and soil contamination and air pollution. However, most dumpsites in developing countries do not have a liner at the base or a top cover for protecting possible water and ground contamination by the leachate (Rafizul and Alamgir 2012).

Table 11.1 Summary of the general characteristics for different type of land disposal facilities around the world. (Source: Joseph et al. 2002 Training Module (2005))

Type	General measures	Engineering measures	Leachate management	Landfill gas management	Operation measures
Open dump	Unplanned, often improperly sited, site capacity is not known, no cell planning	None	Unrestricted contaminant release	None	Few, scavenging, no compaction of waste, and no record keeping
Controlled dump	Hydrogeologic conditions considered, planned capacity, and no cell planning	None	Unrestricted contaminant release	None	Registration and placement, compaction of waste in some cases, basic record keeping
Engineered landfill	Site chosen is based on environmental, community and cost factors planned capacity	Infrastructure and liner in place	Contaminant and some level of leachate management	Passive ventilation or flaring	Registration and placement/compaction of waste; uses daily soil cover
Sanitary landfill	Site chosen is based on environmental, community and cost factors, planned capacity, and cell planning	Proper siting, Infrastructure and liner and leachate treatment in place	Contaminant and leachate treatment (often biological and physico-chemical treatment)	Flaring	Registration and placement/compaction of waste; uses daily soil cover, measures for final top cover, waste compaction, and complete record keeping
Controlled contaminant release landfill	Site chosen is based on environmental, community and cost factors, and planned capacity	Proper siting, infrastructure, with low permeability liner in place, and potentially low permeability final top cover	Controlled release of leachate in to the environment, based on assessment and proper siting	Flaring or passive ventilation through top cover	Registration and placement/compaction of waste; uses daily soil cover, and measures for final top cover
Landfill bioreactor	Site chosen is based on environmental, community and cost factors, and planned capacity	Proper siting, Infrastructure and liner and leachate circulation/generation system	Controlled recirculation of leachate for enhanced degradation and stabilization of waste and leachate	Landfill gas recovery	Registration and placement/compaction/daily cover/closure/mining and material recovery

Fig. 11.2 Uncontrolled scavenging activities and domestic animals roaming on open dumps are common sights in developing countries, which lead to many environmental issues

4. *Sanitary landfills* comprise a series of advanced measures in design, construction, operating, and post-closure steps to have minimum environmental impact. Hence, this technique requires a substantial financial resource compared to other landfilling methods. However, sanitary landfilling is a suitable technique as it imposes minimum adverse impacts on the environment. Strict guidelines are considered based on the environmental, community, and cost for site selection. Emphasis is on fully managing the landfill leachate and gas during operation. For these purposes, geomembrane layers are used to avoid leachate contamination, and gas monitoring/extraction wells are used for landfill gas management. Hence, this method is becoming the most popular landfill model for ultimate disposal sites in developed countries (Ahmed and Lan 2012). In contrast to gasification and anaerobic reactors, sanitary landfilling is a simple disposal procedure with low-cost and landscape restoring effects (Aziz et al. 2010). These factors influenced the popularity of sanitary landfills in many countries. However, landfills must be closely monitored during their design, operation, and post-closure due to the generation of landfill leachate and greenhouse gases (Ahmed and Lan 2012). Liner fractures may lead to groundwater contamination, and atmospheric contamination may occur from gas leaks due to breaks in the landfill cap of an engineered landfill.

11.1.3 Landfill Leachate

Landfill leachate is a water-based solution that has dissolved or entrained environmentally harmful substances that may enter the environment through degrading waste in the landfill. Many groundwater pollution incidents have been reported involving landfill leachate (Christensen et al. 2001). Therefore, leachate is considered as a hazardous liquid and strict regulations have been enacted by many environmental protection authorities around the world (Rafizul and Alamgir 2012). Landfill leachate is generated from rainwater that passes through the waste within the solid waste dumping facility. The moisture that already exists in the waste is also involved in the generation of leachate (El-Fadel et al. 2002).

Leachate consists of different organic and inorganic compounds that may be either dissolved or suspended and transported as a plume into the aquifer or away from the dumpsite following the land gradient. Landfill leachate plumes are not much wider than the landfill and not beyond 2,000 m from the landfill but show narrow plume movement (Christensen et al. 2001). The higher density (~ 1.014 g/cm^{-3} at 10 °C) caused by the high salt content of leachate may lead to an initial sinking of the leachate plume with groundwater while undergoing limited lateral or transverse mixing (Christensen et al. 2001). The viscosities of the leachate also differ from the groundwater, but very few data exist on leachate viscosity. The high electrical conductivity of landfill leachate is also a very important parameter to understand the leachate-contaminated subsurface environment, particularly for predicting leachate flow and transport through the subsurface. These subsurface data can be observed by employing advanced geophysical techniques mainly based on the conductive nature of the landfill leachate.

11.2 Leachate Formation Mechanisms

Landfill leachate is generated through a series of physical, chemical, and microbiological processes. The breakdown of larger waste materials into smaller fractions during the manual mixing of waste, while the liquids elute and percolate, is the main physical process. The oxidation/reduction processes during waste degradation are included in the chemical processes. For example, nitrate and ammonium ion oxidation to nitrogen gas is a dominant chemical process as leachate has considerable nitrate species. However, it is difficult to distinguish a single process in the landfill leachate since a combination of these processes is actively involved in generating the leachate. Landfill leachate is typically a strongly reduced matrix with a great capacity for donating electrons (e.g., donation of electrons via conversion of ammonium ions to nitrate). The electrons produced are accepted by dissolved or solid aquifer electron acceptors (e.g., nitrate, oxygen, sulfate, and ferric ions) (Christensen et al. 2001). Furthermore, organic matter dominates the reduction capacity, and ammonium and methane also contribute significantly (Christensen et al. 2001). A lysimeter-based study has shown a clear pattern between rainfall and the formation of landfill leachate (Rafizul and Alamgir 2012). The natural attenuation involved during transportation of landfill leachate is the main reason for changing its initial characteristics (Christensen et al. 2001; Mayakaduwa et al. 2012).

11.3 Types of Landfill Leachate

11.3.1 Acetogenic Leachate

The microbiological decomposition processes occurring within waste in a landfill play a crucial role determining leachate characteristics (Irene 1996). During the second phase, anaerobic and facultative organisms (acidogenic and acetogenic bacteria) hydrolyze and ferment cellulose and other putrescible materials. The resulting simpler soluble compounds such as volatile fatty acids and alcohols may cause high biochemical oxygen demand (BOD) in leachate which is called as "acetogenic leachate." Acetogenic leachate is characterized by acidic pH, high BOD/chemical oxygen demand (COD) ratio, strong unpleasant smells, and high concentrations of ammonium nitrogen (Table 11.2**)** (Christensen et al. 2001). According to Harmsen (1983), >95 % of the dissolved organic carbon (DOC) in acetogenic leachate consists of volatile fatty acids and only 1.3 % accounts for high molecular weight compounds (MW > 1,000) (Harmsen 1983). Volatile amines and alcohols are also found in acetogenic leachate. Shuokr et al. (2010) reported that the volatile matter content in the acetogenic phase may be the reason for acidic pH in the leachate (Shuokr et al. 2010). In addition, this type of leachate may contain a considerable concentration of inorganic ions such as chloride, sulfate, calcium, and magnesium (Irene 1996).

11.3.2 Methanogenic Leachate

The acidic phase may last for several years and then slow-growing methanogenic bacteria start to establish gradually consuming simple organic compounds released during the second phase. The methanogenic leachate produced during this phase has an alkaline pH (Ehring 1988), lower BOD (Robinson 2007), and lower BOD/COD ratio and a consequent decrease in solubility of inorganics and heavy metals (Irene 1996). In this type of leachate, 32 % of DOC consists of high-molecular-weight compounds (MW > 1,000), such as humic and fulvic acids, which are not easily degradable. In addition, inorganic macrocomponents, such as sulfate, are lower during the methanogenic phase due to the microbial reduction of sulfate to sulfide (Christensen et al. 2001). Moreover, no volatile amines and alcohols can be found and ammonia is present in high concentration, which typically inhibits the biological degradation process (Harmsen 1983; Shuokr et al. 2010). Such stabilized leachate may persist for many decades or centuries. However, several inorganic macrocomponents (e.g., Cl, Na, and K) are not significantly different between acetogenic and methanogenic leachates (Christensen et al. 2001).

Table 11.2 Composition of the acetogenic and methanogenic landfill leachates in the Gohagoda landfill leachate

Parameter*	Values from the literature				
	Acetogenic leachate		Methanogenic leachate		Gohagoda leachate
	Al-Wabel; Christensen (Christensen et al. 2001; Al-Wabel et al. 2011)	Robinson (Robinson 2007)	Hunce; Christensen (Hunce et al. 2012)	Robinson (Robinson 2007)	
pH	5.9–6.3	5.5–7.0	7.9	7.5–8.5	8–8.6
Conductivity	6.3–42.5	7–30	37.2	< 1	8.96–29.6
BOD	–	4,000–30,000	4,250	< 500–1,000	21.6–3,590
COD	13,900–22,350	10,000–50,000	8,038	2,000–6,000	70–69,700
BOD/COD ratio	0.58[a]		0.06[a]		0.15
Alkalinity	–	2,000–10,000	13,200	10,000–30,000	725–39,606
Ammonium nitrogen	–	750–2,000	1,430	1,500–3,000	6–4,095
Nitrate-nitrogen	–	< 1	–	< 0.1	1–765
Phosphate	–	5–20	22.8	1,000–3,000	2–258
Sulphate	70–1,750[a]		10–420[a]		–
Chloride		1,000–2,000	7,000	2,000–4,000	68–723
Zinc	0.108–0.226	5–20	1.767	< 0.01–0.05	0.2–1.15
Cadmium	< 0.002	< 0.1–< 0.2	< 0.005	< 0.02–0.1	0.004–0.062
Nickel	0.384–0.718	< 0.1–< 1	0.597	< 0.05–0.1	0.133–0.532
Chromium	0.21–0.336	1–< 0.5	0.354	0.02–5	0.021–0.323
Copper	0.124–0.246	< 0.1	0.145	< 0.3–2	0.048–0.257
Lead	< 0.04	< 0.1–< 0.5	< 0.05	< 0.05–0.2	0.015–0.416
Magnesium	50–1,150[a]		40–350[a]		20–166
Manganese	0.3–65[a]		0.03–45[a]		0.155–1.203
Iron	20–2,100[a]		3–280[a]		0.3–318

*All in mg/L except pH, BOD/COD ratio and EC (mS cm^{-1}), a) according to Christensen et al. (2001) and Abbas et al. (2009)

11.4 Toxicity of Landfill Leachate

Leachate has been identified by many countries as a toxic surface and groundwater and soil contaminant (Mor et al. 2006; Sun et al. 2001; Abbas et al. 2009). In addition, the landfill leachate liquid possesses a strong reducing ability under methanogenic conditions. Many studies are available on either direct experimental determinations of contaminants or estimates through mathematical modeling (Mor et al. 2006). Landfill leachate is highly toxic to higher plants, algae, invertebrates, fish, and humans (Langler 2004; Natale et al. 2008). Ammonium may be present in leachate at high concentrations for years and can cause considerable toxic effects to fish (Christensen et al. 2001). High toxicity was reported for algae, daphnids, and bacteria in tests of samples collected close to a landfill with a decrease in toxicity identified with increasing distance from the landfill (Christensen et al. 2001).

Landfill leachate is a major source of natural organic matter (NOM) for water particularly in the developing world. The increase in organic compounds, particularly DOC, in the leachate is a source of trihalomethanes (THMs) (Weragoda 2005; Stuart et al. 2001). Most of these THMs have carcinogenic and mutagenic or possibly teratogenic properties (Weragoda 2005). In addition, some of these emerging contaminants may be identified as endocrine-disrupting chemicals (Ramakrishnan et al. 2013).

11.5 General Leachate Composition

The composition of landfill leachate can change due to rainfall or prevailing weather conditions during the waste degradation period, different management practices, waste characteristics, and depth of the MSW column. In addition, landfill design and operation procedures such as the degree of compaction, leachate recirculation steps, and internal landfill processes, such as anaerobic digestion steps, are major factors determining leachate composition (Rafizul and Alamgir 2012; Christensen et al. 2001; El-Fadel et al. 1997). Among these factors, moisture is a critical factor for waste degradation and, hence, for leachate composition (Rafizul and Alamgir 2012). However, no standard protocol for sampling, filtration, or storage of leachate samples exists for analysis (Christensen et al. 2001). For example, colloids have considerable affinity for complexation and this involves measuring the actual metal concentration. Many characterization studies have been based on only a few samples from each landfill as the cost and complexity of the experiments are very high. However, understanding leachate composition is very important for planning and determining remedial measures (Rafizul and Alamgir 2012). Hence, it is necessary to determine the actual pollution state such as the amount of contaminants and their generation and degradation rate in a particular region or country rather than copying the treatment methods from any region. Due to the complexity of landfill leachate, different ways are used to explain its composition based on many criteria. The composition of a landfill leachate can be explained by dividing it into four groups of organics (e.g., Dissolved Organic Matter as total organic carbon (TOC), DOC, and COD), inorganics (e.g., Ca, Mg, NH_4^+, SO_4^{2+}, and Cl^-), heavy metals (e.g., Cd, Pb, Ni, and Zn), and xenobiotic organic compounds (XOC) (e.g., benzene, phenol, and trichloroethene).

11.5.1 DOM

DOM is a bulk parameter comprising a variety of organic degradation products ranging from small volatile acids to refractory fulvic- and humic-like compounds (Christensen et al. 2001). Therefore, TOC, DOC, non-volatile organic carbon

(NVOC), or COD is expressed as DOM. No study has given adequate attention to understanding the composition of DOM in landfill leachate and its fate in the environment. Only a very few studies have been published on DOM in landfill leachate. The DOC in leachate originates from the anaerobic decomposition of organic waste that causes numerous environmental effects, such as decreased removal of heavy metals and depleting dissolved oxygen in groundwater sources (Christensen et al. 1998). DOC remains as non-biodegradable compounds and may even be resistant to biological treatment (Zouboulis et al. 2004). Volatile fatty acids constitute a substantial fraction of DOC and show an easily degrading pattern in laboratory-based studies of the acetogenic leachate. But, similar studies on the methanogenic leachate have revealed the recalcitrant nature of DOM (Christensen et al. 2001). However, according to a study based on DOC and its fate, the DOC concentration in the leachate plume decreases with time (Christensen et al. 2001). Conversely, TOC well described the total amount of organic carbon in the leachate matrices. Leachate in active landfill sites contains higher TOC than that from closed landfill sites due to the high decomposition rate (Irene 1996). The ratio of COD to TOC indirectly reflects the organic matter characteristics of the leachate and the particular ratio can be used to determine the rough age of the landfill (Irene 1996).

11.5.2 BOD–COD

COD describes the organic matter content that is susceptible to oxidation by a strong chemical agent such as potassium dichromate. This parameter reflects the changes in solid waste degradability at dumpsites and the amount of organic contaminant (Irene 1996). Most of the leachates from the early stages (first year) of a landfill operation show high COD (>20,000 mg/L). With time, the landfill material ages and the COD stabilizes at ≤3,000 mg/L (Irene 1996). BOD describes the organic matter content that is susceptible to oxidation by biological activities. High BOD occurs in acetogenic leachate with values of 4,000–30,000 mg/L, whereas methanogenic leachate carries lower values of 500–1,000 mg/L (Robinson 2007).

11.5.3 Solids

Determining the different fractions of solids in a landfill leachate is very important to understand the behavior of microbial degradation processes. For instance, it is interpreted that greater total suspended solid (TSS) concentrations reflect higher enzyme activity. The TSS concentration of leachate depends mostly on the abundance of microorganisms as well as the dilution conditions. Volatile-suspended solids (VSSs) could be directly proportional to microbial mass. In addition, VSS is frequently used as an estimate of the concentration of the active microorganisms in a biological treatment unit, but it is an imperfect measure of the active mass. VSS is also considered a useful design and management parameter for wastewater.

Volatile solids (VSs) are often interpreted as a measure of organic matter. This is not precisely true as the combustion of many pure organic compounds results in the formation of ash and many inorganic salts are volatilized during ignition. It includes losses due to decomposition or volatilization of some mineral salts.

11.5.4 Nutrients

Nitrate, phosphate, sulfate, and ammonium nitrogen concentrations are the principal nutrients of concern in leachate discharge and generally depend on the waste composition in landfills. Robinson and Luo (1991) observed the composition of leachate generated from very large landfills and reported typical concentrations of nitrate and phosphate of 2.5 and 27.6 mg/L, respectively (Robinson and Luo 1991). Bagchi (1990) reported that the overall nitrate concentration range in leachate is up to 250 mg/L (Bagchi 1990). Ranges of 5–10 and 20–40 mg/L total phosphorous and ammonium nitrogen, respectively, are observed in leachates from mature landfills (Shuokr et al. 2010). Sulfate is high in concentration in the landfill leachate, but low concentrations can be found in an active methanogenic leachate because the sulfate reduces to S^{2-} ions (Christensen et al. 2001). Decomposition of waste or ash is the main source of released sulfate. The disposal of plaster board made of gypsum ($CaSO_4 \cdot 2H_2O$) also releases sulfate into the leachate. Discharge of untreated leachate with high nutrient concentrations may accelerate eutrophication of lakes and reservoirs and may lead to other adverse effects such as the depletion of dissolved oxygen in receiving water, the toxicity to aquatic life, and an adverse impact on public health.

11.5.5 Heavy Metals

Heavy metals in landfill leachate are controversial. Many researchers have reported fairly low concentrations of heavy metals and their strong attenuation through precipitation and sorption (e.g., processes such as adsorption, absorption, surface complexation, surface precipitation, and ion exchange) in landfill leachate, suggesting a low risk to the environment (Christensen et al. 2001). Nevertheless, some researchers have reported opposite observations. For example, high concentrations of Cd, Hg, Ni, Mn, Cu, Zn, and Pb have been reported in leachate and these metals show enhanced transportation with DOC derivatives mainly by the anaerobic degradation of organic compounds, such as humic, fulvic, and hydrophilic acids, present in the leachate (Robinson 2007; Asadi 2008; Christensen et al. 1996). In addition, DOC contributes to the leachate color, turning it dark brown due to the complexation of ferric hydroxide colloids with humic and fulvic substances (Chu et al. 1994). Some heavy metals in reduced states (e.g., chromium iron as Cr^{3+}) have been reported in methanogenic leachate.

11.5.6 XOC

Very broad ranges of XOCs have been reported in landfill leachate and most are aromatic hydrocarbons (Christensen et al. 2001). These XOCs are organic chemicals identified as unknown and individual pollutants in the leachate and are reported to cause serious biological effects. Phenols, halogenated hydrocarbons, chlorinated aliphatics Perchloroethylene and Trichloroethene (PCE and TCE), and aromatic hydrocarbons (Mor et al. 2006; Asadi 2008) are included in the group of XOCs common in leachate. In addition, organic waste water contaminants, such as cholesterol, N, N-diethyltoluamide (an insect repellent), and tri(2-chloroethyl) phosphate (a fire retardant), were found in the landfill leachate-affected groundwater samples (Barnes et al. 2004). Newly identified XOCs, such as herbicide Mecoprop or Methylchlorophenoxypropionic acid (MCPP), have frequently been observed in leachate but little attention is given yet to understanding their degradation in the anaerobic environment (Christensen et al. 2001). However, analyzing XOCs is a complicated procedure as poor sampling protocols, high labor, and sampling costs hamper analysis. Aromatic hydrocarbons readily degrade in aerobic environments but a slower degradation rate has been detected in reducing environments (e.g., benzene). Nevertheless, degradation of XOCs and their associated products are still lacking a precise understanding.

11.5.7 Microbial Communities

Although the microorganisms involved in landfill leachate have not been studied in detail, bacteria and their activities in leachate have been investigated in a few studies. Methanogens, sulfate reducers, iron reducers, manganese reducers, and denitrifiers have been identified commonly in leachate plumes. Diverse microbial communities have been identified in leachate plumes and are believed to be responsible for the redox processes (Christensen et al. 2001). Some bacterial species, such as eubacteria and archaea, dominate landfill leachate-contaminated groundwater (Christensen et al. 2001; Ludvigsen et al. 1999). The microbial population closest to the landfill appear to be the most active in response to the pollutants. In addition, the methanogens and sulfate-reducing bacteria are abundant close to the landfill. However, the number of microorganisms decrease with plume length (Ludvigsen et al. 1999).

11.6 Case Study: Gohagoda Landfill Leachate

Many characterization studies and extensive reviews of the composition of landfill leachates are available for developed nations, particularly temperate countries, but only a few studies have reported on the transport and fate of landfill leachate in the tropics, particularly in the developing Asian region (Kale et al. 2010; Mor et al. 2006; Vasanthi et al. 2008). A detailed characterization of the landfill is a main limitation for designing a treatment plant (Tatsi and Zouboulis 2002). The situation of leachates from Sri Lankan dumpsites is typical of Asian countries, and no detailed characterization data are available. However, a few studies have been carried out to characterize leachates generated from the Gohagoda dumpsite in Sri Lanka. A groundwater quality study based on the shallow wells and drains around the Gohagoda dumpsite revealed high contamination in the Mahaweli River with BOD, COD, nitrate, and phosphate values of 20,000, 48,000, 64, and 56 mg/L, respectively (Wimalasuriya et al. 2011). But none of these studies focused on a long-term characterization of the leachate focusing on the interaction between temporal and spatial variation and flow and transport of leachate through subsurface. The following is a case study of such a characterization.

11.6.1 Gohagoda Open Dumpsite

The Gohagoda open dumpsite is situated adjacent to the northwestern boundary of Kandy city, Sri Lanka. It has been used for dumping waste from the world heritage city, Kandy since the 1960s. In 2003, the dumpsite was semi-engineered by extending the landfill area to 25,000 m^2 and including provisions for leachate treatment. However, the design period was only 2–3 years old and, currently, open dumping is taking place and the leachate treatment process is not functioning. About 130 t MSW/day including waste from slaughter houses, fish markets, households, and non-infectious hospital waste are being dumped without any sorting or pretreatment (Welikannage and Liyanage 2009).

11.6.2 Parameters

The landfill leachate used in the experiment was collected from the Gohagoda open dumpsite from June 2011 to October 2012. The leachate samples were collected at four sampling points of the drainage canal with recommended procedures as summarized in Table 11.3. Figure 11.3 shows the sampling points; GS1 and GS4 were located at the start and end points of the canal, whereas GS2 and GS3 were in the middle. The collected leachate samples were characterized for pH, temperature, conductivity, alkalinity, and total dissolved solids (TDS) under field conditions and then immediately transferred to the laboratory at 4 °C for other experiments such as nutrient content, COD, Cl^-, solids, TOC, DOC, and a metal analysis (Table 11.3). A resistivity survey was also performed using ABEM Terameter 300-c SAS, Sweden (one-dimensional (1D) resistivity survey) and AGI (Advanced Geosciences Inc, Austin, TX, USA) Mini-sting system with accessories (2D imaging). Resistivity data were collected by three 1D survey lines and two 2D profile lines covering the point where the leachate collected at the river (Fig. 11.3). The 1D data processing

Table 11.3 Summary of the analytical methods to determine the major chemical constituents in Gohagoda open landfill leachate, Kandy

Constituents	Method/reference
pH	ROSS sure-flow combination epoxy body electrode
EC	Conductivity meter (Orion 5 star series)
BOD_5	Winkler method (American public health association 2005)
COD	Spectrophotometer (HACH DRB 200)
TOC	TOC analyzer (Analytikjena Multi N/C 2100)
Alkalinity	Titrimetric method (American public health association 2005)
Ammonia-nitrogen	Iron selective electrode
Nitrate-nitrogen	Cadmium reduction method
Nitrite-nitrogen	Diazotization method
Phosphate	Ascorbic acid method
Chloride	Iron selective electrode
Zinc Cadmium Nickel Chromium Copper Lead Iron Manganese	Atomic adsorption spectrophotometer (AAS) (GBC 933 Australia)

*All in mg/L except pH and electrical conductivity (EC) (mS cm^{-1})
BOD, Biochemical oxygen demand; COD, chemical oxygen demand; TOC, total organic carbon

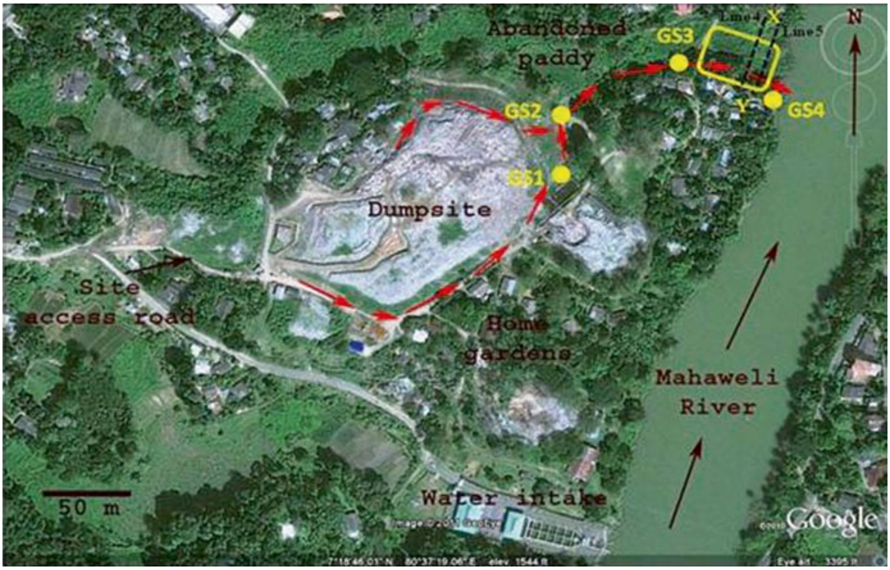

Fig. 11.3 Schematic diagram of the leachate drainage channel (*red arrows*), leachate sampling points (*yellow dots*), resistivity survey area (*yellow rectangle*), and 2D profile lines 4 and 5 with direction X–Y (*black dotted line*) at the Gohagoda dump site

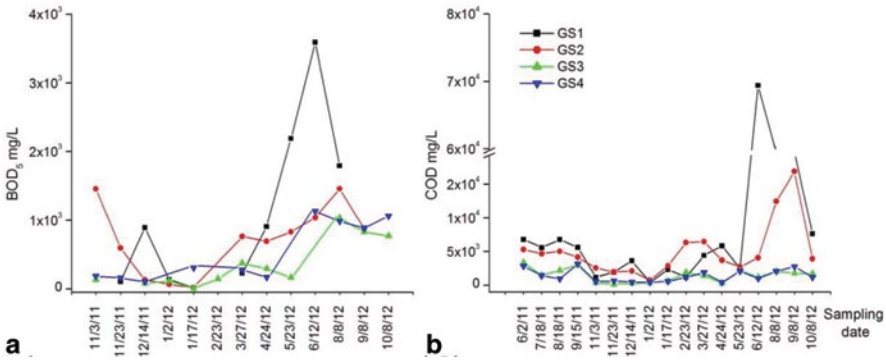

Fig. 11.4 (**a**) pH and (**b**) alkalinity variations in the leachate samples analyzed

was carried out using the Resist freeware package while maintaining the root mean square error < 5 %. The 2D data were processed via Earth Imager licensed software by fixing resistivity at 10–400 Ωm.

11.6.3 Leachate Characteristics

11.6.3.1 pH and Conductivity

Figure 11.4a shows the pH variation during the study period. The pH was 8–8.6 during all samplings with a few exceptions. The pH changed acidic during the later study period. This may be due to the uncontrolled open dumping of MSW with manual mixing of waste and enhancing microbial activity due to the influence of rainfall (Trankler et al. 2005). Degradation of fresh waste can also decrease pH. The alkaline pH was due to mineralization of carbonates, bicarbonates, and hydroxides in the well-established methanogenic phase of the landfill (Robinson 2007; Maqbool et al. 2011). Hence, a phase change from acetogenic to methanogenic can be effectively identified by pH changes in the landfill leachate (Trankler et al. 2005). In addition, the recorded electrical conductivity (EC) of the leachate samples was high at 3.2–31.4 mS/cm, indicating a high content of dissolved salts. However, due to dilution and flushing of organic and inorganic materials, the EC values decreased towards the riverside.

11.6.3.2 Alkalinity and Hardness

The alkalinity in the Gohagoda leachate was 725–39,606 mg/L (Fig. 11.4b). Because the alkalinity is a measure of the acid neutralizing capacity and, hence, is a function of HCO_3^- and CO_3^{2-} content (William 1997), the dissolution of metal carbonates under prevailing pH conditions may have been the reason for the increase in alkalinity with time (Bhambulkar 2011). Hardness is normally expressed as the total concentration of Mg^{2+} and Ca^{2+} in mg/L and it was 15–800 mg/L during the study period. GS2 showed the highest hardness value at the beginning but it decreased rapidly thereafter. The pattern of variation was narrow except GS4. Thus, it was evident that GS1 and GS2 were highly contaminated with Mg^{2+} and Ca^{2+} multivalent cations, which may be due to soaps, detergents, batteries, and other types of industrial and household waste. The reason for the hardness decreasing with time could be infiltration and attenuation by soil. Under alkaline pH conditions, adsorption or precipitation mechanisms attenuate $Mg^{+2}$and Ca^{2+} ions in leachate in surrounding soils that are rich in clay minerals. In addition, chloride was 68–723 mg/L during the study period (Table 11.2). Farm animal waste, household waste, and septic effluent might be sources for the high chloride levels in leachate (Mor et al. 2006).

11.6.3.3 BOD and COD

Figure 11.5a and b illustrates the BOD_5 and COD variation throughout the leachate characterization period at the Gohagoda landfill site. The maximum BOD_5 was 3,590 mg/L at the closest point to the dumpsite. However, the BOD_5 was <2,190 mg/L at all other sampling times, indicating typical methanogenic phase conditions (Robinson 2007). Furthermore, low BOD_5 values with continuously fluctuating patterns were observed during the study period. At the beginning of the characterization, very significantly high BOD_5values of 27,500 mg/L were recorded at the closest point to the landfill (GS1 point), indicating typical acetogenic phase leachate characteristics (Wijesekara et al. 2010). COD stabilized at ≤3,000 mg/L with time at the Gohagoda site. These values are consistent with other studies for typical methanogenic landfill leachate (Irene 1996). A highly concentrated landfill leachate can be generated in biodegradable waste rich landfill cells during the initial period of refuse degradation (Tatsi and Zouboulis 2002; Trankler et al. 2005). As typical South Asian MSW landfills, a composition study at the Gohagoda dumpsite for solid waste revealed that there was a high amount of biodegradable waste, which has a direct relationship with the high organic content of leachate (Trankler et al. 2005; Menikpura and Basnayake 2009).

11.6.3.4 TOC/DOC

Average TOC and DOC values were 36,955 and 28,493 mg/L, respectively, during the dry season, and a low COD/TOC ratio (1.59) was observed in the Gohagoda leachate. These results indirectly indicate the age of the Gohagoda landfill site as >20 years and the presence of a more oxidized state of organic carbon for a less readily available energy source for the growth of microorganisms (Irene 1996).

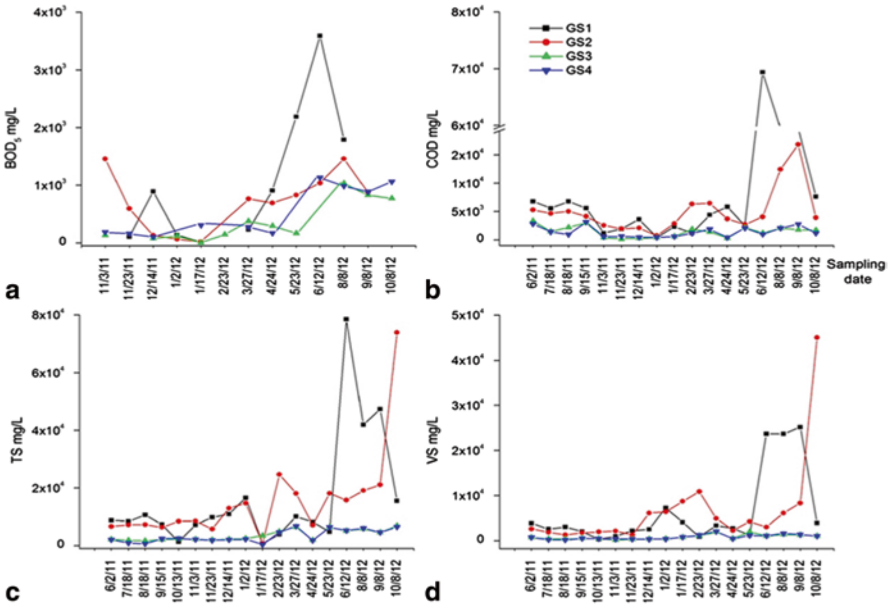

Fig. 11.5 Variation in the concentrations of **a** BOD_5, **b** COD, **c** TSs, and **d** VS in the leachate samples analyzed

11.6.3.5 Solids

Figure 11.5c and d reflects the Total Solids (TS) and Volatile Solids (VS) variations during the study period at the Gohagoda landfill. The TS and VS values were <20,000 and 10,000 mg/L, respectively, which agreed with the previous literature values for methanogenic phase leachate (Chu et al. 1994). However, on a few occasions very high TS and VS concentrations of 80,000 and 45,000 mg/L, respectively, were observed. The spatial variations in TS and VS had many similarities. The average Total Suspended Soilds (TSS) and Volatile Suspended Solids (VSS) concentrations during the study period were 1,493 and 416 mg/L, respectively. The mean VSS values of the leachate at various landfills are 50–200 mg/L, which is close to the observed values (10–4,810 mg/L) (Fan et al. 2006). The VSS value of an old landfill (>10 years) is 7 mg/L (Kang et al. 2002). In addition, the concentration of all analyzed solid parameters decreased from the dumpsite to riverside, and this may have been due to the coagulation and settling of solid particles in the adjoining paddy field soils. Overall, the solid parameters analyzed indicate that the Gohagoda leachate is in the methanogenic stage.

