Rouf Ahmad Bhat
Khalid Rehman Hakeem *Editors*

Bioremediation and Biotechnology, Vol 4

Techniques for Noxious Substances Remediation

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Dedicated to the scientist community of our native land (Jammu and Kashmir), whose outstanding contribution in the field is a moment of gratitude

Foreword

Prof. Dr. Münir Öztürk (M.Sc., Ph.D., D.Sc., FIAS),
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Global sustainability is facing a critical situation due to overpopulation under limited existing natural resources following the changes in our life styles. We need sustainable environmental management systems such as biotechnology for a re-establishment of our resources. One of the problems which need to be tackled is use of biotech in bioremediation, as one of the processes for protection of our environment. However, we are facing difficulties due to ecological and economic reasons. There is need to develop ways for a sustainable restoration of our environment depending on the biochemistry, bioavailability and bioactivity of pollutants.

Bioremediation is considered as a sustainable approach to degrade and detoxify the contaminants in our environment. Although this approach is in use for the last six decades it is often successful but with few desirable results. Sometimes instead of degradation of a contaminant, more toxic daughter products are produced. The key to successful bioremediation is to trap up the naturally occurring potential of microorganisms for an effective transformation of pollutants.

The editors of the current series titled "Bioremediation and Biotechnology" have finished 3 volumes till now. First volume has been edited by Khalid R. Hakeem, Rouf Ahmad Bhat and Humaira Qadri, which presents information on "sustainable approaches to pollution degradation". The second volume has been edited by Rouf Ahmad Bhat, Khalid R. Hakeem and Monisa Aslam Darvish covering chapters on the "degradation of pesticides and heavy metals". The third volume has been edited by Rouf Ahmad Bhat, Khalid R. Hakeem and Najla bint Saud, which includes chapters on "persistent and recalcitrant toxic substances".

This edition is the 4th in line and includes 15 chapters presenting detailed information on "viable techniques for remediation of noxious substances in stressed environs". The contributions include chapters mainly from different states of India, Brazil and Romania.

Chapter 1 addresses the concerns and threats of heavy metals contamination on aquatic ecosystem. The reasons of toxicity are noted as non-degradability and high bioaccumulative potential in aquatic taxa, which of course varies with the metal concentration, speciation and physiology of the target species.

Chapter 2 presents valuable information about the pollution in aquatic environments stressing on the sources and consequences. It is mentioned here that water has the ability to be diverted, transported, stored, and recycled and is one of the most manageable natural resources; however, it is often a difficult task to mitigate some of the water pollution problems, because each case requires its own science and interdisciplinary expertise with its own technological, economic and social facets. The authors stress the fact that in the next few decades the mitigation of these pollutant sources will require huge funding and research into efficient technology for removal.

In Chap. 3, recent scenario of groundwater quality in northwest Himalayas has been highlighted, describing the source of chemical ions and quality of groundwater in parts of Srinagar district, Kashmir. A high positive correlation has been reported among the chemical variables indicating a dominant influence of carbonate as compared to the silicate lithology. The concentrations of major ions of groundwater are reported to lie well within the maximum permissible limits for drinking purpose. Nevertheless, the increasing tendency and enrichment of water with respect to K^+, NO_3^- and Cl^- is given as an alarming indication of contamination of shallow aquifers.

Chapter 4 addresses the work on polycyclic aromatic hydrocarbons (PAHs) and their toxic effects as the highly persistent ubiquitous recalcitrant organic compounds and their bioremediation strategies. These are mutagenic as well as carcinogenic in nature and considered as priority pollutants. Authors point out that large numbers of PAHs in soil are taken up by plants and enter our food chain causing serious health problems. Their removal is needed following microbial bioremediation as a pivotal process. Authors say that this technology needs further attention from the research community to make it successful and economical for its evaluation in cleaning and restoration of the sites contaminated with persistent pollutants.

The authors of Chap. 5 have presented information on the threats and risks of contamination load on different biota. They have discussed the data on various types of pesticides used in agriculture to safeguard the products from various types of heavy metals contaminating different biota. The contamination from these harmful substances in the environment causes various defects not only to the humans but also to other organisms living in association with them.

The Romanian researcher group has discussed the data on the mechanisms and importance of phytoremediation in Chap. 6. They mention about the use of plants as an interesting tool to promote environmental restoration. The chapter focuses on the mechanisms and importance as a strategic method of dealing with the restoration of polluted environs – an essential step towards achieving sustained development in respecting the environment and developing environmental awareness.

The data on the role of soil biota and associated threats has been discussed in Chap. 7 prepared by a group of scientists from Kashmir and Saudi Arabia. The authors have elaborated the values of soil biota which plays an essential role in the proper working of biological systems and for sustaining life on Earth because they are engaged in ecological, biotechnological and metabolic processes vital for human survival. The authors stress that the effects of different ecosystem services, in particular soil microorganisms (bacteria and fungi), have not yet been completely investigated. The physical properties of soils are affecting the activity of microorganisms; for maintenance of soil biota and ecosystem services, environment-friendly management practices need to be followed.

The researchers from Romania are sharing the information on the "viability of in-situ and ex-situ bioremediation approaches for degradation of noxious substances in stressed environs" in Chap. 8. They discuss at length the soil pollution problems, because soil regeneration is one of the main components of sustainable community development. The authors point out that it can be the basis of environmental improvement, social cohesion and economic growth. According to these scientists, it is necessary to consider the introduction of functional regulations regarding the prioritization, investigation and remediation of soils that could present an unacceptable risk to human or environmental health, especially due to the inheritance of industrial activities. Authors are stressing on the remediation of contaminated soils (SCs) which need to be addressed systematically, depending on the degree of pollution, its complexity and risks. A de-pollution solution already used is proposed for implementation in a certain locality, preceded by a stage of pollution assessment and a series of experimental remedial studies at other sites which can determine the viability of the solution for the given situation.

"Bioremediation: a viable approach for degradation of petroleum hydrocarbons" is the topic of Chap. 9 prepared by scientists from Romania. The authors are discussing the bioremediation of soils contaminated with oil and petroleum products where the hydrocarbons are degraded through indigenous microorganisms

(MOs). MOs are reported to degrade the hydrocarbons partially or completely and the result of their microbial activity is non-polluting for the environment, being made up of water, CO_2 and non-toxic substances. They conclude that development of more efficient and sustainable technologies contributing in the improvement of the process of remediation of contaminated soils is essential.

Another group of authors from Kashmir have presented their views on the "application of macrophytes for remediation of wastewater in constructed wetlands" in Chap. 10. The authors mention that the use of macrophytes for pollution cleanup is an emerging technology involving the use of specialized plants for waste removal from natural ecosystems. According to these workers the important parameters that should be kept in mind include macrophyte species, pH, temperature and salinity of the target waters. The chapter stresses on the evaluation of macrophytes for wastewater remediation using constructed wetlands.

The scientists from Brazil have pooled up data on the application of biotechnology for restoration of degraded environs in Chap. 11. It focusses on different strategies offering options available for use in optimized way to remediate different kinds of environs. The use of plants, microorganisms, biochars, nanomaterials and also the genetic manipulation of living beings are discussed as tools to develop efficient and safe protocols to try to repair the damages of our ecosystems.

Chapter 12 titled "Role of Free Floating Aquatic Plants in Abatement of Disturbed Environs" provides information on the use of aquatic macrophytes, as they provide a considerable reinforcement to the structure and functioning of aquatic ecosystems. As per the authors, owing to their noteworthy significance in aquatic environments, exploration on aquatic floras continues to flourish. The macrophytes are presented here as efficient tools for cutting back pollution as compared to other bioagents because of their being cost-effective and manageable.

The title "Genetically Modified Microbes as Biofertilizers" is the topic of Chap. 13. According to the authors of this chapter, utilization of advantageous microorganisms as biofertilizers is of utmost importance in agriculture. They form an important part of nutrient management system in plants and play a vital role in enhancing sustainability as well as productivity of soil. These researchers mention the fact that biofertilizer production by using the tools of molecular biotechnology like recombinant DNA technology can perk up the metabolic pathways of production of significant plant growth promoting factors, if recognized and transmitted to the valuable plant growth promoting microbes. Authors write that the genes of microbes can be optimized or improved by means of various genetic modifications, which offer an improved nutrient accessibility to plants and thus enhance plant development.

The authors of Chap. 14 have presented valuable information on "nanotechnology: a modern waste management approach". They have presented the use of an efficient nanofilter and Ag, Cu, ZnO and TiO_2 nanoparticles (nps), carbon nanotubes, and the manufacturing concept of nanotechnology which is becoming more efficient in the management and safe disposal of hazardous waste constituents.

Chapter 15 "Restoration of Heavy Metal Contaminated Environs Through Ectomycorrhizal Symbiosis" is presented by scientists from North India. The authors discuss the role of specialized fungi in heavy metal remediation. Furthermore, this chapter presents an overview of heavy metals, their influence on living systems and remediation through ectomycorrhizal symbiosis.

This edited volume covers important information of great scientific value. The editors need full appreciation for the commendable work done in bringing out this fourth volume in the series. The editorial team has spent great efforts in bringing together chapters from different parts of world to address pollution problems in a sustainable way with the latest findings related to the biotechnology and bioremediation. I am sure that it will serve as a valuable resource material for scientists working in the fields of biotechnology and related sciences. Great efforts have been spent by the editors for this praiseworthy contribution.

Preface

A healthy environment is a potion to sustain life on Earth. Consequently, its components are the backbone for living creatures. The living organism from microscopic to macroscopic has a good survival rate in quality environs. The population explosion has disturbed the quality of environments from sustainable to unsustainable. Furthermore, rapid thriving of industries, conversion of agricultural land to residential areas, habitat destruction, deforestation and use of synthetic recalcitrant substances enhanced the rate of degradation of the environment. Discharge of untreated sewage, chemical substances, agricultural runoff and crude dumping of solid wastes are further strengthening the issues of degradation of environmental quality.

Nowadays, people are working continuously to overcome the issues/problems raised due to anthropogenic activities. There are numerous conventional techniques available for degradation and cleaning of noxious pollutants from disturbed environs, but their inefficiencies, particularly for removal and degradation of hazardous and toxic substances, offer a gap for treatment technologies. Moreover, these techniques utilize plenty of energy, efforts and are costly to install.

Monitoring and evaluation of pollution load in different environs play a pivotal role, as far as remediation and restoration of disturbed environs are concerned. Biomonitoring by way of evaluating the relationship of biota about polluted/stressed environs has gained wide credibility. Living organisms respond effectively with disturbed environs, hence these organisms could be the asset to detect/check pollution load in disturbed environs and could be valuable indicators for monitoring pollution in stressed environs.

Plant chemistry has a history for being a friend of the environment. Nowadays, it has gained vast popularity concerning the cleaning of toxic substances in disturbed environs in an ecofriendly manner. This kind of property in plants for remediation and restoration of degraded environs always maintains the quality and health status of ecosystems.

This book (4th of its series) is an eloquent group of various chapters, relevant to the veracity of biotechnology and bioremediation as viable techniques for remediation of noxious substances in stressed environs. It is an amalgam of important topics, namely, pollution in aquatic environs – sources and consequences, contamination load in aquatic environs – impacts and challenges, pollution phenomenon in bottom sediments in stressed environs, threats and risks of contamination load on different biota, current scenario of treatment technologies for removal of noxious substances in stressed environs, credibility on biosensors for monitoring the contamination levels in disturbed environs, the role of ecofriendly techniques and approaches for remediation of contamination levels in different environs, phytotechnology – a remediation tool for sustainable environs, the role of plants for degradation of noxious pollutants in stressed environs, values of aquatic plants for removal of toxic substances from aquatic environs, the role of free floating macrophytes in the abatement of disturbed environs, mechanism and importance of phytoremediation, credibility on biotechnology for sustainable degradation of noxious pollutants, bioremediation – a viable approach for degradation of noxious pollutants, the viability of in-situ and ex-situ bioremediation approaches for degradation of noxious substances in stressed environs, phytoremediation technology – a sustainable solution for cleaning up of noxious pollutants from disturbed environs, application of biotechnology for the restoration of degraded environments. Starting chapters of this book bind dealing with the stress of noxious substances and their consequences in different environs, followed by the techniques dealing with the quantitative and qualitative evaluation of noxious substances, and closing chapters address biotechnological role in the remediation of noxious substances in stressed environs.

This book is a meticulous description of the ecofriendly treatment strategies for noxious substances in stressed environs. In general, the book is an essential bind about an intrusion of sustainable technologies for remediation of noxious pollutants and a core guide for academicians, researchers, scientists and students.

Srinagar, Jammu and Kashmir, India Rouf Ahmad Bhat
Jeddah, Saudi Arabia Khalid Rehman Hakeem

About the Book

This book is an articulate group of various chapters, relevant to the veracity of biotechnology and bioremediation as viable techniques for remediation of noxious substances in stressed environs. It is an amalgam of important topics, namely, pollution in aquatic environs – sources and consequences, contamination load in aquatic environs – impacts and challenges, pollution phenomenon in bottom sediments in stressed environs, threats and risks of contamination load on different biota, current scenario of treatment technologies for removal of noxious substances in stressed environs, credibility on biosensors for monitoring the contamination levels in disturbed environs, the role of ecofriendly techniques and approaches for remediation of contamination levels in different environs, phytotechnology – a remediation tool for sustainable environs, the role of plants for degradation of noxious pollutants in stressed environs, values of aquatic plants for removal of toxic substances from aquatic environs, the role of free floating macrophytes in the abatement of disturbed environs, mechanism and importance of phytoremediation, credibility on biotechnology for sustainable degradation of noxious pollutants, bioremediation – a viable approach for degradation of noxious pollutants, the viability of in-situ and ex-situ bioremediation approaches for degradation of noxious substances in stressed environs, phytoremediation technology – a sustainable solution for cleaning up of noxious pollutants from disturbed environs, and application of biotechnology for the restoration of degraded environments. Starting chapters of this book bind dealing with the stress of noxious substances and their consequences in different environs, followed by the techniques dealing with the quantitative and qualitative evaluation of noxious substances, and closing chapters address biotechnological role in the remediation of noxious substances in stressed environs. In general, the book is an essential bind about an intrusion of sustainable technologies for remediation of noxious pollutants and a core guide for academicians, researchers, scientists and students.

Contents

About the Editors

Rouf Ahmad Bhat (Ph.D.) is working at Cluster University of Srinagar, Jammu and Kashmir, India, on the capacity of Assistant Professor and has his specialization in Limnology, Toxicology, Phytochemistry and Phytoremediation. Dr. Bhat has been teaching graduate and post graduate students of Environmental Sciences for the past 3 years. He is an author of more than 50 research papers and 30 book chapters, and has published more than 15 books with international publishers. He has presented and participated in numerous State, National and International conferences, seminars, workshops and symposiums. Dr. Bhat has worked as an associate Environmental Expert in World Bank funded Flood Recovery Project and also Environmental Support Staff in Asian Development Bank (ADB) funded development projects. He has received many awards, appreciations and recognitions for his services to the science of water testing, air and noise analysis. He has served as editorial board member and reviewer of reputed international journals. Dr. Bhat is still writing and experimenting with diverse capacities of plants for use in aquatic pollution.

Khalid Rehman Hakeem (Ph.D.) is Professor at King Abdulaziz University, Jeddah, Saudi Arabia. After completing his doctorate (Botany; specialization in Plant Eco-physiology and Molecular Biology) from Jamia Hamdard, New Delhi, India, in 2011, he worked as a lecturer at the University of Kashmir, Srinagar, for a short period. Later, he joined Universiti Putra Malaysia, Selangor, Malaysia, and worked there as Postdoctoral Fellow in 2012 and Fellow Researcher (Associate Professor) from 2013 to 2016. Dr. Hakeem has more than 10 years of teaching and research experience in plant eco-physiology, biotechnology and molecular biology, medicinal plant research, plant-microbe-soil interactions as well as in environmental studies. He is the recipient of several fellowships at both national and international levels; also, he has served as the visiting scientist at Jinan University, Guangzhou, China. Currently, he is involved with a number of international research projects with different government organizations. So far, Dr. Hakeem has authored and edited more than 45 books with international publishers, including Springer Nature, Academic Press (Elsevier) and CRC Press. He also has to his credit more than 100 research publications in peer-reviewed international journals and 55 book chapters in edited volumes with international publishers. At present, Dr. Hakeem serves as an editorial board member and reviewer of several high-impact international scientific journals from Elsevier, Springer Nature, Taylor and Francis, Cambridge, and John Wiley Publishers. He is included in the advisory board of Cambridge Scholars Publishing, UK. Dr. Hakeem is also a fellow of Plantae group of the American Society of Plant Biologists; member of the World Academy of Sciences; member of the International Society for Development and Sustainability, Japan; and member of Asian Federation of Biotechnology, Korea. Dr. Hakeem has been listed in Marquis Who's Who in the World, since 2014–2019. Currently, Dr. Hakeem is engaged in studying the plant processes at eco-physiological as well as molecular levels.

Chapter 1
Concerns and Threats of Heavy Metals' Contamination on Aquatic Ecosystem

Mehvish Hameed, Zulaykha Khurshid Dijoo, Rouf Ahmad Bhat, and Irteza Qayoom

1.1 Heavy Metal Sources

Heavy metals (HMs) gain their entry into the environs by natural plus anthropogenic sources, thereby impairing the soil, water, and air plus their interface considerably if they are present above certain level. Figure 1.1 shows heavy metal sources and their cycling through various components of environmental settings (Brady et al. 1994).

1.2 Natural Sources

Most studies have reported various natural sources of HMs. The discharge of HMs by natural sources depends on certain environmental conditions. These sources comprise of emissions from volcanoes, sea salt, natural forest fires, breaking of heavy metal containing rocks, biological sources, and windblown soil particles. Heavy metals are released as hydroxides, oxides, sulfides, sulfates, phosphates, silicates, as well as in the form of organic composites. These toxic HMs enter the water bodies and change the water chemistry, thus affecting the aquatic biota present there. The most common HMs are Pb, Ni, Cr, Cd, As, Hg, Zn, and Cu. Even though

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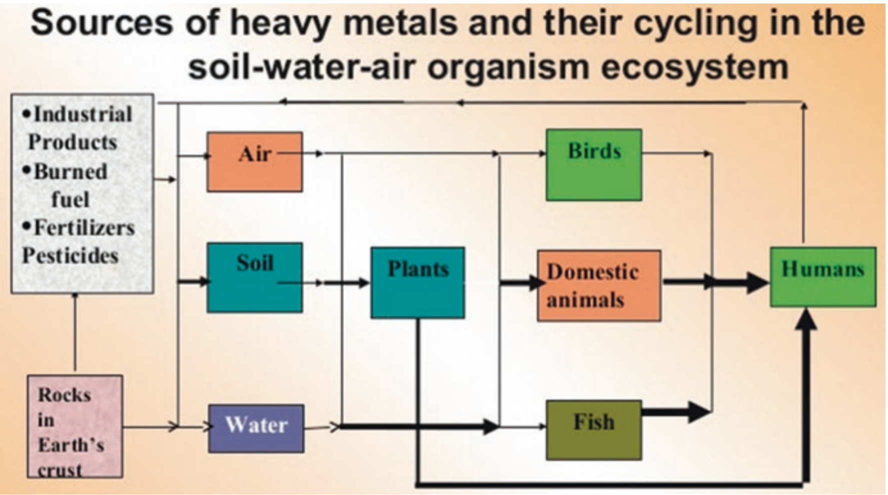

Fig. 1.1 Sources of heavy metals with their cycling in the environment. (Brady et al. 1994)

they are present in trace quantities, these metals have extreme consequences on all organisms (Herawati et al. 2000).