11.6.3.6 Nutrients

Among the nutrients, nitrogenous compounds were observed in high concentrations. Figure 11.6a shows the nitrate-N variation in the leachate samples analyzed.

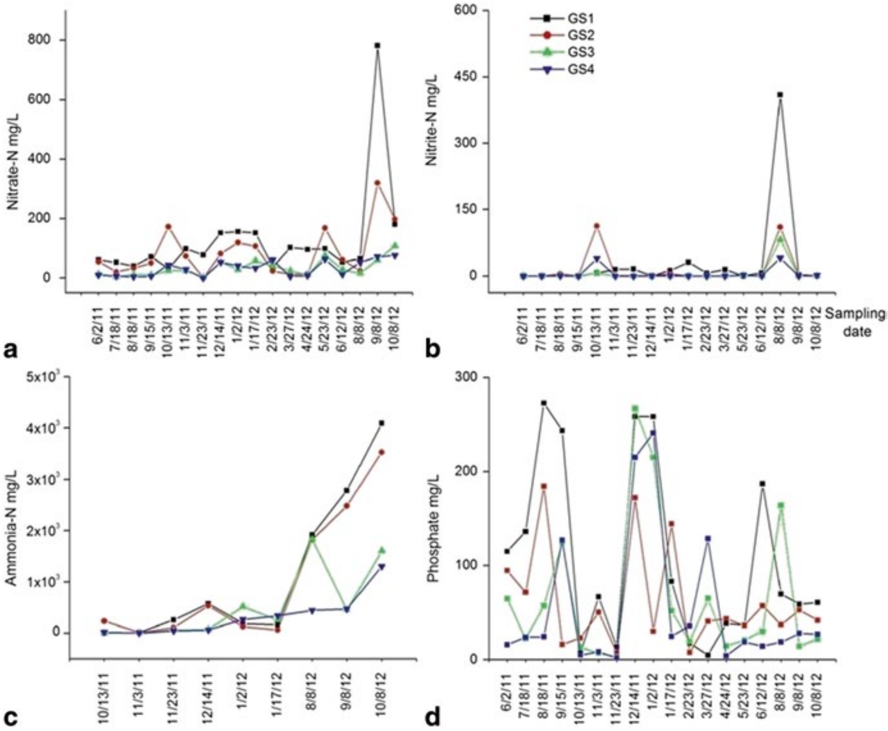

Fig. 11.6 Variations in the concentrations of **a** nitrate-N, **b** nitrite-N, **c** ammonia-N, and **d** phosphate in the leachate samples analyzed

Nitrate-N ranged from 1 to 765 mg/L. Sewage, fertilizer, farm animal waste, and food waste are sources of nitrate in leachate. Higher concentrations of nitrate-N resulting during the final period may have been due to rainwater ingress into the landfill that promoted solubilization of pollutants from actively decomposing waste mass into the leachate. Furthermore, nitrite-N was 0.1–410 mg/L, indicating a complex fluctuation pattern (Fig. 11.6b). A high concentration of nitrite-N is observed in methanogenic leachate worldwide (Robinson 2007**).** Ammonium-N may be present in leachate due to the fermentable organic matter and the high protein concentration (Mor et al. 2006). Ammonium-N is a major reducing agent in the leachate and, thus, is involved in increasing nitrate concentration. The ammonia-N results in the Gohagoda leachate fluctuated widely at 6–4,095 mg/L (Fig. 11.6c). Considerably high concentrations (3,000 mg/L) were observed at the end of the study with heavy rainfall. Because ammonia is a product of anaerobic protein metabolism, stabilizing anaerobic digestion may have led to the accumulation of ammonia during the final time period. Phosphate levels varied considerably within wide ranges exceeding the country's standard values for wastewater discharge to inland waters at 2 mg/L (Fig. 11.6d). All nutrients generally showed a sudden increase in concentrations immediately after the heavy rainfall. This was probably due to enhanced leaching of nutrients from the fresh waste dumped at the site during the study period followed by the dilution effects of rain (El-Fadel et al. 1997).

11.6.3.7 Chloride

Chloride in leachate is a major non-reactive or inert component and, thus, chloride does not undergo any chemical or physicochemical reactions in the leachate plume. Therefore, dilution is the main attenuation mechanism for chloride (Christensen et al. 2001). However, chloride can contribute to the formation of toxic dioxin gas. The chloride concentration during the study period was 68–723 mg/L. Farm animal waste, household waste, and septic effluents could be the high chloride sources in the leachate (Mor et al. 2006). High rainfall during the last sampling period may have caused accelerated run-off from the dumpsite, resulting, insignificantly, increased chloride levels. However, chloride ions are found in the deepest parts of leachate plumes that affect aquifers; thus, it is an important parameter to model.

11.6.3.8 Heavy Metals

The presence of high levels of heavy metals in the Gohagoda leachate suggests their origin could be from various wastes dumped in the landfill (Fig. 11.7). The presence of alloys, paints, lamp filaments, electrical wiring batteries, ceramics, and automotive parts in a dumpsite can be reasons for heavy metal contaminations (Trabelsi et al. 2009; Fetter 1993). A high concentration of Fe in the leachate may be from Fe scraps and Fe-containing carbonates dumped on the landfill. The presence of Pb exceeding the country's wastewater discharge permissible level of 0.1 mg/L may be attributed to the disposal of batteries, lead-based paints, chemicals for photoprocessing, and lead pipe (Mor et al. 2006). High concentrations of Zn suggest the presence of fluorescent tubes, batteries, and a variety of food wastes. Possible sources of cadmium may be dry cell batteries and paint (Aderemi et al. 2011). Aeration by mechanical mixing of waste accelerates the release of heavy metals into the leachate, which contaminates open water bodies such as rivers as well as groundwater resources through percolation (Mor et al. 2006). In contrast, the alkaline pH enhanced precipitation of cations; thus, lower concentrations are reported in methanogenic phase leachate (Christensen et al. 2001). The sulfide-producing conditions also influence the low concentrations of metal ions.

11.6.3.9 Resistivity Survey

The resistivity data revealed that the main outflow pathway of landfill leachate to the nearby Mahaweli River is characterized as a plunging basin towards the river, and its flow is confined to the near surface (Fig. 11.8). The flow pattern may have been influenced by river water inflow at <3 m level, which would prevent delineating possible perch water pockets (Wijesekara et al. 2013).

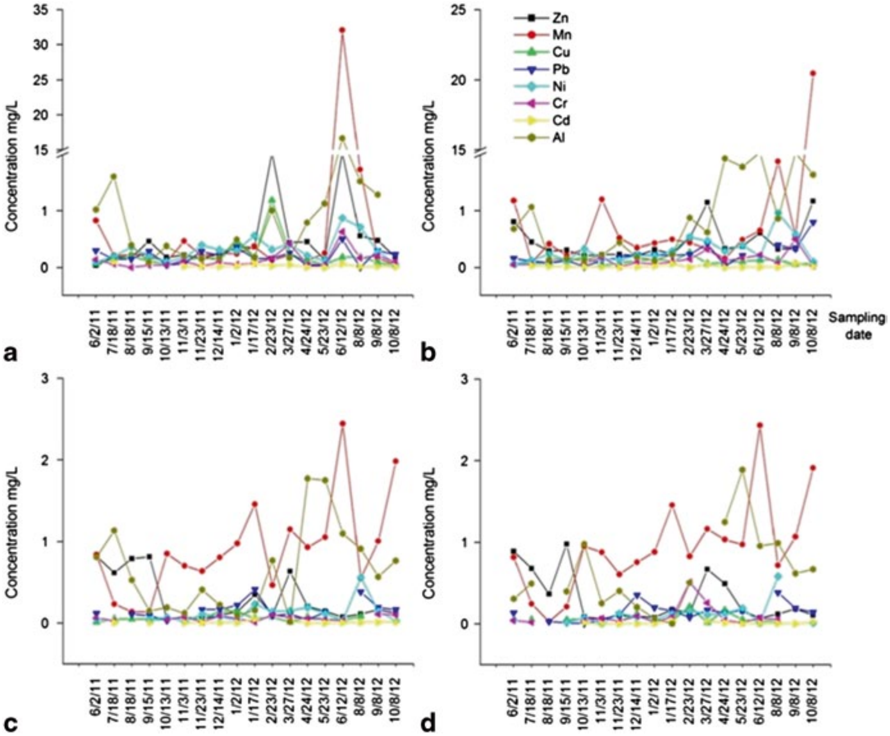

Fig. 11.7 Variations in the heavy metal concentrations at the **a** GS1, **b** GS2, **c** GS3, and **d** GS4 sampling locations

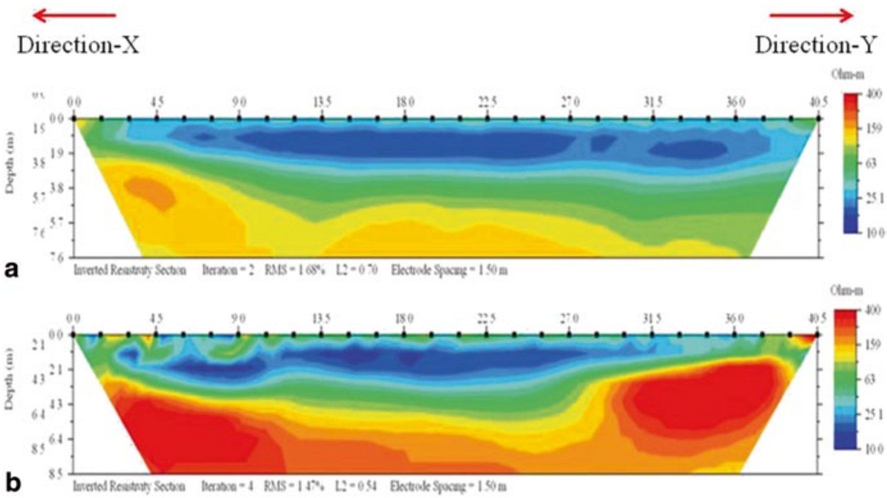

Fig. 11.8 Images of 2D profiles (**a**) line-4 and (**b**) line-5 indicate that the leachate flow is very shallow and limited to the 3-m level. Blue color indicates possible leachate plume with low resistivity values in the Y direction

11.7 Leachate Treatment Technologies

An important part of maintaining a landfill is managing the leachate through proper treatment methods designed to prevent pollution of surrounding ground and surface water. Leachate treatment technologies fall into two basic types of biological and physical/chemical treatments. Integrated systems that combine the two are often used for larger systems depending on treatment goals. The most common biological treatment is activated sludge, which is a suspended-growth process that uses aerobic microorganisms to biodegrade organic contaminants in the leachate. The leachate is aerated in an open tank with diffusers or mechanical aerators. Constructed wetlands are also used for biological treatment (Sundaravadivel and Vigneswaran 2001). However, treating old landfill leachate is a very difficult task using conventional biological treatment processes (Ahmed and Lan 2012). Air or ammonia-stripping, adsorption, and membrane filtration are major physical leachate treatment methods, whereas coagulation–flocculation, chemical precipitation, and chemical and electrochemical oxidation methods are the common chemical methods used for landfill leachate treatment (Ahmed and Lan 2012; Amokrane et al. 1997; Ahn et al. 2002; Chiang et al. 2001; Lin and Chang 2000; Steensen 1997; Marttinen et al. 2002; Cossu et al. 1998). The membrane bioreactor (MBR) (Ahmed and Lan 2012; Amokrane et al. 1997; Cossu et al. 1998; Ahn et al. 2002; Chiang et al. 2001; Lin and Chiang 2000) technique is a promising alternative physical treatment method, as the membrane separation capacity of a MBR allows most microbial cells through the reactor resulting in an efficient biological digestion system (Ahmed and Lan 2012). Li et al. (1999) reported that ammonium removal can be achieved by chemical precipitation. In addition, a 66% COD and 50% ammonia removal were obtained by nanofiltration (Marttinen et al. 2002). Evaporation and reverse osmosis have been used to treat industrial landfill leachate (Di Palma et al. 2002). Further, combined processes successfully applied together include coagulation–flocculation + biological treatment; (Kargi and Pamukoglu 2003) photochemical oxidation + activated sludge; Fe(III) chloride coagulation + photo-oxidation; and ozonation + adsorption (Koh et al. 2004; Wang et al. 2002; Rivas et al. 2003). Several researchers have investigated efficiency of ozonation for treating landfill leachate (Steensen 1997; Baig et al. 1999; Silva et al. 2004). Activated carbon adsorption systems have also been used to treat landfill leachate and remove dissolved organics; however, most of these techniques are generally considered expensive treatment options and must often be combined with other treatment technologies to achieve the desired results. A few studies have demonstrated the use of nano-zero-valent iron (NZVI) as a leachate treatment, but this method is restricted to developed and temperate countries (Jun et al. 2009). However, landfill leachate treatment is a serious issue with no single suitable solution due to the complexity and variation in composition and many local and regional differences.

11.8 Summary

Landfill leachate is composed of a wide range of contaminants: dissolved organic matter, heavy metals, and xenobiotic organic compounds. Exposure of leachate to the soil and groundwater creates significant changes in the environment. Leachate can be categorized into two phases of acetogenic and methanogenic leachates. The dissolved organic matter in the leachate is a bulk parameter comprising a variety of organic degradation products ranging from small volatile acids to refractory fulvic- and humic-like compounds which remain as non-biodegradable compounds for years. The BOD in acetogenic leachate is high indicating presence of readily oxidizable matter for aerobic microorganisms, whereas methanogenic leachate has low BOD values. Most leachate from the early stages (first year) of landfill operation showed a high COD, but as the landfill material aged the COD stabilized at $\leq$3,000 mg/L. Determining solid content is very important to understand the microbial degradation patterns, their abundance (e.g., active microbial mass), and enzyme activities. Nitrate, phosphate, sulfate, and ammonium nitrogen concentrations are the principal nutrients of concern in leachate discharge and generally depend on the waste composition in the landfills and the leachate phase. Among the nutrients, nitrogenous compounds were observed at high concentrations. Sewage, fertilizer, farm animal waste, and food waste may be the sources of nitrates in leachate. The presence of alloys, paints, lamp filaments, electrical wiring, batteries, ceramics, and automotive parts in a dumpsite are the reasons for high heavy metal concentrations in the leachate; hence, high concentrations of Cd, Hg, Ni, Mn, Cu, Zn, and Pb have been reported associated with leachate. Very board ranges of xenobiotic organic compounds have been reported in landfill leachate and most are aromatic hydrocarbons and XOCs, which cause serious biological effects. Phenols, halogenated hydrocarbons, chlorinated aliphatics (e.g., PCE and TCE), and aromatic hydrocarbons are the main XOCs found in leachate. An important part of maintaining a landfill is managing the leachate through proper treatment methods designed to prevent pollution of surrounding ground and surface waters. Hence, two basic categories of leachate treatment methods are biological and physical/chemical technologies used worldwide. The most common biological treatment is activated sludge, which is a suspended-growth process that uses aerobic microorganisms to biodegrade organic contaminants in leachate. Air or ammonia-stripping, adsorption, and membrane filtration are major physical leachate treatment methods, whereas coagulation–flocculation, chemical precipitation, chemical and electrochemical oxidation methods are the most common chemical methods used for landfill leachate treatment. However, no universal leachate treatment methods have been developed due to the complexity of leachate.

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Part III
Climate Change and Health

Chapter 12
Climate Change and Migration: Food Insecurity as a Driver and Outcome of Climate Change-Related Migration

Celia McMichael

Abstract The impacts of human-induced climate change on both population mobility and food security are issues of substantial concern and debate. However, there has been limited consideration of the intersections between these processes. This chapter considers two key areas of concern. First, climate change will adversely affect food security in many regions, and this may contribute to migration where, for example, people move to areas where agricultural livelihoods and food sources are more secure. Second, climate change is projected to cause increases in human population movement in coming decades, and the nature of some anticipated migration pathways may lead to food insecurity in sites of settlement and relocation. However, the effects of climate change on both population mobility and food security will occur through complex pathways. This chapter considers the intersections—both potential and current—between climate change, food security and migration.

Keywords Climate change · Migration · Food security

12.1 Introduction

This chapter examines the relationships between climate change, food security and human migration. The impact of human-induced climate change on both population mobility and food security are issues of substantial concern and debate (Bardsley and Hugo 2010; McMichael et al. 2012). First, climate change is projected to contribute to substantial increases in human population movement in coming decades (Black et al. 2012; Foresight 2011; Scheffran et al. 2011; Tacoli 2009). Second, in many regions, climate change will increase threats to food security through its impacts on food production, ocean acidification and fishery yields, infrastructure, the capacity of countries to import food and the ability of households to purchase food (Badjeck et al. 2010; Dinar 2007; FAO 2011; Grace et al. 2012; Misselhorn et al.

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2012). However, there has been limited consideration of the intersections between these processes. As Warner et al. argue, ‘we know little about the interplay between environmental change and stresses on ecological systems, resulting socio-economic vulnerability and potential outcomes in terms of population displacement or induced migration’ (Warner et al. 2010, pp. 689–690).

The relationships between these factors are not characterised by direct causality but rather constitute a complex interplay. This interplay of diverse factors was apparent recently, for example, during the ‘Arab Spring’ in which food availability, elevated food prices, drought and poor water availability, demographic change, urbanisation and migration contributed to the pressures that underpinned the political upheaval. In spring 2010, record rainfall in Canada reduced the wheat harvest by nearly one quarter. During 2010, drought and bushfires substantially reduced crops in Russia, Ukraine and Kazakhstan—all leading global wheat exporters. In 2010–2011, a ‘once-in-a-century’ winter drought in China led the Chinese government to purchase wheat on the international market to compensate for losses from drought. The USA began to suffer ‘winter kill’ from storms in late January 2011. These factors reduced the global wheat supply and contributed to global wheat shortages (Johnston and Mazo 2013). By February 2011, wheat was trading at US$ 8.50 to US$ 9 a bushel, compared to around US$ 4 in July 2010. Bread prices skyrocketed in Egypt, the world’s largest wheat importer (Sternberg 2013), and citizen protests highlighted political and economic dissatisfaction, including with the high cost of food. Of course, escalating food prices—in part due to climatic changes—were a contributing factor, not the primary cause of the Arab Spring. But as Johnston and Mazo argue controversially, climate change acted as ‘a threat multiplier in the sense that it was a necessary component of any number of possible scenarios, each of them sufficient to have led to the sort of unrest we are now witnessing in the Middle East and North Africa region’ (2013, p. 20). At the same time, migration flows both shaped and resulted from the Arab Spring: in the period immediately preceding the revolts, emigration increased substantially in Arab Mediterranean countries (during 2001–2010, the aggregate number of emigrants to the Organisation for Economic Co-operation and Development (OECD) countries increased by 42 %, from 3.5 to almost 5 million); many countries, such as Egypt, were experiencing urbanisation fed in part by the ‘youth bulge’ with disaffected young people migrating to urban areas in search of employment opportunities; following the Arab Spring, migration within the Southern Mediterranean increased substantially as migrants and refugees fled instability and violence (Fargues and Fandrich 2012). The full impact of the Arab Spring on migration will not be fully understood for some time (Foresight 2011). As this example illustrates, however, there are concurrent processes and complex interactions between climate change, migration, food security and other diverse factors including land and water availability, urbanisation and social, political, demographic and economic stressors.

This chapter seeks to examine the intersections—both potential and current—between climate change, human migration and food (in)security. First, it provides a brief overview of the relationships between climate change and population movement. The chapter is then organised via two key questions: 1) How does climate change-related food insecurity contribute to human migration; and 2) how does climate change-related migration impact on food (in)security? To engage with these questions, the chapter discusses case studies from Mozambique, Ethiopia, Laos, Syria, Sudan, Mexico and Pakistan.

12.2 Background: Climate Change and Population Movement

There is now consensus among scientists that climate change is occurring, and that human-generated emissions of greenhouse gases—associated with industrial activity, burning of fossil fuels, deforestation, the surge in human numbers, land-use patterns, food production and consumption—have resulted in the increase in global average temperatures and other climatic changes, particularly since the middle of the twentieth century (Lenton et al. 2008; Rockström et al. 2009; Smith et al. 2009). The natural environment is more than merely a backdrop to human lives (Black et al. 2011), and there have been many studies of the potential impact of climatic changes on human systems, including migration (Foresight 2011).

Environmental change and deterioration associated with human-induced climate change will shape population movement and forced migration (see, for example, Bates 2002; Black 2001; Perch-Nielsen et al. 2008; Renaud et al. 2007; Warner et al. 2008). Most frameworks start with climate change as a driver of population mobility and consider the potential magnitude, pathways and consequences for migration. Broadly, climate change is anticipated to affect population movement through: (i) an increase in the intensity and frequency of extreme weather events and climate-related disasters; (ii) loss of arable and inhabitable land; and (iii) adverse impacts on ecosystems (Oliver-Smith 2009). These climatic changes will have diverse impacts on population mobility.

First, the frequency and intensity of atmospheric hazards—e.g. floods and cyclones—are expected to increase due to climate change (Krishnamurthy 2012). Migration related to extreme climatic events is typically temporary, short distance and within countries. People tend to return to their original areas or sites of residence to rebuild homes and livelihoods (Black 2001). For example, in the 2010 Pakistan floods, 12 million people lost their homes. Two months into the disaster, around seven million flood victims remained homeless but many returned home after the water subsided to secure their land, salvage possessions and to replant their fields (Lom 2010). During disasters, the structural causes of vulnerability—including economic status, ethnicity and gender—have a substantial impact on the dynamics of displacement and return settlement.

Second, slower onset climatic changes are forecast as a proximate factor in more permanent migration away from places of origin. This will include people who lose habitable islands or coastal or riverine terrestrial land due to sea-level rise. Low-lying islands in the Pacific are widely regarded as being ‘on the front line’ of climate change-related migration and displacement, but populations in low-lying regions of Asia, Africa and Latin America are also considered at risk (Farbotko and Lazrus 2012; McMichael and Lindgren 2011). Two thirds of the world's cities with populations more than five million are at least partially located in coastal zones, including urban centres of Asian and African mega-deltas, and there are more than 220 million people living in the low-elevation coastal zones of the world's 11 largest river deltas (Foresight 2011). While the numbers of people at risk from sea-level rise in small islands and small island states are few in global terms, there is the threat that some low-lying small island states, such as the Maldives, Tuvalu and Kiribati, could ultimately be submerged (McAdam 2010).

Third, climate change has adverse impacts on ecosystems that are an important source of amenity and livelihood, including land degradation, declining abundance of fish, erosion of riverbanks and beaches, declining freshwater availability and coral degradation. Although extreme environmental events result in highly visible and large-scale population displacement, a larger number of people are expected to migrate due to a gradual deterioration of environmental conditions: Between 1979 and 2008, it is estimated that 1.6 billion people were affected by droughts compared to 718 million affected by storms (Walsham 2010). These slower onset environmental changes can be a proximate factor for migration (temporary and permanent). For example, studies have shown a correlation between changing rainfall patterns and migration in Mexico. Dryland Tlaxcala, in Mexico, depends on rain-fed agriculture, and changing rainfall periods have been linked to a decline in crop yields and incomes. Return migration and seasonal migration have been documented as a livelihood diversification strategy in this area (Campbell and Berry 2003). However, other studies indicate that long-distance migration among pastoralists is reduced during drought (van der Geest 2011). And a review by Black et al. (2012) argues that the most vulnerable populations are unable to migrate during environmental disasters.

In sum, climate change (and associated adverse events and environmental deterioration) is widely viewed as a stress factor that increases migration pressure in vulnerable regions (Scheffran et al. 2011). Yet migratory responses to environmental changes are heterogeneous, and studies suggest that some adverse climatic changes can reduce and inhibit migration opportunities. While there is no commonly agreed definition of climate migration, there has been extensive debate regarding present and future numbers of people likely to migrate in response to the effects of climate change, on either a temporary or permanent basis (Boano et al. 2008; Brown 2007; Myers 2002). Estimates range from tens to hundreds of millions of climate change-related migrants by mid-century. Yet critics of these quantitative estimations have pointed to the difficulties in disaggregating 'environmental migration' from other push/pull factors, and the problem of distinguishing populations 'at risk' from those that are likely to migrate (Foresight 2011). There is a need for more localised estimates which take a realistic account of the potential for adaptation and provide the data needed for planning over short-, medium- and long-term time frames (Walsham 2010). Many estimates of climate change migration are challenged as being both speculative and inflated (particularly those estimates at the upper end) (Black et al. 2011), yet substantial climate-related changes in people's living and working environments are occurring, with migration being a likely response now and in the future (Tacoli 2009).

However, many estimates of the impact of climate change on migration do not take into account the extent to which adaptation strategies may reduce population mobility and displacement (Barnett and Webber 2010). Migration is not the mechanical response to environmental degradation and disaster: people living in hazardous environments differentially draw on adaptive strategies and incorporate risk into their lives (McGregor 1994). In Bangladesh, for example, investment in storm shelters and early warning systems in response to a series of devastating cyclones has arguably contributed to people's decision to remain in vulnerable areas (Foresight 2011). Migration is only one of a range of options pursued by people affected by environmental stressors, with other strategies including selling assets, changing livelihoods or short-term movement. A key question is whether adaptive responses to climate change threats are sufficiently robust to withstand future events. Further, there will be many people who are unable to migrate in response to adverse climatic changes due to lack of financial, social, political and physical resources, and accordingly are vulnerable to environmental deterioration and impoverishment. Indeed, people who do not migrate in the face of adverse climatic changes 'are likely to represent an equal if not bigger challenge to policy makers as those who migrate' (Foresight 2011, p. 25). Decisions to migrate or remain in situ depend on available resources, social networks and the perceived alternatives to migration.

Further, while migration can be a manifestation of acute vulnerability, migration can also operate as a form of adaptation in that migrants are active social agents who shape their lives and livelihoods in response to environmental change (Scheffran et al. 2011). Adaptation is defined as 'adjustment in natural or human systems in response to actual or expected climatic stimuli or their effects, which moderates harm or exploits beneficial opportunities' (IPCC 2007a, p. 869). Accordingly, migration can be understood as an adaptive response to climate change that also offers opportunities to access new resources, acquire new knowledge, develop alternative livelihoods, develop social networks and increase the adaptive capacity and resilience of both 'home' and 'host' communities (Scheffran et al. 2011).

Finally, environmental change, and climate change in particular, is one of a number of drivers that interact to produce migration responses (Black et al. 2011). For less developed countries in particular, social, demographic, political and economic stressors—e.g. high population density, limited economic opportunity and employment, inequitable distribution of resources and services and armed conflict—will coexist with climate risks and influence decisions about migration (Tacoli 2009). As illustrated by the example of the Arab Spring discussed previously, environmental change, in combination with other sociopolitical vulnerabilities, creates conditions for displacement and migration. Hence, it is difficult to disaggregate the impacts of climate change from those of other processes, particularly in the case of slow-onset environmental change (Adamo 2010). Indeed, migration is an integral part of broad social and development processes, with current world migration driven largely by non-environmental factors (de Haas 2010). The International Organization for Migration (IOM) estimates that about 214 million people currently live outside their country of birth (i.e. around one out of every 33 persons in the world today), and around 28 million are internally displaced (IOM 2013). With this in mind, it is critical to challenge concerns about climate change-related migration that are framed as a crisis of environmental displacement (Farbotko and Lazrus 2012) and, instead, broadly examine how the effects of climate change exacerbate pre-existing conditions such as poverty and social (in)equity. Environmental change is one among many factors that drive migration, and migration is also one of the numerous possible responses to environmental change (Walsham 2010).

12.3 Intersections Between Climate Change, Migration and Food Insecurity

In the subsequent two sections, the following broad questions are considered: 1) How might climate change-related food insecurity contribute to migration; and 2) how might climate change-related migration contribute to food insecurity (see Fig. 12.1)? This extends a previous assessment of the potential impact of climate change-related migration for human health (see McMichael et al. 2012), with the specific focus here being the food security/migration nexus. As complex realities rarely fit into readily defined categories, the thematic organisation is intended to broadly identify some key intersections between climate change, migration and food insecurity. Through assessing previous experiences of environmental change, food insecurity and migration, lessons are then inferred for responding to the future challenges of human-induced climate change.

12.3.1 The Effect of Climate Change-Related Food Insecurity on Migration

The standard definition of food security is 'when all people, at all times, have physical and economic access to sufficient, safe, and nutritious food to meet their dietary needs and food preferences for an active and healthy life' (FAO 2002). At a household level, food security refers to access by all members at all times to sufficient food for an active and healthy life (Maxwell and Frankenburger 1992). Broader definitions of household-level food security include related concepts of accessibility, sufficiency, security and sustainability (Regassa and Stoecker 2012). At the extreme, food insecurity is experienced as famine and hunger. Although vulnerability to food insecurity is shaped by the contexts and process across different regions, it largely remains a rural and agricultural phenomenon (Bogale 2012). Food (in)security focuses on actual and potential resources available to households based on their own production, assets or reciprocal arrangements. However, a 'forward-looking' approach is also imperative that can identify not only households that are presently food insecure but also those that are vulnerable to future risks, such as natural disasters and extreme climate conditions (Bogale 2012).

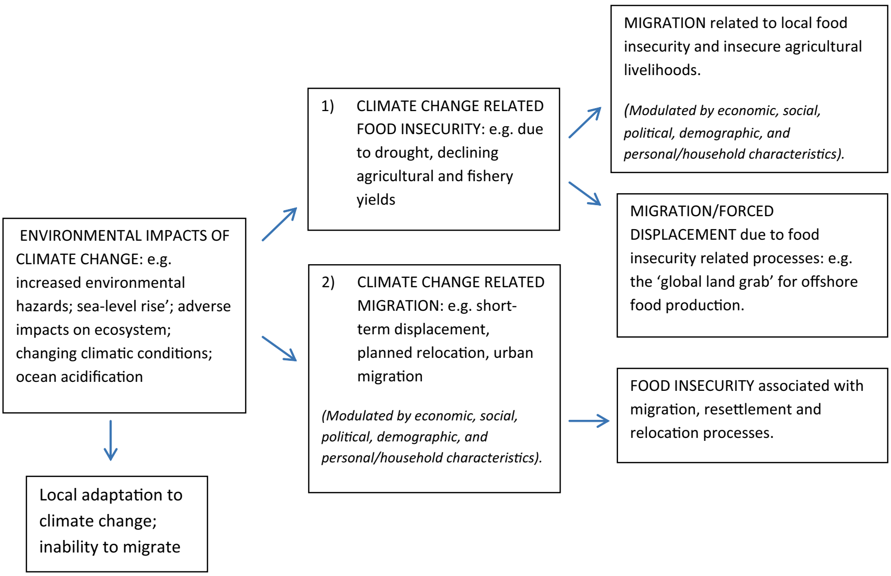

Fig. 12.1 Broad relationships between climate change, migration and food insecurity

There are multiple risk factors for food insecurity, including inaccessibility to productive resources, land tenure insecurity, inaccessibility to transport infrastructure, poorly managed food aid programs, recurrent drought and declining resource productivity as a result of environmental degradation. Climate change, however, is now considered a threat to food security and agricultural productivity, particularly in areas that already experience high levels of food insecurity (FAO 2011). This section considers how climatic change could contribute to food insecurity and combine with other drivers to influence human migration.

12.3.1.1 Climate- Change- Related Food Insecurity and Population Mobility

Climate change effects—changes in flooding and drying cycles, average temperatures, rainfall patterns and amounts and the spread of drought conditions in some regions—are expected to lead to significant changes in the geographic distribution of food production and food prices (Easterling et al. 2007). It is anticipated that 10% less rain will fall in sub-Saharan Africa by 2050, leading to droughts and falling crop yields (IPCC 2007b). Conversely, temperate regions in the higher latitudes will experience marginal increase in food productivity due to extended growing seasons and expansion of areas appropriate for crops (Vincent et al. 2008). However, changes in food production will disproportionately affect low-income regions, including sub-Saharan Africa, South Asia and India, potentially exacerbating preexisting widespread malnutrition (Dinar 2007; Grace et al. 2012; Misselhorn et al. 2012). Warming oceans and ocean acidification will also endanger coral ecosystems and the fish upon which around three billion people depend for food and essential nutrition (FAO 2011; MacNeil et al. 2010). Changing agricultural and fishery yields will largely have adverse repercussions on human health including increased malnutrition (McMichael et al. 2004, 2012; Costello et al. 2009).