1.3 Anthropogenic Sources

Anthropogenic activities are chiefly behind HM pollution. The main sources are untreated water discharge from industries, agricultural inputs, and domestic effluents; mining and metallurgical processes all add a bulk of HMs into the environment. The introduction of these HMs into an ecosystem due to anthropogenic activities has changed the natural fluxes of these metals. Some significant HM contaminants released from anthropogenic sources which considerably add to the biosphere include lead from vehicular exhaust; arsenic, copper, and zinc from smelting processes; arsenic by insecticides; and nickel, vanadium, mercury, tin, and selenium released from combustion of fossil fuels. To meet the needs of rising human population, humans have significantly contributed to the environmental pollution (He et al. 2005; Bhat et al. 2017)

1.4 Pollution by Heavy Metals

Presently, environmental pollution is among the most paramount existential challenges to mankind. HM presence in the environment at such high concentrations poses a great danger to the environment and may harm environmental components if they are present above certain levels. The combination of population growth and economic development has resulted in amassing of hazardous amount of HMs in the environment. In addition to this, heavy metal mobilization as well as transport in the surroundings has significantly augmented ever since 1940. The HM enters the water bodies via numerous means like effluent/waste discharges, surface runoff, and leachates besides atmospheric depositions through various activities taking place in urban and industrial areas. HMs are often cumulative toxins and strongly affect people when ingested. Accumulated toxic substances tend to increase in concentration and are often present in single tissue (Ansari et al. 2004). The bioaccumulative potential of HMs can result into a wide-ranging concerns fluctuating from molecular alterations to elimination of local fish populations (Massaquoi et al. 2015). Moreover, the existence of deadly concentrations of HMs in bottom-dwelling species has considerably decreased their diversity and affected their development as well as reproductive potential. Sediments cast a noteworthy role in growth, development, and evolution of aquatic beings in addition to acting as a pollutant sink. River hydrodynamics and biogeochemical cycles, besides environmental settings, are among the various processes which govern the dynamics of toxic pollutants in the aquatic ecosystem.

1.5 Heavy Metal Pollution in Aquatic Environs

Heavy metals are among the leading hazards to both terrestrial and marine habitats (Slaveykova and Cheloni 2018). Once they are discharged from natural and anthropogenic sources, HMs contaminate water bodies, underlying sediments, air, and the soil (Singh et al. 2018). HMs gain their entry into the air by volcanic eruptions and from industries. This ultimately reaches to the land, thereby resulting in water and soil pollution. Due to its persistent nature in the environs, HMs either accumulate in biota or are leached into groundwater. Globally heavy metal pollution is becoming a grave subject of alarm as it has protracted motivation due to the rise in the usage and handling of HMs during numerous activities to encounter the requirements of the fast increasing populace. Heavy metal concentration in various environments is ruled by its dose plus the contact period (Khan et al. 2011). Hydrosphere, lithosphere, and biosphere are the chief notable constituents of the environment being affected by heavy metal pollution.

1.6 Effect on Water

Heavy metals released from different sources contaminate the water bodies. It is an environmental concern that has a negative influence on flora, fauna, and human well-being (Rezania et al. 2016). Even at lower quantities, heavy metals pose extreme danger to aquatic species (Akif et al. 2002). HMs can be a source for chief histopathological modifications in bodies of aquatic creatures such as fish (Ahmed et al. 2014). Industrialization and urbanization are the two most important sources which have contributed significantly in the heavy metal water contamination. HMs are transported to the water bodies through effluents from industries and sewage inputs besides from agricultural runoff (Afzal et al. 2018), most of which finish up amassing in the soil plus in sediments too (Musilova et al. 2016).The influx of industrial effluents into the aquatic bodies is the principle origin of surface water plus groundwater contamination (Afzal et al. 2018). Effluents from mining operations also result in accumulation of HMs in the aquatic settings (Zhuang et al. 2013). Because of their environmental persistence and bioaccumulation and biomagnification of HMs in food chains, they have become a worldwide problem (Rajaei et al. 2012). Even its presence in smallest amount in aquatic environments can be much toxic to humans as well as other species plus posing serious health challenges. The metal toxicity level depends on various factors like its type, biological functioning, and duration of exposure to the toxic metal. In fact, all aquatic organisms get affected by the contamination of heavy metals. Humans are much susceptible to serious health issues due to the process of biomagnification (Lee et al. 2002) and its presence at upper trophic level. The health impacts of heavy metals are listed in Fig. 1.2.

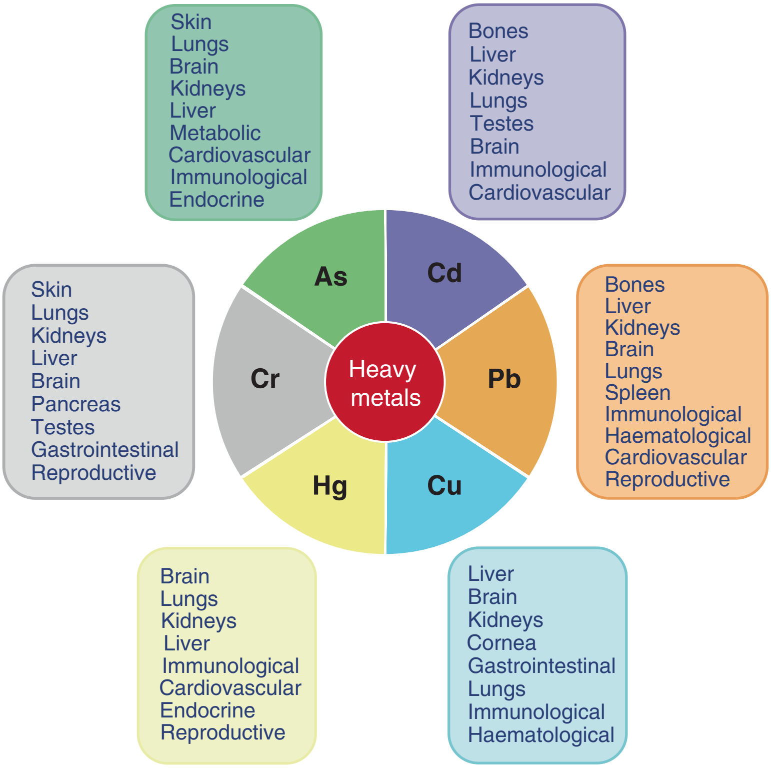

Fig. 1.2 Heavy metal impacts on human health

1.7 Sediments

Sediment in the aquatic systems is the chief repository and source of HMs. Sediments execute a substantial role in the relocation and in storing of potent toxic heavy metals (Yan et al. 2010; Gao and Chen 2012). It is like a needle pointing to the fact that the water is polluted (Zahra et al. 2014). Sediments are the sink and source of HMs, liberating the HMs into the water column back upon any disturbance (Fernandes and Nayak 2012). The HM buildup in sediments nearby inhabited zones can deliver the confirmation of the human influences on this ecological unit and aids in evaluating the threats linked with the discarding of human waste (Demirak et al. 2006; Balls et al. 1997). Sediments contaminated with HMs are an environmental concern having consequences on aquatic species plus human health. Unending accretion of HMs in sediments may likewise add to the pollution of groundwater (Sanyal et al. 2015). A number of physical and chemical factors regulate the adsorption, desorption, and content of HMs in sediments. These factors include temperature, hydrodynamic settings, redox conditions, number of microbes, salt levels, as well as size of sediment particles (Zhao et al. 2014). In addition to these physical and chemical factors, concentration of HMs in sediments is dependent on chemical composition and concentration of organic matter (Azadi et al. 2018). The bioavailability of metal in sediments has a relationship with the pH also. pH decline impacts binding of metal ions and H^+ in sediments resulting in dissolution of metal complexes, thus liberating free heavy metal ions into the water (Nowrouzi et al. 2014). In riverine sediments, if concentration of heavy metals is high, it may be an ecological risk to benthic organisms (Decena et al. 2018).

1.8 Heavy Metals: Bioavailability and Biological Role

Bioavailability of heavy metals is regulated by physical, chemical, as well as biological factors. The physical factors are temperature, phase association, adsorption, and sequestration. The chemical factors are speciation at thermodynamic equilibrium, complexation kinetics, lipid solubility, and octanol/water partition coefficients (Hamelink et al. 1994). Biological factors like species features, trophic connections, and biochemical/physiological variation are influential (Verkleji 1993). In biological systems, it has been reported that heavy metals impact cellular organelles and other constituents like cellular sheath, mitochondria, lysosomes, endoplasmic reticulum (ER), nucleus, and other metabolism-affecting enzymes and detoxification, besides cellular damage repairing (Wang and Shi 2001). Metal ions also influence cellular constituents like DNA and nuclear proteins, resulting in DNA interference plus conformational adjustments leading to the modification of the cell cycle, mutagenesis, or apoptosis (Chang et al. 1996; Wang and Shi 2001; Beyersmann and Hartwig 2008). The accumulation of lethal substances may result in biomagnification in animals. In aquatic ecosystems, heavy metals of utmost alarm are Cu, Zn, Hg, and Pb as well as Al, Cr, Se, Ag, Ar, and Sb. These heavy metals have magnified the issues associated with the aquatic systems (freshwater, coastal, as well as estuarine ecosystems). These heavy metals when present in a concentration exceeding the threshold are detrimental to organisms although few of them like copper and zinc are vital for metabolism at lesser concentrations.

Few heavy metals don't have any influence on any biological processes of living beings. They remain there in the body in the harmful form and elicit harmful effects, thus affecting their biology. HMs cause biotoxic effects (effect of HMs to the body of living organisms when ingested above recommendation limits) as they interact with the body's natural biochemistry in the normal metabolic processes . Most HMs have strong affinity toward sulfur. These toxic chemicals create bonds with S in enzymes, thus inhibiting essential enzyme functioning (Waseem and Arshad 2016).

A brief description of accumulation and physiological role (Ansari et al. 2004) of trace HMs in aquatic species and the potential threats to humans is shown as follows:

1.8.1 Lead (Pb)

Lead is a highly toxic heavy metal; its excessive usage has given rise to major environmental pollution problems and health issues everywhere in the world (Jaishankar et al. 2014).Various sources of environmental lead pollution are as follows: metal plating and finishing, exhaustive emissions from automobiles, pesticides and fertilizers, ores' smelting processes, battery industry effluents, wastes from urban soil, gasoline and dye additives, and chimneys of manufacturing plants (Eick et al. 1999). Humans are exposed through consumption of food and water exposed to lead and also from inhalation (Ferner 2001). Excessive levels of lead cause neurological and physiological effects in humans. The teratogenic effect is particularly a serious consequence of lead toxicity. Lead poisoning inhibits heme synthesis which leads to hematological damage, damage to CNS and PNS, and reproductive, bone, and kidney dysfunction (Ogwuegbu and Muhanga 2005). There is also some evidence pertaining to organolead compounds, regarding their acute toxicities to bottom-dwelling organisms although few studies have stated their chronic effects (Probst 1979).

1.8.2 Mercury (Hg)

Hg is studied extensively due to its toxic behavior. High levels of Hg cause acrodynia, also known as pink disease. The sources of mercury are municipal wastewater, mining activities, incineration of hazardous waste, and discharges from industries (Chen et al. 2012). Mercury is present in the environment in three forms: metallic, organic, and inorganic. Each of these forms of Hg has varying toxicity potential and bioavailability (Jaishankar et al. 2014). Mercury when present in aquatic ecosystems like rivers, streams, and seas is being converted into methylmercury by microbes. Organic forms of mercury are extremely toxic to marine life. Marine mammals amass considerable quantity of mercury coming from various food sources short of any harmful effects. Selenium adversely influences toxicity of mercury in organisms like seals, sea lions, and dolphins. Selenium retains stride with the concentration of mercury. The presence of Hg and Se in connective tissues of dolphin liver is actually a consequence of a purifying advancement for the methyl Hg assimilated through their diet (Price et al. 1972).

Mercury salts are exceedingly toxic. Methylmercury is a neurotoxic substance which causes devastation of microtubules and mitochondria and lipid peroxidation. It also causes accretion of neurotoxins like serotonin and glutamate besides aspartate (Patrick 2002). The chief route through which humans are exposed to methyl Hg is intake of marine species having remarkably high concentrations of Hg (Trasande et al. 2005). Methyl Hg is principally toxic. It provokes teratogenic, carcinogenic, and mutagenic alterations in the organism's body. Therefore, methylmercury is the central toxic form of Hg in the environs. The eating of crustaceans as well as fishes poses a chief danger to humans and other animals. The oxidized mercury resides in the brain, while free metal can be eliminated (Rygg 1985; Rule and Alden 1990). The CNS is severely damaged because of inorganic mercury (II).

1.8.3 Cadmium (Cd)

Cadmium was reported to enhance the growth and photosynthesis of phytoplankton at concentrations up to 100 mg L^{-1}. Cadmium because of its association with phosphates is supposed to be taken up by phytoplankton, although in two studies, it is being reported that it doesn't show any biomagnification and bioaccumulation. Aquatic organisms have small concentrations of cadmium in the food web, of a few PPM. Cadmium is principally concentrated in kidneys. It is excreted when metalloprotein is formed in the kidneys. Exceeding quantities of cadmium occur in mollusks too. Suzuki in 1979 studied the common limpet along the Bristol Channel-Severn estuary and established a relationship between high levels of Cd and a declined use of glucose. Cd is a by-product of the Zn making, leading the workers exposed to it. Cadmium is also bioaccumulative in nature. Cadmium is responsible for causing the *itai-itai* disease. Cadmium is exposed to man through ingestion and inhalation which ultimately leads to acute and chronic toxicity (Jaishankar et al. 2014). The signs of cadmium poisoning are associated with the kidneys, lungs, and bones. The chronic inhalation of cadmium causes kidney proteinuria (Swarzenski et al. 2000; Szefer 1990).

1.8.4 Arsenic (As)

The chemistry of As is multifarious besides being vital in development of aquatic species. Arsenic is present in various chemical forms: arsenate (AsO_3^{4-}), arsenite (AsO_3^{3-}), methyl arsenic acid [$MeAsO(OH)_2$], and dimethyl arsenic acid [Me_2 AsOOH]. AsO_3^{4-} is the main species in the photic zone of water. $MeAsO(OH)_2$ and Me_2AsOOH are present in high concentrations (Tay et al. 1992). Algae have extra accruing capability to arsenic than fish, with crustaceans amassing restrained quantity. The arsenic forms are imperative with reference to toxicity. The toxic potential of the arsenic reduces as per the following pattern with As (III) followed by As (V) and then the organoarsenic. It gives the impression that one of the body's resistance counter to arsenic is alkylation, resulting in generation of alkylarsenic (V) compounds: $CH_3AsO(OH)_2$ and $(CH_3)_2AsO(OH)$, which are less toxic forms of arsenic, and then these products are excreted from the body (Timmreck and Shook 1992). Acute effects of oral arsenic poisoning are strong abdominal pains, nausea, vomiting, and gastric intestinal complications triggering diarrhea, only to end with coma followed by death. Exposure to arsenic through inhalation causes respiratory effects which comprise of nasal and throat irritation, headache, vertigo, restlessness, and irritability (Rinderhagen et al. 2000; Tsuchiya 1981). As and Se are incompatible in the body and thereby separately stabilize the toxicity of each other. As (III) is deliberated as having the utmost toxicity; arsenate can be troublesome by competing with phosphate, consequently resulting in interruption of oxidative phosphorylation process. Arsenic also impedes the DNA repair mechanism by substituting the phosphorus in DNA (Rinderhagen et al. 2000). It may intermingle with the biosynthesis of porphyrin and distress the white blood cells. Arsenic toxicity has been associated with impacts on the reproductive system such as miscarriages/stillbirths. Hearing impairment is also related with arsenic poisoning. Occurrences like milk adulteration in Japan and discharges from Cu smelters have triggered auditory issues (Stauber and Florence 1990). Arsenic attacks the renal system, predominantly the reabsorption process. It causes destruction to peripheral nervous system (PNS) like peripheral neuritis plus motor sensory paralysis (Tsuchiya 1981).

1.8.5 Barium (Ba)

Barium has no part in biological science. As per *The British Pharmaceutical Codex* (1907), barium chloride ["barii chloridum," $BaCl_2.2H_2O$] has a stimulatory effect on cardiac muscles as well as other muscles. It increases blood pressure by narrowing the blood vessels. It has a tendency to empty intestines, urinary bladder, as well as gall bladder. Its toxic nature has also been verified. Barium sulfate ($BaSO_4$) is insoluble and is useful in radiography. All barium combinations should be considered as exceptionally toxic even though there is authorization that its vulnerability is limited and such compounds are not easily accessible to humans. Its toxicity hinges on the solubility of counterions. The nature of the counterions also plays a significant role. Baritosis is one of the forms of pneumoconiosis that is caused by longtime contact with barite and Ba dust. It has been stated that those workers are more prone to it who are being exposed to crushed and ground insoluble barium salts (US EPA 1992).

1.8.6 Zinc (Zn)

Zinc (Zn) is typically existent in plants and animals in concentrations corresponding to iron and generally in far greater concentrations than many other trace elements. Many researches verify that Zn is crucial for bacteria, fungi, and blue-green as well as green algae. Just because Zn isn't considered as highly toxic metal, hence it is being discharged into water bodies in considerable amounts. Limited number of reports shows that some species are susceptible to Zn toxicity at quantities frequently seen in seawater and sediments of estuarine waters. Stauber and Florence (US EPA 1992) observed that the growing of cultural diatoms was restrained by 20 μg L^{-1} of Zn. Impacts on fertilization as well as embryonic growth in Baltic spring-spawning herring at low salt levels were perceived at just 5 μg L^{-1}. On the other hand, many accounts of zinc toxicity were observed in waters having concentrations of Zn beyond 100 μg L^{-1}. Zn and Cd toxicity has an inclination to happen in the environs jointly. Zinc has a great number of biological purposes in humans besides being an essential component of more than 100 enzymes responsible for body's metabolism. Zn is involved in the production and functioning of certain hormones. It also executes an imperative part in reproductive as well as sexual maturity. Zinc is also present in the plasma, erythrocytes, leukocytes, and platelets (Van-Loon and Duffy 2000). Commonly found Zn compounds aren't predominantly toxic, while zinc salts can be carcinogenic.

1.8.7 Copper (Cu)

Copper (Cu) is a necessary element for some animals. A maximum concentration of it is present in gastropods, decapod, crustaceans, and cephalopods as their blood consists of pigment hemocyanin which holds Cu. Extra Cu is typically deposited in the liver (4800 μg g^{-1}). Oysters may have similar extraordinary content of Cu that is hoarded typically in the WBCs consisting of 20,000 μg g^{-1} of Cu and 60,000 μg g^{-1} of Zn in these blood cells. Cu is among the most toxic metal, following Hg and Ag, to marine life despite many purifying and storing systems. It has been experimentally proved that many aquatic species are negatively affected by Cu levels of 1–10 μg L^{-1} (Price et al. 1972). Vandecasteele and Block (1993) detected that 2 μg L^{-1} of Cu had noteworthy impacts on young bay scallops and surf clams. Some bivalves like *Mytilus edulis* were able to tolerate high levels of Cu due to the presence of Cu-binding metallothioneins (Viarengo et al. 1984). Cu-containing proteins in mammals are cerebrocuprein, ceruloplasmin, erythrocuprein, hemocuprein, etc. Copper enzymes also have the capability to openly utilize molecular oxygen. It has been labelled indispensable for cross-linking of elastin. Cu deficit is responsible for anemia plus disparities in bone development. It is commonly found in populations having malnutrition, also in patients getting whole parental nourishment. The consequence of Cu intake in disproportionate concentrations is hemolysis (splitting of RBC) (Van-Loon and Duffy 2000).

1.8.8 Manganese (Mn)

Manganese is among the many vital elements required by plants as well as animals. The biologically functioning form is the Mn^{2+} ion. It is as an enzyme activator widely distributed all over in the body tissues and fluids. In the human body, its content is projected to be 12–20 mg. It is also involved in mucopolysaccharide breakdown. It is also associated with superoxide dismutase. Pyruvate carboxylase is the single identified manganese-containing metalloprotein. Various experiments have been carried out to determine manganese deficiency in animals although none in humans. Manganese deficiency is responsible for skeletal irregularities. It is minimum toxic trace element to animals. Its prolonged exposure causes manganese poisoning that often occurs in mine workers. Manganese being toxic, when inhaled, causes neurological disorders (Van-Loon and Duffy 2000).

1.8.9 Iron (Fe)

Iron is the central constituent of plant and animal life being crucial for their growth and development. In the human body, iron is bound to protein forming complexes as porphyrin or heme compounds, mostly hemoglobin plus myoglobin or as non-heme protein-bound compounds such as ferritin plus transferrin. In humans, Fe binds to oxygen consequently assuring lungs to supply oxygen to the cells. The maximum amount of iron exists in the liver, spleen, kidney, and heart. Fe contamination results in the decrease in the number and abundance of species like periphyton, benthic invertebrates, and fishes (Vuori 1995). The iron precipitation results in substantial impairment to fishes because of clogging action in addition to hindering of respiration (EPA 1993). Iron deficiency is responsible for a number of diseases like anemia, lethargy, headache, as well as anorexia. Children are more susceptible to iron toxicity for the reason that they have maximum exposure to iron-containing products (Albretsen 2006). Excessive intake of soluble iron salts (>0.5 g) results in grave injuries to the digestive track followed by serious problems like hepatitis. Recurrent ingestion of exceedingly abundant quantities of Fe results in hemochromatosis which finally results in liver cirrhosis (Van-Loon and Duffy 2000; Wang et al. 1995).

1.9 Trophic Transfer of Heavy Metals

Being persistent pollutants, HMs amass in organisms and are then transmitted from lower trophic level to subsequently higher trophic levels. Food chains and food webs signify association amid organisms; hence all organisms get affected by contamination. The amount of HMs amassed in biota hinges on their rate of absorption and depuration from the body. HMs are transported to living organisms from the abiotic environment (water, sediments, and soils). This can take place either directly or indirectly from its food/prey, e.g., HMs may come in bodies of fishes straight from water and sediments by way of the gills and/or the skin. It can also come from consuming contaminated prey. The concentration of the heavy metal may either rise or fall in subsequent trophic ranks. The buildup of HMs in organisms varies with metal species in consideration and the biological processes established for the homeostasis. It also depends on the detoxification mechanisms. Methylated forms like that of mercury accumulate in biota to larger levels consequently biomagnified due to affinity toward lipids (Fig.1.3). Metallophytes have developed exceptional mechanisms for enduring exceptionally high content of HMs in soil (Ali et al. 2019a, b).

1.10 Factors Regulating HM Bioaccumulation

Many physical, chemical, biological, and environmental factors influence the intake plus withholding of heavy metals by marine organisms (Rashid et al. 2019). Various organisms are evaluated as indicators of heavy metal pollution owing to the fact that the bodily concentration of metal is proportional to the concentration of metal in seawater. For the evaluation of organisms as bioindicators, various factors like the organisms' rate of metal uptake which in turn is dependent on the chemical species of the metal are taken into notice. The chemical factors affecting the rate of metal uptake are pH, temperature, and hardness besides salt levels. HMs normally influence each other and as a result constrain the uptake of another by a specific organism (Ansari et al. 2004). The metal content in an organism depends upon the size of the individual, age, and growth rate. In addition to this, position in the water column also plays important role (Ansari et al. 2004). Furthermore, seasonal variation of the metal concentrations has been observed because of the changes in the organism's weight without any change in the total metal concentration of the organism. In few cases, the metal concentration is dependent on the organism's sex to some extent.

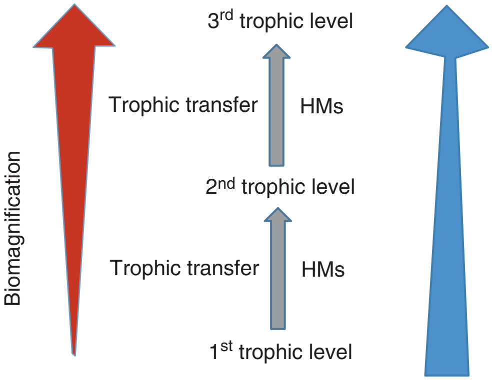

Fig. 1.3 Trophic transfer of heavy metals

1.11 Bioaccumulation of Heavy Metals in Fish

Fishes contaminated by HMs have turned out to be a significant subject all around the globe owing to their antagonistic aftermaths on fish and its consumers (Rahman et al. 2012). Bioaccumulation is regulated by fish age, size, weight, and length, as well as feeding behaviors and body functioning. The environmental factors like content and bioavailability of metals, physicochemical properties of water, and climatic factors also perform a key function. Varying with the structure and functioning of tissues, the degree of heavy metal buildup varies tissue-wise in fishes. In general, organs like gills, liver, and kidneys store much greater concentration of HMs than the skin and muscles because of metal-binding proteins called metallothioneins (MTs) present in these tissues when being exposed to HMs. Fish gills are target tissues for amassing as well as removal of HMs like Ni (Mansouri et al. 2012). Fish muscles don't accumulate HMs in high concentration, but they are important from the viewpoint of human consumption (Khaled 2009). Bioaccumulation of HMs in fish muscles is mostly species specific (Kumar et al. 2010). Elevated level of HMs in aquatic biota poses major health consequences and can result in population decline of aquatic species (Luo et al. 2010). Heavy metals are powerful neurotoxic drivers distressing fish species. The heavy metal interfaces with chemical incitements in fish can interrupt the fish communication with their surroundings (Baatrup 1991). HMs have been connected to fish defects in natural populations. These aberrations have undesirable effects on populace of fish species as these defects impact their morphology, survival, rate of growth, as well as well-being and health. These defects in fish can be explored as exceptional biomarker of heavy metal pollution in the environment (Sfakianakis et al. 2015).

Accretion of toxic HMs in fish has significant environmental and ecological consequences, besides societal concerns; it impacts both humans and aquatic carnivore species feeding on fish (Ali et al. 2017; Ali and Khan 2018a, b, 2019). HMs found in polluted seawater are assimilated in fish, and from there they pass into humans, thereby affecting human health (Dwivedi et al. 2015). In addition, toxic HMs also affect fish health (Javed and Usmani 2015) have reported pollution of river with heavy metals resulting in stress of freshwater fish by weakening it and making it more vulnerable to diseases. Heavy metal pollution is considered among the potential reasons for the decrease in population of freshwater fish and other aquatic organisms (Mehmood et al. 2019). It has been stated that with the rise in pollution levels of Indus, a major river in Pakistan, diversity and abundance of aquatic life were drastically affected (Al-Ghanim et al. 2016).

1.12 Heavy Metal Remediation Techniques

The remediation method for heavy metals should be cautiously evaluated so that the protection of the biotic and abiotic environment is ensured. All remediation procedures entail treatment of extensive sludge quantity which destroys the natural habitats in addition to being very costly (Nleya et al. 2016) (Fig. 1.4).

1.12.1 Precipitation

Numerous alkaline chemical reagents are commonly used for neutralization of acid mine drainage (AMD). It helps in pH elevation which in turn results in the formation of precipitate, thereby helping in recovering of the metals. Commonly used reagents for the recovery of mineral from AMD are limestone ($CaCO_3$), caustic soda (NaOH), soda ash (Na_2CO_3), quicklime (CaO), slaked lime ($Ca(OH)_2$), and magnesium hydroxide ($Mg(OH)_2$) (Masindi et al. 2016). The metal recovery takes place at different pH (Table 1.1). These recycled minerals are vended to metallurgical businesses, thereby offsetting the treatment charges (Nleya et al. 2016).

1.12.2 Adsorption

The process of adsorption starts once an adsorbate collects or adheres against adsorbent's surface. Adsorption is much competent and economical method for metal exclusion from aqueous solutions owing to its reversibility besides desorption abilities. Even though it is efficient, this process fails with concentrated solutions. The reason for it is that the adsorbent gets saturated with the adsorbate easily. This method performs well in case of very dilute solutions. It's a tedious task due to the reason that it entails recurrent regeneration in addition to being nonselective (Nleya et al. 2016). Thus adsorption is not effective in metal remediation on a large scale.

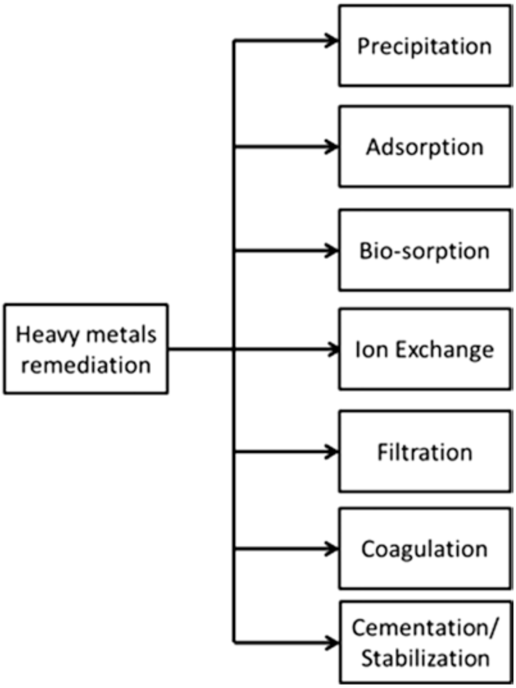

Fig. 1.4 Remediation practices for heavy metals. (Yusuf et al. 2015)

Table 1.1 pH for each metal ion at which precipitates formed in AMD

Metal ion	pH	Metal ion	pH	Metal ion	pH
Al^{3+}	4.1	Hg^{2+}	7.3	Cd^{2+}	6.7
Fe^{3+}	3.5	Na^{+}	6.7	Fe^{2+}	5.5
Mn^{2+}	8.5	Pb^{2+}	6.0	Cu^{2+}	5.3
Cr^{3+}	5.3	Zn^{2+}	7.0		

Masindi et al. (2016)

1.12.3 Ion Exchange

Ion exchange refers to the procedure in which give-and-take of ions takes place among two or more electrolytic solutions. Clay and resins have great cation exchange capability; thus they are frequently employed for metal exchange from aqueous mixtures. The efficacy of this method depends on pH besides temperature. Natural and artificial clays, zeolites, and synthetic resins are utilized for separation and exclusion of metals (Nleya et al. 2016; Masindi 2016).

1.12.4 Biosorption

Biosorption is the process of removing toxins from water systems by making use of biological tools. It includes absorption, adsorption, surface complexation, ion exchange, and precipitation. Biosorbents are advantageous because of their permanence, efficiency, and capability. They are steadily available and can be easily regenerated. However, the process easily reaches a breakthrough, therefore limiting further removal of pollutant (Silvas et al. 2011).

1.12.5 Membrane Technologies

Usage of membrane technologies for the retrieval of AMD is highly resourceful in treating polluted waters having elevated pollutant content. These techniques use the concentration gradient phenomenon or reverse osmosis process. Diverse membranes are used for treating mine waters. These includes ultrafiltration, nano- and micro-separation, reverse osmosis, and particle filtration (Nleya et al. 2016; Buzzi et al. 2013; Park et al. 2015)

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Chapter 2
Pollution in Aquatic Environs: Sources and Consequences

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2.1 Introduction

For the sustenance of life, water is essential either directly or indirectly as it plays an immense important role in all living and biogeochemical processes including solvents, temperature buffers, metabolites, and lubricants (Hanslmeier 2011). Water is however said to be contaminated if unguided, and anomalies of several anthropogenic practices have hindered some of the water quality criteria, making the water unsafe to use. All health and life risks can be caused by water pollution. Depending on your type and source of pollutants, the effects may vary. Some of the pollutants like heavy metals, dyes, and some other organic contaminants act as endocrine-disrupting substances and are carcinogenic having their source of origin from pharmaceuticals, cosmetics, and personal care product wastes. For ecologists and environmentalists, anthropogenic sources are the main cause for invasion of pollutants in water body via various means (Adeogun et al. 2016). Due to rapid population growth and increased speed of industrialization, there has in the last decades been a huge rise in freshwater demand (Ramakrishnaya et al. 2009). The excessive use of fertilizers and toxic practices in particular is endangering human health by most of agricultural growing behaviors (Okeke and Igboanua 2003; Bhat et al. 2017). A decline of water quality has arisen from anthropogenic development in various parts of the world due to widespread urbanization, agricultural operations,

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industrialization, and population expansion (Baig et al. 2009; Wang and Yang 2016). Therefore, poor water supplies have significantly limited water pollution regulation and increased water quality (Bu et al. 2010); hence to the experts, government, and other agencies, water pollution is a subject of concern. Protecting the integrity of the river water is therefore highly important owing to severe water pollution and global water shortages. Industrialization is a big catalyst for growth and urbanization in every community. Although industrialization has countless benefits, it has been described as a major environmental hazard, as it releases to our immediate environment, soil, air, and water numerous toxic chemicals, pollutants, solid waste, and different kinds of microbes. Water pollution is particularly interesting and has now become a global problem and is highly influenced by developing countries as a consequence of their promotion of growth (Inyinbor et al. 2016 and Rana et al. 2017). This occupies 98% of our drinking and is pointless to be consumed because of the high level of salt. Approximately 2% of the planet's water is fresh, while 1.6% is locked up in glaciers and polar ice caps. For aquifers and wells, an estimated 0.36% is contained deep. Therefore, in lakes and rivers, only about 0.036% of total water sources on the earth are available. Across 45 developing countries, the WHO/ UNICEF reported that the bulk (76%) of households are primarily responsible for water collection (Harikishore and Lee 2012).

2.2 Global Scenario of Water Pollution

Waterborne diseases are the major cause of death around the world which are due to unclean drinking water (Clasen et al. 2007; WHO 2010). For the safety and longevity of infants and children, clean drinking water is essential (Anderson et al. 2002; Vidyasagar 2007). According to the estimates, the death rate is 1.8 million worldwide due to diarrhoea. As people with medical conditions like AIDS, diabetic are more prone to get severe infections imposed by waterborne pathogens (Kgalushi et al. 2004; Laurent 2005).The percentage of households using an unclean source of drinking water has decreased throughout the less developed world, but it is extremely unlikely that all households will have a safe source of drinking water in the nearby future (Mintz et al. 2001). It has been estimated that nearly 884 million people in 2010 worldwide used an enhanced drinking water supply and forecasted that 672 million people will continue to use the improved drinking water system in 2015 (UNICEF 2010). So it is important to understand what drives a household to treat its drinking water with an unclean source of water. Nearly about five million deaths are occurring per year due to illnesses caused by waterborne diseases because of lack accessibility to safe drinking water. Oceans are covering nearly about 70% of planet earth, as these vast water bodies are not even now considered to be safe because of oil spillage, dumping of pollutants, and so on and even though the beaches around the world often used to close for solid waste collection along the shoreline.

2.3 Sources of Water Pollution

There are two major sources of water pollution, i.e. point sources and nonpoint sources. Point effluents have a clear detectable source which includes pipe connected to a warehouse, truck oil spill, and chemical effluents. Point contamination causes include liquid effluent (both urban and industrial) and storm sewer runoff and mostly impact the area near it, whereas nonpoint sources of pollution are those that come from different points of origin and number of ways by which chemicals penetrate the soil or surface water and arrive from numerous non-identifiable sources into the ecosystem. Also the water pollutants are further categorized into organic and inorganic pollutants. Inorganic water pollutants have their source of origin from acid mine runoff; heavy metals from metallurgical operations; surface runoff; mining, cutting, and burning activities; ground filling; runoff from the agricultural fields of the fertilizers that include nitrates, phosphates, etc.; and industrial chemical wastes, while the organic pollutants include the food waste, pathogens, biological volatile compounds, and organohalides. Some of the major sources of water pollution are discussed in details.

2.3.1 Load of Heavy Metals

Heavy metals have the capability to accumulate in the body of an organism without undergoing any degradation in any metabolic process. The source of heavy metals in waters includes industrial wastes, municipal wastes, rocks, and soils (Brady et al. 1994). An exposure of the living organisms to the heavy metals alters the physiological reactions inside the body and overall leads to cognitive behavioural changes. The effect of toxicity depends on the various factors like sensitivity of an organism, accumulation rate, etc. (Das et al. 1997). Various metals are essential like zinc (Zn), copper (Cu), manganese (Mn), iron (Fe), and nickel (Ni) as they act as micronutrients in order to carry on the biochemical and physiological functions of the various organisms like microbes and plants. Among various inorganic pollutants, heavy metals are not used to go under degradation process in natural waters like rivers and lakes so easily, thus leading to the process of bioaccumulation in the food web and food chains of various ecosystems (Jain 1978). However, so far as the sources are concerned, it has been estimated that wild animals and plants do contain heavy metal concentrations due to pesticides, fertilizers, mining activities, coal-based power plants, tanneries, steel industries, cement industries, metal chelates, and waste effluents. Excessive use of heavy metal-based pesticides is causing serious threats to various fragile ecosystems, thus affecting the biodiversity (Ghosh and Vass 1997) and human life sustenance. Some of the heavy metals do not have a documented physiological function but have been proven to be lethal if they are found to be more than the allowed consumable limits which mainly include the chromium, cadmium, lead, etc. (Bruins et al. 2000). As the allowed consumable limits for the Cd is 0.01 mg/L, Pb is 0.10 mg/L, and for Cu, it is 0.050 mg/L (ISI 1982). According to Tsuji and Karagatzides (2001), heavy metals lead to various deadlier health ailments like congestion of nasal mucous membranes and pharynx; tumour and cancer; gastrointestinal, muscular, reproductive, neurological, and genetic malfunctions; and oedema of eyelids.

2.3.2 Urbanization

Paul and Meyer (2001) reported that the leading cause for the increased amounts of phosphorus in the urban catchments is urbanization. After every pollutant washout from industries, urban runoff, domestic discharges find their way to reach nearby waterbodies where the problem, of euthrophication and algal blooms arises.

2.3.3 Oxygen-Demanding Wastes and Nutrient Enrichment

Due to lack of efficient waste management handling, both the organic and inorganic wastes get piled up which ultimately are accumulated in nearby water bodies including surface waters and groundwaters and become a source of pathogens (Bhat et al. 2018a, b). As in developing nation, sewage is not being treated from primary to advanced tertiary treatment in order to remove Nitrogen and Phosphorus which both are the leading causes of nutrient enrichment in lakes, rivers and seas which ultimately results in algal blooms and death of fishes by oxygen depletion. Moreover both natural and anthropogenic sources add nutrients especially nitrogen and phosphorus to the surface waters, as natural sources add minimum concentration, while human activities are resulting in the addition of large quantities of nutrients especially N and P where the natural balance entirely got disrupted. Howarth et al. (1996) reported that the North Atlantic ocean which is surrounded by temperate-zone rivers where net anthropogenic N input is highly correlated with total N fluxes. Howarth et al. (1996) reported that net anthropogenic input of N in the oceans and with their watersheds are highly correlated as well as the nitrate fluxes and total nitrogen are directly associated with human population density (Howarth et al. 1996; Goolsby and Battaglin 2001). It is easy to track the point sources, while diffuse sources show more spatial and temporal variation which includes agricultural surface runoff from fields. Despite strong regulation of the point source supplies in reaction to the Clean Water Act, the major source of water pollution in the United States is now contaminants from nonpoint sources (Carpenter et al. 1998).