Drought is a key driver of food insecurity. Long-term and recurrent drought conditions and changes in food production and food security may contribute to population mobility where people seek to migrate to areas where food sources and agricultural livelihoods are more reliable (Mendelsohn et al. 2007; Kloos and Adugna 1989). As such, migration can provide a coping strategy that diversifies and strengthens people's livelihoods, assets and incomes, which in turn helps to reduce food insecurity (Bardsley and Hugo 2010; Black 2001). In recent years, there have been several reports and studies documenting the impact of long-term environmental processes—particularly drought—on population mobility and migration (IFRC 2009; NRC 2011). Drawing on research from drought-prone areas of northern Ethiopia, Ezra (2001) argues that persistent food insecurity has led to outmigration from communities, particularly among youth. Around 84 % of the population in Ethiopia live in rural areas and engage in rain-fed agriculture: In these areas, vulnerability to food insecurity is determined not only by climatic variability but also by land degradation, population density, low levels of rural investment and the global market (Bogale 2012). Similarly, pastoralists from Sahel Africa (e.g. Senegal, southern Mauritania and southern Sudan) have permanently migrated partly in response to prolonged drought that disrupted and degraded people's livelihoods and food security (Afolayan and Adelekan 1998; Davies 1996; Hammer 2004). Irregular rainfalls, prolonged drought periods and vulnerable ecosystems in the Sahel have typically required a high level of adaptation among communities, and population mobility (e.g. nomadic pastoralism and circular migration to urban areas during the dry season) is a common strategy to cope with the variable climate. However, permanent migration (including international migration) is increasingly common due, in part, to changing environmental conditions: For example, in Mauritania, severe droughts in the 1970s contributed to international emigration, initially mainly to neighbouring West African countries (Scheffran et al. 2011).

More recently, during 2006–2011 Syria experienced long-term drought and crop failures. In 2009, the United Nations and the International Federation of Red Cross and Red Crescent Societies reported that more than 800,000 Syrians—including agriculturalists and herders in rain-fed areas of the northeast—had lost their livelihoods as a consequence of the droughts. By 2011, around one million Syrians were estimated to be severely affected and food insecure due to the droughts, with two to three million experiencing extreme poverty. This contributed to large-scale migration of farmers, herders and agriculturalists from rural areas to the cities in search of alternative work (Femia and Werrell 2013; Erian et al. 2010). In one recent report, Hassan Hami Hami, who moved with his family to Damascus after he lost his livelihood as a wheat farmer on the northeast border of Syria, is quoted as saying, 'there is nothing left for us there… Farming stopped and I sold plastic for a while, but it was not enough. We had to borrow so much money from people just to survive' (IRIN 2009). And in Zimbabwe, droughts during 1997–2010 were less severe than those in earlier decades, but they contributed to substantial food insecurity because they occurred in the context of increasing vulnerability associated with the broader political conflict and economic contraction. Hundreds of thousands of people were displaced in this political–economic–environmental crisis, either internally or externally. However, there may also be hidden thousands who were unable to migrate (Foresight 2011).

Other studies have sought to model the future relationships between climate change, agricultural production and migration. In their study of the long-term relationships between climate change, economic impacts and demographic dynamics in Northeast Brazil, Barbieri et al. (2010) argue that climate change will affect agricultural productivity levels, contributing to population movement when adaptation mechanisms are not sufficient to mitigate the economic impacts. Their study models future scenarios (between 2025 and 2050) for climate change impacts on migration. Despite complex connections between migration and other factors—including socio-economic status, sea-level rise and water and energy supply—the authors suggest that migration (particularly rural–urban migration) will be a mechanism to reduce vulnerability to altered agricultural production associated with climatic change (e.g. increased temperatures), particularly among rain-fed smallholder farmers who live in semi-dry areas of Northeast Brazil.

Yet, there is a need for caution in drawing overarching causal connections between drought, declining agricultural productivity and migration. In addition to studies that indicate a connection between drought, declining agricultural productivity, food insecurity and outmigration, research also highlights other migratory responses including socially differentiated migration, declining migration and immobility. For example, a study in Burkina Faso found that, during drought years, the incidence of longer term migration tended to fall, yet the short-term mobility of women and children increased (Henry et al. 2004). Farmers' responses to declining rainfall and agricultural productivity can range from abandonment, diversification (including the introduction of new crops), intensification (including irrigation and industrialisation) and other risk reduction strategies (including insurance schemes), each with distinct consequences for migration patterns (Foresight 2011). Further, while the effects of climate change are expected to lead to significant changes in agricultural and fishery yields, food insecurity and famine are also shaped by social, demographic, political and economic stressors (Ó Gráda 2011). Sen (1999) has argued that famine and famine mortality, rather than being caused by lack of food availability (e.g. due to drought or crop failure), are a result of social, political and economic inequalities that hinder the ability of people to acquire food through purchase, exchange or transfer. Sen's focus on the distributional aspects of famine highlights sources of food and food distribution other than production. Ó Gráda (2011) argues that markets now have effective capacity to move food to where it is most needed. He cites, for example, studies that indicate that grain markets in Niger had sufficient capacity for food distribution during the drought of 2005. These debates indicate that the adverse effects of climate change will increase vulnerability to drought, famine and food insecurity in many regions, but the scale of vulnerability and the nature of migratory pathways will be shaped by the extent to which societies, communities and food markets can adapt.

12.3.1.2 Food Production via the 'Global Land Grab' and Population Mobility

The previous section has considered the pathways by which food insecurity associated with environmental deterioration may become a driver of population mobility. Food insecurity associated with environmental change will also affect population mobility—in particular, forcible migration—through more circuitous pathways. The 'global land grab' (otherwise known as 'large-scale land investment') refers to the rapid increase of (trans)national commercial land transactions and land speculation predominantly, but not solely, relating to the large-scale production and export of food and biofuels (Borras and Franco 2012). It includes the lease, concession or sale of public land to foreign governments and companies. Land can be used for various purposes including as a hedge against crisis-ridden international financial markets, investment in agricultural production for export to finance-rich and resource-poor countries, tourism development or the production of biofuels at a time when global energy prices have been at an unprecedented high (Hall 2011; Zoomers 2010). Economic globalization, combined with the growing global land scarcity and the 'global land grab', increases the complexity of future pathways of land-use change and associated population mobility (Lambin and Mayfroidt 2011). The global land grab has now emerged as a critical development issue (Robertson and Pinstrup-Anderson 2010; Zoomers 2010), with complex links to forced migration and resettlement, food security and climate change.

Large-scale land investment is driven by multiple processes, currently including: the oil price spikes of the mid-2000s; the food price hikes of 2007 and 2008; the crisis in world financial markets in 2008 and the onset of global recession in 2009; the worldwide boom in foreign direct investment (FDI); liberalisation of land markets via the neo-liberal economic model; and the need to increase global food production in order to meet the demands of a growing population (Cotula et al. 2009; Huang et al. 2011; FAO 2012). However, climate change is also a critical factor underlying the global land grab. As discussed earlier, climate change will shape food (in)security and alter the areas suitable for highly productive agriculture. While international trade is regarded as an important means of compensating for falling agricultural and livestock yields in tropical and semi-tropical latitudes, it may only partially compensate. Recent studies suggest that international land acquisition will increasingly be a strategic choice to address the problem of food insecurity (FAO 2012). Recent estimates suggest that around 45 million h of land have been acquired through land acquisition deals, with two thirds of demarcated land in sub-Saharan Africa (Borras and Franco 2012; World Bank 2010). However, some leases or concessions have been granted on land that is already occupied and used for subsistence farming and grazing by local people (Cotula et al. 2009).

There is some evidence that, due to international land acquisition deals, local people are forcibly displaced to alternative, often marginal, locations. Since 2008, Ethiopia has leased more than 3.6 million h of land to foreign and domestic investors, including investors from India, South Korea, China and the Gulf States (HRW 2012). Forced resettlement is taking place in areas where significant land investment is planned or occurring. In Ethiopia's Gambella region, 42% of the land area is marketed for lease or already leased to investors, and up to 45,000 households are being relocated to new 'villages'. Human Rights Watch (HRW 2012) reports that despite government assurances of basic resources and infrastructure, the new villages have inadequate food, agricultural support and health and education facilities. Reduced capacity for shifting cultivation and small-scale farming removes an important brake on hunger and extreme poverty for current and future generations. While such land deals provide direct foreign investment, it is on terms that are creating significant problems, including large-scale population displacement (Hall 2011). In this way, the global land grab—driven in part by climate change-related food insecurity—will contribute to forcible population displacement.

However, as Borras and Franco (2012) articulate, the character and extent of such displacement and dispossession is not uniform, and there is a need for careful empirical investigation to move analysis beyond the somewhat anecdotal current discussion. While there is indeed the threat of displacement of local people and communities as a result of (trans)national commercial land transactions, experiences range from forcible displacement and land dispossession, to short-distance relocation, to land lease-and-labour arrangements. Borras and Franco cite various examples, including: the short-distance relocation of people from the 30,000-hectare Procana sugarcane plantation in Mozambique in which livestock herders' settlements were relocated, their traditional grazing areas re-routed and boundaries redrawn; and small farmers in Indonesia or in São Paulo in Brazil who are linked to emerging plantation enclaves through contract farming and/or land lease-and-labour arrangements via which capitalist investors are able to control land while avoiding dispossessing smallholders. Highlighting the diverse outcomes of land acquisition for migration allows more nuanced understanding of and responses to relocation, livelihood disruption, food insecurity, compensation and labour conditions, all of which are critical issues for affected people (Borras and Franco 2012).

12.3.2 The Effect of Climate Change-Related Migration on Food Insecurity

The previous section has discussed two pathways—both direct and indirect—by which climate change-related food insecurity may contribute to population displacement: climate change-related drought and food insecurity and large-scale land investment. However, the effects of climate change are expected to contribute to population mobility and forced migration through multiple pathways. How, then, will food security be improved or compromised among those who move? In the following sections, three climate change-related migration pathways are considered: planned resettlement, large-scale forced displacement (associated with environmental disaster) and rural–urban migration.

12.3.2.1 Planned Resettlement

Discussions about the risks climate change pose to vulnerable populations—particularly those from low-lying islands and coastal deltas—are increasingly identifying planned resettlement as an adaptation response (Biermann 2010; Byravan and Rajan 2006). These are likely to be at the scale of communities, within countries and (preferably) voluntary in nature. Any plans to relocate human populations in response to current or future threats of climate change must consider both the immediate and long-term impact of planned resettlement on livelihoods, economic security and well-being (Cernea and Schmidt-Soltau 2006; Johnson 2012; Penz et al. 2011). Previous assessment of the outcomes of 'development-forced displacement and resettlement' indicates that resettlement policies typically create new vulnerabilities among resettled populations, particularly among the poor (Cao et al. 2012; Warner et al. 2008; Cernea 1997; Cernea and Schmidt-Soltau 2006).

However, research into planned resettlement has tended to focus on direct economic impacts, including compensation, and to a lesser extent the political and environmental consequences. There is comparatively limited coverage of potentially far-reaching and long-term social costs (Rogers and Wang 2006). In particular, there has been very limited research on the health impacts of planned resettlement schemes and development-induced displacement. As Jayewardene (1995) indicates, health-focused research in the context of development-related displacement is only conducted where health problems reach a crisis level. Yet planned resettlement has been associated with adverse health outcomes, including food insecurity (Cernea 1997). For example, Stal (2011) outlines a case study of planned resettlement as a strategy to cope with flood risk in Mozambique's Zambezi basin in 2001 and 2007. The government initially moved displaced flood-affected people to accommodation centres and then later attempted to relocate them to resettlement centres. The resettlement centres were built in flood-safe areas, close to schools, health centres and low-lying fertile fields. Yet, the flood-safe areas suffered from water scarcity and drought, and people were unable to grow crops and maintain secure food sources and livelihoods. Following the 2007 floods, while many people travelled regularly from resettlement area to the low-lying river areas to grow crops, productivity was reduced and communities required governmental and international aid for survival. In this example, planned resettlement reduced flood risk in Mozambique's Zambesi basin but increased the challenge of maintaining secure food sources. Indeed, a key outcome of planned resettlement is often malnutrition as the environmental, market and social conditions under which people previously secured food typically differ in new locations (Cernea 1997; Kloos 1990; Kloos and Adugna 1989).

Resettlement is a highly disruptive process that should only be considered where other adaptation strategies are ineffective or unavailable (Barnett and Webber 2010). Nonetheless, studies that seek to document 'successful' resettlement suggest that planned resettlement policies are most effective—i.e. they minimise the social and health costs of planned resettlement—when affected populations: have active control and influence over decision-making and processes of resettlement; voluntarily participate in resettlement; are well informed about social, economic and environmental conditions; are provided with adequate compensation (in the form of assets, incomes and economic opportunities); are employed wherever labour is required; and have access to housing, health services, mental health services, employment and education in sites of resettlement (Cernea and Schmidt-Soltau 2006; Johnson and Krishnamurthy 2010; Penz et al. 2011).

12.3.2.2 Environmental Disaster and Large-Scale Forced Displacement

Large-scale forced displacement can occur where immediate environmental disasters—such as floods, cyclones, landslides and wildfires—threaten the physical safety of populations (Krishnamurthy 2012). Climatic change will increase the frequency and intensity of extreme weather events, including cyclones, heatwaves, heavy rainfall events leading to flooding and droughts (Coumou and Rahmstorf 2012; Krishnamurthy 2012). While individual disaster events cannot be attributed specifically to climate change, the increased frequency and intensity of weather-related events is representative of a projected trend associated with climatic change (Comou and Rahmstorf 2012; Vincent et al. 2008). Indeed, Comou and Rahmstorf (2012, p. 495) state that it is very likely that several of the unprecedented weather extremes of the past decade would not have occurred without anthropogenic global warming. Rapid-onset extreme environmental events are highly visible and immediate triggers for population displacement. These displacements tend to be 'forced', short distance and are usually within a state (Black et al. 2011).

Environmental disasters and food insecurity are closely interconnected. Floods, hurricanes and other environmental hazards damage and destroy agriculture, livestock and fishing infrastructure, assets and production capacity. They interrupt market access, trade and food supply, reduce income and erode livelihoods (Vincent et al. 2008). In July 2010, heavy monsoon rains in northwest Pakistan triggered landslides and flash floods that flowed into the southern provinces, submerging entire villages in its course. The floods directly affected one fifth of Pakistan's total land area and 20 million people. The flood destroyed an estimated 3.3 million h of crops and 2.4 million h of agricultural land. Two months into the disaster, around seven million flood-affected people remained displaced (Lom 2010). Many households and villages could not access food stocks through markets. The Food Cluster response, led by World Food Programme (WFP), began within 24 hours of the onset of flooding and distributed an estimated 500,000 mega tonnes of food. The Agriculture Cluster, led by Food and Agriculture Organization (FAO), focused on the provision of seeds, fertilizers and tools, the reconstruction of infrastructure and vaccination of livestock (Maxwell and Parker 2012). As this example illustrates, environmental disasters can have enormous adverse impacts on food security, as well as agriculture-related livelihoods.

More broadly, fast-onset natural disasters are likely to result in population displacement that is 'refugee like' in that large numbers of people are displaced to often marginal and vulnerable locations (Stal 2011). Encampment is a common response during post-disaster assistance. Yet studies among refugees have shown a high prevalence of malnutrition among camp populations, with some studies indicating that nutritional status among camp populations declines over time (McGregor 1994). Food shortage, childhood malnutrition, micronutrient deficiencies and undernutrition are recurring problems for displaced persons, particularly in low-income regions (Toole 2005; UNHCR/WFP 2006). It is likely that displacement in response to environmental disasters—including climate change-related disasters—will occur in food-insecure regions, and many people will be nutritionally compromised at the outset. Disaster risk reduction frameworks seek to both ensure that livelihoods and food production systems are resilient and able to recover from disaster events (FAO 2011).

However, while the health of political refugees who are involved in large-scale displacement and settlement in camp contexts provides some indication of potential health threats, it is critical that people involved in climate change-related movements are not framed as 'climate refugees'. The term 'climate refugee' reinforces the view that climate is an isolated driver of migration that compels the emergence of refugees. This obscures the fact that it is often institutional and human response, and the economic or social circumstances of a marginalised population, that can turn situations such as drought or flooding into a disaster.

12.3.2.3 Rural–Urban Migration

Rural–urban migration is a robust trend at a global level, particularly in low-income countries and constitutes the most significant volume of migration globally (Adamo 2010). Climatic changes will further increase rural–urban migration as adverse environmental changes—e.g. flooding, water shortages and drought—impact upon agricultural activities and livelihoods (IPCC 2007b). Indeed, climate change has begun to amplify rural–urban migration in developing regions (Adamo 2010). Where environmental changes associated with climate change disrupt rural lives and livelihoods, these—in conjunction with other factors—affect migration decisions (Satterthwaite et al. 2010). Marchiori et al. (2012) estimate, for example, that in sub-Saharan Africa between 1960 and 2000, more than five million people have migrated due to anomalies in local weather; they project that towards the end of the twenty-first century, every year an additional 11.8 million people in sub-Saharan Africa may move as a consequence of weather anomalies. And, there is some evidence that migrants from environmentally vulnerable regions of Bangladesh migrate to urban slums, particularly those of Dhaka, yet the data are not detailed enough to identify the role played by environmental factors in driving migration from these areas (Walsham 2010).

Urban areas can offer many potential advantages for improving living conditions including the availability of infrastructure and services. However, urban migration can also expose people to new risks in sites of settlement, notably in low-lying megacities (Foresight 2011). Urbanisation is associated with highly dynamic changes in food systems (Misselhorn et al. 2012). Since the 1970s, there has been increasing ease of access to 'western-style diets' in urban areas (i.e. increased meat and dairy and reduced complex carbohydrates, fruit and vegetables) which contributes to the two billion adults estimated to be overweight and obese (GRNUHE 2010). However, among the urban poor, particularly in low- and middle-income countries, urbanisation is also associated with undernutrition, increases in child malnutrition and poor health (FAO 2011; Satterthwaite et al. 2010). FAO (2011) anticipates that as more people migrate from rural to urban areas, urban poverty and food insecurity will increase. The urban poor often live on marginal land and produce little or no food and frequently lack capacity to buy adequate food supplies. Poor urban settlements are typically neglected by local or national government authorities, have inadequate infrastructure and have high rates of unemployment and underemployment (Campbell 2010).

Nonetheless, it is also important to be cognisant of heterogeneity with regards to specific, localised migration impacts. For example, it is widely recognised that rural–urban migration is often a deliberate decision to improve livelihoods, enable investments, stabilise family income and acquire a wider range of assets to insure against future stresses, including in response to climate variability (de Haas 2010). Indeed, people who lack the capacity to migrate may face increased exposure to adverse impacts of climate change, including food insecurity (O'Brien and Wolf 2010). Further, remittances from urban migrants to communities of origin are regarded as important for protecting against poorly functioning markets, inadequate state policies and a lack of state-provided social security. In addition, while rural–urban migration is widely associated with urban poverty, in most countries rural migrants are not the majority of the urban poor (Tacoli 2009). Accordingly, concerns about potential adverse outcomes or climate change-related urban migration—e.g. food insecurity in urban poor areas—must be balanced by recognition of the positive potential of migration and the challenges of immobility.

12.4 Conclusion

> 'Food is fundamental to human wellbeing, and human development is central to achieving food security' (Misselhorn et al. 2012).

This chapter has focused on the intersections between climate change, migration and food (in)security and has examined the complex connections between these processes within broader social, political and economic contexts. The introduction to this chapter cited the example of the Arab Spring, and the diverse factors—including population mobility, climate change, demographic pressures, political and economic factors and food insecurity—that contributed to the uprisings. The example illustrates the challenges of understanding and forecasting the impacts of climate change for human societies, including in relation to migration and food insecurity. This chapter has considered pathways via which climate change-related food insecurity will contribute to human migration, e.g. drought and reduced agricultural productivity (associated with outmigration, socially differentiated migration and immobility) and the 'global land grab' (associated with forced displacement, short-distance relocation and land lease-and-labour arrangements). It has also examined climate change-related migration and food security in sites of settlement and relocation, including in contexts of planned resettlement, large-scale forced displacement and rural–urban migration. The aim of this chapter is not to provide an exhaustive review of all relevant research but to consider the diverse connections between climate change, migration and food security. Given the complexity of the connections between climate change, migration and food insecurity, what conclusions can be drawn?

First, adaptation is essential to reduce the numbers of people who are projected to become food insecure in coming decades. Currently, around one billion people do not have enough to eat and a further billion lacks adequate nutrition (Misselhorn et al. 2012). Continuing population growth, changing dietary practices and demands and the adverse impacts of environmental changes—including climate change—will place additional pressure on global food security. Increasing agricultural productivity has been highlighted as critical to reducing food insecurity, in order to increase both food availability and rural incomes. Agricultural adaptation will be essential for ameliorating the negative impacts of climatic changes. However, there are important questions to be asked about how agricultural productivity can best be increased (Bogale 2012). There is a critical need for equitable and resilient food production systems that both increase food security and minimise further environmental degradation (Misselhorn et al. 2012). With growing awareness that free markets have failed to deliver food security, there is now increasing emphasis being placed by governments and international agencies on country-led agricultural development programmes, public investment, the key role of small-scale farmers and the challenges of limited resources in a climate-constrained world (Wise and Murphy 2012).

Around 2.5 billion people living in rural areas generate income by managing some 500 million small farms of less than 2 h each (FAO 2011). Globally, small-scale farmers comprise the largest farmer group. Vincent et al. (2008) argue that coping with the adverse impacts of climate change will entail greater attention to the emerging range of social protection measures related to small-scale agricultural production. These include weather-based crop insurance, asset restocking, starter packs and seed banks, transfer of agricultural technologies and cash transfers water and soil conservation practices. Also, the alarming scale and pace of land grab deals requires national governments and international organisations to establish responsible agricultural investment policies that reduce threats to local communities (FAO 2011; Robertson and Pinstrup-Anderson 2010). This will require land deals that emphasise benefits for the rural poor, extend land tenure rights to current land users based on indigenous concepts of occupancy, utilise transparent and consultative processes and ensure food security for local populations (Robertson and Pinstrup-Anderson 2010). However, some warn that such responsible policies may be 'too little too late' (Wise and Murphy 2012). FAO (2011) argues that assisting smallholders is the most direct way to improve resilience to climate change and to protect against hunger and food insecurity. Globally, there is also the challenge of generating alternative livelihoods that are not climate-sensitive, and this requires investing substantially in the education of rural populations (Vincent et al. 2008).

There is, however, a predominant emphasis on increasing crop productivity. It is widely argued that 50 % more food will be needed by 2030 in order to meet the demands of a growing global population (Godfray et al. 2010). Research has typically focused on agronomy (although livestock and fisheries also receive substantial attention) with a view to identifying increases in productivity via technological innovation: For example, average yields of the world's main grains (wheat, barley, maize, rice and oats) have increased threefold since 1960. It is anticipated that new drought-tolerant crop varieties will be required with increasing drought conditions in many regions of the world. Yet agricultural activity is the cause of 12–14 % of total greenhouse gas emissions and a further 18 % of emissions are attributed to land-use change and forestry. Current high-input agro-industry and food system activities have adverse impacts on biodiversity, biogeochemical cycles, freshwater resources and other environmental parameters. Therefore, a key challenge is developing food systems that are significantly more environmentally benign than current approaches (Ingram 2011).

Second, if climate change continues on its current trajectory, then an increase in the numbers of displaced people over the coming decades is likely. Recent debates on climate change and migration have tended to focus on migration as a problem or threat to be managed (Hartmann 2010). Conversely, there is a growing body of academic literature within which migration is framed as an adaptive process in response to the effects of climate change: a process that allows communities to cope with the effects of climate change (Bardsley and Hugo 2010; Barnett and Webber 2010; Black 2001). As discussed earlier, for example, the move to a new location can alleviate health risks associated with food insecurity. Scheffran et al. state that 'migration is an adaptation measure that reduces pressure and offers potential opportunities in climate hot spots… migrant networks can strengthen the social capital, livelihood and resilience of their origin communities and develop innovative approaches for climate adaptation' (2011, p. 126). Yet while climate change and development policies should approach migration as a potential adaptive strategy, migration is not the preferred option for the majority of the world's population.

Climate change adaptation has necessarily become a prominent focus for national and international policy (Reid and Huq 2007). For example, the Climate Change, Agriculture and Food Security (CCAFS) project aims to identify technical and policy interventions to adapt agriculture and food systems to climate change in order to improve food security, livelihoods and environmental benefits. CCAFS efforts range from building capacity for research teams to improve understanding of agricultural system sustainability and to inform policy decisions to the 'seeds-for-needs' project that uses geographic information system (GIS) technologies to support rural Ethiopian women farmers to identify, conserve and access promising local gene-bank resources to enable adaptation to climate change (CCAFS 2012). And the need for planning for climate change-related migration was explicitly recognised in the 2010 Cancun Adaptation Framework, inviting parties to undertake 'measures to enhance understanding, coordination and cooperation with regard to climate change-induced displacement, migration and planned relocation, where appropriate, at national, regional and international levels' (see IOM 2011). Migration, which has often been regarded as a substantive problem or threat by policymakers and governments, is increasingly understood as part of the climate change 'adaptation portfolio' (Tacoli and Mabala 2010; Walsham 2010). However, adaptation policy frameworks require cross-sectoral approaches that address connections—for example—between migration and food security in the context of changing climatic conditions.

Finally, the primary focus of international policy in relation to human-induced climate change must remain on the critical issue of reducing carbon emissions through mitigation efforts (McMichael et al. 2012). Globally, climate change poses significant challenges to societies, ecosystems and economies. Almost all countries in the world (194 in total) are engaged in negotiations on how to mitigate and adapt to climate change, as parties to the United Nations Framework Convention on Climate Change (UNFCCC) (Foresight 2011). In-depth understanding of the risks associated with climate change, including the way in which food insecurity will be both a driver and outcome of climate change-related migration, could strengthen international commitments to reduce greenhouse gas emissions and abate climate change. Indeed, a recent study indicates that public health concerns are more likely to elicit reactions consistent with support for climate change mitigation and adaptation than a focus on risks to environment, national security or the benefits of mitigation and adaptation-related actions (Myers et al. 2012). If the world is to stay below 2 °C of warming, then emissions must be held below 450 parts per million (ppm) of carbon dioxide in the atmosphere. The level is currently around 400 ppm—an amount not seen in at least three to five million years—and climate change is already occurring, with future temperature changes 'locked in'. Through deep cuts in global greenhouse gas emissions, together with comprehensive socioecological adaptation strategies, adverse climate-related impacts for migration and health—including food insecurity—could be greatly reduced.

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Chapter 13
Climate Change and Vector Borne Diseases in Latin America

Ulisses EC Confalonieri and Flávia RL Suassuna Dutra

Abstract The Latin American and Caribbean (LAC) region is very heterogeneous from the perspectives of physical geography, ecosystems, social, cultural, and economic characteristics, and also health profiles. Global climate change is projected to affect this region in several ways, either through changes in climatic baseline conditions or by changing the pattern of occurrence of extreme weather events.

The most important vector-borne diseases (VBDs) caused by climate factors in the region are malaria, dengue fever, leishmaniases, yellow fever, Carrion's disease, plague, and filarial infections. Several studies in Latin America have pointed that the incidence of these infections is modulated by climate variability phenomena such as the El Niño-Southern Oscillation (ENSO).

Keywords Tropical diseases · Vectors · Malaria · Dengue fever · Leishmaniases · Climate change

13.1 Introduction

The Latin American and Caribbean (LAC) region has a total population of about 596,650,000 people and almost 80 % of them live in cities (UN habitat 2012). The projected population for 2020 is 1,027 billion or 13.4 % of the expected population for that year. By 2025, nine out of the 30 largest cities in the world will be in LAC region. Life expectancy in 2010 was estimated to be 76.2 years for both sexes and the regional infant mortality rate was estimated as 14.8/1,000 live births (range: from 4.8 in Cuba to 57.0 in Haiti) (PAHO 2011).

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A satellite-based survey pointed that South America has the most diverse climate, geology, and biological diversity among all continents (GVM 2002). Recently, the United Nations Development Programme published a report indicating that around 40 % of the global terrestrial biodiversity is in Latin America (UNDP 2010).

With regard to the climate of South America, Reboita et al. have described the most important atmospheric systems that determine the precipitation and its seasonal variation in this region. The large latitudinal extension of the continent, associated to a diverse elevation, determines a high climatic variation that has been divided into eight zones, according to the precipitation regimes. The rainiest subregion is its northwestern part (Colombia) while the driest is a coastal strip in Peru and Chile, with an average of 350 mm/year (Reboita et al. 2010). With regard to the interannual variability of climate, it is well established that precipitation over South America is modulated by the El Niño-Southern Oscillation (ENSO) phenomenon, which is observed in the tropics globally. A 5-year oscillation was observed predominating over the equatorial region of LAC while a 3.7-year oscillation period has its strongest influence over the southern part of Brazil (Obregón 2002). Based on various climate models, it was projected that, for 2090–2099, Latin America would experience a temperature increase ranging between 1 and 4 °C, under scenario B2; under scenario A2, the increase would range between 2 and 6 °C (ECLAC 2010). Projections of precipitation for LAC region involve a high degree of uncertainty and large heterogeneity. Summer climate projections, under scenario A1B, show a regional reduction in precipitation varying from 5 to 20 % in Central America and parts of South America. A summer time increase in rainfall (5–10 %) is projected for parts of Ecuador, Peru, Colombia, and Argentina. For the winter season, projections of rainfall decrease of up to 20 % are expected for parts of Mexico, Brazil, Venezuela, and Central America (ECLAC 2010).

Marengo et al. (2009), using the Providing *Regional Climates* for Impacts Studies (PRECIS) regional climate modeling system, have analyzed the distribution of extremes of temperature and precipitation in a future (2071–2100) climate, under the Intergovernmental Panel on Climate Change – Special Report on Emission Scenarios A2 and B2 emission scenarios. They have found that, in all future scenarios, all parts of the region would experience significant changes in both rainfall and temperature. The occurrence of warm nights was projected to be more frequent in the entire tropical South America, while cold nights were likely to decrease. Increased intensity of extreme precipitation events over most of southern South America and western Amazonia was also projected.

13.2 VBDs in LAC Region

The LAC region has several endemic infections that are transmitted by vectors; the two diseases which account for the majority of cases are malaria and dengue fever. For the latter, 637,801 cases were reported in 2011 (PAHO 2011); about 3 % of the regional population is exposed to malaria transmission and, in 2010, the estimated

Table 13.1 Other vector-borne diseases (VBDs) in the region

Disease	Number of cases	Reference
Cutaneous leishmaniases	66,941	Alvar 2012
Chagas disease	8–9 million	Hotez 2008
Visceral leishmaniases	3,662	Alvar 2012
Onchocerciasis	500,000 (exposed to infection)	Gustavsen 2011

number of malaria cases in LAC was 1,100,000 (WHO 2012). Chagas disease infects millions of people in Latin America but its incidence seems to be much more influenced by deforestation and changes in land use than due to climatic phenomena.

All these VBDs can be influenced by climatic factors, such as temperature, rainfall, and humidity, to varying degrees. Some are affected also by hydrological processes resulting from rainfall, such as malaria in the Amazon (Olson et al. 2009).

13.2.1 Dengue Fever

Interannual climate variability, such as the ENSO phenomenon, is known to affect the dynamics of VBDs in LAC region (Rodriguez-Morales 2010).

Recent studies have pointed to a significant increase in the incidence of dengue fever in the tropical Americas (Shephard et al. 2011; Tapia-Conyer et al. 2009). Climatic variability affects dengue incidence especially by increasing the population density of the vector *Aedes aegypti* (Dibo et al. 2008). Outbreaks of dengue fever in some LAC countries, such as Honduras and Nicaragua (Rodriguez-Morales et al. 2010) and Costa Rica (Fuller et al. 2009; Mena et al. 2011), were associated to climatic variability and environmental change.

In Bolivia, dengue fever serotype 1 reemerged during the strong El Niño event of 1997–1998 and cases due to serotype 2 have increased dramatically, also during this period. Also in Bolivia, it was observed that dengue cases respond to indices associating minimum temperature, rainfall, and humidity (Arana and Aparicio 2007). Carbajo et al. (2012) have modeled the annual dengue risk in Argentina, using a temperature-based mechanistic model, for the period 1998–2011. It was found that, although temperature was useful to estimate the annual transmission risk, it did not describe adequately the occurrence of the disease on a national scale; climatic variables separately performed worse than geographic or demographic variables.

Johansson et al. (2009) have analyzed a time series of 20 years of dengue incidence data and, by using a statistical approach to control seasonality, have showed a positive and statistically significant association between monthly changes in temperature and precipitation and monthly changes in dengue transmission in Puerto Rico. However, while they have reported a significant association between climate and dengue, it was on a month-to-month timescale and did not demonstrate that warmer years consistently exhibited higher overall incidence of the disease.