2.3.4 Industrial Wastes

As in the manufacturing process of various industries like paper and steel industries, huge quantity of water is used and carries various organic and inorganic chemicals like acids, alkanes, and dyes to the nearby waters in the effluents. Huge quantity of flouride is added to rivers and lakes from the discharge points of aluminium industries while steel industries release huge amounts of cyanide and Ammonia by fertilizer plants, thus all these chemical pollutants affect the physiological as well as biological properties of nearby waterbodies. Fertilizers and pesticides are used to increase the productivity of the fields, but these chemicals like DDT, aldrin, dieldrin, malathion, parathion, etc. are involved in the production of toxins in the environment. These chemicals do not undergo breakdown to simple compounds but remain for longer period of time among the living organisms and in the environment via the process of bioaccumulation and biodegradation.

2.3.4.1 Oil Spillage

Oil discharges from carriers carrying petrol, diesel, and their derivatives to the surface of the sea, by means of accident or leakage, pollute the seawater to a large extent. Offshore oil drilling frequently contributes to marine resource contamination. The waste oil extends across the surface of the water and creates a thin layer of water emulsion into the liquid.

2.3.4.2 Acid Rain Pollution

Various anthropogenic activities like thermal power plants emit lots of sulphur dioxide and nitrogen dioxide into the atmosphere which react with rain and lower the pH of the normal rain water below 5 that results in fallout of acidic rain which damages building structures and carbonate and bicarbonate balance of soil and hence ultimately affects the plants and other life forms of inland waters and marine ecosystems.

2.3.4.3 Radioactive Waste

The radioactive materials come from the nuclear power plants, nuclear atomic plants, radioactive sediment, and radioactive minerals' exploitation in the environment. These wastes pose serious threat to soil, water, and living organisms even if they are present in very small concentrations. The half-life of some hazardous radioactive elements like cesium-137 and strontium-90 is about 30 years while for plutonium-239 is about 24,000 years. Hence these radioactive elements will remain active for many generations to cause deadlier diseases like bone cancer, premature delivery, and other serious ailments to human beings.

2.4 Micro- and Macropollutants of Water

There are two types of chemical water pollutants which include macro- and micropollutants, a relatively small number of macro-polishing agents usually occurring to milligrams per liter that are nutrients such as nitrogen (Gruber and Galloway 2008) and phosphorus (Filippelli 2008) and other natural organic agents which are listed under macropollutant category (Jorgenson 2009), while micropollutants are another listed category including organic and inorganic trace compounds in the quantity of mg per liter. As per Larsen et al. (2007), the challenging task for the scientists and other experts is to classify and to detect the effects of those micropollutants which are being added except the classical common pollutants whose sources are known, although the design of sustainable thermotechnology continues to classify newer compounds which are being added to waters and other ecosystems. The primary biomass production goes on increasing due to high nutrient pollution load to inland and ultimately to marine ecosystems like seas and oceans which results in depletion of oxygen levels in the upper layers of lakes, rivers, and seas, and hence anoxic conditions result in release of toxic gases and other toxins which are harmful for beneficial microbes and native vegetation of waters (Lohse et al. 2009; Heisler et al. 2008), and also due to disproportionate irrigation, heavy load of salts are being added to inland waters, thus leading to enduring problems (Kaushal et al. 2005). As due to climate change, sea level rise and extreme use of chemical pollutants are the leading cause for deterioration of groundwater qualtity as reported by Post (2005) in the coastal waters of China and India. Micropollutants can be harmful even at minimal concentrations, and their structural diversity is difficult to assess which leads to short-term and long-term effects (Schwarzenbach et al. 2006). Cosgrove and Rijsberman (2000) have reported that the identified sources are very scanty for micropollutants as various kinds of industrial estates use huge quantity of good quality of water for the manufacturing processes and lead to flow out pollutant effluents into the nearby water bodies containing both known and unidentified micropollutants. Nearly about all the developing nations lack the treatment facilities at the end of industrial effluents to remove or achieve goal of allowed limits of EPA and in countries like India and China where outlets are being directly discharged without any secondary or tertiary treatment, thus micropollutants in the milligram per litre for urban wastewater, though remain as such and affects the whole equilibrium balance of all the aquatic and terrestrial habitats (Shao et al. 2006).

Agricultural sector is among the major source of trace pollutants in the form of residues which varies from the various concentrations of nanogram to microgram per litre but although allowed limit varies as per rules of different countries (Bockstaller et al. 2009, Eliopoulou and Papanikolaou 2007). According to Watson (2004), the naturally occurring micropollutants bear odour, taste and undergoes series of reaction and may form various toxicants while the dumping municipal waste sites, military operation sites, and estates contaminate quality of groundwater via the process of leaching are being added to waterbodies. As more than 100,000 chemicals are registered which are being released into the nearby water bodies without complying with standard and norms, thus urgent need to provide a representational image of the size and nature of different types of micropollutants from different sources in order to address this global problem of water pollution (Schwarzman and Wilson 2009). Without promises of completeness, we seek to provide a representational image of the size and nature of this global problem of water pollution by discussing a set of very different types of micropollutants from different sources. Schwarzenbach et al. (2003) reported that it is quite challenging task to determine the detrimental effects of heavy metals including mercury, lead, chromium, cadmium, etc. which needs broad interdisciplinary approach to assess the quantity of micropollutants in aquatic ecosystems. After introduction of these invasive chemicals to the environment undergoes series of reactions like adsorption, absorption, oxidation/reduction, complexation and precipitation/dissolution and ultimately determines fate of these inorganic or organic micropollutants. The solubility of metallic minerals and metals depends upon the oxygen concentration and pressure. Manganese and iron are abundant and fragile to the varying oxygen levels as they easily get adsorbed under low oxygen availability and become more toxic under reductive conditions (Roberts et al. 2010). These reactive and toxic compounds can be dissolved and finally precipitated by microbes, by use of stable isotopes along with the mass spectroscopic techniques new analytical window through which microbial processes can be tracked by signatures of metallic elements, such as iron and manganese concentrations can be traced inn (Teutsch et al. 2009). As per Plumlee et al. (2006), X-ray diffraction techniques can be employed for the molecular characterization and to determine concentrations of metal ions as adsorbed on surfaces of the minerals and finally the mobility of toxic ions in the ecosystems can be tracked (Manceau et al. 2002). Hence the mobility of toxicants can be directly linked to the ability of that toxin to pass through the cell membranes of the organisms, and specific methods have been developed for metal pollutants according to their reacting sites with abiotic environments (van Leeuwen et al. 2005). Finally on-site observation along with molecular characterization with the integration of biological and physicochemical processes can be used to access the ultimate fate of micropollutants in aquatic ecosystems.

2.4.1 Persistent Organic Pollutants

Long back to the dates, persistent organic pollutants are the chemicals of serious concern as they contain intermediate products of various reactions which are unintentional in the origin as from heavy mechanical works and other combustion processes (Bhat et al. 2018a, b). Some criterion has been kept to include chemicals in the persistent organic pollutant category as some of the conditions are discussed below:

1. The POPs will remain in the environment for longer period of time because any chemical or biological reaction will not affect their concentrations.

2. Due to their persistence, the disposal rate of such chemicals is almost negligible.
3. Biomagnification.
4. With high rate of toxicity toward the flora and fauna including humans as well.

In the international convections, namely, Stockholm Convention and Aarhus Protocol, numerous persistent organic pollutants have been included in order to cut the emission rates on the global level (Lohmann et al. 2007). Highly chlorinated compounds like polychlorinated biphenyls, dichlorodiphenyltrichloroethane, and polycyclic aromatic hydrocarbons are the top priority persistent organic pollutants (Muir and Howard 2006). Moreover there are other diffuse sources of persistent organic pollutants which are not even included in the list as due to the recent occurrence of polybrominated diphenyl ethers and perfluoroalkyl-associated chemicals as alarming persistent organic pollutants (Vonderheide et al. 2008; Yoga and Sericano 2009) which have wide industrial application due to their properties of use (Goss and Bronner 2006). Many persistent organic pollutants have shown that they remain active in the atmosphere for hundreds of years, but due to lack of knowledge, they cannot be eliminated from the source in use (Richardson 2009; Giger 2009). Various health ailments like obesity, diabetes, or thyroid, fertility, and immune problems are associated with exposure to the persistent organic pollutants. The marine biota have been found to act as storing bodies where concentration goes on increasing with the rate of consumption (Kelly et al. 2007, 2009). After conducting various histopathological studies, huge concentrations of persistent organic pollutants have been found in marine biota and ultimately find its way to the humans especially in the human milk (Hites 2004 and Porta et al. 2008). In the Arctic region, persistent organic pollutants have shown the marked presence due to huge travel range (Brown and Wania 2008). DDT and PCB are being most traditionally used chemicals as an insecticides which have long persistence but are still in use when banned dates back. In many regions of the world including North America, Europe, and Japan where hundreds of persistent organic pollutants has shown detrimental effects within the human body along with the exposure in 5 years of period and PBDEs have shown their more effects on terrestrial organisms as well as same case has been observed among the mammals of marine ecosystems in the Northern Europe and America (Hites 2004). Hence in order to achieve the goal of complete elimination of persistent organic pollutants, there is a need for the remediation of previous contaminated sites then the newly added chemicals to the environment can be achieved by remediation strategies.

2.4.1.1 Occurrence of Toxic Algae

Due to the availablity of suitable Conditions as algae can flourish and leads to production of various toxins which are hazardous chemicals posing threats to aquatic and terrestrial animals as these algae produces both the toxins, i.e. intracellular and extracellular. These extracellular toxins are being released into the surrounding waters while other organisms become fragile to these contaminants by either feeding on these algal cells or by water absorption cause death to those organsims. All the organisms in any ecosystems whether terrestrial and aquatic organisms are directly or indirectly interlinked via the food chains and food webs as though these toxins can be transferred and accumulated from one organism to another one, for example, from zooplanktons to large fishes and lastly get bioaccumulated into the humans body; hence, affects every single organism. The production of microscopic algae like dinoflagellates, diatoms, and cyanobacteria can be stimulated by inorganic nitrogen contamination which triggers their metabolism to generate more toxins (Anderson et al. 2002).

2.5 Consequences of Water Pollutants

2.5.1 Chemicals in Water that Affect Human Health

Exposure of human beings to the toxicants in their day-to-day life results in acute and chronic diseases as the allowed limit for the fluoride in water should be less than 0.5 mg/litre of water which is essential against the tooth decay and weakening of bones, but exposure to higher levels especially in the age group of 5–6 years causes disease called fluorosis. Tanneries, insecticide for plants, ceramics, coal-fired power plants, and other industries release arsenic into the water bodies, and it also has some natural source of origin like the rocks rich in such metals. It has been already reported in various districts of West Bengal where allowed limits for arsenic have found to be more thus many cases has been registered for complaint of various cancers like prostate and lung cancers and other heart ailments. The plumbing pipes and other sanitary domestic fittings add arsenic to the drinking waters which causes kidney diseases and affects central nervous systems as children and pregnant women are more prone to the lead contaminations. Another toxic metal is the mercury which comes from the smelters, battery production, pesticides, and fungicides; as in 1938, significant amounts of mercury have been dumped from the factory into the Minamata Bay which resulted in the mercury pollution, and fishes accumulated the dumped mercury which found its way to human body after the consumption of these contaminated fishes, and the affected humans has been diagnosed with varying levels of mercury in their blood and tissues; hence the disease is named as Minamata disease due to presence of methyl mercury, as around two thousand were poisoned and hundreds of people were left dead, disabled and ultimately resulted in the chromosomal aberrations and human neurological disorders (Akio 1992). Another breakout was the long-term consumption of rice contaminated with cadmium in regions of Japan which resulted into the disease known as “itai-itai” or “ouch-ouch” as people complained of nephritis and nephrosis (Friberg et al. 1974).

2.5.2 Waterborne Disease

Presence of microorganisms indicates the quality of water as some of the microbes, namely, *Vibrio cholera*, *Salmonella* sp., *Shigella* sp., and *E. coli*, if present in the water will cause diseases like typhoid, diarrhoea, and dysentery after consumption because they are pathogenic microbes in nature (Adetunde and Glover 2010). The main source for these pathogenic microbes is the faeces and untreated sewage which, after direct oral transmission through water or food induce above-mentioned diseases (Adetunde and Glover 2010). It has been reported worldwide that more than 14,000 deaths occurs in a day mostly children of age 5 due to contamination of groundwater (Larry 2006) and also more than 1.1 million children are estimated to die each year because of their low immunity (Steiner et al. 2006).

2.5.3 Acidification of Freshwater Ecosystems

Baker et al. (1991) reported that the cause of acidification in inland waters is due to presence of nitrogen dioxide and sulphur dioxide as they react with water to form nitric acid (HNO_3) and sulphuric acid (H_2SO_4), respectively, after following the various reactions (Mason 1989). Due to fallout from the atmosphere consisting mainly of $SO_4^{2-}$and NO^{3-}, where the concentration of H^+ in freshwater environments with no high acid neutralizing potential (i.e. with moderate or low alkalinity) (Baker et al. 1991). The pH of water decreases on addition of these acids, and acidic pH will lead to accumulation and/or reduced sedimentation of metals like aluminium (Al^{2+}) and other trace metals like zinc, copper, lead, and cadmium. In the acidified lakes, aluminium gets deposited on sediments (Borg et al. 1989; Nelson and Campbell 1991). According to the Skjelkvale et al. (2001), the emission rates for the sulphur dioxide and nitrogen oxides from the Europe and North America in the 1980s and 1990s have been eliminated but their levels remain unregulated and caused acidification of freshwaters (Skjelkvale et al. 2001). Ammonium ions (NH_4^+) lead to release of H^+ ions under the acidic conditions (Wetzel 2001). Hence the inland water bodies around the world has been classified on the basis of their pH values between 4.5 and 5.8, and these lakes and streams are found in the various regions of Northern and Central Europe and North America (Skjelkvale et al. 2001; Doka et al. 2003). The productivity of primary and secondary vegetation of lakes and streams got declined due to acceleration of acidification because of human interventions and in turn affected the invertebrate and important fishes of the lakes and streams (Allan 1995). As per the reports of Doka et al. (2003), when the pH levels of water drops to 6.0 to 5.5, all the biota gets affected because of their fragile enzymatic reactions inside the body. Ultimately the equilibrium of the ecosystem of lakes and streams gets disturbed, hence regulating the concentrations of chlorides, sodium, potassium, and calcium (Allan 1995). As it has been found in various experimental studies conducted over some lakes of Canada with pH below 5.6, the nitrification process of NH_4+ gets hampered (Rudd et al. 1998, 1990).

2.5.4 Ocean Garbage Patches

The flow rate of plastics in the North Pacific Ocean has been estimated around 5–10 million tons that too around the Japan and California as estimated by the UN (Livingeco 2011). The North Pacific Subtropical Gyre is often recognized as "the Great Pacific Ocean Garbage Patch" which is measured to be twofold the size of Texas. Kostigen and Magazine (2008) reported that at the depth of 100 feet large, small plastics in clusters have been found in the Pacific Ocean Gyre and in other associated gyres like of the Southern Atlantic subtropical gyre (SG), North Pacific subtropical Gyre (NPG), and Indian Ocean subtropical gyre. As in Caribbean Seas and parts of the North Atlantic Ocean, two lack tons of plastic per km^2 has been found after surveillance of 20 years (Gill 2010) The major sources for the plastics into the oceans comes from the beaches which accounts for eighty percent 10% from fishing gear and other percent from vessels and ship as well as the cargo ships add containers (McLendon 2010). Nearly about thousands of plastic ducks were lost in the Pacific Ocean between Hong Kong and America, and these are reported to be circulated in oceanic waters as Great Pacific Garbage Patch around the waters of Alaska, South America, Hawaii, Australia, and Pacific Northwest (Nelson 2011).

2.5.5 Marine Biodiversity and Plastic Pollution

Over the last several decades, addition of plastic waste in to the water bodies has significantly increased as the wildlife is often injured due to plastics found in the environment whether intertwined or ingested (Hameed et al. 2020). As per reports of Blight and Burger (1997), a marine class, namely, Procellariiformes, such as the petrels, albatrosses, and shearwaters used to feed on food as the broken plastics seems similar to their food particles i.e. phytoplankton's as after engulfment of these plastic materials moreover these organisms are in turn eaten by small and finally large fishes as per trophic levels. The assimilation of these plastic wastes into the body decreases ability to digest and inhibit progress, causes internal damage, and creates intestinal blockage (Plot and Georges 2010). Fishing nets, or other ring-shaped materials, can contribute to strangulation, feeding efficiency loss, often drowning as of natural curiosity of the pinnipeds which are interwoven into aquatic waste at a young age, thus hinders their body size decreases due to accumulation of marine debris (Allen et al. 2012). All around the world, it has been estimated that 23% of marine mammals especially sea turtles and large population of seabirds ingest plastic debris and tar from oil spills which leads to death of marine mammals as many plastic scraps has been removed after autopsies (Stamper et al. 2009). Ingested plastic debris and tar from oil spills is the leading cause for the death of sea turtles as many plastic scraps has been removed after the autopsies including Styrofoam, fishing lines, plastic bags, etc. as the floating plastic bags seem to be jelly fishes for these turtles (Stamper et al. 2009; Mascarenhas et al. 2004).

Henceforth the population of the *Dermochelys coriacea* (leatherback sea turtles) has declined as now listed as the critically endangered species of IUCN (Shillinger et al. 2012).

2.5.6 Coral Reefs and Water Pollution

The most diverse ecosystem on the planet earth is the coral reefs with the presence of species from algae to the higher mammals with high levels of interaction at diverse levels of hierarchy. Although diverse coral reefs are very fragile for the very small change in their abiotic factors or the available basic necessities like temperature, nutrients etc. which varies from the organism to organism and also with the different age groups. The coral reefs are the organisms which lives in symbiotic association between the hosts coral which is polyps (*Symbiodine* sp.) belonging to the class of Cnidaria and with the algae (Hoegh-Guldberg 1999 and Fabricius et al. 2005). From the past decade, due to high levels of water pollution and global climate change, the temperature and the sea level rise have threatened these coral reef ecosystems all around the world especially of the reefs of Pacific oceans. According to the reports of Stebbing and Brown (1984), the branching coral species appears more susceptible than massive corals to a certain amount of chemical contaminants, and also the small polp species seems more susceptible to pollution stress than large polyp corals on comparison of stage of life, reproductive strategy, mucus and lipid content are used to access the sensitivity of coral groups due to pollutant stress (Scott 1990; Peters et al. 1997). The optimum temperature for the corals should be between 20 and 40 °C on an average, but from the past few years, the temperature of the shallow seas has found to be more by 2 degrees which results in the loss of symbiotic association of coral polyps and algal species and finally the bleaching of corals. Also the washout from the farm fields finds its way to the oceans which consists of fertilizers and pesticides of the chlorinated compounds like DDT, HCB, dieldrin, and chlordane, as the residues remain in the sediments of water and soil for longer periods of time thus affecting the natural balance of coastal waters around the world especially in the developing nations (Mitchell et al. 2005; Packett et al. 2009). The distribution and fate of pesticides and their toxicity to non-targeting populations is therefore critical to the secure evaluation of application-related threats in specific tropical areas with trends of use of pesticides typically well exceeding temperate areas (Ecobichon 2001).

2.6 Climate Change and Water Pollution

According to the Intergovernmental Panel on Climate Change (IPCC), global surface temperature rose by 0.74 °C in the last 100 years (1906–2005). Global warming is thus actually an incontrovertible fact, and the annual warming trend for the last 50 years is almost double that recorded over the previous 100 years (Trenberth et al. 2007). All the biological and even physic-chemical processes of water ecosystems on the globe may get directly or indirectly affected by climate change (Dalla et al. 2007; Delpla et al. 2009; Whitehead et al. 2009). Understanding the different hydrodynamics and biochemistries taking place in numerous waters is the key to understanding the interaction between climate change and water quality in various bodies in water (Delpla et al. 2009; Mooij et al. 2009). Till date so many studies has been conducted to identify and classify the source, origin, and effects of various types of pollutants like eutrophication, salinization, nutrient release, aquatic plant growth, and long-term climate change effects on the inland waters, surface waters, seas, and oceans. As due to temperature rise or the global climate change, the hydrodynamics of the water system including thermoprofile and chemoprofile of entire water column gets totally disturbed in the deep lakes and reservoirs (Brooks et al. 2011).

It has been observed that for some North American and European Lakes since the 1960s, the stratification process has been extended from 20 days to 40 days (Rosenzweig et al. 2007; Delpla et al. 2009). The exchange of surface and groundwater has hampered for the process of thermal stratification due to reduction of dissolved oxygen levels and excessive accumulation of carbon dioxide which leads to easy formation of a reductive environment (Rasmussen et al. 2009). However, several scientific reports have shown that the loss of nutrients and other toxins from the soil due to low water hypoxia (Gantzer et al. 2009). In recent times, the temperature rose by 3.8 °C in 2019 to 2100 under the A2 scenario in contrast to the reference duration from 1991 to 2001after conducting experiments over Shimajigawa's reservoir of Western Japan. According to Komatsu et al. (2007) by deepening of an anaerobic layers in the waters by 6.6 meters will ultimately advance the PO^4 concentration from 1.7 to 5.6 μg/L in the surface water due to more fluxes of phosphorus and an increase in the chlorophyll a concentration from 7.8 to 16.5 μg/L. Though mineralization and salinization for the long run will eventually affect equilibrium conditions of lakes and streams due to climate change which will lead the waters unfit for drinking purposes. According to the results obtained by Liu et al. (2004), on the Hei River Basin, an increase in the temperature and a decrease in the runoff have been the major reasons for the mineralization of lakes since the early 1960s. Liu et al. (2004) deduced that the mineralization of Chaiwobao Lake and Hongjianzhuo Lake in Xinjiang Province was also associated with climate change.

2.7 Conclusions

Pollution of water is an alarming problem in the world and must be dealt with sustainably. The framework of research and development should be strengthened in order to develop and develop new innovative technologies with financial feasibility. In river basins and catering areas of bodies of water, the construction practices of factories, industrial projects, irrigation, and other infrastructures should not be allowed to limit the contamination of rivers, lakes, and others. In addition, the comprehensive environmental preparation should be applied with legal support through well-defined simulation models with the main aim of preserving or restoring water quality.

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Chapter 3
A Recent Scenario of Groundwater Quality in Kashmir, Northwest Himalaya, India

Riyaz Ahmad Mir and Khurshid Ahmad Lone

3.1 Introduction

Groundwater is considered the largest resource of freshwater after the glaciers and ice sheets of the polar regions of the world. It plays a significant role in shaping the socioeconomic conditions of the human life. In Kashmir valley, the ground has a huge potential to provide major resource of freshwater supply that can be used for all domestic, horticultural, agricultural, and hydropower generation purposes significantly. However, the value of groundwater is not determined by its widespread occurrence and availability, but its value depends on its consistent and good quality (UNESCO 2000; Jeelani et al. 2014; Mir and Jeelani 2015). The suitability of groundwater for different uses depends upon the inputs of chemical species from the atmosphere, from soil and rock weathering, as well as from anthropogenic activities (Jeelani et al. 2014; Mir and Jeelani 2015). Nearly all groundwater originates as rain, snow melt, or surface water that infiltrates through the soil or geological material and reaches the phreatic zone. Rain and snow are naturally slightly acidic due to chemical reactions with CO_2 in the atmosphere. However, it is in the soil zone that the water interacts with the inorganic and organic solids while infiltrating through it. The inorganic material may be fairly fresh rock material as found on the steeper slopes of a mountain, or more likely, it is weathered material composed of fairly reactive secondary minerals that may equilibrate with the infiltrating water, thus imparting its chemistry (Deutsch 1997; Jeelani et al. 2014). The groundwater's chemical composition is determined by its sources and sinks along its flow path (Deutsch 1997). Moreover, the relative concentration of dissolved constituents is

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also a function of its availability from the solid phases as well as its solubility of secondary minerals produced due to weathering processes. In general, the groundwater during its flow tends to acquire a similar chemical composition as that of the seawater. This tendency is generally associated with a significant change from a dominant bicarbonate (HCO_3^-) type or anion species to a chloride (Cl^-) type (Chebotarev 1955). During recent decades, the anthropogenic activities have significantly affected the groundwater resources and are therefore considered a major hazard in the evolution of chemical quality of groundwater. The increased and rapid urbanization and conversion of agricultural lands into the urbanized settlements have resulted in the dreadful conditions of water quality (Mir et al. 2016). Rapid and increased use of fertilizers, pesticides, huge production of house hold effluents or effluents discharged from industries, and other municipal sewage are the main contaminants of groundwater (Mir and Gani 2019).

Nonetheless, any imbalance in the chemical quality of groundwater is responsible for many diseases in humans. For example, the lower values of pH can cause gastrointestinal disorders, hence limiting its domestic uses. Similarly, the groundwater with higher TDS values cannot be used for irrigation and drinking purposes (Fetters 1990; Freeze and Cherry 1979; Jehangir et al. 2011). The presence of F higher than a threshold value of 1.5 ppm results in fluorosis (Subba and John 2003), and the presence of nitrate, nitrite, and phosphate above certain permissible limits makes water unsuitable for drinking purpose (Lee et al. 2003; Rajmohan and Elango 2005). Furthermore, the study of major ions explains the source of ions in groundwater and gives an insight into the level of contamination that is either from natural or anthropogenic sources (Jalali 2005; Subba 2006; Jeelani et al. 2014). For this purpose, several indices, ratios, and diagrams are used. For example, the Wilcox diagram and US Salinity Laboratory diagrams are used to find out the nature of water and to check out whether the water is useful for irrigation (Subramani et al. 2005; Singh et al. 2005; Jeelani et al. 2014; Mir and Jeelani 2015). Thus, using the chemical budget of major ions, the quality of water can be easily assessed (Mir and Jeelani 2015; Mir et al. 2016).

Thus keeping in view the above discussion, the present study has been carried out in parts of Srinagar district, Kashmir valley, northwest Himalaya, India. The main objectives of the study include to determine sources of the major ions of the groundwater of the area using statistical analysis and to determine the suitability of the groundwater for domestic as well as agricultural purposes using the standard indices and other international guidelines.

3.2 Groundwater Pollution in Kashmir

There are a number of studies which reported a general degradation and deteriorating conditions of water resources of the Kashmir valley (Mushtaq and Pandey 2014; Showqi et al. 2014, Rashid et al. 2017; Rashid and Romshoo 2013). There are several studies on the chemical quality of the River Jhelum and its tributaries also which suggest that the water of the river is chemically good but the nature is trending toward degrading quality (Mir et al. 2016; Mir and Jeelani 2015; Mir and Gani 2019; Rather et al. 2016). However, there are a least number of studies on the groundwater resources of the Kashmir valley and its quality status. Some sporadic studies have been carried out previously on the groundwater resources of the Kashmir valley. For instance, Jehangir et al. (2011) studied groundwater quality for irrigation in southern parts of the Kashmir valley. They suggested that majority of groundwater in the aquifers of this area is of marginal to harmful quality for irrigation purposes. Gulzar et al. (2017) studied the groundwater quality of Anantnag district, Kashmir valley, and suggested that although the water is suitable for domestic and irrigational purposes, there are certain locations which indicated its unsuitable nature. Bhat et al. (2013) studied the water quality of the Srinagar district, Jammu and Kashmir, and concluded on the basis of physicochemical properties that the groundwater of the area is suitable for domestic as well as agricultural purposes with few exceptions. Sarah et al. (2011) studied the water quality of a groundwater-fed Manasbal Lake of Kashmir Himalayas and concluded that the water is safe for domestic uses based on chemical quality. Jeelani et al. (2014) carried out a detailed hydrochemical assessment of groundwater throughout the Kashmir valley and suggested that the groundwater of shallow as well as deep aquifers is good for drinking, livestock, and irrigation purposes with the exception of one site located in Sopore areas of the valley.

Central Groundwater Board has reported a groundwater potential of the valley of 2400 million m^3/year which is being currently exploited at 2.4 million m^3/year (Gulzar et al. 2017). This groundwater resource poses a huge potential to supply water for both urban and rural areas in the valley. However, keeping in view the higher demand for water in response to rapid population growth and industrialization, high tourism pressures and continuous landform degradation (Mushtaq and Pandey 2014; Zaz and Romshoo 2012), uncontrolled use of fertilizers and pesticides (Mir et al. 2016), spontaneous urbanization (Sajjad and Iqbal 2012), frequent expansion of the settlements into the agricultural lands vis-à-vis shifting the land use land cover pattern, and overall ever-rising anthropogenic activities (Mir et al. 2016, Mir and Jeelani 2015) in the valley, the health of the groundwaters is highly jeopardized, and its biological as well as physicochemical properties may also be seriously affected.

3.3 Location of the Study Area

The study area covers a part of the Srinagar district of the Kashmir valley, northwest Himalaya, India. The area comprising both urban and rural areas lies between 34° 3′–34° 20′ N latitudes and 74° 40′–75°15′ E longitudes and covers an area of 2228 km^2 (Fig. 3.1). The study area is connected to the other parts of the valley by all-weather motorable roads and to the rest of India by National Highway No.1A (NH 1A) and the air route. The study area is bounded in the north by Sonawari

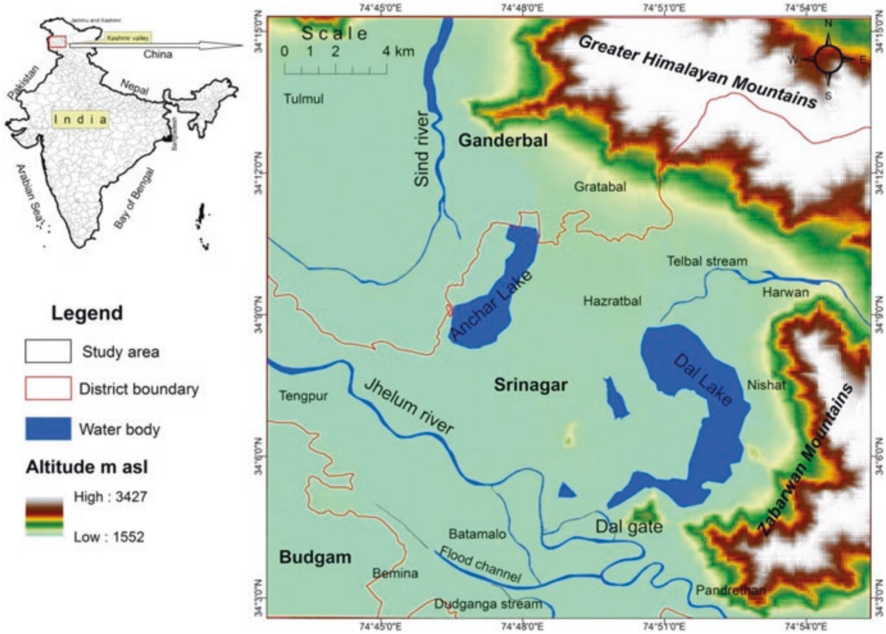


Fig. 3.1 Location map of the study area

(Baramulla district), in the northeast and east by district Kargil, in the south by district Pulwama, and in the southwest and west by Budgam and Baramulla districts, respectively. The total population of the district is ~12,02,447 which comprises a rural population of ~17,313,281 and urban population of ~121,9516 (Census 2001). In the study area, hand pumps are being widely used to pump out groundwater for domestic and other related purposes. Most of the wells are shallow, hence liable to contamination from the sources like sewage drains, septic tanks, polluted surface water bodies, and agricultural farmlands and/or floating gardens of the Dal Lake where huge pesticides are being used.

3.4 Climate of the Area

The study area has a distinctive character with its own climatic peculiarities. The area witnesses a continental climate system, characterized with marked seasonality linked with the mechanism of weather in the Indian sub-continent (Hussain 2005). In general, it has a long period of winter and spring seasons. Based on general characteristics of weather, i.e., precipitation and temperature, four seasons have been described for the area as (a) winter season (November–February), (b) spring season (March–mid-May), (c) summer season (mid-May–mid-September), and (d) autumn season (mid-September–mid-November). January is the coldest month whereas the month of July is generally the warmest. Normally, the temperature varies between −5 and >30 °C in the area. The precipitation is highly variable round the year with more rains occurring during summer season and snowfall during winter season. Overall, the precipitation is higher during winter season with a total annual precipitation of ~1100 mm. March receives maximum rainfall and October the least and September–November is usually a dry season (Mir and Jeelani 2015).

3.5 Geology of Study Area

The main lithological units exposed in the area include the Agglomeratic Slate, Panjal volcanic, Gangmopteris beds, Zewan Formation, Triassic Formation, Karewa Formation, and Alluvial deposits (Fig. 3.2). The Agglomeratic Slate is comprised of pyroclastic slates and conglomerates and underlies the lower part of the Panjal volcanics that are generally basaltic in composition with grayish to dark green in color. The Panjal volcanics are called the Panjal Traps generally. Thin Gangmopteris beds of light-colored shale conformably overlie the Panjal volcanics. The Panjal volcanics are overlain by Gangmopteris beds which are followed by the Zewan Formation. The Zewan Formation is followed by the homogeneous compact, light gray-colored limestone of Triassic Formation with shale in the lower parts, shale and sandstone intercalated with limestone in the middle parts, and massive limestone in the upper part. The Plio-Pleistocene deposits called as Karewa sediments overlie the Triassic and pre-Triassic rocks, flanking the surrounding mountain precipices of the study area. The Lower Karewas comprise blue, gray, and buff silts and sands, conglomerates, alternating laminated yellow marls, and silts and sands. In the low-lying areas, adjoining the Jhelum River and its local streams, the recent alluvium comprised of the finely compacted detrital sediments of loam, clay, silt, and sand is present. The geological map is shown in Fig. 3.2.

3.6 Materials and Methods

In this study, 140 groundwater samples were collected seasonally, 70 each in pre-melting (December, 2004) and post-melting (June/July, 2005) seasons between 10.00 h and 15.00 h from different sampling stations in one liter polyethylene bottles (Fig. 3.3). Samples were collected from bore wells, springs, and dug wells that represent the main sources of groundwater in the area. In order to avoid the stagnant water and to collect the rust-free and running water samples from bore wells, the pumping was carried out for 5 to 10 min, while in the case of springs and dug wells to avoid floating debris, the samples were collected at depths greater than 30 cm below the water surface. Prior to sample collection, the containers were also washed with conc. HNO_3 followed by complete removal with distilled water. The sample

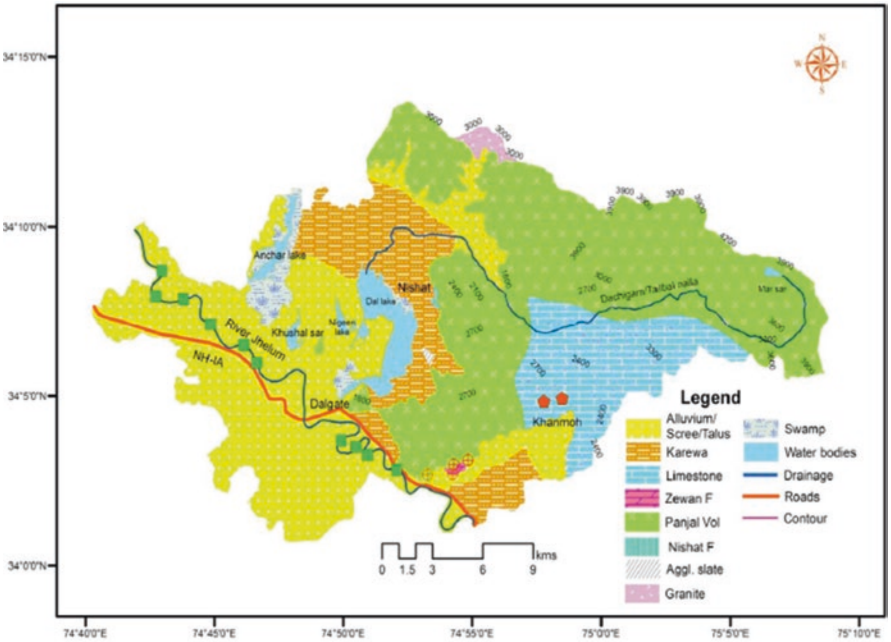


Fig. 3.2 Geological map of the study area

bottles were also rinsed by the sample water that was to be sampled. Water temperature, pH, and electrical conductivity (EC) measurements were carried out in situ at the sampling sites, whereas further chemical analysis was carried out at the Center of Research for Development (CORD) and Department of Geology and Geophysics, University of Kashmir, Srinagar.

The chemical analysis was carried out following the standard methods of Trivedy and Goel (1984) and APHA (2001). Water temperature, pH, and EC were determined by the potable laboratory thermometer, digital pH meter, and conductivity meter in situ. The Ca^{2+} and Mg^{2+} ions were determined by EDTA titration wherein the Eriochrome Black T and murexide were used as indicators. The Cl^- ion was determined by titration against $AgNO_3$ (0.02 N) using potassium chromate (5%) as indicator, whereas the HCO_3^- ion was determined by again titration method against HCl (0.01 N) using methyl orange as an indicator. Na^+ and K^+ ions were estimated by Flame Emission Photometry. The Spectrophotometric method was used for the determination of SO_4^{2-} and NO_3^- ions. It is important to mention that the results were obtained in mg/L that was converted into milliequivalents during the data processing and interpretations. Furthermore, a standard computer program Minitab was used for statistical data analysis such as for the determination of descriptive statistics, correlation matrix, and principal component or factor analysis (FA). Prior to conducting FA, the raw data was normalized as the first step in factor coefficient matrix. By examining the factor loadings and their Eigen values, the variables belonging to a specific process were identified and explained.

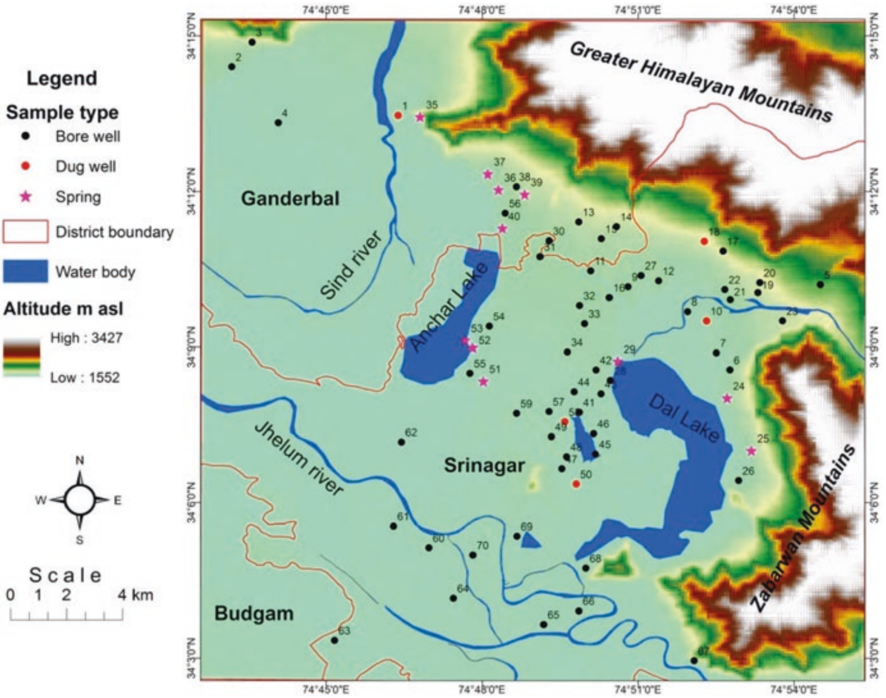


Fig. 3.3 Sample site map of the study area

3.7 Findings

3.7.1 Geochemistry of Groundwater

The physicochemical parameters analyzed in this study include pH, EC, total dissolved solids (TDS), total hardness, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO$_4^{2-}$, HCO$_3^{-}$, and NO$_3^{-}$. The statistical overview of the results is presented in Table 3.1.