Colón-Gonzalez et al. (2011) used multiple linear regression models to assess the linkages between climate variability and dengue fever in tropical Mexico. Using data from 1985 to 2007, they have shown that the incidence rate or risk of infection was higher during El Niño events and in the warm and wet season. During the cool and dry season, dengue incidence was positively associated with the strength of ENSO and the minimum temperature.

Lowe et al. (2010), in a preliminary modeling of dengue fever and climatic covariates in Brazil, for 2001–2008, found that the model performed well in some regions of the country, but not in others. The authors concluded that seasonal climate forecasts could have potential value for the design of a dengue early warning system, capable of predicting the climatic conditions that favor dengue outbreaks. Degallier et al. (2010), in a pilot study, used monthly means of the pressure vapor deficit and temperature (the CARIS dengue risk model) to produce a risk index, based on the suitability of the climate for the completion of mosquito cycle and for the virus to be transmitted. The authors have produced maps of the months of maximum risk index for dengue transmission in South America, for different months of the year.

Roseghini et al. (2011) have studied the association of different climatic variables, on a monthly and daily basis, to dengue incidence, in three Brazilian cities. Daily temperature records had a significant correlation with dengue incidence, with a 7-day lag time; most epidemics have occurred after intense rainfall episodes in the summer time. Other factors determining dengue incidence that were acknowledged by the authors were the immune status of the population as well as human migration and garbage disposal practices, which can facilitate the formation of mosquito breeding sites.

13.2.2 Malaria

A survey of data related to highland malaria in Ecuador (Pinault and Hunter 2012)—both entomological data and disease cases—pointed to the existence of endemic malaria in this area since the early twentieth century, basically driven by human migration and land conversion. The disease foci were eliminated as a consequence of habitat destruction, due to environmental interventions, and also due to the spraying of insecticides. The existence of high-altitude malaria a century ago, in this area, precludes the attribution of local transmission of malaria to climatic changes.

Poveda et al. (2011) and Arevalo-Herrera et al. (2012), in Colombia, have explained a steady increase in malaria incidence in the country, in the past 50 years, by a historical increasing trend in average air temperatures due to global and also local and regional warming. Also in this country, peaks of malaria incidence, in specific years, seem to be associated to higher temperatures linked to El Niño years. This is a quasi periodic event (every 3–4 years), which appears to have become more frequent, in the past four decades, as a possible consequence of global warming.

Arana and Aparicio (2007), in Bolivia, have reported the presence of malaria vectors (*Anopheles pseudopunctipennis*) and cases in high-altitude villages (2,615–3,592 m.o.s.l), localities where the disease has not been recorded before 1998. Since this event occurred in association with several ecosystem changes and also an increase in average atmospheric temperature of 0.85 °C, the authors raise the possibility of an influence of climate change in this process.

In the Amazon, studies have indicated the influence of climate-driven river flow variations on the dynamics of malaria. Olson et al. (2009) have observed that, in the uplands of Brazilian Amazon, malaria risk in relation to rainfall can either increase or decrease, in a given locality. In areas dominated by wetlands and large rivers, the relation was negative, that is, more precipitation, less malaria. Wolfhart (2011) has observed that increases in malaria incidence occurred after 1–2 months of peaks in temperature, in localities of the Brazilian Amazon. Sudden oscillations in the water level of rivers (a hydrological phenomenon known locally as "repiquete") also had an influence in malaria increase, with a few days of lag time.

Mantilla et al. (2009) used historical climate data and annual malaria case number data from 1960 to 2006, to develop statistical models to isolate the effects of climate on this disease in Colombia. They have found that the trend variables as well as the El Niño measures were significant predictors of malaria cases in the entire country and also in two of its five subregions. A 20 % increase in malaria cases was associated to a 1 °C increase in temperature of the Pacific Ocean (sea surface temperature (SST)), which indicates a weak to moderate ENSO event.

Blanco and Hernandez (2007) have formally evaluated the impact of climate change on the incidence of malaria and dengue fever in Colombia. They have used a statistical model, based on temperature and precipitation (1995–2005), as well as malaria incidence for 715 municipalities (data from 2000 to 2005). After calculating the additional number of malaria and dengue cases that could be attributed to climatic change (50- and 100-year scenarios), they multiplied the number of cases obtained by the corresponding unit costs to estimate the total cost of the impact. The direct and indirect costs for both diseases were estimated to be US$ 2.5 million and US$ 7.6 million, for the 50- and 100-year scenarios, respectively. The direct additional costs for malaria (2015–2100) were estimated to be about US$ 800,000.00.

13.2.3 Leishmaniasis

Gomez et al. (2006) have observed that, for the period 1991–2000, cutaneous leishmaniases in Bolivia have increased in incidence by 67 % during La Niña years; during El Niño periods, a decrease of 40 % was reported. Aparicio and Ortiz (2000) have suggested that, in the northern part of Bolivia, climate variability could explain an increase in 34 % of the new cases of cutaneous leishmaniases.

The impact of the El Niño phenomenon on leishmaniases (visceral and cutaneous) was studied in Colombia by Cárdenas et al. (2006). For the period 1985–2002, the authors found that the disease has increased by 15 % during El Niño and has decreased by 12 % during La Niña. The largest outbreak of this disease in Colombia (2003) had, as statistically significant variables, mean temperatures and precipitation, besides elevation and land use as possible determinants of the infection (Valderrama-Ardilla 2010).

Solomon et al. (2012) presented the results of the eco-epidemiology of leishmaniasis in Argentina, in relation to climate variables, at different scales. The authors report that, in several foci of the disease, Phlebotomine species presented population peaks associated with periods of rain; these increases in vector population could be observed up to 12 months after the rainfall events. These effects of abiotic factors upon the seasonal variations of population dynamics of *Lutzomyia longipalpis*, vector of kala-azar, were also observed in Brazil (Ximenes et al. 2006). Also in Brazil, drought-induced rural-to-urban migration in the northeastern region has been associated to peri-urban outbreaks of kala-azar (Confalonieri 2003; Rabelo 2008).

Chaves and Pascual (2006) have analyzed the historical trends in cutaneous leishmaniases in Costa Rica, for 1991–2001. Using advanced statistical models, they investigated the role played by climate variables in the dynamics of the disease and found that the 3-year cycles of the disease match with climatic cycles of similar length. Models were able to predict, with 12 months lead time, variations in disease incidence, with an accuracy of 75 %.

Some ecological niche modeling exercises have projected changes in the geographical distribution of Phlebotomine sandflies, vectors of leishmaniases in Brazil, in response to expected climatic changes (Peterson and Shaw 2003).

13.2.4 Filarial Infections

The most important filarial infections of humans in LAC are onchocerciasis, caused by the worm species *Onchocerca volvulus* and mansonelosis, caused by *Mansonella ozzardii*. Both have a focal distribution in the region (southern Mexico, northern Central America, and northern South America) and have blackflies (*Simulium* sp.) as vectors. These are aquatic insects that breed in fast-flowing watercourses, such as rapids and waterfalls, since their immature forms need high levels of dissolved oxygen in the water. Although no studies have been published on the effects of climate on these parasitic infections, it has been suggested that environmental changes driven by climate variability and change, as well as land-use change, would affect these diseases due to their impacts on water flow and quality, which are critical for the breeding of these vectors (Confalonieri et al., submitted).

13.2.5 Carrion's Disease

Carrion's disease or Bartonellosis occur in high-altitude valleys of the Andes mountain range in South America (Peru, Ecuador, and Colombia) and the causative agent, *Bartonella baciliformis*, is transmitted by the bite of sand fly vectors. Chinga-Alayo et al. (2004) have studied the association of the incidence of bartonellosis in Peru with selected climatic factors. For the periods 1983–1988 and 1995–1999, a fourfold increased risk was reported for a specific Peruvian locality, in association with the occurrence of El Niño events.

13.2.6 Other VBDs

Two other VBDs that occur sporadically in Latin America and are affected by climatic variability and change are yellow fever and plague. Confalonieri (2003) analyzing a 40-year time series of plague incidence data in the northeastern part of Brazil has observed that most incidence peaks have occurred at the end of the dry season, with a 3-month lag period. The possible explanation was that, after many weeks without precipitation, a sharp decline in the primary production of the dry-land ecosystem forced the wild rodents to the periphery of human dwellings in rural areas. In their approach in search of food, wild rodent species which were reservoirs of the plague bacterium have dropped their flea vectors close to humans, where they transmitted the disease.

Also in Brazil, recent reports have associated the amount of rainfall either with the dynamics of mosquito species vectors of jungle yellow fever in the Amazon (Pinto et al. 2009) or with local outbreaks in the central part of the country (Vasconcelos et al. 2000; Vasconcelos 2010).

13.3 Discussion and Conclusions

The LAC region has a very diverse climate and models have projected, for the next few decades, changes in climatic baseline conditions as well as in the frequency and intensity of extreme events. The LAC region has several endemic VBDs which are sensitive to variations in the climatic conditions. Outstanding among these are malaria and dengue fever, due to their large area of distribution of cases and also the number of people infected each year. Several studies, in different countries, have pointed to the relative influence of climatic conditions affecting the epidemiological dynamics of these diseases, as well as of the leishmaniases. Most of these studies have analyzed time series of historical data of both climatic and epidemiological variables. Therefore, most have addressed issues relative to the effects of climate variability and not climate change. Positive associations between climatic and epidemiological variables of VBDs were found in specific localities and times of the year but not in others; this heterogeneity could be found within the same country. In several countries, the climatic variations associated to the ENSO phenomenon were found to have a clearly discernible influence on the incidence of some VBDs. A few global models of future risks of malaria and dengue fever, in relation to climatic scenarios, have been developed in countries outside the LAC region, but these have failed to address the local and regional specificities of VBD and their control in the LAC continent. There is no clear evidence that a few cases of high-altitude malaria reported in the Andes Mountains were associated to global climatic change.

As endemic infections were strongly influenced by climate variability and change, VBDs have been considered as important components in the assessment of the social vulnerability to the impacts of climate change. Recent assessments developed in Brazil (Confalonieri et al. 2009, 2013) have included malaria, dengue fever, and cutaneous and visceral leishmaniases as determinants of the sensitivity of the population to the impacts of climatic change. Those population groups and territories where these VBDs were more prevalent were considered to be more vulnerable, when compared with disease-free areas.

Most local, regional, and subregional studies on the influence of climate on VBD have acknowledged the importance of non-climatic factors in determining the incidence and distribution of VBD in LAC—such as human migration, disease control activities, environmental change, immunological status of the population, etc. However, few of them have included these variables in their analyses. In general, studies conducted with data for smaller areas performed better than those which have analyzed data from large areas. More studies are needed, at different spatial scales, using improved multivariate models, in order to produce the knowledge necessary to inform epidemiological surveillance systems targeted to the possibility of climate-driven reemergence of VBD in Latin America.

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Chapter 14
Climate Change and Geoenvironmental Problems in Indian Desert

H. S. Sharma

Abstract This chapter deals with the micro-climatic changes and some of man-induced environmental hazards of the Indian arid regions. The study of rainfall trends for the last 100 years in Rajasthan shows that certain stations have recently experienced apparent downward trend in rainfall, whereas others have shown a high variability from year to year, but no constant trend has yet been noticed. Some studies in Rajasthan show that there has been an increasing trend of rainfall in western part and a decreasing trend in the eastern part of the Aravallis in the last 50 years. Recurring drought and acceleration of desertification processes; drinking water scarcity; occurrence of brackish groundwater; presence of fluoride in the groundwater in most parts of the desert; salinity hazards; water logging and rising water table in the vicinity of canal-irrigated areas, especially Indira Gandhi Nahar Pariyojana (IGNP) and high flood propensity, in desert districts; destruction of natural vegetation by deforestation for fuel and fodder; mining activities and overgrazing; creation of scarred and derelict landscape due to open cast mining of minerals and raw material resources and depletion of biodiversity and stress on wildlife habitat are some of the geo-environmental hazards which need immediate attention.

Key words Climate change · Geo-environmental problems · Global warming · Anthropogenic forces · Aerosol · Solar radiation

14.1 Introduction

Climate change refers to the variation in the Earth's global climate or in regional climates over time. It describes changes in the variability or average state of the atmosphere over time scales ranging from decades to millions of years. These changes can be caused by processes internal to the Earth, external forces (e.g., variations in sunlight intensity) or, more recently, human activities.

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In recent usage, especially in the context of environmental policy, the term "climate change" often refers to changes in modern climate which, according to the IPCC, are 90–95 % likely to have been, in part, caused by human action. Consequently, the term anthropogenic climate change is frequently adopted; this phenomenon is also referred to in the mainstream media as global warming. In some cases, the term is also used with a presumption of human causation, as in the United Nations Framework Convention on Climate Change (UNFCCC). The UNFCCC uses "climate variability" for non-human-caused variations.

14.1.1 Climate Change Factors

Climate changes reflect variations within the Earth's atmosphere, processes in other parts of the Earth, such as oceans and ice caps, and the impact of human activity. The external factors that can shape climate are often called climate forcings and include such processes as variations in solar radiation, the Earth's orbit and greenhouse gas concentrations.

14.1.2 Greenhouse Gases

Current studies indicate that the radioactive forcing by greenhouse gases is the primary cause of global warming. Greenhouse gases are also important in understanding Earth's climate history. According to these studies, the greenhouse effect, which is the warming effect produced as greenhouse gases trap heat, plays a key role in regulating the Earth's temperature.

Beginning with the industrial revolution in the 1850s and accelerating ever since, the human consumption of fossil fuels has elevated CO_2 levels from a concentration of ~280 ppm to more than 380 ppm today. These increases are projected to reach more than 560 ppm before the end of the twenty-first century. It is known that carbon dioxide levels are substantially higher now than at any time in the last 800,000 years. Along with rising methane levels, these changes are anticipated to cause an increase of 1.4–5.6 °C between 1990 and 2100.

The biggest factor of present concern is the increase in CO_2 levels due to emissions from fossil fuel combustion, followed by aerosols (particulate matter in the atmosphere) which exert a cooling effect and cement manufacture. Other factors, including land use, ozone depletion, animal agriculture and deforestation, also impact climate.

During the modern era, the naturally rising carbon dioxide levels are implicated as the primary cause of global warming since 1950. According to the Intergovernmental Panel on Climate Change (IPCC 2007), the atmospheric concentration of CO_2 in 2005 was 379 ppm compared to the pre-industrial levels of 280 ppm; in other words, it is 0.02–0.03 % in the atmosphere; this has been much higher in the long history of the Earth.

The evidence for climate changes is now overwhelming. Emissions of carbon dioxide and other pollutants into the atmosphere are causing changes to the global climate in ways that we do not fully understand, and the consequences of which we comprehend even less.

Ice caps and glaciers are melting, causing sea levels to rise. Ocean temperatures are rising, causing stronger hurricanes and killing coral reefs. Rainfall is much heavier in some regions, perhaps in the Seychelles, much less frequent in others, causing drought, flood and shifts in agricultural productivity that can spell disaster for subsistence farming.

The effects are global, and climate change will affect every part of our planet. No one can stand by and do nothing.

But, ironically, the parts of the globe that are likely to be hit hardest by climate change are those who are least able to do anything to prevent it. These are the poorest countries and the smallest states, whose carbon emissions are tiny, but who, by virtue of geography and poverty, are most vulnerable to the impact of climate change. The aim is not to present yet more evidence of climate change, nor is it to urge larger nations to speed up their actions towards mitigation—much though this may be needed. The aim is to promote awareness, preparedness and adaptation so that when ecological changes do occur, as we believe they will, we will be better prepared to take action and, thus, save the lives and livelihoods of this poor nations.

The United Nations Development Programme (UNDP) report released in India and Brazil on 27 November 2007, *Fighting Climate Change: Human Solidarity in Divided World*, reveals that the impact of climate change on the poor is "significantly underestimated." The report reveals that INDIA'S POOR would be among the world's 40-million poor people to be adversely hit if the 10-year window for initiating major programmes on climate-change mitigation and adaptation are missed.

"**The world is drifting towards a tipping point that could lock the poorest countries in a downward spiral, leaving hundreds of millions facing malnutrition, water scarcity, ecological threats and loss of livelihood,**" said Maxine Olson, UNDP's resident representative in India.

14.1.3 Geo-Environmental Problems in the Indian Desert

The Rajasthan desert is characterized by various types of sand dunes of high velocity and rolling sand; high diurnal variation of temperature, scarce rainfall (less than 300 mm p.a.); high wind speed, intense solar radiation; and high rate of evaporation. The soils of desert are poor in fertility, rapid infiltration rate of water, low humus content due to rapid oxidation and high salinity. Despite very hostile conditions for existence of life, this region supports large human and livestock population.

The geomorphological and archeological evidences suggest that the desert region was once a flourishing green countryside with thick forest and well-integrated drainage system, of which Saraswati and Yamuna were the main rivers. The study of landset data also confirms it. The onslaught of man and his domestic animals on the local ecosystem changed the panorama of the region from the land of plenty to the land of poverty in less than 5,000 years (Sharma 1999; Singh 1977; Sood and Pathan 1982).

The Indian desert during last few decades has witnessed rapid growth of population, modernisation in agriculture, accelerated urbanisation, changes in land use system, industrialisation and enhanced mining activities. This rapid transformation in nature by human activities has contributed to damage physical environment leading to land degradation, droughts, deforestation and depletion of water resources which together resulted in an ecological imbalance with catastrophic effects.

The most obvious problem of the Indian arid zone is land degradation resulting from climatic vagaries and its unplanned and ruthless exploitation due to increasing pressure of human and livestock population. It is, therefore, necessary to address these issues and provide possible solutions for mitigating droughts, desertification and floods.

The man-induced environmental hazards that riddle the arid regions need priority consideration in planning. These are provided as follows:

1. Recurring drought and acceleration of desertification processes
2. Drinking water scarcity
3. Occurrence of brackish groundwater
4. Presence of fluoride in the groundwater in most parts of the desert
5. Salinity hazards, water logging and rising water table in the vicinity of canal-irrigated areas, especially Indira Gandhi Nahar Pariyojana (IGNP) and high flood propensity, in desert districts
6. Destruction of natural vegetation by deforestation for fuel and fodder, mining activities and overgrazing
7. Creation of scarred and derelict landscape due to open cast mining of minerals and raw material resources
8. Depletion of biodiversity and stress on wildlife habitat

14.2 Rainfall Treads and Freak Weather Conditions

The study of rainfall trends for the last 100 years in Rajasthan shows that certain stations have recently experienced apparent downward trend in rainfall, whereas others have shown a high variability from year to year, but no constant trend has been noticed. Some studies in Rajasthan show that there has been an increasing trend of rainfall in the western part and decreasing trend in the eastern part of the Aravallis in the last 50 years. Now the question arises, is there any widespread evidence that rainfall in the Indian desert and adjoining areas is decreasing or increasing? If so, is a fluctuation in progress, or is the decrease a lasting change? On a very long time scale, there have certainly been great changes in climate, especially within the Quaternary Period. During the past 10,000 years, Rajasthan has seen alternating between arid and humid phases, resulting in the accumulation of sand dunes, especially during the arid phase.

There is, thus, plenty of evidence of past desiccation of climate that led to the spread of the desert surface in the north-eastern part of the present desert boundary. Is there evidence of a similar desiccation in progress today? Is the widespread desertification now in progress due to such a downward trend of rainfall? There is strong evidence to suspect that more and more humid and sub-humid zones of the country, which had earlier experienced no significant moisture stress, are now under the intensification of man-induced desertification process.

The unprecedented drought situation that has occurred within the last few decades in Rajasthan is not a new thing. There are plenty of references of such a situation in the Vedic literature and in the recorded history of India. The droughts of 1877, 1900, 1918, 1940, 1965, 1972, 1979, 1984–85 and 1986–87 are well known because of their disastrous consequences. The most notable characteristics of such droughts are random distribution in time, spatial coherence over large areas and in some regions and persistence for years at an end.

Heavy rainfall in the desert region is rare. Whether the Barmer floods in 2006 were produced by freak weather or by global warming is a matter of further research. The data suggest that in the last 60 years, there have been five recorded instances of rainfall on a single day that exceeded the deluge of 2006 in Barmer. In September 1968, 302 mm of rainfall was recorded, almost double the 160-mm of rainfall, which wreaked havoc in Barmer on 22 August 2006. There was heavy rainfall in Jodhpur in 1979 and 1981, and 308.0 mm and 240.0 mm of rainfall in Jaisalmer and Barmer in 1998 (10 June 1998), respectively. In 2000, unprecedented rainfall of about 433.0 mm occurred at Loonkaransar, Bikaner. This gives the trends of weather pattern that there could be floods in Rajasthan desert every third or fourth year.

In view of this, it is stated that the data of over 100 years are not enough to conclude that the climate of the planet and the Indian sub-continent is changing. Weather pattern fluctuations that occur over a few decades are unusual, after that they could reverse themselves. Therefore, there is a need to analyse more data to conclude the changing climate in this region.

14.3 Drought-Desertification Lineages

M.S. Swaminathan in a personal interview with DNA (20 July 2008) has said that "deterrence against drought is more important than the nuclear deal". He further stated that in our country "we are reactive and not pro-active."

The prolonged drought in the 1990s and beginning of this century has prompted the question whether the climate is being affected by human action. There are two mechanisms whereby this might happen. First, overgrazing, unwise use of land and stripping of forest cover all tend to make the surface more reflective to solar radiation in this part of the country. Dynamic modelling indicates that such raised albedos tend to diminish rainfall and further a potential disastrous positive feedback. Second, in regions like Rajasthan, far from the ocean, much of the rainfall is caused by re-evaporated soil moisture. Faulty land use practices have reduced the storage capacity and enhanced evaporation.

It is a matter for enquiry and scientific analysis, whether man-induced changes can thus permanently alter climate. There is no doubt, however, that overgrazing and unwise use of land alter the surface micro-climates adversely. Reduction of permanent vegetation cover has the consequences cited earlier.

14.4 Drought/Deforestation

The process of forest destruction is a worldwide tragedy. It is estimated that a forest, the size of Cuba, is being destroyed every year. The yearly losses are estimated to be between 10 million and 15 million hectares. The global assault on forests carries a disaster potential resulting in a serious crisis in food supplies and fuel. Moreover, no one would be able to escape the adverse effects of balding the Earth.

The disappearance of forests from the Aravallis and discontinuous isolated hills of Rajasthan has resulted in changing rainfall patterns and has caused drought conditions in large areas. The country stands denuded of its best forests. Today less than 11 % of its land area has some tree cover worth the name, against official claims of 23 % and the optimum requirement of 33 %. The study of landsat imageries has revealed that the country is losing its forest cover at an alarming rate, and its total area under forests today may be as low as 40 million hectares. The state of affairs in Rajasthan is still worse. Only 1.5 % area is under forest cover against official figures of 9.5 %.

The above analysis makes it clear that drought and desertification are serious threats to the sustainability of arid and semi-arid areas of Rajasthan. Therefore, some appropriate action plan has to be evolved to combat desertification. With this objective, in the year 2000, the UN convention to combat desertification (UNCCD) has chalked out a Regional Action Programme (RAP) to combat desertification. Accordingly, the RAP for Asian region has been initiated as a collective effort by the member countries. The aim of RAP is to strengthen the existing capacities of the member countries of the Asian Region to the suitable measures for combating desertification. Under RAP, six thematic programme areas were identified. The first one, Thematic Programme Network 1 (TPN-1), is on desertification monitoring and assessment. The overall objective of TPN-1 is to enhance the desertification monitoring and assessment capacities in the region through the establishment of a network and the harmonization of approaches for its conduct in the region. China has been identified as the host country to coordinate TPN-1 activities among the member countries in establishing the Asian Regional Desertification Monitoring and Assessment Network (TPN-1). In India, Space Applications Centre (Indian Space Research Organisation (ISRO)), Ahmedabad has been identified as the national focal institution to coordinate TPN-1 activities within the country and establish the national network for desertification monitoring and assessment. Under this activity, a major case study project on desertification status mapping involving 17 institutions of the country has been completed under the financial support of the Ministry of Environment and Forests, Government of India. Under this scheme, Desertification and Land Degradation Atlas of India (2008) has been brought out. This study reveals that 67 % of area in Rajasthan is under serious threat of desertification and land degradation. The most significant process of desertification is wind erosion which accounts for 44.42 % mainly in the desert region followed by water erosion (11.22 %), vegetal degradation (6.25 %) and salinisation (1.07 %).

The picture that emerges from the above description is, thus, one of unending gloom. Meteorological drought in arid and semi-arid parts of the country being a regular phenomenon, it is an immediate necessity to evolve long-term planning measures to mitigate the problem of drought and other natural and man-induced calamities.

The control of human misery and economic losses resulting from drought is possible only when the ecological roots of this problem are properly identified. At present, it is not yet possible to predict either the onset of drought or the end of the present dry condition. Drought is an inevitable part of climate and all available scientific evidence indicates that its temporal and spatial occurrence is still unpredictable. There is, thus, a need to establish long-term drought plans that are capable of mitigating the consequences of drought. Such drought control plans are necessarily the work of an interdisciplinary team comprising geo-scientists and social scientists. Emphasis should be placed on the establishment of climate research groups to continuously monitor the occurrence and progress of drought at least on a seasonal basis. Such monitoring of drought could be used to forewarn farmers and the government of possible severe drought.

14.5 The Need for Long-Term Drought and Desertification Planning

In order to systematically undertake the various soil and water conservation measures at the ground, the Central Government initiated a centrally sponsored programme like Drought Prone Area Programme (DPAP), Combating Desertification Programme (CDP) and Desert Development Programme (DDP). The measures fall under the following broad categories:

1. Judicious use of limited irrigation water
2. Rainwater harvesting
3. Management of surface and groundwater resources
4. Improved agronomic practices
5. Contingency crop planning
6. Integrated watershed development

The Ministry of Rural Development has undertaken major initiative in drought and flood mitigation by way of undertaking a **micro-watershed development programme** under DPAP/DDP/CDP programmes since 1994. A micro-watershed of about 500 ha has been considered as a unit. The task of undertaking surveys was given to non-governmental organisations (NGO's) working in the desert areas. Measures like afforestation, pasture development livestock management, field crops and water storage have been initiated. **Rainwater harvesting** techniques has been a major thrust area for successful crop production and recharging of groundwater. The Rajeev Gandhi Drinking Water Mission has been a sustainable approach by the Government during the last decade.

The Indian desert is a major beneficiary under the DDP programme as out of 36 DDP districts in India, 16 districts with 93 development blocks fall in Rajasthan. Another 10 districts with 32 blocks are under DPAP. Under this programme, there are about 1447 projects at various stages of development, out of which more than 500 have been completed. Evaluation study of 462 watershed projects in 26 districts of Rajasthan conducted by Tayleor Nelson Mode New Delhi (Sponsored by Ministry of Rural Development, Government of India) indicates that good results are available from several project areas where the water table has gone up and the per hectare yield of crop and grasses has also improved.

14.6 Controlled Land Use

The overriding priority, therefore, from the standpoint of climate–desertification relationships, is to avoid further destruction of forest cover and surface cover by poor pastural and agricultural practices. Whether or not such practices are really leading to a lasting deterioration of large-scale arid zone climate is still open to question. What is certain is that unwise land-use practices worsen the local climate and, therefore, aggravate the bad effects of prolonged drought that may occur. It may not be true that "**desert feeds on desert**," as is often said, but it is profoundly true that "**drought feeds on poor land use**," and is thereby worsened. Thus, the future of drought-prone states like Rajasthan lies in controlled land-use planning.

14.7 Water Harvesting

It has been seen that most of the official water development projects in drought prone regions fail to see that groundwater storage ultimately needs to be recharged. The surface water policy in drought-prone regions has encouraged increased withdrawal of groundwater much beyond recharge rates. This has caused groundwater mining, and drying up of surface tanks, shallow and deep wells, increasing the level of human misery. **Nature is not Kamdhenu, the mythical celestial cow yielding inexhaustible milk. We are sucking her dry out of our own greed.** The only way out is to husband the groundwater resources by rationing their use, providing protective irrigation in the form of limited quantities of water at critical stages of crop growth. The first step in any rational water-management policy must be soil conservation. To retain more of the water than it does at present, the ground must have vegetation on it and for this the soil must be healthy. The best way of increasing groundwater recharge is to provide good forest cover. Collecting water is equally important. Perhaps the most efficient and economical method of water harvesting is through tanks. All places, especially in Rajasthan with an annual rainfall below 500 mm, can be taken care of by collecting the rainwater in situ.

14.8 Conclusion

This chapter brings out some of the geo-environmental hazards in the Indian desert such as drought and desertification, problem of groundwater depletion, groundwater quality, deforestation and depletion of biodiversity. It is also evident from the above analysis that rainfall trends for the last 100 years in Rajasthan show that certain stations have recently experienced an apparent downward trend in rainfall, whereas others have shown a high variability from year to year, but no constant trend has been noticed. It may be concluded that there has been an increasing trend of rainfall in western part and decreasing trend in the eastern part of the Aravallis in the last 50 years. Now the question arises, is there any widespread evidence that rainfall in the Indian desert and adjoining areas is decreasing or increasing? If so, is a fluctuation in progress, or is the decrease a lasting change? On a very long time scale, there have certainly been great changes in climate, especially within the Quaternary Period. During the past 10,000 years, Rajasthan has been alternating between arid and humid phases resulting in the accumulation of sand dunes, especially during the arid phase. However, more data are needed in order to bring out climatic change in the Indian desert.

To sum up, it may be stated that despite the known drought proneness of the Indian desert, it has made noteworthy economic progress in the last few decades, which is reinforced in no small measure by the benefit being derived from the largest drought-proofing measures in the shape of IGNP. However, the low rating of human development index (HDI) of this region is a matter of serious concern. A consistent effort at improving HDI could itself help in facing any disaster in the future with great resilience.

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Chapter 15
Geoecology of Malaria in India: Historical Perspective and a Case Study of Western Rajasthan

Rais Akhtar

Abstract Malaria has plagued India since antiquity. In the twentieth century, both man-made and physical environments have contributed to the establishment of different malaria intensity zones. All the development and progress in science has not been able to conquer this disease, although it has been held at bay for at least half a century in many regions of the world. However, India is not among these regions; its conducive climate, lack of resources and fluxes in political will and stability have rendered it highly malaria prone. Considering that this risk of malaria persists to this day despite multiple and sustained efforts, an attempt has been made to highlight India's past experience in order to mount an informed and organized offensive to combat malaria. A 1948 Malaria Distribution Map of India indicated malaria-free, endemic and variable endemic zones. The malaria-free zone was associated with higher elevations, e. g. the Himalayas and coastal lands. The endemic zone was considered to be places where the average annual rainfall exceeded 80 cm. A malaria control program was started in India immediately after independence in 1947. Spraying of *Anopheles*-killing insecticides was the main control activity. Although the disease was largely controlled by 1965, resurgence took place from several pockets. Monsoon rains, higher humidity, vegetation, tribal habitats and rice cultivation have definitive associations with the disease in those two states. Eradication will have to await the discovery of an effective vaccine, but the disease has been drastically controlled since the mid-1980s with the existing techniques. However, the Intergovernmental Panel on Climate Change (IPCC) Assessment Report of 2007 asserts that climate change contributes to the global burden of disease and premature deaths. Population is exposed to climate change through changing weather pattern—temperature, precipitation and more frequent extreme events such as heat waves, cyclones and flooding.

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In the context of health, there is emerging evidence that climate change has altered the distribution of some infectious disease vectors and has increased heat wave-related deaths.

This chapter discusses the outbreak of malaria in the desert region of Rajasthan and also focuses on the study of people's perception about climate change and its impact.

Keywords Malaria · Hyperendemic areas · Rice cultivation · Physical environment · Climate change · People's perception · Thar desert · Waterborne diseases

15.1 Introduction

Malaria has plagued India since antiquity. In the twentieth century, both man-made and physical environments have contributed to the establishment of different malaria intensity zones. All the development and progress in science has not been able to conquer this disease, although it has been held at bay for at least half a century in many regions of the world. However, India is not among these regions; its conducive climate, lack of resources and fluxes in political will and stability have rendered it highly malaria prone. Considering that this risk of malaria persists to this day despite multiple and sustained efforts, an attempt has been made to highlight India's past experience in order to mount an informed and organized offensive to combat malaria. A 1948 Malaria Distribution Map of India indicated malaria-free, endemic and variable endemic zones. The malaria-free zone was associated with higher elevations, e. g. the Himalayas and coastal lands. The endemic zone was considered to be places where the average annual rainfall exceeded 80 cm. A malaria control program was started in India immediately after independence in 1947. Spraying of *Anopheles*-killing insecticides was the main control activity. Although the disease was largely controlled by 1965, resurgence took place from several pockets. Monsoon rains, higher humidity, vegetation, tribal habitats and rice cultivation have definitive associations with the disease in those two states. Eradication will have to await the discovery of an effective vaccine, but the disease has been drastically controlled since the mid-1980s with the existing techniques.