The temperature of groundwater ranged from 11° C to 15° C with a mean of 13.06 °C. The TDS of groundwater samples ranged from 107 to 710 mg/L with a mean value of 382.21 mg/L, being low in springs (107 mg/L–429 mg/L) and moderate in dug wells (141–704 mg/L) and high in tube wells (136–710 mg/L). The EC of groundwater varied between 168 μS/cm and 1110 μS/cm with a mean of 587.65 μS/cm, being lower in springs (168–670 μS/cm) and higher in dug wells (220–1100 μS/cm) and tube wells (212– 1110 μS/cm). The pH of the groundwater samples was moderately alkaline and ranged between 7.10 and 8.30 with an average of 7.62. pH of the springs ranged between 7.1 and 8.07; that of dug wells ranged between 7.16

Table 3.1 Statistical overview of hydrochemical characteristics of groundwater, Srinagar district. The sampling for pre-melting season was carried out during December, 2004 and for post-melting season during June–July, 2005

Parameter/ constituent	Spring		Dug well		Bore well		Overall range	Overall mean
	Range	Mean	Range	Mean	Range	Mean		
(a) Pre-melting season								
pH	7.10–8.07	7.85	7.16–8.03	7.62	7.10–8.30	7.58	7.10–8.30	7.62
Temp. (°C)	11–15	12.64	10–13	12.4	12–15	13.20	11–15	13.06
EC (µS/cm)	168–670	515.18	220–1100	635	212–1110	598.03	168–1110	587.65
TDS (mg/L)	107.429	329.54	141–704	406.4	136–710	387	107–710	382.21
Ca^{2+} (mg/L)	36–105	66.18	27–100	66.80	20–127	73.77	20–127	72.09
Mg^{2+} (mg/L)	5–25	14.27	8–28	19.40	6–35	17.77	5–35	17.34
Na^{+} (mg/L)	3–42	17.63	7–70	37.0	6–80	30.93	3–80	28.28
K^{+} (mg/L)	0.5–9.0	3.07	2.2–8.0	5.94	0–10	3.58	0–9	3.67
Cl^{-} (mg/L)	13–60	30.09	9–93	40.20	7–120	14.61	7–120	39.7
HCO_3^{-} (mg/L)	120–350	266.81	185 + 455	326	95–450	304.17	95–455	299.87
SO_4^{2-} (mg/L)	1.5–4.0	5.59	2.1–4.2	3.24	1.5–5.0	2.65	1.5–5.0	3.15
NO_3^{-} (mg/L)	1.4–4.0.0	2.59	0.9–8.5	4.54	0.5–6.8	2.55	0.5–8.5	2.7
Hardness (mg/L)	115–340	231.18	105–365	250.20	86–410	250.73	86–410	247.64
(b) Post-melting season								
pH	6.95–7.91	7.61	7.01–8.27	7.52	6.98–8.36	7.47	6.95–8.36	7.50
Temp. (°C)	15–19	16.90	15–21	17.20	14–20	16.27	14–21	16.20
EC (µS/cm)	140–698	431.18	160–1290	598.0	143–1305	543.13	140–1305	529.46
TDS (mg/L)	90–447	276.09	102–826	383.0	92–835	345.75	90–835	345.75
Ca^{2+} (mg/L)	25–97	42.82	21–75	52.0	23–128	58.39	21–128	55.50
Mg^{2+} (mg/L)	3–22	11.82	9–55	22.20	5–56	16.77	3–56	16.38
Na^{+} (mg/L)	2.1–30	14.69	4–74	30.0	3.5–106	28.39	2.1–106	26.34
K^{+} (mg/L)	0.25–6.5	2.17	0.9–8.9	4.90	0–11.8	2.86	0–11.8	2.74
Cl^{-} (mg/L)	7.2–43	21.68	7–95	36.80	3–105	31.10	3–105	30.3
HCO_3^{-} (mg/L)	85–315	187.64	145–515	288	105–525	237.15	85–505	265
SO_4^{2-} (mg/L)	1.1–3.3	2.11	1.15–3.1	2.27	0.3–4.15	2.38	0.3–4.15	2.33
NO_3^{-} (mg/L)	0.9–4.0.3	2.03	0.3–8.8	4.05	0–6.3	2.02	0.-8.5	2.17
Hardness (mg/L)	79–300	214.54	94–405	224.8	80–410	215.5 1	79–410	211.79

and 8.03, while that of the tube wells ranged between 7.10 and 8.30. The groundwater hardness ranged between 86 and 410 mg/L with an average of 218 mg/L. The lower values have been found in spring water with the exception of location no. 29 (340 mg/L) and high in tube wells with the exception of well no. 4 (94 mg/L).

The Ca^{2+} concentration in groundwater varied from 20 mg/L to 127 mg/L with an average of 73.77 mg/L, being high in tube wells (20–127 mg/L) with the exception of location no. 4 (20 mg/L); moderate in springs (36–105 mg/L) with the exception of location no. 29 (105 mg/L); and relatively low in dug wells (27–100 mg/L) with the exception of well no. 50 and 58 (100 mg/L). The Mg^{2+} concentration of groundwater ranged from 5 mg/L to 35 mg/L with an average of 17.34 mg/L. Mg^{2+} did not fluctuate much, being low in springs (5 mg/l–25 mg/L) with the exception of location no. 53 (25 mg/L), intermediate in dug wells (8 mg/L–28 mg/L), and relatively high in tube wells (6–35 mg/L) with the exception of well no. 5 (7 mg/L) and 6 and 7 (6 mg/L). Na^+ concentration in groundwater varied from 3 mg/L to 80 mg/L with an average value of 28.28 mg/L, being high in tube wells (6–80 mg/L) with the exception of location no. 14 (9 mg/L), 15 (10 mg/L), 19 and 20 (10 mg/L), 27 (9 mg/L), 30 (6 mg/L), 31 (8 mg/L), 32 (10 mg/L), and 34 (8 mg/L), moderate in dug wells (7–70 mg/L) with the exception of location no. 50 (70 mg/L), and low in springs (3–42 mg/L) with the exception of location no. 52 (42 mg/L). The K^+ concentration found in groundwater varied from 0 to 10 mg/L with the mean of 3.67 mg/L. K^+ exhibited rather uniformity in variation, ranging from 0.5 mg/L to 9 mg/L in springs being relatively higher at location no. 39 (9 mg/L), 2.2 mg/L to 8.0 mg/L in dug wells being higher at location no. 10 and 50 (8 mg/L), and 0 to 10 mg/L in tube wells being higher at location no. 12 (10 mg/L). However, the mean concentration is relatively high in dug wells (5.94 mg/L); moderate in tube wells (3.58 mg/L); and low in springs (3.07 mg/L).

Among the anions, HCO_3^- was the dominant anion and represented the total alkalinity of the water in the study area. The phenolphthalein alkalinity was found to be zero. HCO_3^- in groundwater varied between 95 and 455 mg/L with an average value of 2.99.87 mg/L, being high in dug wells (185 to 455 mg/L) with the exception of location no. 10 (185 mg/L); moderate in tube wells (95–450 mg/L) with the exception of location no. 6 and 7 (95–105 mg/L), respectively; and low in springs (120–350 mg/L) with the exception of location no. 29 (350 mg/L) and 37 (345 mg/L). The Cl^- content in groundwater varied from 7 to 120 mg/L with a mean of 39.7 mg/L. The higher values have been found in tube wells with the exception of well no. 14, 15, and 17 (7 mg/L) and 13 (9 mg/L), moderate in dug wells with anomalous values at location no. 50 (93 mg/l) and 58 (60 mg/L), and low in springs with the exception of location no. 51 (60 mg/L), 52 (50 mg/L), and 53(55 mg/L). SO_4^{2-} in groundwater has been found to be at lower levels ranging from 1.5 mg/L to 6.6 mg/L with a mean value of 3.15 mg/L. No exceptional concentration has been found in the study area. The NO_3^- levels found in groundwater varied from 0.4 mg/L to 8.5 mg/L with a mean concentration of 2.70 mg/L. The lower values have been found in spring waters (0.9–8.5 mg/L) with a relatively high values at location no. 29 (4 mg/L) and 39 (3.9 mg/L); high concentration in waters of dug wells (0.9 to 8.5 mg/L) with the exception of well 18(0.9 mg/L); and moderate values of waters in tube wells (0.4 mg/L–6.8 mg/L) with relatively high values at location no. 12 (6.00 mg/L), 47 (6.80 mg/L), 56 and 57 (4.0 mg/L), 64 (4.10 mg/L), and 69 (5.0 mg/L).

3.8 Analyzing the Source of Ions Using Statistical Analysis

3.8.1 Correlation Matrix of Hydrogeochemical Data

The statistical correlation matrix developed for the geochemical data of groundwater for pre-melting and post-melting seasons is given in Table 3.2. The correlation shows high positive and significant relation between Ca^{2+} and HCO_3^- (0.86, 0.74), Ca^{2+} and hardness (0.94, 0.85), and HCO_3^- and hardness (0.92, 0.94) suggesting the predominant source of these ions be carbonate lithology mainly coming through dissolution of calcite, and a relatively lower positive correlation between Mg^{2+} and HCO_3^- (0.62, 0.73) and Mg^{2+} and hardness (0.62, 0.69) indicating some contribution coming through dissolution of dolomite as well. Besides, a positive correlation between Na^+ and HCO_3^- (0.44, 0.73), Mg^{2+} and Na^+ (0.31, 0.78), and Mg^{2+} and Cl^- (0.43, 0.86) though relatively low in pre-melting season indicates the dissolution of silicates (primary and/or secondary silicates). The possible minerals furnishing these ions could be the pyroxenes, amphiboles (containing ferromagnesian minerals), and/or their altered products. Moreover, a positive and significant correlation between Na^+ and Cl^- (0.74, 0.87) cannot be related solely to the dissolution of soil salts; a significant contribution may be furnished from anthropogenic sources in the form of domestic wastes, polluted surface water bodies, and/or evaporation of waterlogged bodies, thereby increasing the salinity of groundwater. pH is moderately correlated with HCO_3^- (0.38, 0.51), Mg^{2+} (0.36, 0.37), Ca^{2+} (0.34, 0.36), Cl^- (0.35, 0.38), and Na^+ (0.15, 0.30), while K^+ and SO_4^{2-} show negative to very low correlation with pH. Ca^{2+} and K^+ show negative correlation in both the seasons.

The positive correlations of K^+ (0.57, 0.60), Na^+ (0.49, 0.42), SO_4^{2-} (0.41, 0.55), and Cl^- (0.41, 0.51) with NO_3^- manifest the possible anthropogenic inputs from agricultural activities, domestic wastes, and seepage from polluted surface water bodies. The high positive correlation among the variables thus indicates the influence of lithology of the area particularly carbonate lithology and silicate lithology. However, a modifying influence to the chemistry of groundwater is also imparted through human influence.

3.8.2 Factor Analysis of Hydrogeochemical Data

The factor analysis of hydrogeochemical data explains the observed relations in simpler terms that are expressed as a new set of variants called factors. FA is used as a numerical method of discovering variables that are more important than others

Table 3.2 Correlation coefficient matrix of hydrogeochemical variables

z	pH	EC	TDS	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	Hardness	HCO_3^-	SO_4^{2-}	NO_3^-
(a) Pre-melting season												
pH	1.00	0.40	0.45	0.34	0.36	0.15	−0.03	0.35	0.40	0.38	−0.01	0.21
EC		1.00	0.96	0.76	0.57	0.59	0.21	0.76	0.82	0.88	0.15	0.36
TDS			1.00	0.76	0.64	0.60	0.22	0.78	0.85	0.92	0.19	0.40
Ca^{2+}				1.00	0.34	0.10	−0.06	0.47	0.94	0.86	0.05	0.13
Mg^{2+}					1.00	0.31	0.23	0.43	0.62	0.62	0.05	0.21
Na^+						1.00	0.34	0.74	0.19	0.44	0.23	0.49
K^+							1.00	0.20	0.04	0.17	0.21	0.57
Cl^-								1.00	0.54	0.58	0.19	0.41
Hard.									1.00	0.92	0.07	0.18
HCO_3^-										1.00	0.13	0.29
SO_4^{2-}											1.00	0.47
NO_3^-												1.00
(b) Post-melting season												
pH	1.00	0.48	0.47	0.36	0.37	0.30	0.12	0.38	0.47	0.51	0.09	0.31
EC		1.00	0.99	0.65	0.80	0.80	0.15	0.87	0.92	0.96	0.33	0.43
TDS			1.00	0.65	0.80	0.79	0.15	0.87	0.92	0.96	0.32	0.43
Ca^{2+}				1.00	0.23	0.17	−0.03	0.37	0.85	0.74	0.17	0.12
Mg^{2+}					1.00	0.78	0.13	0.86	0.69	0.73	0.29	0.39
Na^+						1.00	0.16	0.87	0.54	0.73	0.27	0.42
K^+							1.00	0.18	0.08	0.15	0.39	0.60
Cl^-								1.00	0.73	0.78	0.34	0.51
Hard.									1.00	0.94	0.28	0.33
HCO_3^-										1.00	0.28	0.37
SO_4^{2-}											1.00	0.55
NO_3^-												1.00

that represent parameter variation and identify the hydrochemical processes (Bakac 2000; Mir and Gani 2019). The results of the FA are given in Table 3.3. In order to have a better interpretation and understanding and to determine the mechanisms, processes, and sources that control the chemistry of the groundwater of the area, FA has been carried out in this study.

The FA performed on 12 different parameters indicated the 3 different trends in the present area. The FA of the groundwater samples explained that 75.68% of the total variability is accounted by first three factors with Eigen values greater than 1. Factor 1 explained 50.99% of total variance followed by 16.77% and 7.91% by the factors 2 and 3, respectively. Factor 1 includes EC, TDS, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, and hardness with very high factor loadings of Ca^{2+}, HCO_3^-, hardness, EC, and TDS and less pronounced values of Mg^{2+} and Cl^- (also obvious from their moderate correlation with Ca^{2+}). The possible source of Mg^{2+} and Cl^- ions could be the carbonate minerals, pyroxenes, and/or amphiboles (present in the carbonate and silicate lithology in the catchment areas). Factor 1 therefore seems to be related to the dissolution

Table 3.3 Variables, communalities, and factor loadings after varimax rotation

	Pre-melting season				Post-melting season			
Parameter	Factor 1	Factor 2	Factor 3	Communalities	Factor 1	Factor 2	Factor 3	Communalities
pH	0.45	0.30	0.17	0.32	0.22	0.52	0.17	0.35
EC (µS/cm)	0.83	0.45	0.14	0.91	0.73	0.64	0.17	0.98
TDS (mg/L)	0.85	0.46	0.17	0.96	0.73	0.64	0.16	0.97
Ca^{2+} (mg/L)	0.95	−0.11	0.04	0.93	0.04	0.97	−0.02	0.94
Mg^{2+} (mg/L)	0.56	0.42	−0.02	0.49	0.88	0.24	0.14	0.86
Na^{+} (mg/L)	0.17	0.84	0.26	0.81	0.92	0.13	0.16	0.90
K^{+} (mg/L)	−0.08	0.45	0.57	0.53	0.01	−0.02	0.85	0.72
Cl^{-} mg/L)	0.52	0.68	0.14	0.76	0.87	0.32	0.22	0.92
Hardness (mg/L)	0.98	0.05	0.04	0.97	0.50	0.84	0.09	0.96
HCO_3^{-} (mg/L)	0.92	0.24	0.13	0.92	0.63	0.74	0.13	0.96
SO_4^{2-} (mg/L)	0.09	−0.09	0.85	0.74	0.15	0.16	0.73	0.58
NO_3^{-} (mg/L)	0.12	0.43	0.74	0.74	0.31	0.12	0.82	0.79
Eigen value	6.12	2.01	0.95	–	7.01	1.78	1.14	
% of total variance	50.99	16.77	7.91	–	58.41	14.83	9.52	
Cumulative	50.99	67.76	75.67	–	58.41	73.24	82.76	

of carbonate minerals/lithology dominantly calcite as indicated by the high factor loadings and strong positive correlation of Ca^{2+}, HCO_3^-, and hardness. Factor 1, therefore, mainly measured the hardness, alkalinity, and dissolution of alkaline earths. Therefore, this factor seems to be lithologically controlled.

Factor 2 includes very high loading of Na^+ and relatively less pronounced loading of Cl^-. This factor indicated a possible dissolution of secondary silicates and soil salts, leading to the enrichment of Na^+ and Cl^- in finer detrital sediments comprising clay/silt/sandy-clay/sandy-silt. The fine-grade sediments provide a subsurface hydrogeological environment that extends residence time of groundwater due to low hydraulic conductivity and thereby promotes large residence time and contact surface, hence greater soil-water interaction. High positive correlation between Na^+ and Cl^- also indicated this phenomenon. Moreover, moderate loadings of Mg^{2+}, K^+, and NO_3^- on factor 2 (F_2) and the moderate correlation between Na^+ and NO_3^-, Cl^- and NO_3^-, Na^+ and K^+, and Na^+ and Mg^{2+} indicated some contribution from the possible anthropogenic sources (domestic wastes, waterlogged bodies, leaching from sewage drains, and/or agricultural inputs) to factor loading 2 (F_2) as well. Factor 2, therefore, seems both lithologically and non-lithologically controlled.

Factor 3 includes SO_4^{2-}, NO_3^-, and K^+ with feeble loadings of Na^+ and Cl^-. This factor indicated influence of anthropogenic activities/sources on groundwater chemistry. The possible provenances of these nutrients include leaching from surface soils of the agricultural farmlands, domestic wastes, leakage from sewer drains, and/or influx from polluted surface water bodies.

FA was also performed on the water samples collected in the post-melting season. About 82.75% of the total variability is accounted by three factors (F_1, F_2, F_3) having Eigen value greater than unity. Factor 1 explained 58.40% of total variance followed by 14.83% and 9.52% by factors 2 and 3, respectively. Unlike pre-melting season, here, factor 1 (F_1) showed the high loading of Na^+ followed by Mg^{2+} and Cl^- and also a moderate to low loadings of HCO_3^-, hardness, and NO_3^- as well. These variables also exhibit a high to moderate correlation coefficient. This factor may be attributed to the influence of weathering and dissolution of secondary silicates, thereby imparting their chemical character to the groundwater chemistry. Surface alluvium and/or clay/slit strata/sandy slit/sandy-clay lenses seem to be the most influential sources that provided the highly reactive secondary minerals and/or soil salts to groundwater moving vertically or horizontally.

Factor 2 exhibited very high loading of Ca^{2+}, hardness, and HCO_3^-, reflecting dissolution of carbonate minerals particularly calcite, thereby controlling the alkalinity and hardness of groundwater. High positive correlation between Ca^{2+}, hardness, and HCO_3^- also confirms the dissolution of carbonate minerals particularly calcite as the dominant contributor to the factor 2 (i.e., controlling hardness and alkalinity of groundwater). There is also a moderate influence of Cl^- and Mg^{2+} as indicated by their moderate F_2 values and correlation coefficient.

Like pre-melting season, factor 3 included K^+, NO_3^-, and SO_4^{2-} indicating possible input from anthropogenic sources, viz., agricultural farmlands, domestic wastes, leakage from sewer drains, and polluted surface water bodies and vegetable gardens. The above variables also showed good-moderate correlation coefficient indicating the possibility of their source being mainly non-lithological, i.e., anthropogenic sources.