15.2 Climate and Malaria: Nineteenth-Century Observations

Before the discovery by Ronald Ross (1897) and Alphonse Laveran (1884), confusion prevailed about the real cause of malaria (Akhtar et al. 2010). In 1872, ***Indian Medical Gazette*** discussed the great confusion about the cause or causes of fevers in India. It states, "There is no fact connected with the medical history of India more freely conceded by the most advanced thinkers in this country and indeed by any of those at home who take an interest in the matter, than the obscurity which surrounds

Table 15.1 Month-wise malaria mortality in northern and western India

Year 1869	July	August	September	October	November
Number of deaths	13,734	15,595	31,307	44,221	36,332

many forms of Indian fevers. Of all the causes which have tended to obscure them, none appears to us to have been so powerful for evil as the too frequent use of term malaria. In every attempt at scientific diagnosis, we are met by the old bugbear malaria as either the cause of fever or it has imprinted its mark so indelibly on the disease that the original characters of the complaint are totally lost" (Jaggi, 1979).

F.N. Macnamara, based on 1869 data, provided an account on the climatic conditions and malaria outbreaks in northern and western India (Macnamara 1884). It is surprising to note that S.R. Christopher and J.A. Sinton, who prepared the first map of malaria in India, published in 1926, have not mentioned this pioneering attempt by Macnamara (Christophers and Sinton 1926). Macnamara noted, "At several stations in the upper Gangetic plains and in the Punjab as well as in Bengal, the rise in the number of admissions for fever is very marked during July and August, the most equally months in respect to temperature of the year, and the admissions attain their maximum frequency peak in September" (Macnamara 1880). He further observed that, "probably, throughout Bengal, much of the north-Western Provinces, and parts of the Punjab, the average rainfall quite suffices to foster as abundant a production of miasma where, however, as in parts of Punjab, the average rainfall is slight it may be ordinarily insufficient in quantity to develop the full amount of malaria which might otherwise be produced" (Macnamara 1880).

Macnamara cited month-wise mortality figures (due to malaria) as reported in northern and western India (Table 15.1).

Macnamara successfully showed that mortality rises with increase in rainfall and starts declining from November onwards.

However, the first scientific description of malaria in India came from Sir Joseph Fayrer's paper on the climate and fevers in India published in the *British Medical Journal* in 1882. Feyrer asserts that malaria is prevalent in low-lying, marshy or waterlogged ground, or on soil drying up after rains, or on land that is rendered damp by interrupted drainage; it is also found on dry, sandy or rocky ground, where there is little or no moisture or vegetation of any kind. About the regional distribution of malaria, Fayrer stated that:

"There are certain tribes in the Terai and other forest districts of India who acquire some immunity, the non-Aryan races, inhabiting Assam, suffer, it is said, to a greater extent from malarial disease than the Aryans in the same province. The Tharoos live where it would be death to others but even they are not altogether exempt" (Fayrer 1882).

Malaria is very intense in the belt of low swampy forest ground at the foot of the Himalaya mountains, where the porous soil has a substratum of clay, through which the water is brought near the surface, and where there is dense vegetation and a high temperature; in certain jungle districts, waterlogged land and where the tides encroach; in the river valleys, deltas and debouchures of rivers; and near rice cultivation in the Sunder bunds of Bengal, is probably exaggerated, where the mud is covered with dense jungle and frequently washed by the tide; in the jungles lying at the foot of hill ranges, and along the sea coast where salt and freshwater mingle. But it is scarcely less active on high and arid ground, as in the Deccan, Sind, Bicaneer, Peshawur, the Punjab and Bhawulpore (Fayrer 1882).

J.R. Adie's paper on infection among troops and native children in Delhi describes the ecology of malaria in Delhi and notes that Delhi Fort is notoriously unhealthy, and both the British troops within the Fort and the Native infantry at Daryaganj are heavily infected each year with malaria. The fever season in this part of India being at its height in October and November, the figures for British troops probably represent the highest degree of infection for the year 1910; those for the children taken at the end of September represent the condition of affairs at or near the commencement of the fever season (Adie 1911).

Thus, Patrick Hehir has rightly postulated that, in general terms, it may be stated that malaria fever is most prevalent in India during the years of the heaviest monsoon rain. There are the years in which we get outbursts of high endemicity, and this is particularly the case in the level plains and localities in which the drainage is slow or in any way obstructed (Hehir 1927).

The geographical distribution of malaria, using mapping technique, was first drawn by S.R. Christophers and J.A. Sinton and published in 1926 (Fig. 15.1). In the field of tropical medicine, S.R. Christophers was considered the last of the great polymaths. He was one of the great pioneers to rank equally with his famous peers Sir Patrick Manson and Sir Ronald Ross (Shortt and Garnham 1979).

According to Service, Christophers was a complete naturalist, not a specialist in a narrow field but an expert in many, and he was the first, and probably last, of all-round scientific malariologists. In studying malaria, he encompassed many disciplines, such as parasitology, entomology and sociology and also took into consideration the history and geography of the area. He was responsible for the survey approach to malaria problems and made important discoveries related to the mechanism of immunity in hyperendemic malaria (Service 1978). Christophers' joint paper with Sinton on 'A Map of Malaria in India' published in 1926 was the reflection of Christophers' holistic approach to understanding the spatial distribution of malaria. The map was prepared in colour to display the major epidemiological features of malaria in India based on variations in endemicity.

A high spleen rate when present in such areas is usually the result of abnormally heavy monsoon rainfall (epidemic tracts) or the existence of special local conditions favouring the enhanced prevalence of the disease, such as improperly controlled irrigation, waterlogging, etc. (Christophers and Sinton 1926).

The impacts of climate change, temperature rise and increased rainfall have a positive association with the prevalence of malaria. Christophers and Sinton assert that it is characteristic of such areas that there is some enhanced malaria prevalence in early summer, when the increasing temperature more or less favours the breeding of *Anopheles*, followed by a lull due to desiccation and a still more marked increase in the autumn following the monsoon rainfall (Christophers and Sinton 1926). Regarding general causes of malaria occurrence, Christophers and Sinton stated,

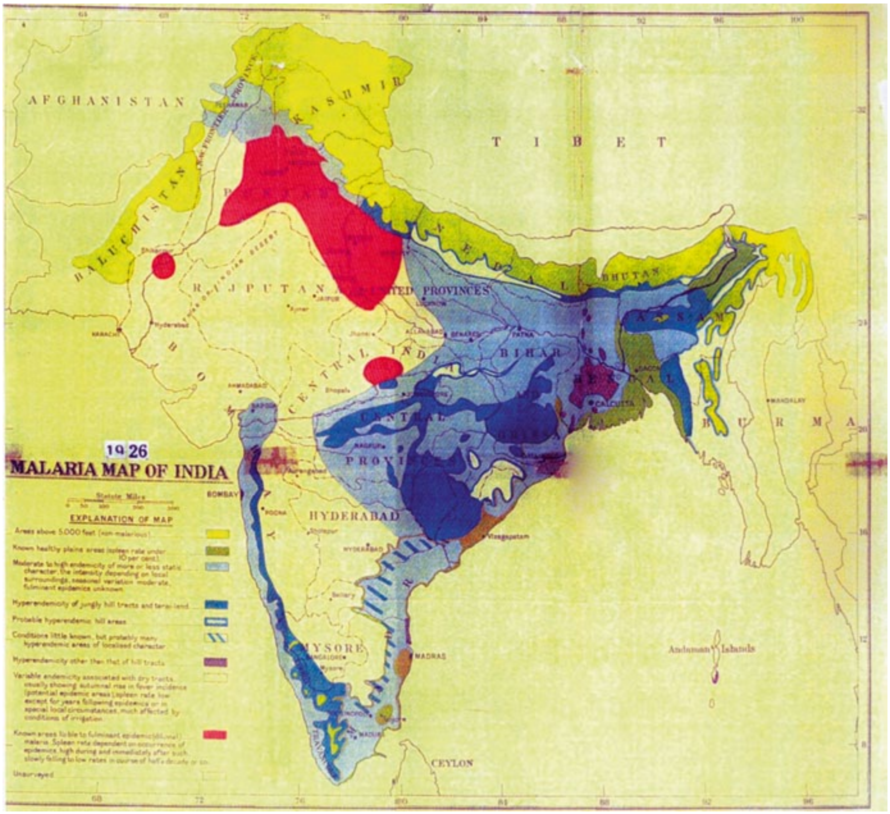

Fig. 15.1 Malaria map of India. (Source: Christophers and Sinton (1926))

"malaria here is largely a reflex of a multiplicity of natural features of the country, rainwater collections, streams and rivers, swamps, ponds and lakes (tanks). In addition, rice fields and irrigation play their part" (Christophers and Sinton 1926). Christophers and Sinton pinpoint that hyperendemicity is associated with and appears to be an essential feature of low jungles or forest-clad hills.

Learmonth provided geographical sciences for the occurrence of malaria in India during the 1940s and the 1950s. Malaria according to Learmonth, like many other diseases, may occur in endemic form that is constantly, by fairly regular increments, or in epidemic form, by occasional but commonly in the form of severe outbreaks. There is a broad division on the map of India between the more endemic areas, roughly corresponding to pluviose India, and the more epidemic areas, roughly corresponding to the semiarid areas of India. But some lowland and pluviose areas are relatively free from malaria, while malaria ceases over about 6,500 feet. Within the epidemic areas, some tracts are subject to catastrophic or 'fulminant' epidemics. Within the endemic areas, some tracts are so severely affected that they are classed as ‘hyperendemic’, and these include two contrasting types: forested hill tracts, such as the Western Ghats, and lowlands, usually deltaic, areas such as West Bengal.

Learmonth in his research on geoecology of malaria in the Indian subcontinent identified the following regions with varying malaria intensity (Learmonth 1957):

1. Areas over 5,000 feet (non-malarious).
2. Known healthy plains (spleen rates less than 10 %). (Now somewhat smaller area in East Bengal than shown on the map.)
3. Moderate to high endemicity of more or less static character, the intensity depending on local surroundings, seasonal variation moderate and fulminant epidemics unknown.
4. Hyperendemicity of jungly hilly tracts and *Terai* land.
5. Probably hyperendemic hill areas.
6. Hyperendemicity other than hill areas. Variable endemicity associated with dry tracts, usually showing autumnal rise in fever incidence (potential epidemic areas), spleen rate low except for years following epidemics, or in special local circumstances, much effected by conditions of irrigation.
7. Known areas liable to fulminant epidemicity (diluvial) malaria. Spleen rate dependent on occurrence of epidemics, high during and immediately after such an outbreak, slowly subsiding to low rates in course of half a decade or so.

Learmonth also quoted from G. Covel and laid emphasis on the importance of ecological perspective of *Anopheles* mosquitoes:

15.3 The Report of the Health Survey and Development Committee of 1946 stated

“Endemic malaria is believed to cause one million deaths in British India” (GOI 1946). The report described the spatial pattern of non-malarious and malarious regions. “Areas 5,000 feet above sea level are non-malarious and four widely separated regions, viz., Eastern Bengal, the north-eastern portion of Brahmaputra valley in Assam and two narrow strips of territory in Madras Presidency, in the Northern Circars and Madras city, are relatively free from the disease. The malaria tracts can be divided into the following five main types representing varying degrees of prevalence of the disease (GOI 1946).

1. Coastal regions of the maritime provinces of Bombay, Madras and Orissa.
2. Gangetic valley of the United Provinces and Bihar and the large tracts in the Central Provinces and the eastern portion of Central India. In these areas, malaria is prevalent in a more or less static form of moderate to high intensity.
3. Hyperendemic malarious regions associated with jungly hill tracts and *terai* land. These areas are widely scattered in the sub-Himalayan regions of the United Provinces and Bengal bordering on Nepal and Bhutan, respectively, and in Assam, the Chittagong Hill Tracts, the Central Provinces and the Chota Nagpur.
4. Hills and in the Western Ghats form a point well to the north of Bombay to the southern tip of the Indian peninsula.

5. Extensive tract of dry area running across India from north to south and comprises Sind, Rajputana, the south-western portion of the United Provinces, large part of Central India, Gujarat, Bombay, Deccan, Hyderabad and Mysore States and area in Madras Presidency to the east and southeast of Mysore. This region is characterized by varying degrees of malarial endemicity depending on local factors such as irrigation. There is usually an autumnal rise in fever incidence and epidemics of malaria may take place at intervals of a few years.
6. A territory consisting of a considerable part of the Punjab, Delhi Provinces and the south-western part of the United Provinces, the boundary running well to the east of Agra and Bareilly. This region is liable to outbreaks of fulminant epidemic malaria.

A fifth type of region showing hyperendemicity unassociated with hilly conditions exists in strictly localized areas, for example, the Tanjore district of Madras Presidency, a thin coastal strip above Madras city, and isolated spots in Orissa and Bengal.

15.4 Case Study of the Desert Region of Western Rajasthan

In the context of the historical perspective of malaria outbreaks in India, and the identification of vulnerable areas, particularly those which suffer from environmental degradation and hyperendemic malaria as described by Christophers and Sinton, the author of this chapter conducted a case study of the desert region of western Rajasthan highlighting changing malaria ecology due to flooding in the region.

The study on the outbreak of malaria epidemic in four districts of the desert region of western Rajasthan state—Bikaner, Jodhpur, Barmer and Jaisalmer—in 1994 has broken the myth that desert zone is less prone to malaria epidemic (Akhtar and McMichael 1996; Bouma and Vander Kaay 1995). This wrong notion over the years led to laxity on the part of the Department of Health Services, Government of Rajasthan and National Malaria Eradication Programme (now National Vector Borne Disease Control Programme) to adopt preventive measures.

Several studies pertaining to this outbreak appeared in 1995. Two different hypotheses—meteorological correlation and the canal irrigation system—were put forward in different studies (Sharma 1995). Significantly, almost all studies lack empirical bases both on the malaria incidence and on the meteorological data.

15.5 Changing Pattern of Rainfall in the Thar Desert: Historical Context

It is worthwhile to study the changing rainfall pattern in the desert region. Goudie, who studied the changing rainfall pattern in arid areas, including the Thar, noted a noticeable change in rainfall from 1890 to 1895. Conditions had been relatively wet in the 1880s and the 1890s (June–September summer monsoon rainfall—1818–1890

Table 15.2 Five-year running mean percentage of normal summer monsoonal seasonal rainfall centred on 1957 and 1970. (Source: Goudie, Environmental Change, Clarendon Press, Oxford, 1983, p. 156)

	1957	1970
Bikaner	114	71
Jodhpur	115	68

(2,422 mm) and 1891–1900 (2,472 mm), but then there followed a period of low precipitation, with precipitation in the driest decadal period being generally only between 52 and 69 % of that for the wettest decade of this century. The decreases in the summer rainfall were also noted during 1957–1970. The analysis of data for Bikaner and Jodhpur of the Thar Desert showed that summer monsoon rainfall decreased steadily by more than 45 % since 1957 (Table 15.2).

Analysis of flood years (Parthasarathy et al. 1987) in the desert region during the period of 123 years since 1871 showed that only 5 years (flood years) recorded summer monsoon rainfall above 500 mm. These years were 1908 (573 mm), 1917 (564 mm) 1944 (542 mm), 1990 (777 mm) and 1994 (544 mm), with 1994 being the year of the severe malaria outbreak in the region. Similarly, malaria was also reported in epidemic form during the 1990 flood year. This argument can be supported with empirical evidences as shown in Figs. 15.2 and 15.3. Thus, it is evident that the rainfall pattern in the desert region has been changing. However, the summer monsoonal rainfall of 500 mm and above may be taken as an indicator in forecasting malaria outbreak in the Thar Desert.

15.6 Role of Irrigation Canals

The construction of canals in the desert area commenced in 1962, and the first phase was completed in 1990. By this time, there was a network of canals with a total length of more than 8,000 km. These canals have created a waterlogging problem in vast areas. As a result of irrigation facilities, the soil structure has been changed with increased moisture-retaining capacity. Due to these environmental changes (man-made), a new vector (*Anopheles culicifacies*) is expanding in these areas, which was earlier dominated by *A. stephensi*. *A. culicifacies* remains active throughout the year. Recent studies also suggest that both 'tanka' and 'ber', the well-like structures made for storing drinking water by the rural communities in the desert region, have been found to be breeding habitats for *A. stephensi*, the confirmed malaria vector in the desert region (RSAPCC 2011; TERI 2010). Such an environment must have contributed to the increased incidence of malaria in the Thar Desert. However, the outbreak of malaria in the region, particularly in 1994, cannot be associated with the changed environment due to the canal irrigation network. Sudden rainfall due to El Nino Southern Oscillation created flooding conditions, and poor drainage in the

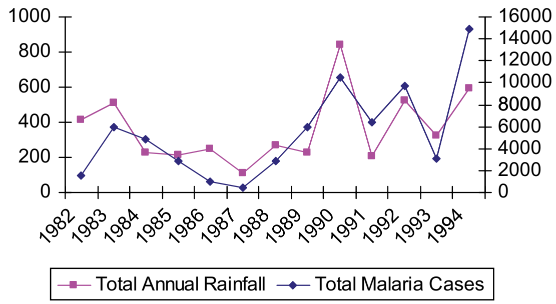

Fig. 15.2 Rainfall distribution and incidence of malaria in Jodhpur, Thar Desert (1982–1994)

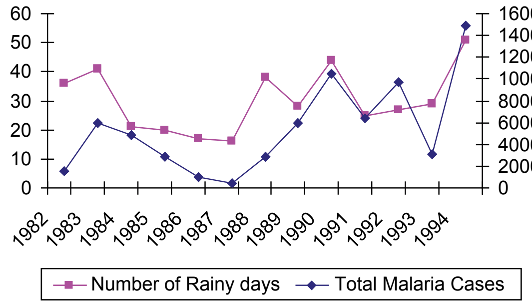

Fig. 15.3 Rainy Days and Incidence of Malaria in Jodhpur

Thar Desert resulted in the creation of breeding places. This has caused both high morbidity and mortality in 1994. In 1993, there were 354 deaths in India attributed to malaria. However, in 1994, some 372 deaths were officially reported in the four districts of Thar deserts, which accounts for about 0.6 % of India's population.

It should also be noted that the state of Punjab, which has about 2.4 % of India's total population with 98 % irrigated cultivated area, reports only 185 cases of *Plasmodium falciparum* with no death, compared with 88,310 *P. falciparum* cases with 452 deaths in the state of Rajasthan. Thus, the hypothesis that canal irrigation and waterlogging are the main reasons for malarial outbreak could not be proved.

Based on data of 13 years, an attempt has been made to study the association between rainfall conditions and the incidence of malaria. Figures 15.2 and 15.3, and Table 15.3 show that both the total annual rainfall and the number of rainy days are positively correlated with the total number of cases of malaria in the epidemic years of 1983, 1990 and 1994. Thus, the hypothesis of meteorological correlation has been proved.

An attempt has also been made to correlate the average November temperature (average of mean minimum and maximum) with the incidence of *P. falciparum* cases during 1982–1994. The correlation has been negative, as there is hardly any positive correlation in any year except in 1988 and 1989. Regarding the epidemic correlation with the rainfall in 1994, the total monsoon rainfall (June–September) in the year 1994 should be noted. Since 1871, the year 1994 was one of the 4 years which experienced the highest rains (other years being 1917, 1944 and 1990).

Table 15.3 Rainfall, rainy days and incidence of malaria in Jodhpur

	1982	*1983*	*1984*	*1985*	*1986*	*1987*	*1988*	*1989*	*1990*	*1991*	*1992*	*1993*	*1994*
Average November temperature	24.0	21.0	23.0	24.5	24.0	24.6	23.2	24.2	23.0	23.0	22.4	24.1	22.7
Total annual rainfall (in mm)	417	513	231	214	249	111	270	230	844	204	526	326	595
Number of rainy days	36	41	21	20	17	16	38	28	44	25	27	29	51
Total malaria cases	1,509	5,934	4,803	2,918	1,034	399	2,877	6,011	10,462	6,374	9,685	3,096	14,919
Percentage of *P. falciparum* cases to total cases	15	25	9	10	11	7	9.5	23	28.7	16.3	48.3	26.0	64.2

Table 15.2 reveals that since 1982, the highest number of rainy days occurred (i. e. 51) in 1994 (Hindustan Times 1994). Therefore, the contention of Tyagi et al. does not hold good that the epidemic occurred in the desert region irrespective of high rainfall (Tyagi et al. 1995). Patrick Hehir in his book *Malaria in India*, published in 1927, noted the desert region as a moderate epidemic zone. He further said that malaria is markedly seasonal in character (usually autumnal) and moderately prevalent. It may be mentioned that no study was conducted in the desert area in the past except the one by Green who studied the distribution of malaria parasites in Nasirabad (near Ajmer), a border zone with desert area. Green stated that, in 1909, 90% of malaria occurred due to *P. vivax*, with the remaining 10% due to *P. falciparum* (Green, quoted from Hehir 1927).

In a recently conducted field survey (100 households each in sample villages from Jodhpur and Sikar districts) in the rural area of the desert region, under the Council of Scientific and Industrial Research (CSIR) emeritus scientist grant, an attempt has been made to study the perception of the population regarding climate change and its impact on human health.

The analysis of data showed that nearly 100% of the people interviewed perceive that the temperature has risen in the last 20 years. As much as 73% revealed that the intensity of temperature increase is of medium level, while 10 and 17% of the population felt it is of high and low levels, respectively. At the same time, people feel that human activities are responsible for global warming and climate change. Almost all of those who were interviewed asserted that the decrease in the water table is the result of increased temperature. The study also noted a change in the pattern of diseases in the last 10–20 years. Nearly 98% of the population opined that temperature rise and shortage of potable water resulted in the emergence of new diseases. As much as 99% perceived that the intensity of heat waves has increased in the last 20 years resulting in increased heatstroke deaths. Of the people interviewed, 47 and 26% opined an increase in waterborne and deficiency diseases, respectively.

In the context of the outbreak of malaria in the region in 1994, only 39% of the people could recollect this malaria epidemic. However, when questioned about the causes of the malaria outbreak, about 59% indicated heavy rainfall, lack of health and sanitation facilities, and waterlogging as the causes of malaria outbreak.

It is interesting to note that in this field survey, conducted during 2010–2011, nearly 57% of the people opined that malaria is not being reported in the region. Thus, changing climatic conditions, particularly the precipitation scenario, are positively associated with the outbreak of malaria in the desert region of Rajasthan.

The study was based on 100 households selected on the basis of stratified random sampling from Jodhpur and Sikar districts. The objective of the paper was to understand people's perception about climate change and its impact on health in the desert region of Rajasthan. The knowledge of local communities, which have been coping with environmental changes since the millennia, is important in comparison with scientific community's assessment of climate change in the past two decades.

The region suffers from water shortages, but sometimes experiences heavy precipitation that causes flooding in the region. Groundwater level has gone down to a seriously critical level.

The study revealed that almost 100 % of the population believes that the ambient temperature has risen in the past 20 years. Nearly 100 % of the population relate the decrease in the water table to the rise in temperature. The region has also experienced a change in the disease pattern in the last 10–20 years with increase in waterborne diseases. The population also suffers from a number of deficiency diseases. As much as 90 % of the people perceived that the intensity of heat waves has increased in the region.

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Part IV
Water Quality, Exposure and Health

Chapter 16
Spring Water Quality and Human Health in Foothill Settlements of Pir Panjal Range in Anantnag and Kulgam Districts of Jammu and Kashmir State, India

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Abstract The present research work attempts to investigate the water quality of some selected springs in the foot hill settlements of Pir Panjal range in the Anantnag and Kulgam districts of Jammu and Kashmir state, to determine the suitability of water for drinking purposes and impact on human health. Since the area is rural in character, people generally go for open defecation and open solid waste/sewage/other waste disposal that ultimately find way into springs. Investigation reveals that the water quality of some of the springs has been deteriorated because of human impact. During the health survey of sample villages where the water of these springs is used for domestic purposes, it has been noted that about 72.6 % of the people were suffering from different water borne diseases like diarrhoea (24.3 %), dysentery (16.4 %), typhoid (6.4 %), gastroenteritis (15.6 %), infectious hepatitis (9.8 %) and poliomyelitis (0.14 %). In this context, some suggestions have been made to restore the ecological balance of these water bodies that will help to maintain the water quality and health of the people.

Keywords Spring water · Foothill settlements · Water quality · Permissible limits · Waterborne diseases · Water contamination

16.1 Introduction

Springs are concentrated discharge of ground water appearing at the ground surface as a current of flowing water as compared to seepage areas which are slower movement of ground water to the surface. They occur in many forms and are classified on the basis of cause, rock structure, discharge, temperature and variability (Todd 2001). Springs are assumed to be stable ecosystems and once ground water flows as a spring it loses the natural protection provided by the overlying rock layers and is

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more vulnerable to contamination threats from surface and atmospheric conditions (Van der Kamp 1995).

Water, the universal solvent, has the property of dissolving most of the substances because of its high dielectric constant but the excess or deficiency of these substances leads to water pollution (Gautam 1990). The possible pollutants in ground water are virtually limitless and most of the pollutants stem from disposal of waste on/into the ground (Anjaneyula and Lakhshmi 2002), but the most important factor is human activity (Tripathi and Pandey 1990). The exploding illiterate population following the unsustainable activities such as open defecation, free disposal of sewage/solid waste, faulty agricultural activity including animal husbandry, etc. has not only enormous impact on the ecology, morphology and discharge of the springs but it also leads to the inevitable reduction in water quality. The addition of human or animal waste leads to not only contamination but also pollution of water (Sharma 1987). Untreated sewage discharge is not only damage for aquatic life but also hazardous to human health. Water is really called the elixir of life. It is the essential and predominant constituent of the human body. Not a single metabolic process occurs in its absence. Supply of safe and potable drinking water to the community is of utmost importance in maintaining public health. The physicochemical and biological composition of water determines its use for different purposes. Provision of safe and portable drinking water to the community can go a long way in eradication of many diseases especially cholera, enteric fever, diarrhoea, dysentery, infective hepatitis and other water borne diseases. The World Health Organization and the United Nations Children's Fund estimated that at the beginning of the year 2000, one-sixth of the world population including 75 % population in rural areas of Asia lacked access to safe water supply (WHO and UNICEF 2000). In these countries, water is extracted from shallow aquifers that are highly susceptible to toxic chemical, microbial and nitrate contamination due to limited access to improved sanitation combined with poor hygiene practices (WHO 2004). Bacterial contamination of water continues to be a widespread problem across the country and round 37.7 million Indians are affected by waterborne diseases annually and over 5 million people die of water related diseases in India every year (WHO 1993; Tebutt 1998). The major pathogenic organisms responsible for water borne diseases in India are bacteria (*E. coli*, *Shigella*, *Vibrio cholerae*), viruses (Hepatitis A, Polio Virus, Rota Virus) and parasites (*Entamoeba histolytica*, *Giardia*, Hookworm). The Central Pollution Control Board (CPCB) monitoring results obtained during 2005 indicate that organic pollution continues to be predominant in aquatic resources. *Escherichia coli* are the major species in the faecal coliform group. *E. coli* is considered to be the species of coliform bacteria that is the best indicator of faecal pollution and the possible presence of pathogens. Run-off is the main carrier of pollutants from land to water. The water bodies with substantial animal inputs can result in potential health risks on par with those that result from human faecal inputs (Dufour 2012).

Springs are one of the important water resources in the foothill and piedmont areas in the world in general and in India in particular. Human settlements have come up near the springs since time immemorial for the availability of fresh water resource in the foothills of Pir Panjal range, due to growth in population and settlements without commensurate improvement of infrastructure and civic amenities, the dependency on water from natural springs is increasing. As always is the consequence of ill-planned anthropogenic activities, surface water resources were first to be affected (Jeelani 2010).

Though a remarkable contribution has been made in this direction and a large number of research works were carried out on the water quality of Himalayan Rivers and Indian springs, so far not a single research work has been done in Jammu and Kashmir state which may highlight the impact of the deteriorating water quality of surface and sub-surface waters on the human health.

Sub-surface water (spring water) though believed to be of better quality is now losing quality at the selfish interests of man. Ground water is reported to be polluted by agricultural and industrial activities in Punjab, Haryana, Andhra Pradesh, West Bengal, etc. It has also been found that ground water in Ludhiana contained 1–2 mg/L cyanide due to the cyanide containing effluent discharged from electroplating units (Ghosh 2002).

Studies conducted by Amathussalam et al. (2002) on the physicochemical and microbiological characteristics of sugar mill effluent polluted ground water in the Eraiyur area of the Permbalur District, Tamil Nadu indicated that electrical conductivity, total dissolved solids, total hardness in terms of calcium carbonate ($CaCO_3$), biological oxygen demand, chemical oxygen demand ion level values are on the higher side of permissible limits of WHO standards. Microbiological studies revealed the presence of specific fungal species which are capable of growing in higher concentrations of bicarbonate and nitrates which in turn serve as indicator organism of such pollutants.

Kumar et al. (1997) highlighted that the population density leading to unplanned sewage disposal has a close relation with the deterioration of spring water quality. While working on the natural springs of Almora town, they found that springs located in the densely populated area had higher concentrations of nitrates, chlorides, sulphates, sulphides and higher electrical conductivity. Concentrations of nitrates up to 60 ppm were observed in some springs, making water unsuitable for human consumption. No significant changes were observed in spring water quality during different seasons.

The chemical properties of the natural springs of the Nainital district are within the maximum permissible limits but are to a certain extent bacteriologically contaminated (Jain et al. 2010).

Ahmad and Alam (2002) conducted a study to evaluate the impact of different types of chemical, electroplating, textile and dyeing industry waste water on the river and ground water. Water samples from the localities located on the side of the Yamuna River and other areas in Delhi and industrial effluents of different types of industries were collected and analysed. Water quality parameters were very poor, except the samples collected from upstream.

Brainerd and Menon (2012) conducted a very important investigation of the impact of fertilizers used in agricultural practices in water on infant and child health using data on water quality pooled with data on the health outcomes of infants and children from the 1992–93, 1998–99, and 2005–06 Demographic and Health Surveys of India. They found that children exposed to higher concentrations of agrichemicals during their first trimester experience worse health outcomes on a variety of measures such as infant mortality, neonatal mortality, height-for-age z-scores and weight-for-age z-scores. The most vulnerable groups are children of uneducated poor people living in rural India.

From the earlier journey through the literature on the water quality of springs, it becomes clear that on one hand, the natural springs of the Himalayan region are still safe from the grave pollution problems but process of deterioration has started and on the other, a lot of work has been done on the assessment of water quality of the springs with only a little treatment of the consequences of deteriorating water quality on the human health. The present study is an attempt to quantify the change in the quality of the water of the springs in comparison to water quality standards of the Central Pollution Control Board, Government of India and the impact of the same on the health of the people in some selected springs in the foothill settlements of Pir Panjal range in the Anantnag and Kulgam districts of Jammu and Kashmir state. Planning strategies for maintaining the ecology of the springs and health of the people have also been suggested.

16.2 Study Area

The present study area is a part of the Kashmir region that falls in the great northwestern complex of the Himalayan ranges with marked relief variation, antecedent drainage, complex and varied geological structure and numerous springs. The bowl shaped valley is 135 km long with the maximum width being 40 km. Its floor called as plain area stands 1,585–1,800 m above the mean sea level (a.m.s.l.) in the flood plain of river Jhelum. The foothills or the sloping Karewa are located roughly between the elevations of 1,800–3,000 m above the mean sea level. Beyond that are located the mountains and the hills. Foothills of Pir Panjal range (westernmost mountain range of middle Himalayas separating Kashmir division from the Jammu division) facing the Kashmir valley thus form an important physiographic division of the region. The foothills, the transitional, gentler, fertile and resource rich tracts between plain areas and mountainous areas, are studded with numerous springs which serve as primary water resource for the people living in these areas. Most of the springs of Kashmir valley are concentrated in the foothill zone of the Pir Panjal range. The area lies between 33° 23′ 08″ N to 33° 40′ 16″ N latitudes and 74° 55′ 17″ E to 75° 23′ 31″ E longitudes and covers an area of about 597 km^2 (Fig. 16.1) with a population of about 1 million (provisional estimate). The area experiences temperate climate with an average annual rainfall of about 1,230 mm. Paleozoic sedimentary rocks, Triassic limestone, Karawa and alluvium are the predominant geological formations of the area with limestone, shale, sandstone and unconsolidated sediments as the dominant lithology (Wadia 1976). The mountainous

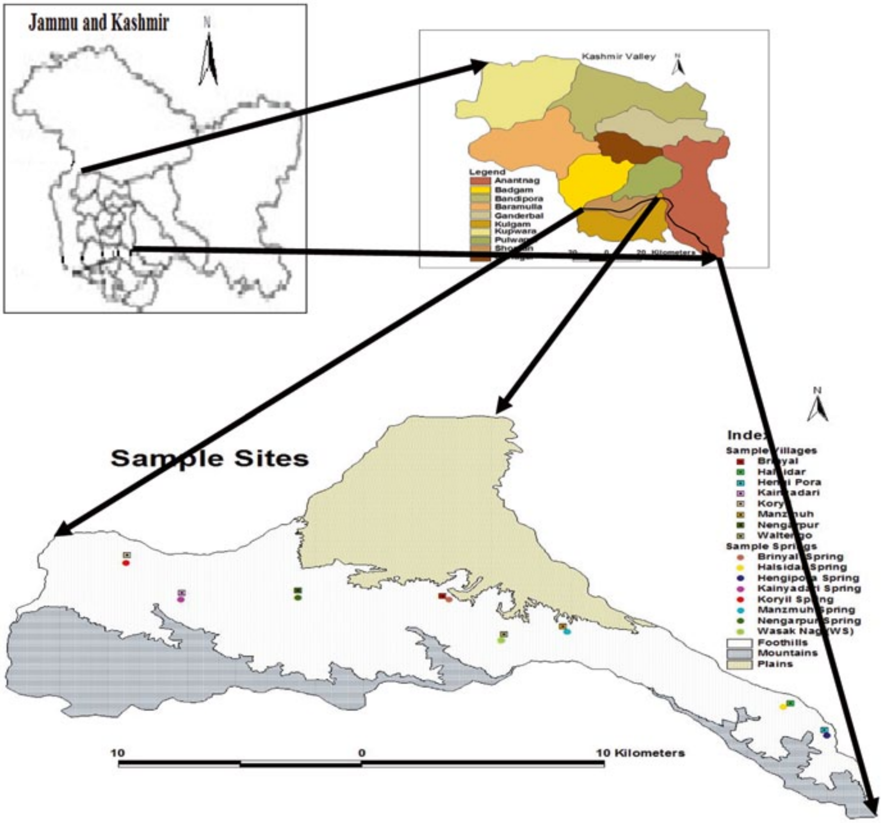


Fig. 16.1 Location map of the study area. (Source: Delineated from SOI toposheets in GIS environment)

regions (>3,000 m a.m.s.l.), the recharge areas, are mostly occupied by the Panjal Traps and the Triassic limestone (Jeelani 2010). The Valley is filled up with a great thickness (>2,000 m) of fluvio-lacustrine sediments of quaternary age belonging to the Karawa Group and the stream deposited alluvium of recent age. Two types of springs were found: karst and Karawa springs. Spring discharges were highly variable from about 5–1,880 L/s. (Jeelani 2005). In general, karst springs have higher discharges (~1,000 L/s) and Karewa springs lower (~7 L/s). However, in the present study, only the Karawa springs were selected which are well distributed with good concentration for they are located very near the human settlements or the later have flourished near the former and have more pollution chances than the karst springs. The extensive foothill zones under the present study have served as the suitable site for human occupancy since the ancient times. But for the last two–three decades, human conflict with this natural setting has led to deterioration of water quality of drinking water sources.

16.3 Data Base and Methodology (Fig. 16.2)

16.3.1 Sources of Data

The present study is based mainly on primary and partly on secondary data. The secondary data include the SOI of toposheets from which the study area was delineated and District Census Handbook of 2001. The primary data was obtained from water quality analysis of sample springs and household survey of sample villages with structured questionnaires.

16.3.2 Delineation of the Study Area

The study area was delineated from the SOI toposheets of 1:50,000 scale of 1961 with numbers as 43 K/14, 43 O/2, 43 O/3, 43 O/6 and 43 O/7 under GIS environment with the help of Arc View 3.2a software. The basis of delineation of foothills was contours. The lower or base contour and the upper or top contour taken were 1,800 and 3,000 m a.m.s.l., respectively. Most of the foothill area (95 %) falls within these two contours (Raza et al. 1978).

16.3.3 Selection of Sample Sites

Out of the whole study area eight sample sites were selected. The sample sites comprise of sample villages and sample springs. Eight sample villages (Table 16.1) were selected for health survey to assess the waterborne disease prevalence, each sample village containing one spring for water quality analysis to develop the relationship between the spring water quality and human health in the area.

16.3.4 Health Survey

To assess the health status of the people of the study area, eight sample villages (20 % of total villages) namely Brinyal, Halsidar, Hengi pora, Kainyadari, Koreal, Manzmuh, Nengarpora and Waltengo were selected by using probability sampling technique. From each sample village, 18 % of sample households were taken randomly for sample health survey.

16.3.5 Collection of Water Samples

On a fair weather day, water samples were taken from eight sample spring located in the sample villages in one litre sampling bottles (polyethylene) and were brought within 24 h from the sampling site to the Hydrological laboratory, Centre of Re-

Table 16.1 Sample villages and sample springs with altitude and geo-coordinates. (Source: Generated from SOI toposheets in GIS environment)

S. No.	Sample villages	Altitude (m above mean sea level)	Sample springs	Altitude (m above mean sea level)	Co-ordinates (latitude/longitude)
1	Brinyal	1,900	Brinyal	1,890	33° 35′ 23″ N and 75° 04′ 54″ E
2	Halsidar	2,100	Halsidar	2,089	33° 28′ 34″ N and 75° 20′ 17″ E
3	Hengi Pora	2,400	Hengi Pora	2,410	33° 26′ 40″ N and 75° 22′ 07″ E
4	Kainyadari	2,250	Kainyadari	2,250	33° 35′ 24″ N and 74° 52′ 26″ E
5	Koreal	2,150	Koreal	2,200	33° 37′ 38″ N and 74° 50′ 24″ E
6	Manzmuh	1,900	Manzmuh	1,900	33° 33′ 15″ N and 75° 10′ 08″ E
7	Nengarpora	2,000	Nengarpora	1,985	33° 35′ 35″ N and 74° 57′ 56″ E
8	Waltengo	1,990	Wasak Nag	2,000	33° 32′ 56″ N and 75° 06′ 56″ E

search for Development (CORD), University of Kashmir for chemical and microbial analysis.

16.3.6 Water Quality Analysis Methodology

The standard methodology recommended by American Public Health Association (APHA 1998) has been employed for analyzing the water samples (Table 16.2).

16.4 Statistical Analysis and Diagrammatic Representation

Data regarding water quality and incidence of waterborne diseases were tabulated and represented graphically (Figs. 16.2, 16.3, 16.4, 16.5, 16.6, 16.7, 16.8, 16.9, 16.10, 16.11, 16.12, 16.13, 16.14 and 16.15).

16.5 Results and Discussions

The analysis of Table 16.4 showing the chemical and microbiological characteristics of water samples and Table 16.3 reveals that there is an insignificant change in the water quality parameters like dissolved oxygen, free carbon dioxide, chloride, total alkalinity, total hardness and calcium hardness and they are within the permissible limits prescribed by the Central Pollution Control Board, Government of

Table 16.2 Water quality analysis methodology. (Source: APHA 1998)

S. No.	Parameters	Method (APHA 1998)	Description of method	Formulae used
1	Dissolved oxygen (DO) (mg/L)	Iodometric	50 mL of the sample was titrated against 0.025 N sodium thiosulphate using starch as indicator	$DO = \frac{V_1 \times N \times e \times 1000}{V_2}$ Where V_1 = Volume of sodium thiosulphate used V_2 = volume of the sample taken for titration N = normality of sodium thiosulphate e = equivalent weight of oxygen
2	Free CO_2 (mg/L)	Titrimetric	To 50 mL of water sample, two drops of phenolphthalein indicator were added and titrated against 0.02 N NaOH	$CO_2 = \frac{Titrant\ used\ (mL) \times 1000}{Volume\ of\ sample}$
3	Chloride (Cl−) (mg/L)	Argentometric Titration	100 mL of sample was titrated against 0.0141 N silver nitrate solution using potassium chromate as indicator solution, till brick red colour end point was attained	$Chloride = \frac{V_1 - V_2 \times N \times e \times 1000}{V_3}$ V_1 = volume of silver nitrate used for sample (mL) V_2 = volume of silver nitrate used for blank (mL) V_3 = volume of the sample taken for titration (mL) N = normality of silver nitrate solution. e = equivalent weight of Chlorine
4	Total alkalinity as $CaCO_3$ (mg/L)	Titrimetric (methyl orange)	100 mL of water sample was titrated against 0.02 N H_2SO_4 using methyl orange as indicator	$Total\ Alkalinity = \frac{V_1 - V_2 \times N \times 1000 \times 50}{V_3}$ V_1 = volume of titrant used for the sample V_2 = volume of titrant used for the blank (mL) V_3 = volume of the sample taken for titration (mL) N = normality of H_2SO_4
5	Total hardness as $CaCO_3$ (mg/L)	EDTA titrimetric	To 50 mL of water sample, 1–2 mL of buffer solution (NH_4-NH_4OH) and a pinch of EBT indicator was added and was then titrated against 0.01 M EDTA within 5 min after buffer addition till wine red colour changed to blue	$Total\ hardness = \frac{V_1 - V_2 \times 1000}{V_3}$ V_1 = volume of EDTA used for the sample (mL) V_2 = volume of EDTA used for the blank (mL) V_3 = volume of the sample taken for titration (mL)

Table 16.2 (continued)

6	Calcium hardness (Ca^{2}+) (mg/L)	EDTA titrimetric	To 50 mL of water sample, 2 mL of 1 N sodium hydroxide and a pinch of murexide indicator was added and then titrated against 0.01 N EDTA till colour changes from pink to purple	Calcium $== \frac{V_1 - V_2 \times 400 \times 1.05}{V_3}$ V_1 = volume of EDTA used for the sample (mL) V_2 = volume of EDTA used for the blank (mL) V_3 = volume of the sample taken for titration (mL)
7	Nitrate-nitrogen (mg/L)	Salicylate	To 100 mL of water sample, 1 mL of sodium salicylate was added and evaporated to dryness on water bath. The residue was treated with 1 mL of concentrated sulphuric acid and after 5–10 min, 6 mL of distilled water and 7 mL of 30 % NaOH solution was added. After development of yellow colour, the intensity was measured at 410 nm and the results were expressed in mg/L	Absorbance was measured at 410 nm using double beam spectrophotometer
8	Coliform (MPN/100 mL)	Multiple-tube fermentation	MacConkey's broth was prepared for each sample. First set of tubes (double strength of broth) was inoculated by 10 mL of sample. Second set of tubes (single strength of broth) was inoculated by 1 mL of sample. Third set of tubes (single strength) was inoculated by 0.1 mL sample. All tubes were incubated (1st, 2nd and 3rd sets) in an incubator for about (24 h) at 35–37 °C. After incubation period, the positive and negative results were recorded by production of gas inside the Durham's tubes and changing colour of media from red to yellow, indicating the positive results. Positive tubes were recorded and then cell numbers were calculated by using (MPN) table, then total number of bacteria per 100 mL sample was counted	–

MPN most probable number, EDTA ethylenediaminetetraacetic acid, EBT eriochrome black T

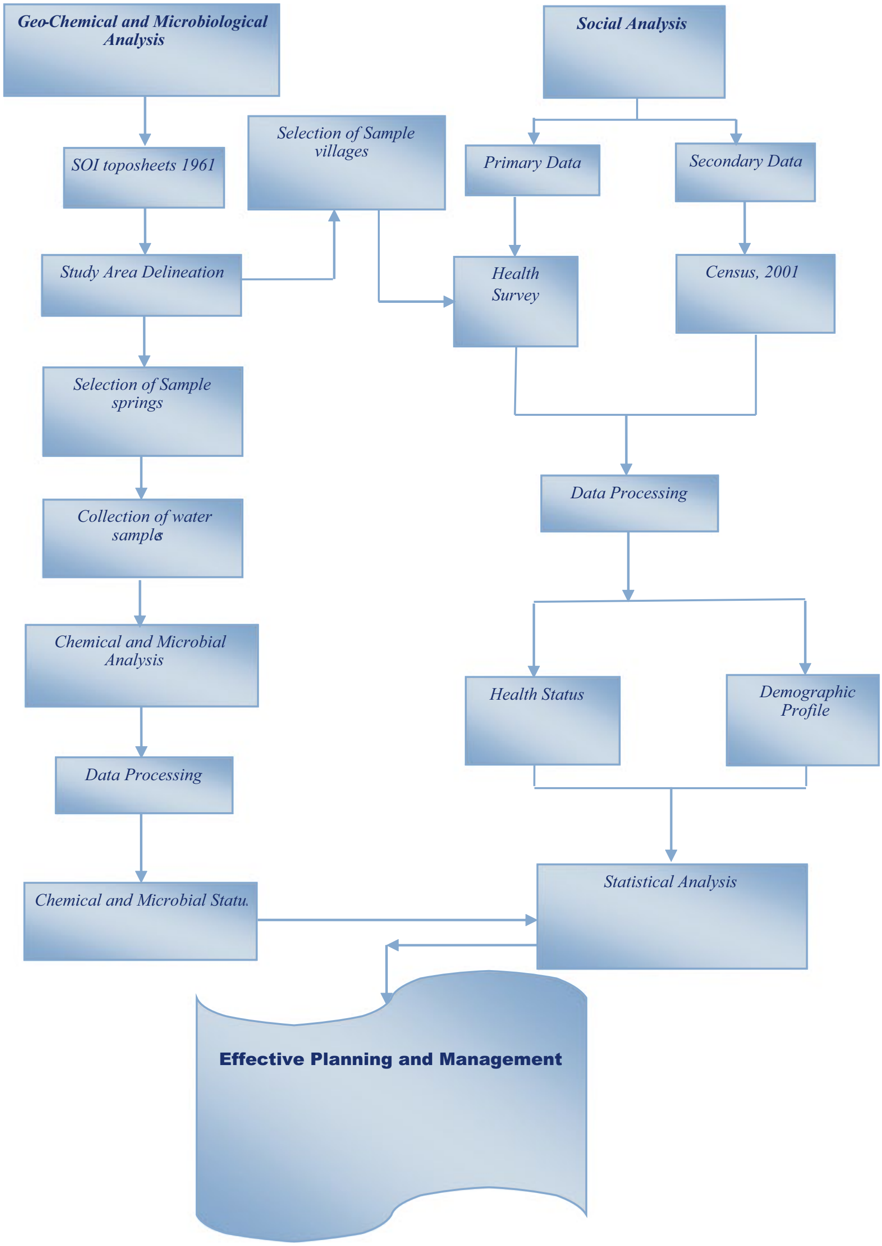


Fig. 16.2 Outline of the methodology

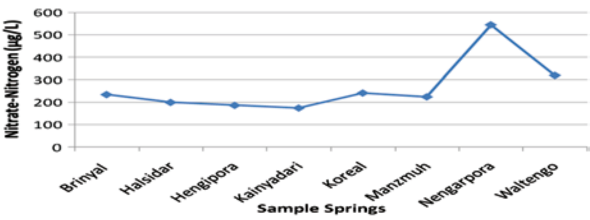


Fig. 16.3 Nitrate-nitrogen content (mg/L)

India. However, a drastic change has been noticed in the nitrate-nitrogen concentration and the coliform content (Table 16.4).

The DO ranges from 3.4 mg/L in Nengar pora spring to 4.8 mg/L in Hengi pora spring while as free carbon dioxide ranges from 12 mg/L in Hengi pora spring to 28 mg/L in Nengar pora spring. Low values may be attributed to high temperature (because of its low altitudinal location and compactness of settlements). The chloride content varies from 21 mg/L in Kainyadari spring to 45 mg/L in Nengarpora spring. The high concentration of chloride in springs of low altitude located in dense settlements is because of relatively more cultural activities in the immediate catchment (Bhat et al. 2010). There may be supporting geological reasons (calcareous sediments) as well.

The alkalinity for the eight springs ranged from 101 mg/L in Brinyal spring to 138 mg/L in Koreal spring. The assimilation of carbon dioxide from rain water and the carbonate origin of some of the springs (rise from underground water and meanwhile dissolute the surrounding carbonate rocks) may be probable cause of increasing bicarbonate concentration (Wadia 1976). The total hardness values range from 85 mg/L in Brinyal spring to 127 mg/L in Halsidar spring. The hardness directly seems related to the source of Ca^{++} and Mg^{++} which owes the origin to the carbonate deposits in the foothills of Pir Panjal range in the valley (Wadia 1976). The concentration of calcium ranges from 58 to 77 mg/L. The Halsidar spring depicts high calcium content above the permissible limits.

The nitrate-nitrogen content of the springs is attributed to the aerobic decomposition of organic nitrogenous matter as decayed vegetables and animal matter are significant source of nitrate. Nitrates constitute an important drinking water standard and its higher concentration is fatal for infants (Steel and McGhee 1984).The WHO standards prescribe 50 mg/L as maximum permissible nitrate concentration for potable water (Fresenius et al. 1988). The relatively higher concentration of nitrogen compounds may be due to domestic sewage which enters into groundwater through leaching from soil and run-off generated from agriculture fields wherein urea is used as a major inorganic fertilizer (Voznaya 1981; Chhathawal et al. 1989). The nitrate-nitrogen values range from 175 to 245 µg/L. Out of eight springs under study, three springs namely Brinyal, Halsidar and Nengarpora have nitrate concentration above 200 µg/L each, much above the permissible limits. It may be attributed to the location of these springs at a lower altitude of the village around their surroundings and thus decomposition of organic matter may directly find way into them. The leaching of nitrogenous compounds from the soil could be an additional factor for higher values of nitrate-nitrogen.

Table 16.3 Water quality standards for different users. (Source: Central Pollution Control Board, Government of India; Subramanian 2002)

S. No.	Designated best-use	Class of water	Criteria
1	Drinking water source without conventional treatment but after disinfection	A	Total coliform organism MPN/100 mL shall be 50 or less, pH between 6.5 and 8. Dissolved oxygen 6 mg/L or more. Biochemical oxygen demand at 20 °C 2 mg/L or less
2	Outdoor bathing	B	Total coliform organism MPN/100 mL shall be 500 or less, pH between 6.5 and 8.5. Dissolved oxygen 5 mg/L or more. Biochemical oxygen demand at 20 °C 3 mg/L or less
3	Drinking water source after conventional treatment and disinfection	C	Total coliform organism MPN/100 mL shall be 5,000 or less, pH between 6 and 9. Dissolved oxygen 4 mg/L or less. Biochemical oxygen demand at 20 °C 3 mg/L or less

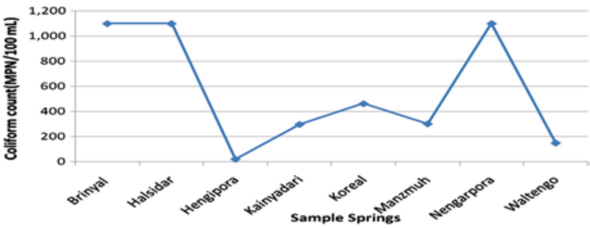
MPN most probable number

Table 16.4 Water quality analysis-2013 (chemical and microbiological). (Source: Based on data obtained from water quality analysis)

S. No.	Chemical and microbiological parameters	Sample springs								Central Pollution Control Board[a]
		Brinyal	Halsidar	Hengi Pora	Kainyadari	Koreal	Manzmuh	Nengar Pora	Wasak Nag	
1	Dissolved oxygen (DO) (mg/L)	4.2	4.6	4.8	4.7	4.4	4.6	3.4	4.4	Six or more
2	Free CO_2 (mg/L)	22	18	12	14	22	16	28	22	No health-based guideline
3	Chloride (Cl^-) (mg/L)	38	41	29	21	18	25	45	22	250
4	Total alkalinity (mg/L)	101	119	128	122	138	125	122	116	200
5	Total hardness (mg/L)	85	127	104	97	117	100	95	97	200
6	Calcium hardness ($Ca2^+$) (mg/L)	58	77	74	64	65	58	52	67	75
7	Nitrate-nitrogen (µg/L)	235	205	187	175	142	125	245	180	10–50 (mg/L)
8	Coliform (MPN/100 mL)	1,100	1,100	200	297	462	302	>1,100	149	Less than 50

MPN most probable number
[a] Water Quality Standards (acceptable limit)

Fig. 16.4 Coliform counts (MPN/100 mL)



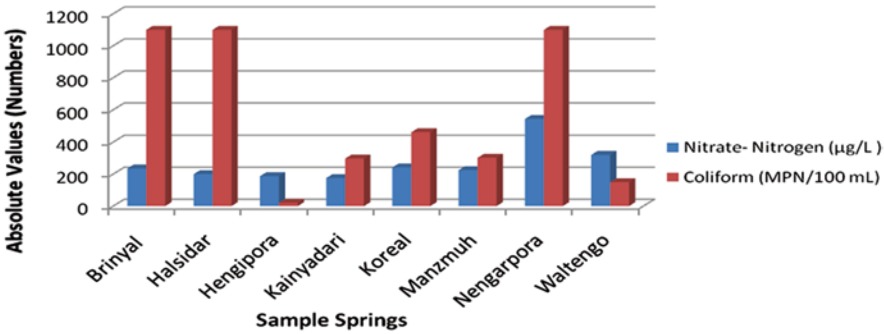


Fig. 16.5 Correlation between NO_3^- and coliform counts

The concentration of coliform bacteria in all the spring waters (Table 16.4 and Fig. 16.4) was well above the drinking water quality standards. The faecal coliform, classic microbiological indicator, count was found very high and above the permissible limit. The values varied from 200 MPN/mL in Hengi pora spring to 1,100 MPN/mL in Nengar pora spring (Fig. 16.4). The concentration of the coliform bacteria was found to be lowest in the Hengi pora spring, which may be attributed to its aloofness to the population for it is located at high altitude than the surrounding human settlements. Among all the springs studied, three springs namely Brinyal spring (1,100), Halsidar spring (1,100) and Nengar pora spring (> 1,100) showed very high concentration of coliform bacteria. These very high values are simply attributed to the rural character (open defecation, manure spreading, cattle rearing, waste disposal, etc. near the springs) of the very dense population in the villages and low altitude of these springs than the surrounding settlements (run-off supported by slope plays its role). It is pertinent to mention that a positive correlation was found among the indicator bacteria (*E. coli*) and NO_3 concentration (Fig. 16.5) indicating common source. Although the relationship between the hydrogeological/geological characteristics of aquifers and bacterial contamination of groundwater has received considerable attention, the bacterial contamination was high in all the springs and varied irrespective of lithology (Yates 1990; Thorn and Coxon 1992). Since, the area is predominantly rural with animal waste spreading nearer to springs that could be the cause of microbial contamination.

The analysis of Table 16.5 reveals that irrespective of age-sex about 72.6 % of the people surveyed were suffering from different water borne diseases like diarrhoea (24.3 %) followed by dysentery (16.4 %), gastroenteritis (15.6 %), infectious hepatitis (9.8 %), typhoid (6.4 %), and poliomyelitis (0.14 %). The incidence of water borne diseases was highest in the sample villages of Nengarpora (87.9 %) followed by Halsidar (86.4 %), Brinyal (81.2 %), Koreal (58.8 %), Kainyadari (53.7 %), Manzmuh (52.1 %), Hengi Pora (47.6 %) and Waltengo (47.4 %). There are remarkable contrasts in the incidence of each waterborne disease among the sample villages (Table 16.5) which could be attributed to the variation in the levels of contamination of spring water used for drinking purposes (Figs. 16.6, 16.7, 16.8, 16.9, 16.10, 16.11, 16.12, 16.13, 16.14 and 16.15).

The drinking water purification practices in the area include boiling followed by sedimentation and muslin cloth filtration. No continuous chlorination or any other disinfection process is employed either by the government or by the people. Out of the sample of 2,842 persons only 28.30 % were found using traditionally purified water for drinking purposes, among which 21.50 % used boiled water (Table 16.6 and Fig. 16.15). The low percentage of people using purified water practices could be due to the lack of knowledge about the importance of purified drinking water for human health.

16.6 Conclusions and Suggestions

The study leads to the conclusion that the water of sample springs of Brinyal, Halsidar and Nengarpora with coliform counts of about 1,100 MPN/100 mL is highly polluted. All the three springs are located at lower altitude than the surrounding village and get contaminated because of anthropogenic impact. The water of these three springs cannot be used for drinking purposes except after proper conventional treatment and disinfection. The quality of the water of the rest of the sample springs is within permissible limits.

It has been noted that the incidence of water borne diseases is very high. 72.6 % of the people were suffering from different water borne diseases like diarrhoea (24.3 %), dysentery (16.4 %), typhoid (6.4 %), gastroenteritis (15.6 %), infectious hepatitis (9.8 %) and poliomyelitis (0.14 %).

Drinking water purification practices followed by people in the area are not satisfactory. Only 21.5 % of the people surveyed were reported using boiled water. No continuous chlorination or any other disinfection process is carried out either by the government or by the people.

In the light of the earlier findings, the following planning measures have been suggested:

- Proper management of all the springs in general and of the three highly contaminated springs namely Brinyal, Halsidar and Nengarpora in particular, needs to be carried out on priority basis. That includes avoiding the free and direct

Table 16.5 Incidence of waterborne diseases in the sample villages. (Source: Data obtained through field work, 2013, by the authors)

Villages	No. of persons suffering (%)						Total (%)	PSNWbD (%)	PSMWbD (%)	NOHS	NOPS	TPOVs (2001)
	Dr	Dn	T	Ge	Py	Ih						
Brinyal	210 (24.5)	150 (17.5)	48 (5.6)	168 (19.6)	01 (0.12)	120 (13.9)	697 (81.2)	161 (18.8)	198 (23.1)	144	858	6,745
Halsidar	93 (30)	79 (25.5)	14 (4.5)	55 (17.7)	00 (00)	27 (8.7)	268 (86.4)	42 (13.6)	92 (29.7)	50	310	2,661
Hengi Pora	16 (15.2)	07 (6.7)	03 (2.8)	18 (17.2)	00 (00)	06 (5.7)	50 (47.6)	55 (52.4)	09 (8.6)	18	105	680
Kainyadari	21 (15.7)	10 (7.5)	06 (4.4)	23 (17.2)	00 (00)	12 (8.9)	72 (53.7)	62 (46.3)	13 (9.7)	22	134	780
Koreal	31 (18.8)	15 (9.1)	09 (5.5)	29 (17.6)	00 (00)	13 (7.8)	97 (58.8)	68 (41.2)	18 (10.9)	24	165	898
Manzmuh	57 (16.4)	36 (10.3)	15 (4.3)	52 (14.9)	01 (0.28)	20 (5.7)	181 (52.1)	167 (47.9)	34 (9.8)	52	348	3,261
Nengarpora	220 (33.9)	152 (23.5)	72 (11.2)	60 (9.3)	02 (0.31)	64 (9.8)	570 (87.9)	78 (12.1)	130 (20.1)	96	648	4,506
Waltengo	44 (16.1)	16 (5.8)	14 (5.1)	38 (13.8)	00 (00)	18 (6.5)	130 (47.4)	144 (52.6)	36 (13.3)	36	274	2,631
Total	692 (24.3)	465 (16.4)	181 (6.4)	443 (15.6)	04 (0.14)	280 (9.8)	*2,065 (72.6)*	777 (27.4)	530 (18.6)	442	*2,842*	*22,162*

Dr diarrhoea, *Dn* dysentery, *T* typhoid, *Ge* gastroenteritis, *Py* poliomyelitis, *Ih* infectious hepatitis, *PSNWbD* persons suffering from no waterborne disease, *PSMWbD* persons suffering from more than one waterborne disease, *NOHS* number of households surveyed, *NOPS* number of people surveyed, *TPOVs* total population of the villages

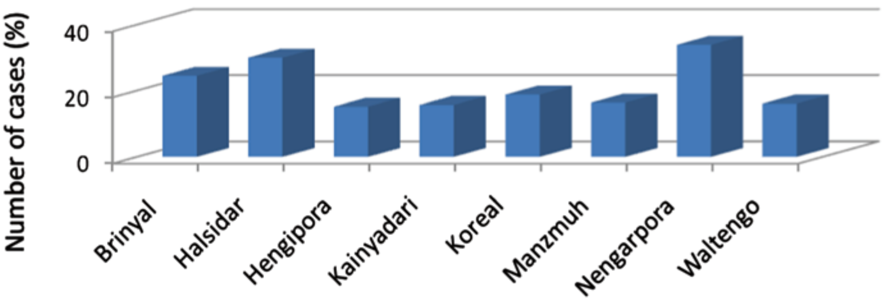


Fig. 16.6 Incidence of diarrhoea—2013

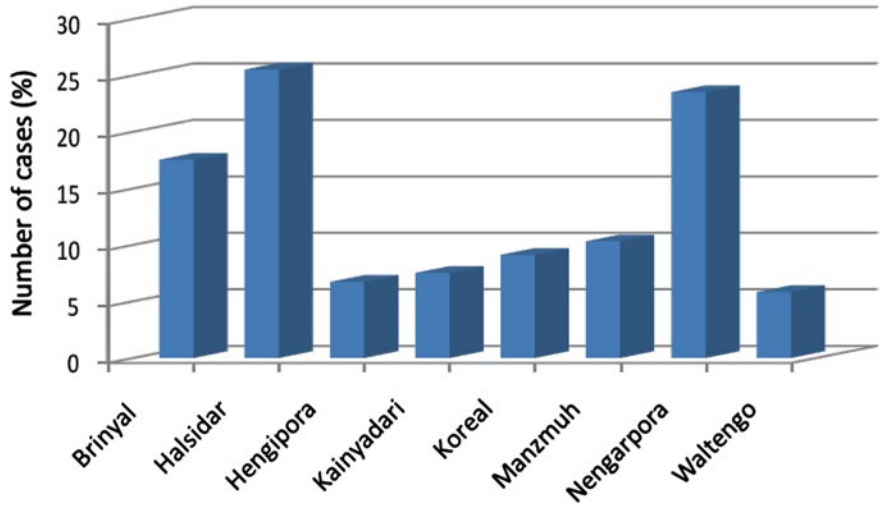


Fig. 16.7 Incidence of dysentery—2013

contamination of spring water by animals. A concrete drain needs to be constructed around each spring.

- Since the area is rural with low literacy levels, mass awareness programmes need to be conducted at the village and school level to sensitize the people about the causes and consequences of water deterioration and management practices. Health institutions, local bodies like panchayats and educational institutions should be involved in this activity.
- Sanitation schemes under MGNREGA need to be launched in the area for building low cost latrines, community latrines and drains for proper disposal of the domestic and other wastes. Community dust bins should be provided to the villagers.

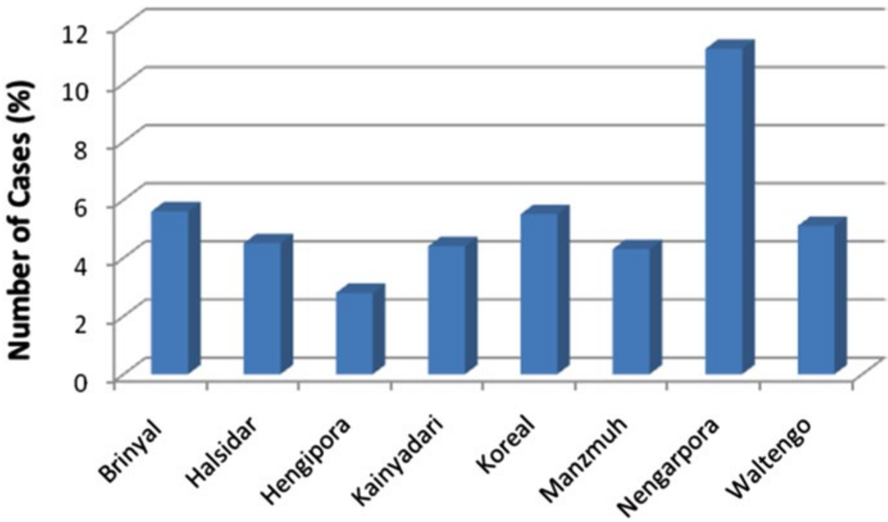


Fig. 16.8 Incidence of typhoid—2013

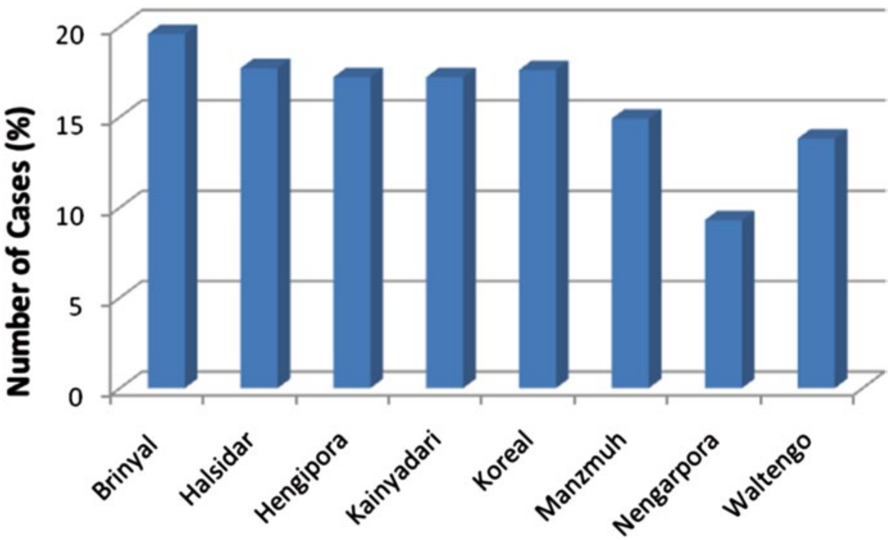


Fig. 16.9 Incidence of gastroenteritis—2013

- A sewage treatment plant is required to be established in the study area which collects waste and impure water from the area of different sources through pipes, treats the water and supplies the treated and pure water to the people through non-leaded and pollution free pipes.