3.9 Analyzing the Suitability of Groundwater for Various Uses

3.9.1 Suitability Criteria for Domestic Purposes

The quality of water plays a prominent role in promoting the standard human health as well as agricultural production. Whether groundwater of a given quality is suitable for a particular purpose depends on the criteria or standards of acceptable quality for the intended use (USEPA 1976). The chemical quality of water is an important factor to be considered in evaluating its usefulness for irrigation as well. Furthermore, the large numbers of health problems in developing areas are reported to be because of ignorance of water quality conditions (Niranjan et al. 1997). Human activity such as urbanization, industrialization, and mining may produce effluents, which pollute the environment as well as the groundwater. The quality standards established (WHO 2006; ISI 2012) for domestic purposes are summarized in Table 3.4.

Table 3.4 Summary of results of physicochemical characters and their permissible limits

Parameter	Range		WHO (2006)		ISI (2012)	
	Pre-melting season	Post-melting season	Acceptable level	Max. permissible level	Acceptable level	Max. permissible level
Temperature ºC	11.0–15.0	14.00–21.00	–	–	–	–
TDS mg/L	107–710	90–835	500	1500	500	3000
EC µS/cm	168–1110	140–1305	–	1600	800	4800
pH	7.10–8.36	6.95–8.36	7–8.5	6.5–9.2	6.5–9.2	9.2
Ca^{2+}	20–127	21–128	75	200	75	200
Mg^{2+}	5–35	3–56	<30 (if SO_4. Is 250 mg/L	150 (if SO_4. Is 250 mg/L	30	100
Na^+	3–80	2.1–106	–	200	–	–
K^+	0–9	0–11.8	–	12	–	–
Cl^-	7–120	3–105	200	250	250	1000
HCO_3^-	30–455	85–505	–	–	–	–
SO_4^{2-}	1.5–6.61	0.2–6.5	200	400	150	400
NO_3^-	0.5–8.5	0–8.8	–	50	45	–
Total hardness (mg/L)	86–410	79–410	100	500	300	600

In the present study, the range of the various parameters as given in the table showed that the concentrations of various constituents are well within the guidelines established by the WHO (2006) and ISI (2012) for drinking and domestic purposes. The results indicated that in the study area, the range of pH (7.1–8.36 and 6.95–8.36) of groundwater indicated an alkaline nature of groundwater. The groundwater is also colorless, odorless, and falls under freshwater (TDS <1000 mg/L) category (Carrol 1962; Freeze and Cherry 1979). Groundwater is moderately hard to very hard, with 14% of samples falling in moderately hard water and 37% as very hard water (Sawyer and MaCarty 1967). However, in the post-melting season, 23% of samples fall in moderately hard class, 63% in hard water class, and 14% in very hard water class (Tables 3.5 and 3.6). The overall hardness (86–410 and 79–410 mg/L) of all the samples fall within the maximum permissible limits (500 mg/L) of the WHO (2006) and ISI (2012). The concentration of Ca^{2+} and Mg^{2+} (alkaline earths) exceeds alkalis (Na + K). On the one hand, low concentration of Ca^{2+} may cause dental problems like tooth cavities and skeletal problems like bone fracture. On the other hand, high concentration is disadvantageous because of the hardness it imparts to the water that interferes with almost every cleaning task in the household and leads to incrustation of water-using appliances and boilers in industrial use. However, in this perspective, Ca^{2+} and Mg^{2+} concentrations found in groundwater are neither too low nor high and falls within the prescribed limits of the WHO and ISI. The range of Na^{+} (3–80 and 2.1–106 mg/L) in groundwater remains at lower levels and is quite below the permissible limits of the WHO and ISI. K^{+} concentration (0–9 and 0–11.8 mg/L) is relatively low; however, some locations showed increasing trend of K^{+} in groundwater which is an alarming indication of the increasing influx of K^{+} from agricultural farmlands. The concentration level, however, is within the maximum permissible limits of the WHO (12 mg/L).

In the case of anions, HCO_3^{-} is the dominant anion and exceeds over strong acids (Cl^{-}, SO_4^{2-} NO_3^{-}), thereby imparting basic nature to groundwater. Bicarbonates are not generally regarded as undesirable for municipal supplies, but are highly objectionable for some of the industrial uses because of the problem of scale formation and if used for sprinkler irrigation, it may cause white deposits on fruits and leaves

Table 3.5 Water classes (in terms of hardness) at different locations

Hardness (mg/L)	Water class	Pre-melting season	Post-melting season
75–150	Moderately hard	4, 5, 6, 8, 10, 14, 15, 20, 24, 25	4, 5, 6, 7, 8, 9, 10, 14, 15, 17, 19, 20, 21, 23, 24, 25
150–300	Hard	1, 2, 3, 7, 9, 13, 17, 18, 19, 21, 22, 23, 27, 30, 35, 36, 37, 39, 40, 45, 51, 52, 53, 54, 55, 59, 63, 64, 65, 66, 67, 68, 69	1, 2, 3, 11, 12, 13, 18, 22, 26, 27, 29, 30, 31, 32, 33, 34, 35, 36, 37, 39, 40, 41, 42, 43, 44, 47, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 63, 64, 65, 66, 67, 68, 69, 70
>300	Very hard	12, 16, 26, 28, 29, 31, 32, 33, 34, 38, 41, 42, 43, 44, 46, 47, 48, 49, 50, 58, 60, 61, 62	16, 28, 38, 45, 46, 48, 49, 50, 61, 62

Table 3.6 Water classes based on Wilcox (1955)

Water class	Na^+ (%)	Pre-melting season			Post-melting season		
		Spring	Dug well	Bore well	Spring	Dug well	Bore well
Excellent	20	24, 25, 29, 35, 36, 37, 39, 40, 51, 52	1, 18	13, 14, 15, 16, 17, 19, 20, 22, 26, 27, 28, 30, 31, 32, 33, 34, 38, 41, 42, 43, 44, 45, 46, 54, 59, 60, 61, 63	24, 25, 29, 35, 36, 37, 39, 40, 51	1, 18	13, 14, 15, 16, 17, 19, 20, 22, 27, 30, 31, 32, 33, 34, 38, 44, 45, 54, 59, 60, 61, 68
Good	21–40	53	50, 58	2, 3, 4, 5, 7, 8, 9, 11, 12, 21, 23, 47, 48, 49, 55, 56, 57, 62, 65, 66, 67, 68, 70	52, 53	10, 50, 58	2, 3, 4, 5, 6, 7, 8, 9, 11, 12, 21, 23, 26, 28, 41, 42, 43, 46, 47, 48, 49, 55, 56, 57, 62, 63, 64, 65, 66, 67, 69, 70
Permissible	41–60	–	10	64, 6, 69	–	–	–

(Subrahmanyam and Yadaiah 2001). The range of HCO_3^- (30–455 and 85–505 mg/L) in groundwater indicated generally the relatively lower levels and cannot pose any such nuisance as mentioned above. The concentration of Cl^- (7–120 and 3–105 mg/L) falls within the permissible limits of the WHO and ISI. However, anomalous values at certain localized areas (particularly in urban Srinagar) are of concern because the inputs from anthropogenic sources have increased the concentration levels of Cl^- against its natural background concentrations and/or atmospheric inputs. The high concentration at some locations may increase the salinity of groundwater, but the levels are much below the maximum permissible limits of the WHO and ISI and, therefore, cannot cause laxative effects and/or corrosive effects to equipments or pipelines. SO_4^{2-} concentration (1.5–6.61 and 0.2–6.5 mg/L) of groundwater is very low and is well below the prescribed limits of the WHO and ISI. NO_3^- concentration (0.5–8.5 and 0–8.8 mg/L) in groundwater is also at lower levels and is quite below the maximum permissible limits of the WHO and ISI and does not pose any threat of methemoglobinemia in infants.

Since the dissolved loading of various ionic parameters is generally within the maximum acceptable limits of the WHO and ISI guidelines, the groundwater tapped in Srinagar and its adjoining rural areas can be regarded as potable and suitable for domestic and drinking purposes with respect to major ions. Nevertheless, the increasing tendency and enrichment of water with respect to K^+, NO_3^-, and Cl^- at some locations is an alarming indication of contamination of shallow aquifers. However, the extent of contamination has not yet reached the level of pollution and is still within the limits of potable water, in terms of national and international drinking water standards.

3.9.2 Suitability Criteria for Agricultural Purposes

For agricultural purposes, the total concentration of dissolved matter in water (salinity), the relative proportion of sodium to other principal cations (Na %), and sodium adsorption ratio (SAR), bicarbonate, etc. are used for the evaluation (Hem 1985). Wilcox (1955) also classified groundwater for irrigation purposes based on percent sodium and EC. Eaton (1950) recommended the concentration of residual sodium carbonate (RSC) to determine the suitability of water for irrigation purpose. The US Salinity Laboratory of the Department of Agriculture adopted salinity hazard diagram for agriculture quality check (US Salinity Laboratory 1954). In the study area, the groundwater samples have been checked for both the irrigation and agricultural purposes. The different indices considered are discussed as sodium percent (Na%), residual sodium carbonate (RSC), sodium adsorption ratio (SAR), salinity hazard diagram, etc.

(a) Sodium Percent: Na % was calculated after Wilcox (1955) equation:

$$\%\mathrm{Na} = \left(\mathrm{Na} + \mathrm{K} / \mathrm{Ca} + \mathrm{Mg} + \mathrm{Na} + \mathrm{K}\right) \times 100$$

The Na % values are generally low to intermediate (4.08 to 49.71, pre-melting, and 3.96 to 40.51, post-melting) in the groundwater and falls in excellent to permissible water class. The total calcium and magnesium ion content of groundwater exceeds that of sodium. Such water is suitable for irrigation, even though the total mineral content may be quite high.

(b) Residual Sodium Carbonate (RSC): RSC is calculated using the following relation (Eaton 1950) where all ionic concentrations are expressed in epm.

$$\mathrm{RSC} = \left(\mathrm{CO_3}^{2-} + \mathrm{HCO_3}^{-}\right) - \left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right)$$

According to the US Department of Agriculture, water having more than 2.5 epm of RSC is not suitable for irrigation purposes. Groundwater of the study area was classified based on RSC, and the results are presented in Table 3.7 for both seasons. Based on RSC values, over 69 samples (98.57%) fall in the safe category, and 1 sample (1.43%) falls in the moderate category (pre-melting season), while over 94% of the samples (RSC < 1.25) fall in the safe category and 6% in moderate (RSC: 1.25–2.5) category in the post-melting season.

Table 3.7 Distribution of residual sodium carbonate (RSC) in groundwater

RSC	Suitability for irrigation	Percentage of samples in this category	
		Pre-melting season	Post-melting season
<1.25	Safe	98.57%	94.29%
1.25–2.50	Moderate	1.43%	5.71%
>2.5	Unsuitable	0	0

(c) Sodium Adsorption Ratio (SAR): The US Salinity Laboratory (1954) defined the sodium adsorption ratio (SAR) of water where the concentrations are expressed in milliequivalent per liter.

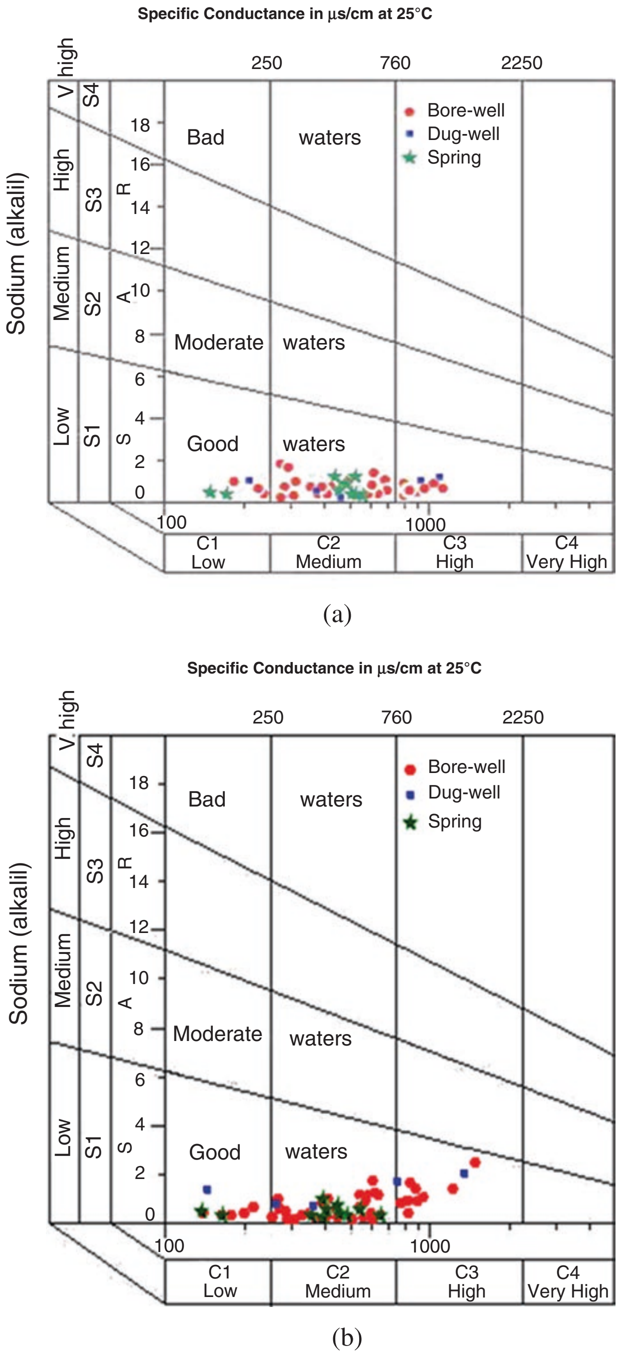
$$\mathrm{SAR} = \frac{\mathrm{Na}^{+}}{\left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} / 2\right)^{1/2}}$$

The classification of groundwater samples from the study area with respect to SAR is represented in Table 3.8. During both the sampling seasons, the SAR values of the samples were found to be less than 10 and fall in the "excellent" field.

The suitability of water for irrigation was evaluated based on the SAR and specific conductance by plotting the data in on the US Salinity Laboratory (USSL) diagrams as shown in Fig. 3.4a, b and Table 3.8. The USSL diagram best explains the combined effect of sodium and salinity hazard. According to this diagram, all the samples of pre- and post-melting season fall in low sodium (alkali) hazard and low to high salinity hazard. The waters are found mostly confined in three classes of water type, i.e., C_2S_1, C_3S_1, and C_1S_1. In the pre-melting season, 9% of samples fall under C_1S_1 class (low sodium and salinity hazard); 50% in C_2S_1 class (low sodium and medium salinity hazard); and 41% in C_3S_1 class (low sodium and high salinity hazard), whereas in the post-melting season, 13% of samples lie in C_1S_1 class; 70% in C_2S_1 class; and 17% in C_3S_1 class. Thus, the groundwater in the study area falls in the category of the good to moderate class in terms of the quality of water for irrigation. The water class C_3S_1 (high salinity and low sodium hazard) is found at locations that lie either in the vicinity of polluted water bodies and/or agricultural farmlands, thereby reflecting the possible influence of anthropogenic activities that lead to the slight enrichment of solutes. However, the high salinity waters possess low sodium hazard (SAR), with little danger to the development of harmful level of the exchangeable sodium. Thus, the groundwater can be used for irrigation in almost all soils. Moreover, the total Ca^{2+} and Mg^{2+} ion content of groundwater equals and/or exceeds that of Na^{+} that could favor the maintenance of good tilth and permeability despite the relatively high salinity (an index of dissolved solids concentration). Though there is an increase in salinity at some locations (6, 7, 47, 48, 49, 50, 62, 69), the SAR, %Na, and RSC are well below the permissible limits for the irrigation purposes, and the water is mostly suitable for agricultural purposes (Table 3.9).

Table 3.8 Suitability of water for irrigation purpose based on USSL classification

		Percentage of samples in this category	
SAR	Class	Pre-melting season	Post-melting season
<10	Excellent	100	100
10–18	Good	0	0
18–26	Fair	0	0
>26	Poor	0	0



(a)

(b)

Fig. 3.4 US salinity hazard diagram of (**a**) pre-melting season and (**b**) post-melting season

Table 3.9 Water class according to SAR and salinity hazard

	Pre-melting season			Post-melting season		
Water class	Spring	Dug well	Bore well	Spring	Dug well	Bore well
C1S1	24, 25	10	4, 8, 15	24, 25	10	4, 6, 8, 14, 15, 19, 20
C2S1	29, 35, 36, 37, 39, 40, 51, 52, 53,	1, 18	2, 3, 5, 6, 7, 9, 11, 12, 13, 14, 16, 17, 19, 20, 21, 22, 23, 26, 27, 30, 31, 32, 34, 42, 45, 54, 55, 56, 59, 63, 65, 67, 68, 69, 70	29, 35, 36, 37, 39, 40, 51, 52, 53	1, 18	2, 3, 5, 7, 9, 11, 12, 13, 17, 21, 22, 23, 26, 27, 30, 31, 32, 33, 34, 38, 41, 42, 44, 54, 55, 56, 57, 59, 60, 63, 64, 65, 66, 67, 68, 69, 70
C3S1		50, 58	28, 33, 38, 41, 43, 44, 46, 47, 48, 49, 57, 60, 61, 62, 64, 66, 70		50, 58	16, 28, 43, 45, 46, 47, 48, 49, 61, 62

3.10 Discussion

In the present study area, the higher concentration of Ca^{2+} and HCO_3^- ions in the groundwater indicated the intense chemical weathering and dissolution of minerals mainly carbonate rocks in the area. In general, the interaction of carbonate rocks with carbonic acid that is produced due to the reaction between the CO_2 with meteoric water liberates abundance of HCO_3^- ions into water. This phenomenon may also produce Ca^{2+} ions resulting in the high concentration of Ca^{2+} in the groundwater of the area. The statistical analysis also suggested that Ca^{2+} ion is mainly derived by the dissolution of carbonate minerals such as the calcite minerals in the area. In spite of similarities in the inorganic chemistry of Ca^{2+} and Mg^{2+}, there is no pronounced correlation between these two ions in the area. A moderate to weak correlation exists between the Ca^{2+} and Mg^{2+} (0.34; 0.23). Therefore, the origin of Mg^{2+} may probably be attributed to the dissolution of alumino-silicates, pyroxenes, and amphiboles of the volcanic rocks and their weathered products. An appreciable amount of volcanics rocks and their weathered products are present in the watershed areas of study area. However, the study of Ca/Mg ratio suggested the dissolution of calcite and some contribution from dolomite as well (Fig. 3.5). Maya and Loucks (1995) have reported that the dissolution of dolomite should happen if the ratio Ca/Mg =1, whereas a higher ratio indicates the greater calcite contribution. Furthermore, a higher Ca/Mg molar ratio (>2) indicates the dissolution of silicate minerals which contribute both Ca^{2+} and Mg^{2+} ions to groundwater (Katz et al. 1998). For the present study area, the location of the points closer to the line (Ca/Mg = 1) indicated the dissolution of dolomite (Fig. 3.5). Most of the points having a ratio between 1 and 2 and/or closer to 2 indicate the dissolution of calcite. Those with values on the higher side indicated pronounced input from the dissolution of silicate minerals. The ionic ratio of Ca/Mg, therefore, explained the contribution of dissolution of carbonate rocks as well as the silicate minerals as the possible sources of Ca^{2+} and Mg^{2+} in the water. However, the results also indicated some modifying influence of possible cation-exchange reactions on the Ca^{2+} and Mg^{2+} concentration in the

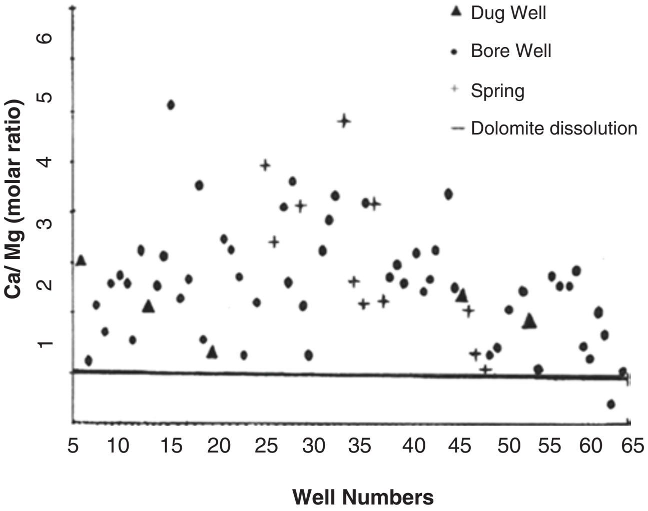


Fig. 3.5 Plot of Ca/Mg molar ratio (Maya and Loucks 1995)

weathered material and/or alluvium present within the sedimentary unconsolidated formations of the area.