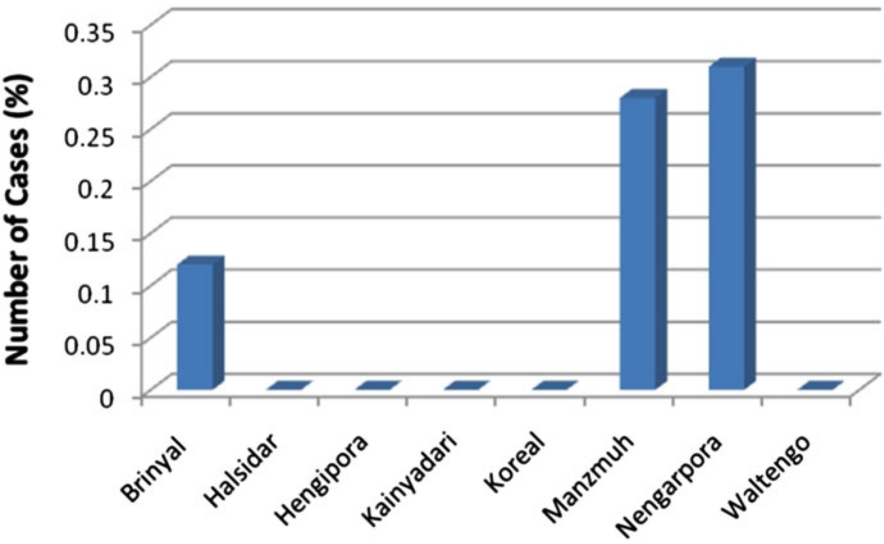


Fig. 16.10 Incidence of poliomyelitis—2013

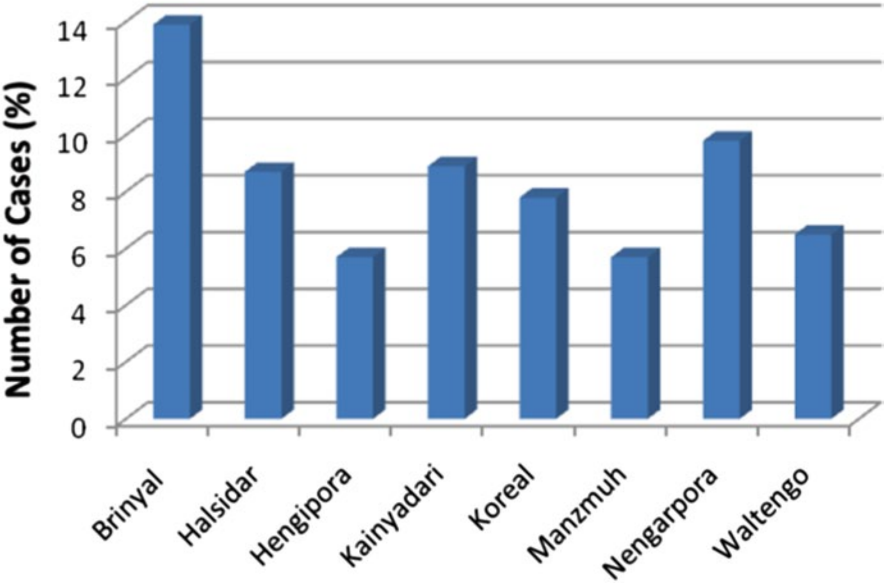


Fig. 16.11 Incidence of infectious hepatitis—2013

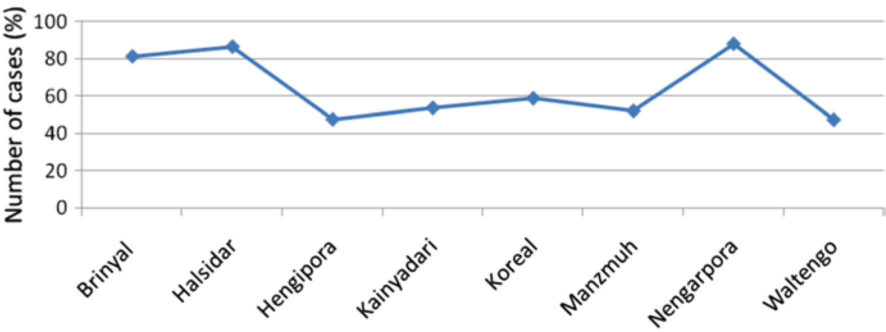


Fig. 16.12 Incidence of waterborne diseases—2013

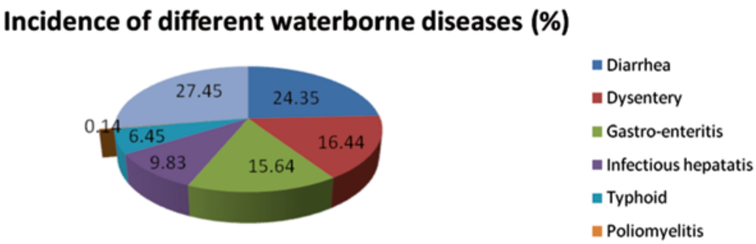


Fig. 16.13 Incidence of different waterborne diseases

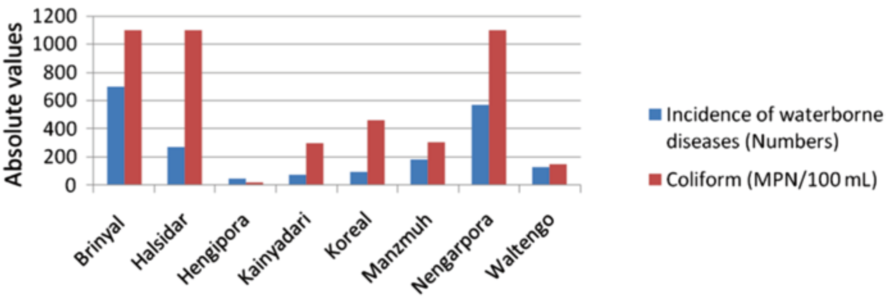


Fig. 16.14 Correlation between persons suffering from waterborne diseases and coliform counts

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Table 16.6 Drinking water purification practices in the sample villages

Villages	Number of house-holds surveyed	Number of households		Average family size	People using unpuri-fied water	Method of purification		
		Using purified water	Using unpurified water			Boiling (% to NOPS)	Muslin cloth filtration (%)	Sedi-menta-tion (%)
Brinyal	144	42	102	5.9	608	200 (23.3)	20	30
Halsidar	50	16	34	6.2	211	80 (25.8)	05	14
Hengi Pora	18	03	15	5.8	87	12 (11.4)	04	02
Kainyadari	22	05	17	6.1	103	24 (17.9)	03	04
Koreal	24	08	16	6.8	110	40 (24.2)	05	10
Manzmuh	52	15	37	6.7	248	71 (20.4)	15	14
Nengarpora	96	28	68	6.7	559	140 (21.6)	10	39
Waltengo	36	08	28	7.6	211	43 (15.7)	07	13
Total	442	125	317	6.5	2,037	610 (21.5) 805	69 (2.4)	126 (4.4)

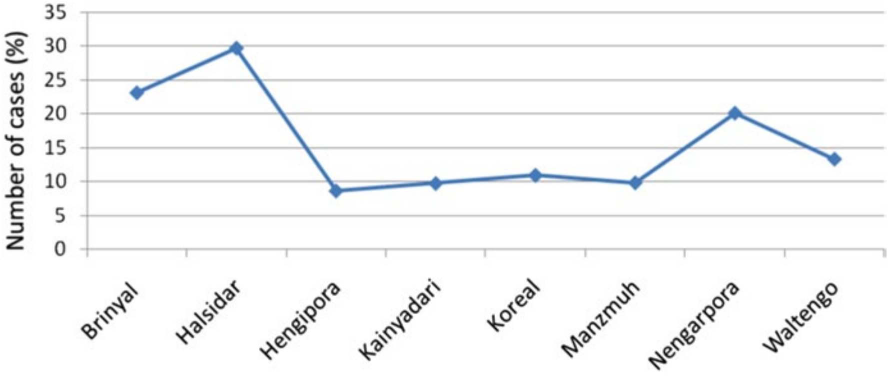

Fig. 16.15 Persons suffering from more than one waterborne disease—2013

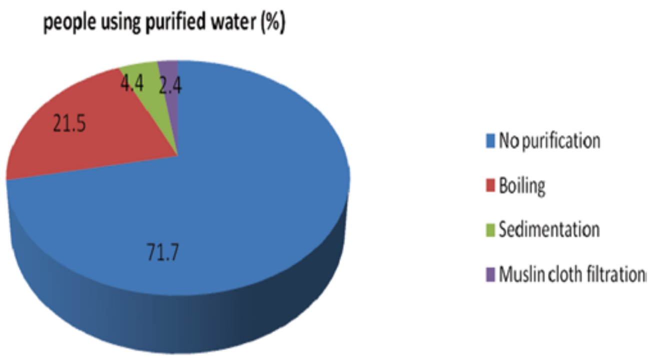

Fig. 16.16 People using purified water—2013

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Chapter 17
Dietary Exposure to Arsenic as an Anthropogenic Factor: Beyond the Recommended Diet

Rebeca Monroy Torres

Abstract Arsenic contamination of groundwater is a public health problem. In Mexico, the problem of arsenicosis is increasing due to overexploitation of aquifers and lack of regulations governing water extraction from new wells. Arsenic causes serious health damages, such as cancer, diabetes mellitus, and hypertension, in addition to being considered an endocrine disruptor. Food plays an important role, especially traditional Mexican food, which is high in soluble fiber, antioxidants, and inorganic nutrients. Furthermore, cooking practices are key to identifying risks of arsenic pollution due to human manipulation. Monroy-Torres et al. Rev Méd UV 9:10–13, 2009, found that dietary intake was the main route of exposure to arsenic, due to contamination of the drinking water used in food preparation. Obesity and malnutrition have been found to coexist in several Mexican communities studied by the author. These diseases, together with anemia and chronic degenerative illnesses that disrupt metabolic balance so as to increase arsenic absorption, promote greater arsenic concentrations, leading to the aforementioned metabolic alterations and carcinogenicity. As mentioned, contamination and dietary exposure are the most common arsenic sources. We propose an analysis of their anthropogenic causes in order to generate ideas and proposals for action towards reducing this hazard.

Keywords Arsenic · Food security · Nutritional status · Micronutrients · Well water

Introduction This chapter has been prepared with evidence gathered by the author and her team, from the standpoint of food security and its impact on health and nutrition. The current global problem of arsenic needs to change. It is of key interest that it be addressed from a multidisciplinary approach. Such an approach would allow several different experts to contribute to a comprehensive analysis of proposals for mitigating the problem. For example, dietary analysis as well as the pharmacokinetics of arsenic in different foodstuffs and in different health and nutritional

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conditions should be factored into possible explanations and solutions. Why is it that some communities with increased exposure to arsenic present less health risks than others? What role does a good nutritional status play as a defense mechanism or in the detoxification of arsenic? What foods or cooking techniques allow higher arsenic absorption? Which allow the least? What other risk factors are present in addition to arsenic? How should we face the current epidemic of obesity and diabetes in the presence of arsenic as an endocrine disruptor?

These and other questions need to be addressed from the collective perspectives of nutrition, medicine, and the social sciences, with policies that lead to mitigating the arsenic problem, based on an understanding of the right to food security which includes quality water supplies and foods that do not harm health. We present an overview of the characteristics of drinking water and the sources of water pollution; we approach the role and importance of nutrition and food from microbiological aspects, and offer scientific evidence gathered by the author, who has been working with communities exposed to arsenic at varying concentrations in the state of Guanajuato, Mexico, since 2004. Finally, we suggest a social and political approach to the problem. At the end of each topic, we offer thoughts and opinions on the evidence presented.

17.1 Features of Drinking Water

Drinking water should be free of harmful chemical and biological agents. The consumption of polluted water is an important risk factor for enteric disease, but there are other environmental conditions to consider, such as (UTEHA 1968):

- Poor health education
- Primitive methods of housing and sewage disposal
- Damaged water supply networks
- Difficult access to water or limited availability
- Lack of a water culture
- Unsanitary techniques in handling and disposing of garbage
- Failure to mitigate the impact and transmission of vermin
- Problems with design and implementation of public policies in rural areas

Contaminated water can provide conditions for the survival of various infectious agents. It is a means of physical protection as well as a source of nutrients for enteric pathogens. This is the reason drinking water must meet public health standards. The water used to prepare or wash food must also meet bacteriological standards for drinking water. It is generally agreed that the water provided by public services for domestic and industrial purposes should be clear, palatable, at a reasonable temperature, not corrosive or scale forming, free of minerals, metals, and the undesirable effects of potentially infectious organisms (UTEHA 1968; Tapia 2001). However, contamination of groundwater and drinking water with metals, such as arsenic, chromium, lead, fluoride, mercury, etc., is increasingly prevalent.

Contamination with arsenic and other metals demands toxicological methods different from those used for the elimination of microbiological risk. Chronic exposure to arsenic is associated with several toxic effects (skin lesions, development of several types of cancers, especially skin, lung, bladder, lung, prostate, liver, and kidney), in addition to damage to various organs and systems (reproductive and neurological disorders).

According to the Mexican Official Standard NOM-043-SSA2-2012, a proper diet is defined by the number of meals a day that meet the following characteristics (FUNSALUD 2001): (a) Complete: including all food groups; (b) varied: including a different food of each food group; (c) balanced: Nutrients from the different food groups balance proteins, fats, and carbohydrates; (d) adequate: suitable for physiological state of the person; (e) sufficient: according to age, sex, and physical activity; (f) harmless: free of biological (bacteria, viruses, fungi, and parasites) and toxic agents (metals and carcinogenic additives).

17.1.1 Water Pollution by Arsenic

17.1.1.1 Arsenic

Arsenic (As) is a naturally occurring contaminant that seeps into filtered water. Toxicologically, the chemical species of arsenic are elemental arsenic, organic, inorganic, and arsine gas (UTEHA 1968). Groundwater pollution is a significant health problem around the world, as in the case of Bangladesh, where the presence of As threatens the health of about 30 million people. The World Health Organization (WHO) describes the water supply of Bangladesh as one of the most polluted in the world due to its exceptionally high levels of As (Heikens 2006). Other countries afflicted are India, China, Vietnam, Mexico, Chile, Argentina, Brazil to name a few (Smith et al. 2000; Chan et al. 2009).

In Mexico, there are several states where contamination of drinking water by arsenic and other metals represents a health hazard. In the state of Guanajuato, the rocks are of volcanic origin, so that arsenic contamination of water is a common problem. Wells in municipalities such as Irapuato and Salamanca show concentrations above those permissible according to the NOM-127-SSA-1994 (Mexican Official Norm of Environmental Health, water for human use and consumption: permissible limits of quality and treatments to which water must be subjected for purification). Such is the case of the community of El Copal, Irapuato, where concentrations of up to 0.3 mg/L have been found (Rodriguez 2006). Studies have also been conducted in the aquifer Irapuato-Valle, where the values are found to significantly exceed those stipulated in environmental regulations (Rahman et al. 2001).

In the past, arsenic compounds were widely used in medicine to treat infectious diseases, but they have been largely replaced by antibiotics, which are less toxic and equally effective (Navas-Acien et al. 2008). Chronic exposure to arsenic is associated with damage to human health, including skin lesions, development of skin, lung, bladder, prostate, liver, and kidney cancer, reproductive harm, endocrine (diabetes mellitus) and neurological disorders, cognitive impairment, and hypertension (Chan 2009; NOM-127-SSA-1994; Rodríguez 2006; Rahman et al. 2001). Some studies mention that the prevalence of skin lesions caused by arsenic may increase with poor nutrition (deficiencies in zinc, selenium, and folate) (Mitra et al. 2004).

17.1.1.2 Incorporation of Arsenic in Children in Communities in the State of Guanajuato

In 2004, the State Laboratory of Public Health in Guanajuato found non-standard levels of arsenic (0.025 mg/L) in the water wells of populations belonging to the state of Guanajuato. A study conducted in 2005 (Monroy-Torres et al. 2009b) found non-standard levels of arsenic in the hair of children exposed to contaminated water, with a maximum of 5,939 mg/kg.

Arsenic in high concentrations has been shown to have harmful effects on human health, including noncarcinogenic adverse effects from exposure to its derivatives. The effects of chronic exposure are hyperpigmentation, hypopigmentation, hyperkeratosis, cardiovascular system damage, kidney and liver disorders, and peripheral neuropathies. According to recent developments, arsenic has been associated with endocrine disruptor capacity, related to the development of type 2 diabetes mellitus (DM2) (Coronado-González et al. 2008). There are also studies linking arsenic exposure in drinking water to the presence of proteinuria (Chen et al. 2011). In animal models, it is well established that arsenic significantly increases oxidative stress, which, in turn, has been associated with chronic degenerative diseases like diabetes, etc.

A study published by Monroy et al. analyzed the nutritional diagnosis and some metabolic markers associated with arsenic exposure in a cohort of children less than 5 years of age in a rural community. The findings show 35 % of the children were obese and 13 % suffered from malnutrition. We also found altered levels of hemoglobin, glucose, triglycerides, cholesterol, and low micronutrient intakes (vitamin A, C, folic acid, and flavonoids), all markers which reflect a risk for developing diabetes and hypertension (Chen et al. 2011; Coronado-González et al. 2008; Evans-Graham et al. 2004; Navas-Acien et al. 2008).

17.1.2 Microbiological Contamination of Water

17.1.2.1 Characteristics of Microorganisms

Bacteria are the most numerous of all living species. Although algae and flagellate protozoa are not uncommon in rain-, surface-, or groundwater, bacteria are the most frequently found microorganisms and of special interest to this protocol. Bacteria can be found even in atmospheric water that has never come into contact with the earth, and they abound in bodies of water that intermittently receive large loads of waste from land.

Hospital water must meet strict requirements, including the water used for the personal hygiene of patients and staff. Otherwise, there is a risk of acquiring bacteremia caused by enteric gram-negative bacilli from the *Klebsiella* group (*Klebsiella*, *Enterobacter*, and *Serratia*) (Macias et al. 1999; WHO 2011). Enterobacteriaceae are perfectly equipped to survive in polluted water and, in the past, wreaked havoc on the population. The significant association between poor water chlorination and contamination of parenteral infusions in hospitals points to the importance of solving this problem, since contamination can occur after invasive procedures through contaminated skin. An association between Gram-negative bacteremia and low levels of chlorine in the water has been reported in Guatemala and Mexico (Pegues et al. 1994). In a study by Macías et al. 2006, microbiological analysis discovered 33.3 % contaminated specimens of water, while chemical analysis revealed that only 54.5 % of specimens were adequately chlorinated (Macías et al. 2006).

Waterborne diseases can be prevented with the following actions: boiling water, adding liquid chlorine or chlorine tablets to drinking water stored in airtight containers, filtering water, using ceramic filters, for example, solar disinfection, and coagulation and flocculation (NOM-012-SSA1-1993; WHO 2004, 2011).

The bactericidal effectiveness of chlorine and its compounds depends on factors like concentration, temperature, and reaction time. The dosage should never be 2 mg of Cl/L of water and allowed limits for residual chlorine should be 0.2–1.5 mg/L. The goal of purification is the destruction of microorganisms. Correct application of chlorine is a guarantee that drinking water will become safe to drink. In the case of Mexico, this has been the main disinfection method, due to its low cost (NOM-012-SSA1-1993; NOM-041-SSA1-1993; NOM-127-SSA-1994; NOM-041-SSA1-1993).

17.1.3 Afterthoughts

Water pollution by both organic materials and metals must be addressed as a whole in order to understand possible synergies. This would also help reduce the impact of arsenic in water and food when it interacts with other substances or microorganisms. This approach is rare and would constitute a very specialized analysis of the health and environmental impacts of arsenic. The assumption would be that the effects of arsenic on health are modified by interaction with other risk factors.

17.2 Impact on Health, Nutrition, and Diet in Some Locations in Guanajuato: Main Evidence

The health of the population reflects many risks. Diarrheal diseases, cancer, respiratory diseases, low birth weight, prematurity, abortions, hypertension, and metabolic diseases, such as diabetes, have all been associated with exposure to water contaminated by either toxic compounds or microbial agents. According to the 2009 INEGI statistics (statistics Perspective Guanajuato, INEGI 2011), the main causes of death in the state of Guanajuato were those presented later, pointing to a probable causal factor. Studies explain that the lack of basic water services has serious implications in many areas, particularly in health, environment, and economy. Among the implications are deaths and serious illnesses caused by water scarcity and/or poor water quality, and furthered by nonexistent or partial sewerage and sanitation, with the consequent continuous contact between people and excreta. According to the WHO (2004), in 2003 there were 1.6 million deaths attributable to unsafe water or inadequate sanitation and hygiene; 90 % of this mortality was concentrated on the population less than 5 years of age, mostly from developing countries. Some of the diseases related to lack of water services or poor water quality are diarrhea, cholera, typhoid, dysentery, gastroenteritis, hepatitis A, polio, amoebic dysentery, schistosomiasis, and salmonellosis. Diarrhea is the most important public health problem (WHO 2000). Negative environmental impacts result from continuous breaching of environmental regulations. Abatement of groundwater is a serious problem in countries that depend on groundwater for urban water supply (Arrojo 2006). The problem of water quality adds to the list of environmental problems underdeveloped countries face. Further, the low priority given to wastewater can continue the spiral of degradation of water sources (Dourojeanni and Jouravlev 1999).

17.2.1 Nutritional Status and Micronutrients

Arsenic found in soil either naturally or from anthropogenic activity forms insoluble complexes with iron, aluminum, and magnesium oxides present in soil; in this form, arsenic is relatively stable. However, under reducing conditions, arsenic can be released from the solid phase, resulting in soluble mobile forms of arsenic, which may potentially leach into groundwater or result in runoff of arsenic into surface waters. Low levels of arsenic are commonly found in food; the highest levels are found in seafood, meats, and grains. For most people, diet is the main source of arsenic. Mean dietary intakes of arsenic of 50.6 µg/day and 58.5 µg/day have been reported in females and males, respectively (MacIntosh et al.1997). In the USA, dietary intake of inorganic arsenic has been estimated to range from 1 to 20 µg/day. Grains are thought to be the main contributors to total dietary arsenic intake (Basu et al. 2011; Schoof et al. 1999).

17.2.2 Main Evidence in the State of Guanajuato

We present the findings from a cohort followed since 2004. We have sought to reduce exposure to arsenic through dietary mechanisms, through food and nutritional care. Suggestions for approaching the study of arsenic arise from different viewpoints, in a multidisciplinary approach.

When arsenic is ingested in contaminated food or drink or from other surfaces (such as hand-to-mouth ingestion, in children), gastrointestinal absorption varies with the chemical form of the metal and the individual's nutritional status (Basu et al. 2011). Once ingested, arsenic is absorbed through the gastrointestinal tract and accumulates in the liver, spleen, kidneys, lungs, heart, and, to a lesser extent, in the muscles and nervous system (Evans-Graham et al. 2004). The main form of excretion of arsenic is via the urine as dimethylarsinic acid (DMA) and methylarsenic acid, 65 % and 20 % respectively.

Chronic exposure to arsenic is associated with many toxic effects, including skin lesions and the development of several types of cancer, particularly skin, lung, bladder, prostate, liver, and kidney. It also damages the reproductive system and can cause neurological disorders and cognitive impairment in children (Evans-Graham et al. 2004; Parvez et al. 2006). These effects have been attributed especially to inorganic arsenic, which increases the frequency of chromosomal aberrations and chromatid exchanges and inhibits DNA repair (Evans-Graham et al. 2004).

Some studies have found an increased susceptibility to the toxic effects of arsenic in individuals with malnutrition. For instance, low intake of micronutrients, especially zinc, selenium, and folic acid, has been associated with increased risk of disease caused by arsenic (Mitra et al. 2004; Smith et al. 2000). Experimental studies have shown that low-protein diets cause a decrease in the excretion of dimethylarsinous acid (DMA), a form of arsenic that favors arsenic retention in keratinized tissues (Smith et al. 2000). Milton et al. (Milton et al. 2004) concluded that malnutrition or poor micronutrient intake may increase the toxicity of arsenic and, therefore, make malnourished populations highly susceptible to complications from the chronic toxicity of the metal (Islam et al. 2004; Smith et al. 2000). A low intake of calcium, protein, folate, and fiber may increase the susceptibility to skin lesions produced by arsenic (Islam et al. 2004; Mitra et al. 2004). Vitamin A is involved in the differentiation of various tissues especially in skin, and deficiency of this vitamin may also increase susceptibility to arsenic (Milton et al. 2004). Thus, malnutrition or inadequate levels of certain specific nutrients may increase susceptibility to arsenicosis (Rahman et al. 2001). Conversely, adequate nutrient levels in the diet may be protective against chronic arsenic toxicity. For example, folic acid protects against the cytotoxic effects of arsenic. The mechanism for this protective effect may involve folate-dependent one-carbon metabolism, which facilitates urinary arsenic excretion through methylation of ingested inorganic arsenic into monomethylarsonic acid and DMA; methylation of arsenic facilitates urinary excretion (Gamble et al. 2007). One-carbon metabolism is dependent on folate, vitamin B12, and vitamin B6 for the recruitment and transfer of methyl groups as well as other nutrients such as betaine, choline, riboflavin, and serine, which contribute to the availability of methyl groups (Hall and Gamble 2012). Moreover, vitamin E enhances the protective effect of vitamin A to the toxicity of arsenic (Milton et al. 2004). It has also been seen that vitamin C and methionine reduce the toxicity of arsenic (Smith et al. 2000).

The first study listed in Table 17.1 was performed after detecting the presence of arsenic in two rural children from a previous study (Monroy-Torres et al. 2009a),

Table 17.1 Summary of evidence regarding nutrition and diet in two rural communities exposed to arsenic in the state of Guanajuato, Mexico. (Source: Monroy-Torres et al., Rev Med UV 2009a; Supp 1;9(1):10–13, Monroy-Torres et al., Ecol Food Nutr 2009b;48:59–75)

Study	Main outcomes
Accessibility of safe water for drinking and preparing food in a community exposed to water contaminated with arsenic. *(Monroy et al., Rev Med UV 2009; Supp 1;9(1):10–13)*	Sample size = 55 90 % of the housewives used well water for drinking and food preparation. Regarding milk, 24 (44 %) consumed brand milk and 31 (44 %) consumed cow's milk. Well water was used for livestock and to irrigate crops.
Arsenic in Mexican children exposed to contaminated well water. (*Monroy et al., Ecol Food Nutr 2009;48:59–75)*	Overall, 110 children were included (10 years old on average).Among 55 exposed children, the mean level of arsenic in hair was 1.3 mg/kg (range <0.006–5.9). All unexposed children had undetectable arsenic levels. The high level of arsenic in water was associated to the level in hair.
Nutritional status and metabolic abnormalities in a cohort of adolescents exposed to arsenic for 5 years.*(Monroy-Torres R, et al. Forthcoming publication)*	The average was 24 ± 4; 35 % were obese and 13 % had malnutrition. There were low intakes of protein, vitamins A, C, folic acid, flavonoids, along with a high intake of saturated fats and refined sugars. The study found several risk markers for diabetes and hypertension.
Eating and nutritional status of children with high levels of arsenic in hair *(Monroy-Torres R, et al. Forthcoming publication)*	The average energy intake was 1717 ± 288 kcal. Protein, folic acid, iron, and zinc intakes were low, according to recommended dietary allowances (RDA). Sources of dietary exposure to arsenic were water and cow milk.

despite the use of tap water. The objective of the study was to describe the accessibility of water and the safety of the water used for drinking and food preparation in a community exposed to arsenic-contaminated water. We applied a 55 cross-sectional surveys aimed at housewives between 27 and 55 years old. They were questioned as to the use of well water in the preparation of foods such as broths, soups, beans, flavored water, and fruits: We also asked about milk intake and origin, major crops in the community, raising cattle, and water source for these activities. The main findings were that more than 90 % of homemakers used well water for drinking and preparing food. Regarding milk, it was consumed 5 days a week, with 24 (44 %) purchasing brand milk, while 31 (44 %) drank cow milk. The milk was acquired within the community, where only four families reported breeding cattle. Regarding food preparation, 50 (90 %) of the mothers said they used well water to prepare broth, 50 (90 %) for soups, 52 (94 %) for beans, and only 10 (18 %) used it for drinking. They reported boiling food to disinfect it. Well water was given to cattle and used for irrigating crops. The main crops were corn, peas, beans, and sorghum. Another important aspect noted was that people knew the water had arsenic and were aware of its effects on health, such as cancer; they pointed out that they used this water due to lack of financial resources. We also found a community that had a filter for treating arsenic-contaminated water, but was unable to use it since those individuals trained and qualified to operate it had migrated to the USA.

These findings have been the cause of an ongoing search for strategies to ensure that people have food and water that are both biologically and toxicologically safe. The health risks of exposure to contaminants in food and water are predictable and serious, with outcomes like cancer, diabetes, and hypertension.

Afterthoughts Some studies have found an increased vulnerability to the toxic effects of arsenic in people with malnutrition (Mitra et al. 2004). For example, a low intake of micronutrients, especially zinc, selenium, and folic acid, has been linked with an increased risk of disease caused by arsenic. A low intake of calcium, protein, folate, and fiber may increase susceptibility to skin lesions caused by arsenic. Folate, vitamin B12, and vitamin B6 are necessary for recruitment and methyl transfer, as well as nutrients like betaine, choline, riboflavin, and serine, which contribute methyl groups. By contrast, vitamin E increases the protective effect of vitamin A against toxicity from contaminants. Vitamin A is involved in the differentiation of various tissues particularly skin lesions. Vitamin C and methionine reduce arsenic toxicity. Nutritional aspects can modify the risk for cancer.

All the listed shortcomings may promote susceptibility to arsenicosis (Islam et al. 2004; Milton et al. 2004; Smith et al. 2000). Nutrition, therefore, contributes to proper growth and development of children and to reduce the risk of toxicity from metals like arsenic. Some children in that study showed detectable arsenic levels despite reporting no well water consumption; however, it was found that cooking food in well water remained a risk factor for exposure.

Mejia (Mejía et al. 1999) had previously pointed out the high bioavailability of arsenic in the pediatric population, due to contaminated surface soil, household dust, and water in a mining zone in Mexico. The experiences of studies conducted in Bangladesh indicate that implications of this exposure in the Mexican communities could be even more alarming in the future.

17.2.3 Arsenic and Metabolic Risk

The prevalence of obesity in children has increased exponentially in recent years, reaching epidemic levels in both developed and developing countries. The data from the national nutrition survey show the combined national prevalence of excess weight and obesity in adolescents is around 35.8 % for females and 34.1 % for males; between 2006 and 2012, there was a 5 % increase for both sexes (Gutierrez et al. 2012).

In general, overweight and obesity are the result of a positive energy balance, resulting from an imbalance between the total calories consumed and calories expended. The etiology is a complex interaction between genetics, diet, metabolism, and physical activity levels (Ettinger et al. 2009). The presence of obesity promotes the development of type 2 diabetes.

Arsenic is linked with the onset of DM2. Some studies found an association between levels of arsenic and the presence of DM2 in adults in the USA. As an endocrine disruptor, arsenic could play a significant role in the incidence of diabetes mellitus (Chan et al. 2009; Ettinger et al. 2009; Navas-Acien et al. 2008).

Arsenic induces diabetes through insulin resistance and beta cell dysfunction; arsenic or its methylated metabolites can induce oxidative stress pathways or interfere with gene expression. Individual factors such as the presence of obesity or malnutrition contribute to the toxicity of arsenic (Ettinger et al. 2009), as do the presence of inflammatory processes and metabolic stress. This also promotes insulin resistance as well as diseases such as hypertension and atherosclerosis.

17.2.3.1 Pathophysiology of Arsenic and its Relation to the Development of Gestational Diabetes Mellitus

In gestational diabetes mellitus (GDM), glucose intolerance is present and there is a 30–60 % risk that the mother will develop diabetes in approximately 5 years into the future. It is considered a complication of pregnancy, with metabolic effects upon fetal development. Studies have been conducted in populations exposed to arsenic concentrations above the levels stipulated by the Environmental Protection Agency (10 mg/L), where residents are mostly Native Americans, frequently affected by DM2. Studies of blood and hair samples from pregnant women revealed arsenic levels between 0.2 and 24.1 mg/L and 1.1 to 72.4 mg/g, respectively. They also showed glucose values between 40 and 284 mg/dl between weeks 24 and 28 of gestation (Ettinger et al. 2009; Soo et al. 2009)

It is not only arsenic exposure that causes these alterations but also persistent organic pollutants (POPs) that contaminate soil and water accumulate in the tissues of animals, then make their way through the food chain until they reach humans. Depending on the concentration, some of these POPs have recently been associated with the development of DM2 (Chasan-Taber et al. 2009). For example, it is believed that metabolites of atrazine, an artificial herbicide used to control the growth of weeds in farming by inhibiting photosynthetic processes, are introduced into the human body via contaminated air, water, and food, and they accumulate in various tissues. The same applies to the animals that are in contact with food contaminated with these elements, which, in turn, will be incorporated into the food chain (Chasan-Taber et al. 2009).

In a study of mice exposed to inorganic arsenic-contaminated water, the mice developed glucose intolerance. The mechanisms for the alteration involve trivalent metabolites of inorganic arsenic, which inhibit insulin-stimulated glucose uptake in cultured adipose cells. Toxic levels of trivalent inorganic arsenic (AsIII) and methylarsonous acid (MAsIII) inhibit insulin-dependent phosphorylation of the protein PKB/Akt, which regulates translocation of GLUT4 to the plasma membrane. The effects of arsenic on glucose metabolism have been examined by numerous laboratory studies. However, these studies have been conducted with other heavy metals, mostly in animal cell cultures or mice. Navas-Acien et al. (2006) indicated that these data require further review with other study designs, where these mechanisms are evaluated in populations with environmental or occupational exposure to arsenic.

17.2.3.2 Gestational Diabetes Mellitus

GDM is defined as an intolerance to carbohydrates which is first detected during pregnancy. GDM has an estimated prevalence of 1–14 %, depending on the type and the diagnostic criteria use resulting in numbers greater than 200,000 cases per year. The prevalence of GDM in Mexico varies; figures range from 0.15 to 12.3 % and 3–4 % of pregnant women (Hernández-Zavala et al. 2007; Setji et al. 2005).

The effects of GDM on the mother during labor are a predisposition to cesarean section and long-term risk of DM2. The effects on the fetus during the first trimester are abortions, intrauterine growth restriction, and malformations (Setji et al. 2005) and during the second and third quarter, macrosomia, polyhydramnios, neonatal hypoglycemia, perinatal mortality, hyperbilirubinemia, hypocalcemia, polycythemia, and respiratory distress syndrome (Nicholson et al. 2005). The effects of macrosomia, defined as weight for gestational age above the 90th percentile or greater than 4,000 grams, are adverse events due to constant hyperglycemia in pregnant women with GDM, which leads to excessive fetal glucose and hyperinsulinemia with consequent adiposity that affects the growth and development of the fetus in utero (Ettinger et al. 2009).

Exposure to environmental pollutants, especially arsenic, alters the normal metabolism of glucose, adding to the risk factors for developing DM2. As an endocrine disruptor, arsenic is known to damage the glucocorticoid receptor that regulates a variety of biological processes in human beings, including insulin sensitivity (Barrett 2009).

Other studies have focused on explaining how oxidative stress and insulin resistance are induced by arsenic, suggesting the biological plausibility of arsenic-induced diabetes. The analysis of the National Survey of Health and Nutrition in the USA showed urinary arsenic concentrations of 8.3 mg/L, with a confidence interval of 7.19–9.57. It was found that 26 % of the higher concentrations were from people who had DM2 (Barrett 2009).

Afterthoughts Arsenic is greatly relevant because its involvement in key signaling pathways can result in metabolic disturbances, diabetes mellitus for example. The challenge becomes greater and requires integrated risk analysis methodologies and multi-causal variables to explain the impact and develop treatment options.

17.3 Sociodemographic Causes and Impact

In this chapter, we must consider the economic costs and time spent due to the lack of basic water services. The social and environmental costs associated with deficient water management fall primarily on the most vulnerable groups. Population groups that lack these services are forced to buy water from vendors, often at a price higher than that charged by either private suppliers or the public water company. They are sometimes forced to seek yet other sources that involve dedicating a greater amount of time to carrying water. This type of expenditure on vulnerable social groups implies that they remain in a continuous spiral of poverty.

The right to clean water and sanitation involves establishing mechanisms for its implementation and ongoing management (Arrojo 2006; Caldera-Ortega and Torregrosa 2010). Mexico announced in late 2008 that it had reached the targeted seven "Millennium Development Goals" with access to clean water and sanitation. When performing an analysis on the regional or local field, the data show a very different picture: In our country, this problem remains unsolved; coverage is far from adequate in marginalized areas, mainly rural, but also some urban areas. This is due largely to a lack of local institutional capacity (Balanye et al. 2005).

For many years, international institutions have acknowledged that the water crisis is a management crisis, rather than an issue of scarcity, and the problems and solutions occur in an environment of political and power processes (Balanye et al. 2005; Hutton and Haller 2004). A review of the literature related to water management usually reveals a series of figures showing the severe water crisis facing many countries, especially those least developed.

Institutional agreements have been established that should allow for a fair and equitable allocation of water for all users, ensuring quality to each of them, with a promise to find effective regulations for environmental and resource sustainability, and including social participation (Balanye et al. 2005; Hutton and Haller 2004). A sixth paragraph was added to Article 4 of the Constitution of the United Mexican States (February 2012), ascertaining that everyone has the right to access to sanitation and water for personal and domestic use; the supply should be sufficient, safe, acceptable, and affordable. The State is forced to uphold this law, while the law will define the bases, support, and arrangements for access and equitable, sustainable use of water resources, with the participation of the Federation, the states, and municipalities, as well as the citizens.

It is evident that the health and economic benefits from adequate public services such as access to clean water result in permanent benefits and a positive economic impact.

Analysis and Context The problem of access to water in sufficient quantity and proper quality is very important, as this is vital for the development of any region. Failure to ensure universal access to drinking water generates negative impacts on the social, economic, and environmental domains. The urgency of solving this problem is determinant, since it involves the fulfillment of a fundamental human right: the right to water. Timely solutions would preclude social conflicts in the dispute over water quantity and quality and prevent negative impacts on the health of the population.

The state of Guanajuato is located in the center of the country. It has a population of 5, 485, 372 inhabitants, with 46 municipalities. León is the most densely populated city, representing 26 % of the population, followed by the municipalities of Irapuato, Celaya, Salamanca, and Silao. The state of Guanajuato is located in a region considered low in water availability due to its geoclimatic features (INEGI 2011). The state is fully aware of its water management issues. León has a serious

Table 17.2 Economic benefits of investing in water and sanitation. (Source: Hutton and Haller 2004)

Beneficiary	Direct economic benefits of preventing diarrheal disease	Indirect economic benefits associated with improved health	Non-health-related benefits of improving water and sanitation services
Health Sector	Decrease in expenses related to diarrhea treatments.	Decreased number of workers ill from diarrhea.	Ecosystems benefit from more efficient management of water resources.
Patients	Costs of treating diarrheal disease and other related expenses are reduced. Decreased costs associated with seeking treatment. Less time is spent in seeking treatment.	Reduction in school days lost. Reduction of time lost by parents of children with diarrheal diseases. Reduced number of deaths.	Ecosystems benefit from more efficient management of water resources.
Consumers			Less time is spent on collecting water and gaining access to health services. Money is saved by reducing payment for water service. No need to buy water from water vendors.
Industrial and commercial sectors	Decreased treatment costs for employees with diarrheal diseases	Less impact on productivity due to workers' health	Benefits to agriculture and industry due to water supply improvements and technological improvements.

problem of water availability, hence, the urgency of building the Zapotillo dam, regardless of possible issues with the quality of water. The municipality of Irapuato is known to have problems with arsenic exposure; previous studies have also reported problems with access to clean water. In the communities belonging to the Upper Temascatio basin, the consumption of unpurified surface water is common. Also, there have been microbiological concerns about water in some León hospitals since 2004. These problems persist in spite of the evidence of arsenic incorporation in the population and the health risks derived from its presence in water and food. The scientific evidence put forth by health studies should be enough to take action towards improving water management in order to ensure the human right to water, based on the academic contributions of various scientific communities within the University of Guanajuato, including the social sciences.

The scope of this chapter provides a comprehensive assessment of water issues in the local case of Guanajuato, Mexico, but the component or causal factor is the same in worldwide problems of arsenic contamination (Table 17.2). Its impact on health should be addressed from a multidisciplinary approach, so that several disciplines converge in providing a solution. This should provide a basis for undertaking short-term water management and pollution prevention strategies. The diagnosis is that there is no institutional framework:

- To give voice to the affected population (so that it is not a priority on the public agenda).
- To hold the "providers" of basic services accountable.
- To make a point of ensuring the human right to water enshrined in our Constitution.
- To provide a multidisciplinary approach to the problem.
- To address nutritional issues, since exposure to arsenic occurs through food and drink.

A comprehensive diagnosis based on the findings can allow the advancement of management strategies for ensuring the human right to water. The strategies could focus on the following steps:

1. Analyzing aspects of quality issues considering physical, chemical, and microbiological water properties and analyzing and characterizing the risks; the ultimate goal pursued by this methodology is to facilitate decisions aimed at reducing risks to acceptable levels. All this information allows researchers to generate enough data to make recommendations to the resident population of a contaminated site for reducing exposure and to suggest activities to follow up on identified health problems.
2. Analyzing direct health risks by measuring metabolic and clinical markers in the population.
3. Diagnosing socio-environmental problems and economic and institutional issues related to water management that impede the fulfillment of the human right to water.
4. Describing aspects of the population's perception of water in the community.
5. Designing a multidisciplinary water management proposal.

Conclusions and Perspectives Promoting a good nutritional status and eating a proper diet are factors that contribute to protect the body upon exposure to metals or other contaminants. Arsenic contamination and its association with the development of metabolic diseases have been little studied, especially with regard to pathophysiological mechanisms and the intervention strategies that should be followed in exposed populations. A proposed intervention strategy should be based geared towards public benefit and prevention of obesity and malnutrition. Obesity and malnutrition expose the organism to inflammatory processes. Under these conditions, the immune system's capacity for dealing with toxic substances like arsenic is diminished. Such is the case with methylation reactions, which normally contribute to the detoxification of arsenic.

Further studies are required in our country to reinforce these hypotheses and define appropriate nutritional intervention strategies. In addition, it is important to keep in mind that the safest solution is to remove arsenic from drinking water. However, this involves great costs and technology that has yet to be developed. As health workers, we must contribute with different solution strategies.

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Chapter 18
Land-Use Changes and Their Impact on Water Resources in Himalaya

Bhagwati Joshi and Prakash C. Tiwari

Abstract This chapter attempts to assess the impacts of land-use dynamics on the environmental status and availability of water resources in Himalaya with a case illustration of Upper Kosi catchment in Kumaon Himalaya. The study used remote sensing and field-based techniques along with qualitative and quantitative empirical methods. The results indicated that population growth and the resultant increased demand of natural resources have brought about rapid land-use changes decreasing forests (4.36 %), extending cultivation (14.33 %) and increasing wastelands and degraded lands (2.18 %). These land-use changes have disrupted the hydrological regime of the catchment through increased run-off and decreased groundwater recharge and caused severe depletion of water resources. Nearly 33 % of natural springs have dried and 11 % have become seasonal, and 7.36 km stream length has dried during the last 30 years. Consequently, as many as 61 % villages have been facing great scarcity of water for drinking, sanitation as well as for crop production, and this situation turns into a severe water crisis during dry summer months. The catchment has lost 18 % of its irrigation potential due to drying of streams and springs resulting in a 25 % decline in food production which has resulted in a 32 % food deficit during 1981 and 2011. A comprehensive land-use policy based on the integrated management of land, water and forest resources needs to be evolved and implemented for the conservation and sustainable development of water resources in the region.

Keywords Headwaters · Subsistence agriculture · Population growth · Reduced groundwater recharge · Food deficit · Reduced irrigation potential · Comprehensive land-use policy

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18.1 Introduction

Himalaya is tectonically alive, economically underdeveloped and the most densely populated mountain ecosystems on the planet. Hence, Himalaya is highly vulnerable to the impacts of global environmental changes (ICIMOD 2010). Constituting headwaters of some of the largest trans-boundary river basins of the planet and one of the major global forests and biodiversity hotspots, Himalaya provides a variety of ecosystem services including water, genetic resources, soils and natural beauty (Viviroli and Weingartner 2003). These ecosystem services not only support livelihood of upstream communities but also sustain subsistence agricultural economy in its vast lowland all across Pakistan, India, Nepal, Bhutan, China and Bangladesh. The nature of terrain imposes severe limitations on the scale of productive activities as well as on efficiency of infrastructural facilities in the region. As a result, biomass-based subsistence agriculture constitutes the main source of rural livelihood and food even though the availability of arable land is severely limited and crop production is low (Maithani 1986; Singh et al. 1984). More than 75 % of the population of the region depends on traditional subsistence agriculture even though the availability of arable land is severely limited (Tiwari 2007). During recent years, a variety of changes have emerged in traditional resource-use structure in response to population growth and the resultant increased demand of natural resources, economic globalization, growth of tourism, rapid urban development, improved access to market and exploitation of natural resources. Moreover, there is a regional shift from traditional crop farming and animal husbandry system to village-based production of fruits, vegetables, flowers and milk for sale, and this has large impact on the traditional resource development process and land-use pattern (Moench 1989; Singh et al. 1984). These changes are leading to land-use intensification through rapid changes in land cover in Himalayan headwaters. As a result, natural forests, wetlands and rangelands have deteriorated and degraded steadily significantly leading to their conversion into degraded and non-productive lands (Tiwari 2000; Tiwari and Joshi 2005; Bisht and Tiwari 1996). This has an unprecedented adverse impact on basic ecosystem services, particularly water, biomass and soil nutrients leading to a decline in the productivity of the rural ecosystem and undermining food and livelihood insecurities in Himalaya (Ives 1989; Valdiya and Bartarya 1991; Joshi et al. 2003).

These changes are disrupting the hydrological system of headwaters through reduced groundwater recharge, drying of natural springs and decreased stream flow and, consequently, increasing vulnerability of large parts of the population dependent on subsistence agriculture to water, food, livelihood and health insecurity, in both upstreams and downstreams (FAO 2005). Moreover, the changing climatic conditions have already stressed the Himalayan ecosystems through higher mean annual temperatures and melting of glaciers and snow, altered precipitation patterns and hydrological disruptions and more frequent and extreme weather events. In this context, the climate change acts as an additional stress which can multiply existing development deficits and may also reverse the process of socio-economic development in the region (UNDP 2010). Further, these changes are likely to undermine the inherent capacity of mountain communities to respond and adapt to changing environmental conditions including climate change. This may increase the proportion of health-, food- and livelihood-insecure population in both upstreams and downstreams, which includes some of the poorest people of the world with access to less than 5 % of planet's freshwater resources. This will have enormous regional implications for fundamental human endeavours ranging from poverty alleviation to environmental sustainability and climate change adaptation, and even to human security. In view of this, the Himalaya is highly critical from the viewpoint of marginality, environmental sensitivity, climate change, constraints of terrain, geographical inaccessibility and low infrastructural development. The main objective of this chapter is to interpret the trends of land-use dynamics in Himalaya in its ecological and socio-economic backdrop and assess their impacts on the environmental status and availability of water resources with a case illustration of Upper Kosi Catchment in Kumaon Himalaya.

18.2 The Study Area

The Upper Kosi Catchment (upstream Someshwer), which encompasses an area of 107.94 km^2, lying between 1,405 and 2,720 m altitude above mean sea level in the Kumaon Lesser Himalaya within the newly carved Himalayan state of Uttarakhand has been selected for the present study (Fig. 18.1). The Upper Kosi Catchment is situated in the district of Almora, which, together with 12 other districts, constitutes the Himalayan state of Uttarakhand. Kosi is one of the major rivers of the west Ramganga system of Kumaon Himalaya which ultimately drains into the Ganges system. The catchment is one of the most densely populated and agriculturally colonized tracts of Kumaon Himalaya. There are in total 65 villages in the catchment and the density of the population has been calculated to be 149 persons/km^2 in 2011. Consequently, the availability of per capita cultivated land is merely 0.17 ha, and more than 90 % land holdings are of less than 1 ha. This shows that the pressure on land and other natural resources has been increasing in the region. As in other parts of Kumaon Himalaya, the traditional process of natural resource development has been changing rapidly mainly in response to the growth of the population and the resultant increased exploitation of natural resources for the past few decades. Consequently, the activities of cultivation, grazing and deforestation are extended over large areas of the region with the result that the proportion of degraded lands and wastelands have been increasing. Consequently, the critical natural resources, such as land, forests and water, have degraded and depleted steadily. The study area has been divided into four micro-watersheds for detailed study of various research parameters.

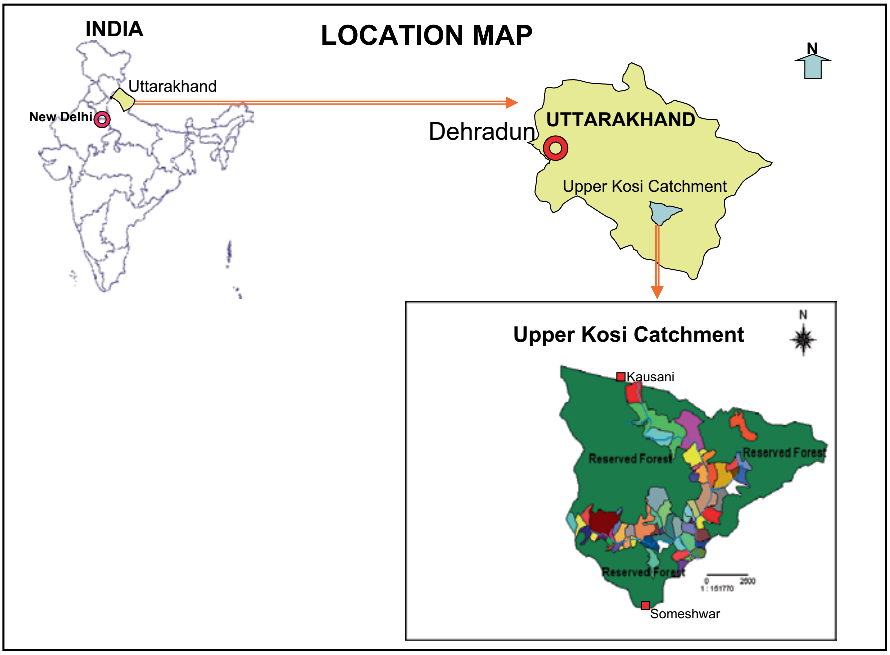

Fig. 18.1 Location map of upper Kosi catchment

18.3 Methodology

Interpretation of land use has been carried out for the years 1981 and 2011. A survey of India Topographical Maps at scale 1:50,000 has been used for land-use mapping for 1981, whereas, high-resolution satellite data were used for interpretation of land use for 2011. Digital interpretation techniques supported by intensive ground validation have been used for this purpose. The first step involved the preparation of the visual interpretation key based on preliminary interpretation of satellite data and extensive ground truth collection. This was followed by the digital classification of land cover/land use through on-screen visual recording and rectification. In order to enhance the interpretability of the remote-sensing data for digital analysis, several image-enhancement techniques, such as principal component analysis (PCA), normalized difference vegetation index (NDVI), etc., were employed. The land-use map of 1981 was digitized and a thematic layer was created, and, finally, the land-use changes that took place in the region between 1981 and 2011 were detected using change detection techniques in geographic information system (GIS; Fig. 18.2). Besides, various qualitative and quantitative empirical methods have been used for the analysis and interpretation of a range of research parameters. Necessary data and information required for the assessment of the impacts on land-use dynamics on the status and availability of water resources have been generated through primary sources employing field observations and monitoring methods, and through con-

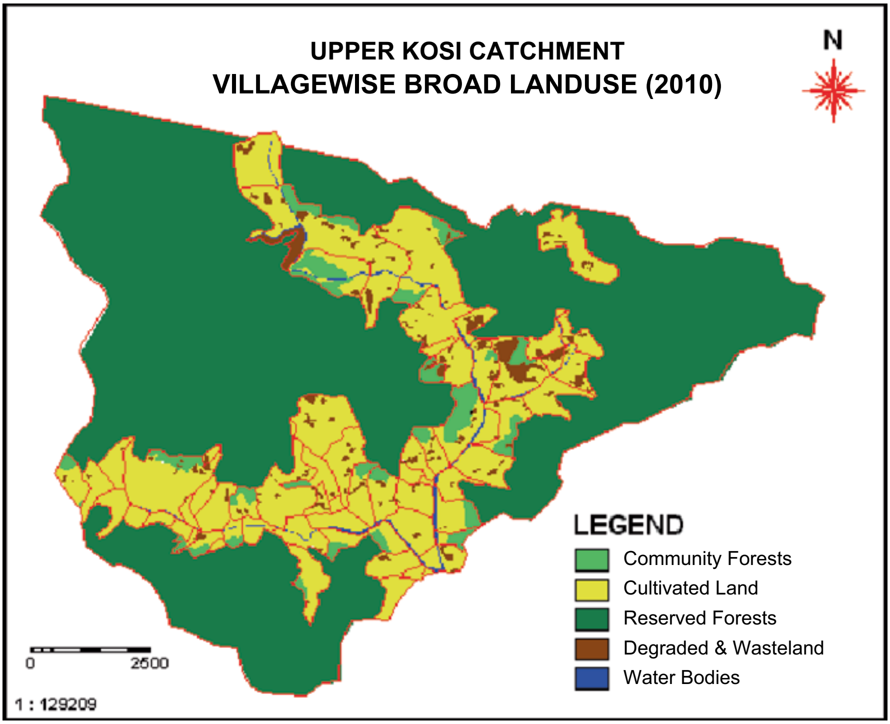

Fig. 18.2 Upper Kosi catchment: villagewise broad land use (2010)

ducting comprehensive socio-economic surveys using exclusively designed schedules and questionnaires.

18.4 Current Land Use

The current land-use pattern (2011) of the catchment has been broadly classified into (i) reserved forests, (ii) community forests, (iii) cultivated land, (iv) degraded land and wasteland and (v) water bodies which respectively constitute 68.21, 3.12, 25.73, 2.18 and 0.76 % of the total area (107.94 km^2) of the region (Table 18.1 and Fig. 18.2). The reserved forests are state property resource and they are situated outside village boundaries and supposed to be completely free from all kinds of resource-use pressures and encroachments. However, traditionally, the rural communities living interspersed in the reserved forests have enjoyed limited rights and concessions, but now these facilities have been withdrawn or limited in most of the reserved forests of Uttarakhand, particularly after the creation of a network of protected areas and the prohibition of green felling above an altitude of 1,000 m in Himalaya. Community forests, which broadly include all those forests and forest

Table 18.1 Land use changes in upper Kosi catchment between1981 & 2011 (in km^2)

Land use classes in 2011	Land use classes in 191					
	Forests area	Cultivated land	Degraded & wasteland land	Water bodies	Total (2011)	
					in km^2	% of total area
Reserved forests	73.63	–	–	–	73.63	68.21
Community forests	2.07	–	1.30	–	3.37	3.12
Cultivated land	3.34	24.23	0.20	–	27.77	25.73
Waste & de-graded Land	1.47	0.06	0.82	–	2.35	2.18
Water bodies	–	–	–	00.82	0.82	0.76
Total (1981) in km^2	80.51	24.29	2.32	00.82	107.94	100.00
Total (1981) % of total area	74.58	22.50	02.14	0.76	100.00	

land which fall inside the village boundary, except the private forests, are under common pool resources (CPRs**).** In order to involve the local people in the protection and conservation of these forests, the control of some of the community forests has now been transferred to the respective villages after reviving the system of Forest *Panchayats* (Forest *Panchayat* is a constitutional village-level institution created for participatory management of village forests in India during the British regime). During recent years, some of the village forests have also been brought under the Joint Forest Management (JFM**)** in the region. This is a recent experiment in the process of participatory forest management in the region which is currently being implemented under project mode with financial support of the World Bank. The JFM projects are being executed by non-governmental organizations (NGOs**)** through community participation. Interestingly, only 3.37 km^2 or 3.12 % of the total area of the catchment is under community forests (Table 18.1). But the availability of merely 3.37 km^2 of community forests for as many as 65 villages is highly inadequate in the region where forest-based subsistence constitutes the main source of rural livelihood. Practically, this is the only forest available to the local population for fulfilment of their all forest-based resource needs. Nevertheless, as many as 36 villages (out of total 65) in the region do not have any community forest. As a result, more than 55 % of the villages of the region are practically dependent on reserved forests for the fulfilment of their various resource needs.

As mentioned in the preceding sections, the Catchment represents one of the densely populated and intensively cultivated regions of Kumaon Himalaya (Joshi et al. 1983**).** An area of 27.77 km^{2}or 25.73 % is under cultivation of which only 15 % is irrigated. The remaining cultivated land, mainly lying upslope, and ridges are never irrigated because of non-availability of water and its inappropriate management. Although the availability of arable land is severely limited, yet, in the absence of other viable means of livelihood, dependence on agriculture is considerably high. As a result, intensity of cropping is very high (150 %). The higher cropping intensity in low agricultural potential areas symbolizes distress of cultivation of land (Maithani 1986**).** Out of the total 65 villages, 47 % are intensively cultivated with more than 75 % of their total area under cultivation, 15 have cultivated land ranging from 45 to 75 % and only 3 villages of the watershed have less than 45 % of their area under cultivation. Out of the total area of the watershed (107.94 km^2), 2.35 km^2 or 2.18 % were identified as wastelands and 0.82 km^2 or 0.76 % are under waterbodies that mainly include stream beds and tiny mountain canals.

18.5 Resource-Use Dynamics

The traditional resource utilization pattern in the region has been changing fast mainly in response to population growth (average more than 1.5 %/year) and increasing economic and social marginalization. The impacts of changes in the community resource utilization structure are clearly discernible in terms of rapid land-use changes (Tiwari 1995). Agriculture is being extended to forests and marginal and sub-marginal lands, and pastures are turning into wasteland and degraded land due to overexploitation and the resultant decline in productivity. With rapid growth of population, the pressure on cultivated land has increased, and more than 90 % of the land holdings are of less than 1 ha. Consequently, the availability of cultivated land is merely 0.14 ha/person against a minimum of 0.2 ha/person as required for practising agriculture on a sustainable basis in the high Himalayan mountain ecosystem (Ashish 1983).

Out of the total 65 villages of Upper Kosi Catchment, as many as 36 have no forests within their boundaries, and per capita availability of forests in the remaining 29 villages is below 0.15 ha. In Himalaya, 5–10 ha well-stocked forest is required to support biomass requirement of 1 ha of agricultural land on sustainable basis (Singh et al. 1984), whereas in the Upper Kosi Catchment, the availability of forest to per hectare of cultivated land ranges between 0.10 and 2.07 ha. The grazing pressure is also very acute as only 0.02–1.67 ha/cattle grazing area is available in the catchment against the ecologically recommended norm of a minimum of 3.5 ha/cattle (Singh et al. 1984).

18.6 Land-Use Changes

Results of land-use change detection exercise revealed that out of a total area (107.94 km^2) of the region, 8.44 km^2 or 7.81 % have changed from one land use to another during 1981–2011. Table 18.1 makes it clear that in contrast to the general conception, the agricultural land in the region has not increased much during the last 30 years. The total cultivated land has increased from 24.29 km^2 in 1981 to 27.77 km^2in 2011, and, thus, registered an overall increase of 14.33 %. This increase in cultivated land has been brought through the extension of cultivation in forests (3.34 km^2) and wastelands (0.20 km^2). The area under forests in the catchment has declined from 80.51 km^2 in 1978 to 77.00 km^2 (73.63 km^2 reserved forest and 3.37 km^2 community forests) in 2008 mainly due to diversion of 3.34 km^2 forest land to agriculture and turning of 1.47 km^2 community forests into degraded lands

Table 18.2 Changes in status of water resources in upper Kosi catchment (1981–2011)

Micro-watersheds	Total area (km^2)	Springs dried (in %)	Springs become seasonal (in %)	Stream-length dried (in m)
North Kosi	44.23	41	17	311
East Kosi	29.18	36	11	227
West Kosi	23.37	47	21	114
South Kosi	11.16	11	05	84
Total	107.94	33.75	10.80	736

and wastelands, thus registering a total decrease of 4.36 %. Wasteland has increased from 2.32 km^2 or 2.14 % in 1978 to 2.35 km^2 or 2.18 % in 2008 as 1.47 km^2 forests and 0.06 km^2 cultivated land were converted into wasteland in the catchment. But, at the same time, 0.20 km^2 and 1.30 km^2 wasteland have been brought, respectively, under cultivation and community forests in the region during the last 30 years (Table 18.1).

18.7 Impact of Land-Use Changes on Water Resources

These land-use changes are of great significance in the ecologically fragile, tectonically live and economically underdeveloped Himalaya as the ecosystem services that it provides support one of the most densely populated regions of the world dependent on subsistence agriculture. Excavation of fragile slopes for road and house construction, removal of vegetal cover, extension of agriculture to marginal and sub-marginal areas and forests and intensification of land use under the impact of changing resource-use practices are leading to rapid environmental changes in the Himalayan watersheds (Tiwari and Joshi 2007, 2005). The decrease in forests has disrupted the hydrological regime of the Himalayan watershed. Studies indicate that the amount of surface run-off from cultivated (80 %) and barren land (85 %) is much higher compared to that from forests (25 %; Tiwari 1995, 2000). These hydrological disruptions are now clearly discernible in (i) a long-term decreasing trend of stream discharge, (ii) a diminishing discharge and drying of springs and (iii) biotic impact on the surface run-off flow system and channel network capacity (Ives 1985; Rawat 2009; Tiwari and Joshi 2012).

The study revealed that out of a total of 107 springs of the Kosi headwater, nearly 33 % have completely dried up and more than 11 % have become seasonal during the last 30 years (Table 18.2), mainly due to large-scale deforestation and the resultant loss of water-generating capacity of the soil (Tiwari 2000; Rawat 2009). It was observed that more than 75 % of the dried springs are located in areas where the forests have been either brought under agriculture or converted into degraded land. The application of change detection techniques using remote-sensing data also revealed that a stream length of 7.36 km has completely dried up out of the total of 26 km of stream length in the Kosi headwater due to rapid land-use changes as a dried stream length of more than 2.5 km lies in wastelands and degraded lands. The

Table 18.3 Changes in water availability, biomass supply and irrigation potential in upper Kosi catchment (1981–2011)

Micro-watersheds	% Villages facing water scarcity	% Decrease in biomass supply to agriculture	% Irrigation potential reduced	% Agricultural productivity declined
North Kosi	67	35	14	25
East Kosi	51	29	17	33
West Kosi	69	41	21	19
South Kosi	57	58	19	24
Total	61	41	18	25

degradation of land and forests is not only reducing groundwater recharge resulting in the decline of water-generating capacity of land, but also rendering the degraded and fragile mountain slopes highly vulnerable to landslides and other such natural hazards in the headwater. As many as 17 active landslides have been identified on the deforested and degraded slopes in the region.

Moreover, the rapid degradation of forests and the resultant decline in the availability of water resources have increased the vulnerability of the region to resource deficiency resulting in food and livelihood insecurity. Currently, the region faces a huge deficit of food (42 %), fodder (46 %) and fuelwood (44 %). Table 18.3 shows that as many as 61 % of villages have been facing a great scarcity of water for all purposes where the situation turns into severe water crisis during dry months. As a result, people of the headwater have to walk up to 5, 7 and 2 km for the collection of fodder, fuelwood and water, respectively. A study revealed that the depletion of forests and the resultant hydrological disruptions have caused a 29 % (East Kosi) to 58 % (South Kosi) decline in supply of biomass to agro-ecosystems and a loss of 14 % (East Kosi) to 21 % (South Kosi) of irrigation potential (in terms of irrigated area) in different micro-watersheds of the Upper Kosi Catchment during the last 30 years (Table 18.3). The loss of primary ecosystem services, particularly water and biomass, has a direct adverse impact on the productivity of the subsistence agricultural system. The different micro-watersheds of the Upper Kosi Catchment have lost their agricultural productivity ranging from 19 % in West Kosi to 25 % in North Kosi with an overall decline of 25 % (Table 18.3).

The study made clear that the entire Kosi headwater is now facing severe water deficiency, which is evinced by inadequate or even non-availability of water for various domestic needs and decline of irrigated land in the region. The main reason investigated for increasing the scarcity of water for both domestic and irrigation was the rapid depletion of water resources in the watershed. However, it was also observed that improper management, conservation and utilization of available water resources are also contributing towards increased water stress in the region to some extent. For instance, no measures have so far been taken for converting huge amounts of run-off during the monsoon season into water resource, wider rain water harvesting and inter-catchment transfer of water (particularly transfer of water from snow-fed rivers to rain-fed water scarcity basins) for meeting the growing demand of drinking and irrigation water, and even effective strategies for replenishing, regeneration and conservation of dwindling water resources are extremely lacking in the entire region. Furthermore, it was observed during the field surveys that in a number of villages, the water supply is irregular and mainly due to inappropriate maintenance and inefficient governance of the water supply system causing great hardship to local people and resulting in the underdevelopment of the entire region.

18.8 Conclusions

During the last three decades, there has been significant conversion of forests into cultivated and degraded land in the Himalaya. As a result, the proportion of both agricultural lands and wastelands have increased, while the area under forests has declined in the region. The main driving forces of these land-use dynamics are the population growth and the resultant changes in community resource-use structure. These land-use changes have shown an unprecedented adverse impact on the water-generating capacity of land to springs and streams, biomass supplies to agro-ecosystems and productivity of natural resources in the region. As a result, a considerably large proportion of natural springs and heads of a number of perennial streams have dried affecting rural water supplies, leading to a loss of irrigation potential and rendering rural areas highly deficit in food, fodder and fuelwood. These ecological impacts of ongoing land-use changes have not only undermined community health, threatened the livelihood and food securities of rural poor but also increased the trends of outmigration of entrepreneuring rural male youths and, thus, have contributed to further worsening the quality of rural life in the region. The conservation of water resources is, therefore, closely interlinked with rationalizing rural resource utilization patterns and management of land and forest resources in the region. In view of this, it is highly imperative to evolve integrated land-use policies, which are conservation oriented, and also attune to community resource needs and developmental priorities.

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Index

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