Similarly, the lower Na^+ and K^+ content also reflected the major influence on their origin by the catchment lithology. Na^+ fluctuated irregularly, while K^+ showed a definite regularity in its seasonal distributional pattern which may be attributed to its low geochemical mobility. However, increasing concentration of K^+ against its background levels at some locations (2, 3, 10, 12, 21, 23, 37, 39, 50, 58, 62, 64, 66, 69, and 70) indicated an alarming anthropogenic influence, however, yet in the offing. Soil amendments applied on paddy fields and floating gardens of Dal Lake are the possible secondary sources of increased K^+ concentration relative to normal background low levels at certain locations. The Na^+ ions in groundwater originate from the interaction of meteoric water with primary silicates in the outcrops of catchment areas and/or secondary alumino-silicates (clay minerals) with some modifying influence because of cation-exchange reactions as well. However, some enrichment from waterlogged bodies and anthropogenic sources cannot be overlooked, particularly in the low-lying areas (locations 6, 7, 47, 48, 49, 50, 62, and 69). This is also evident from the positive correlation and high factor loadings (F_2, pre-melting, and F_1, post-melting) of these two ions.

Relatively low concentration of Cl^- manifests low background levels of the lithological source in the area. No clearly defined linear relationship between concentration of Cl^- and Na^+ is apparent in the groundwater samples under consideration. This suggests that the concentrations of the two constituents are heavily influenced by factors other than the dissolution of halite. Nevertheless, the anomalous concentrations observed in the lower reaches in urban localities and near polluted surface water bodies and/or waterlogged bodies are indicative of the increasing anthropogenic influence in the form of domestic wastes, via improper sewage disposal, faulty drainage systems, etc. as there are no apparent Cl^- sources in the aquifer-matrix of the area. Hence, anthropogenic activities locally affect Cl^- concentrations in groundwater in both the sampling seasons. This is also evident from the positive and significant correlation and high factor loadings in both the sampling seasons.

In Srinagar, NO_3^- levels are generally low and fall in the concentration ranges that represent the possible low natural/background levels (Madison and Brunett 1984). However, high concentrations of NO_3^-, which may suggest human influences, appear to occur in isolated wells and/or localized areas (locations 12, 29, 39, 47, 50, 56, 57, 58, 64, and 69). Moreover, seasonal variation of NO_3^- and K^+ exhibited more or less identical behavior suggesting that relatively high levels of K^+ are generally present in the areas where agricultural activities are more intensive. The relatively high concentration of NO_3^- suggested the possible input from domestic wastes coupled with leaching of the nutrients from agricultural farmlands as NO_3^- fertilizers are often added to cultivated soils as an important plant nutrient. K^+ and NO_3^- may originate mostly from fertilizers and domestic wastes (point sources and non-point sources). However, due to the very different chemistry of K^+ and NO_3^-, there may be a considerable time lag between their rates of movement in the unsaturated zone of the groundwater aquifer. This could also explain the anomalous concentration levels of these ions. The higher concentrations of these constituents, though not alarming at this stage, may go to higher levels in the near future. SO_4^{2-} content in percentage of total anions has no tendency to increase from recharge to discharge areas. Ideally, the SO_4^{2-} content in groundwater should increase toward the discharge areas (Toth 1966). The temporo-spatial variation (indicates general dilution effect, in the summer season) besides, no exceptional variation and concentration have been found in the study area. SO_4^{2-} high (relatively) may be attributed to the possible input from swamp areas/waterlogged bodies and/or topsoil layers. Apart from atmospheric input, some enrichment from anthropogenic sources (though not conspicuous) cannot be overlooked as is evident from high loading of SO_4^{2-} in factor 3 (possible anthropogenic factor).

3.11 Conclusion

The chemical quality of groundwater is very important in determining its suitability for a sustainable use such as public water supply, irrigation, and industrial applications. Furthermore, the physical and chemical parameters also play a significant role in classifying and assessing water quality. The physicochemical parameters of groundwater of the present study area after comparing with the prescribed specifications or standards show that groundwater is suitable for drinking and domestic purposes as most of the constituents are within the permissible limits. The values of TDS and EC fall in the freshwater and low salinity category. The range of hardness of groundwater samples indicates moderately hard to very hard water types and falls within the maximum permissible limits. The groundwater shows basic nature with alkaline earths and weak acids exceeding alkalis and strong acids. Overall the results indicated the suitability of the water for domestic purposes. Nevertheless, the increasing tendency and enrichment of water with respect to K^+, NO_3^-, and Cl^- at some locations is an alarming indication of contamination of shallow aquifers. The low sodium hazard and low to slightly high salinity along with safe to moderate category of water with respect to RSC indicated the portability and suitability of groundwater for agricultural purposes. However, relatively an increase in salinity at some locations is a matter of concern and should be assessed and monitored in the future.

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Chapter 4
Polycyclic Aromatic Hydrocarbons: Toxic Effects and Their Bioremediation Strategies

Mir Sajad Rabani, Aukib Habib, and Mahendra Kumar Gupta

4.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of toxic non-polar organic contaminants, which consist of fused aromatic rings containing hydrogen and carbon atoms. PAHs are of serious concern due to their toxic, carcinogenic, mutagenic properties and cosmopolitan distribution (Harvey 1998). They are a large class of organic pollutants released mainly from anthropogenic sources, including automobiles and incomplete combustion of fossils, power plants, and also from natural sources like forest fires and volcanic eruptions as well (Samanta et al. 2002). These compounds can enter water and soil through irrigation with polluted waters (Labana et al. 2007). Because of their high hydrophobicity, PAHs get adsorbed into the surface soil or marine sediments and bind strongly to the organic matter. The adsorption on to sediments and high hydrophobicity prolong the life span of these contaminants in the environment (Kohl and Rice1998). The dense cloud of π electrons in a PAH compound on both sides of ring structures is mainly responsible for their biochemical persistence. Thus, these compounds are highly resistant to the nucleophilic attack (Haritash and Kaushik 2009). Due to high toxicity, persistence and prevalence in the environment PAHs are studied thoroughly (Blumer 1976). PAHs are often deposited in the sediments because of their low volatility and greater affinity for sediments and may affect bottom fishes and sediment in fauna adversely (McElroy et al. 1989). PAHs may persist for prolonged period until these contaminants are degraded, bioaccumulated or resuspended (Heitkamp and Cerniglia 1987). Additionally, PAHs are reported as priority pollutants by the United States Environmental Protection Agency (USEPA), as many of these are known teratogenic, mutagenic and carcinogenic in nature (Keith and Telliard 1979). PAHs are

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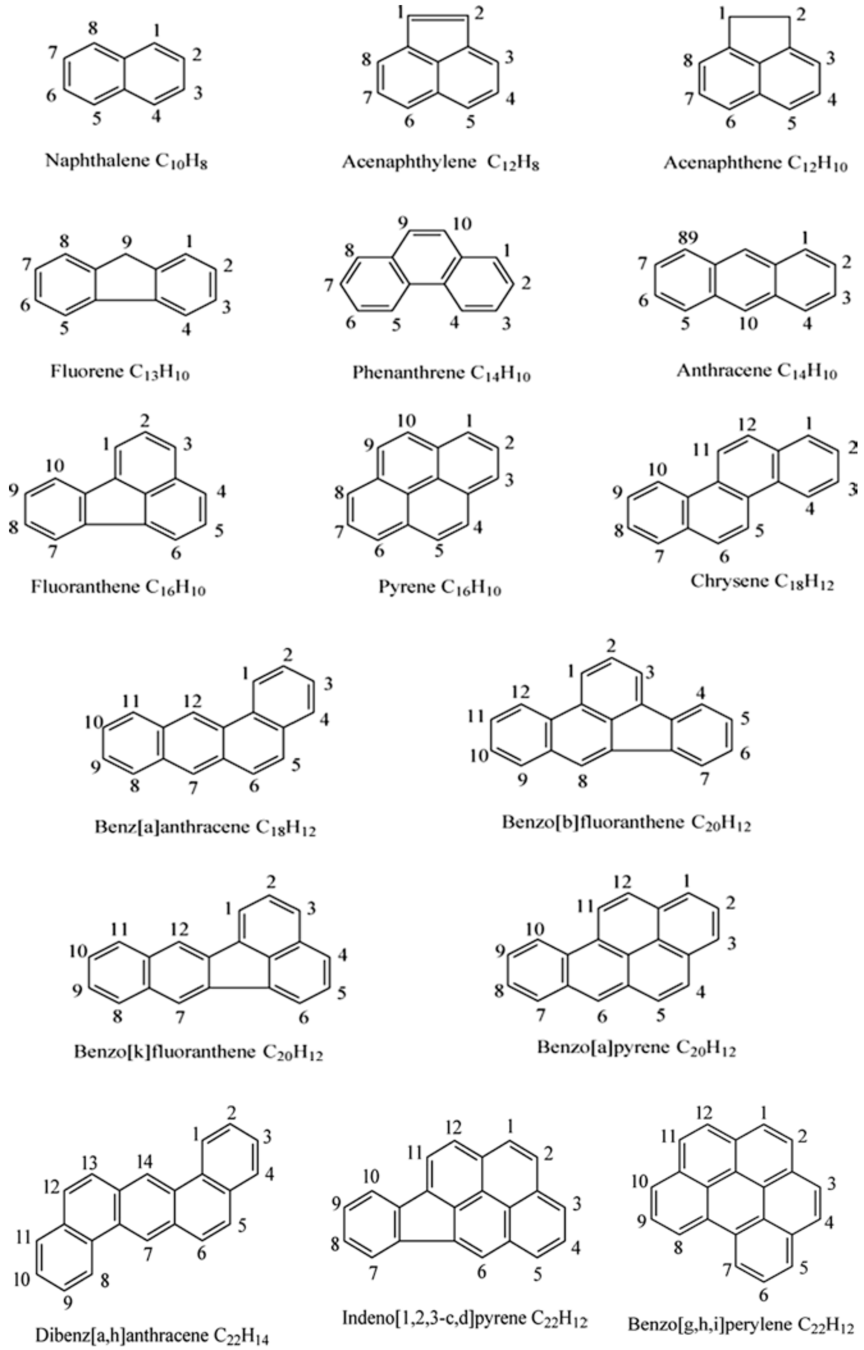
widespread contaminants found everywhere and of great environmental concern (Uyttebroek et al. 2007). The PAHs generally consist of carbon and hydrogen atoms. However, atoms like oxygen, nitrogen and sulphur may often get substituted in the aromatic rings and converted to heterocyclic aromatic compounds (Cutright and Hwang 2006). These heterocyclic compounds are grouped together with PAHs (Wilson and Jones 1993). Further, unsubstituted PAHs are neutral, hydrophobic and non-polar compounds that are scattered randomly during energy conversion (Juhasz et al. 2000a, b).

The term ‘PAH’ basically refers to compounds containing carbon and hydrogen atoms. However, sometimes it may be substituted by oxygen, nitrogen or sulphur atoms in the aromatic rings to form heterocyclic aromatic compounds. Chemically, they comprise of two or more fused benzene rings in linear, cluster or sometimes angular arrangements as illustrated in Fig. 4.1 (Di Toro et al. 2000; Arey and Atkinson 2003). The persistence of PAHs decides their fate in the environment that contributes towards serious environmental concerns (Martens 1995). The role of PAHs in the atmospheric is another issue, since they react with pollutants like nitrogen oxides, sulphur dioxide and ozone to form nitro- and dinitro-PAHs, sulfonic acids and diones, respectively.

PAHs are among the most important classes of aromatic compounds that have caused a serious concern due to their toxic effects to mankind and ecosystem. Thus, are considered a great threat to the ecosystem stability because of their persistent nature. The USEPA has enlisted 16 PAHs as toxic and priority pollutants (Perelo 2010). These contaminants are highly hydrophobic with low water solubility and tend to get adsorbed onto the soil surfaces. The PAHs with two to six rings are of greater significance with respect to the human health and ecosystem stability.

Most of the research has been conducted on small or low-molecular-weight PAHs due to the sample availability. PAHs are natural pollutants of soil, water and air formed mainly due to incomplete combustion of fossil fuels, such as coal, wood and oil. They are component parts of pesticides, dyes and plastic products. Crude oil and coal are known as the natural repositories of PAHs. They are not synthesized for industrial purposes chemically. Nevertheless, they are also used for various purposes. They are mainly used as intermediates in pharmaceuticals, thermosetting plastics, agricultural products, lubricating materials, photographic products, etc. (Kaminski et al. 2008). PAHs are also present in asphalt used for road construction, additionally to roofing tar. Further, various refined products of PAHs are also used in the field of electronics, liquid crystals and functional plastics (Abdel-Shafy and Mansour 2016).

PAHs persist in soil for longer periods of time due to their hydrophobicity, persistence and aggregation property. The PAH concentrations in soil reflects the pollution to some ambient degree (Guo et al. 2011). The presence of PAHs in the atmospheric varies with the relative humidity, temperature and solar radiations. PAH distribution in soil is also related to biological degradation and various physicochemical processes like photooxidation and volatilization pattern of a site. These types of processes are observed in tropical soils frequently that may be a reason for varying concentrations of PAHs between tropical and temperate soils. PAHs in



Naphthalene $C_{10}H_8$

Acenaphthylene $C_{12}H_8$

Acenaphthene $C_{12}H_{10}$

Fluorene $C_{13}H_{10}$

Phenanthrene $C_{14}H_{10}$

Anthracene $C_{14}H_{10}$

Fluoranthene $C_{16}H_{10}$

Pyrene $C_{16}H_{10}$

Chrysene $C_{18}H_{12}$

Benz[a]anthracene $C_{18}H_{12}$

Benzo[b]fluoranthene $C_{20}H_{12}$

Benzo[k]fluoranthene $C_{20}H_{12}$

Benzo[a]pyrene $C_{20}H_{12}$

Dibenz[a,h]anthracene $C_{22}H_{14}$

Indeno[1,2,3-c,d]pyrene $C_{22}H_{12}$

Benzo[g,h,i]perylene $C_{22}H_{12}$

Fig. 4.1 Structure, numbering system and chemical formula of 16 PAHs priority pollutants enlisted by the USEPA marine sediments are highly persistent than soils and other places, since they are less subjected to photochemical or biological oxidation. PAH pollutants can bioaccumulate in terrestrial and aquatic habitats also. As a result of bioaccumulation and persistence, they are harmful to ecosystem and mankind; however, little information is available about the exposure of humans and the PAHs levels found in humans (Samanta et al. 2002).

4.2 Properties of PAH Compounds

The PAH compounds exhibit different physicochemical properties because of their nature and chemical structure. Their properties depend on molecular weight, number of rings and linkage arrangement. A change in the ring structure of PAHs results in change in their properties and hence in biological activity and their fate in the environment (Kanalay and Harayama 2000). The biochemical persistence of the PAH molecules is because of the dense cloud of π electrons present on both sides of the ring structures and are also resistant to nucleophilic attack (Haritashand Kaushik 2009). The aqueous solubility, volatility, chemical reactivity, resistance to oxidation and reduction decrease with the increase in the number of aromatic rings while increasing the boiling point, melting point, stability, hydrophobicity and solubility in fats and lipids (Eisler 1987; Leys 2004, Haritash and Kaushik 2009). Although there are several PAH pollutants, most regulations and data reporting focus on only few PAHs, generally 14 to 20 individual PAH compounds. But majority of them are of the view that there are 16 PAHs (Fig. 4.1) that are enlisted as toxic and priority pollutants by the USEPA (Perelo 2010). PAHs generally contain two or more than two fused benzene rings, where a pair of carbon atoms is shared between the rings in the molecules. The PAHs, which contain two to six benzene rings in their structure, are known as low-molecular-weight or small PAHs, and those with more than six aromatic rings in their structure are called high-molecular-weight or large PAHs. The IARC has defined phenanthrene and anthracene as the simplest PAHs, which contain three rings in their structure (IARC 2010). Naphthalene, which is the basic and first member of PAHs, comprised of two coplanar benzene rings is another aromatic hydrocarbon. But it is not considered a true PAH, though it is referred as an aromatic hydrocarbon with two rings. The PAHs with high molecular weight are highly lipophilic with low water solubility and are soluble in organic solvents, while low-molecular-weight PAHs have high aqueous solubility and are partly volatile (Mackay et al. 1992). The semi-volatile nature of low-molecular-weight (LMW) PAHs means that they exist partly as vapours in the atmosphere and are highly susceptible to degradation processes. Similarly, they are partly dissolved in aqueous environments that make these PAHs available for various physicochemical and biological degradation processes. Contrarily to which, the high-molecular-weight (HMW) PAHs are associated primarily with particles in the atmosphere, soil, and water; thereby less available for degradation.

Table 4.1 Various physicochemical properties of the USEPA enlisted 16 PAHs priority pollutants

Name	Chemical formula	Molecular weight(g/mol)	Aqueous solubility (mg l^{-1})	Vapour pressure (pa)	Log[c] Kow	MP[a] (°C)	BP[b] (°C)	Density g/cm^3
Naphthalene	$C_{10}H_8$	128.2	31	11.86	3.37	80.26	218	1.14
Acenaphthylene	$C_{12}H_8$	152.2	16	0.500	3.93	91.8	280	0.898
Acenaphthene	$C_{12}H_{10}$	154.2	3.8	3.866	4.00	93.4	279	1.024
Fluorene	$C_{13}H_{10}$	166.2	1.9	3.40×10^{-3}	4.54	116	295	1.2
Anthracene	$C_{14}H_{10}$	178.2	0.045	0.432	4.18	217.5	340	1.25
Phenanthrene	$C_{14}H_{10}$	178.2	1.1	9.07×10^{-2}	4.57	101	336	1.18
Fluoranthene	$C_{16}H_{10}$	202.3	0.26	2.05×10^{-5}	5.91	110.8	375	1.25
Pyrene	$C_{16}H_{10}$	202.3	0.13	1.08×10^{-3}	5.22	145–148	404	1.271
Chrysene	$C_{18}H_{12}$	228.3	0.006	5.67×10^{-4}	5.18	254	448	1.27
Benz[*a*] anthracene	$C_{18}H_{12}$	228.3	0.011	1.04×10^{-6}	5.61	158	438	1.19
Benzo[*b*] fluoranthene	$C_{20}H_{12}$	252.3	0.0015	6.52×10^{-7}	5.91	166	481	1.286
Benzo[*k*] fluoranthene	$C_{20}H_{12}$	252.3	0.0008	1.07×10^{-5}	5.80	217	480	1.286
Benzo[*a*]pyrene	$C_{20}H_{12}$	252.3	0.0038	1.28×10^{-8}	6.00	179	495	1.24
Dibenz[*a,h*] anthracene	$C_{22}H_{14}$	278.4	0.006	2.80×10^{-9}	6.75	262	524	1.232
Indeno[1,2,3-c,d]pyrene	$C_{22}H_{12}$	276.3	0.00019	1.33×10^{-8}	6.50	164	536	1.378
Benzo[*g,h,i*] perylene	$C_{22}H_{12}$	276.3	0.00026	1.87×10^{-8}	6.50	278	550	1.38

Where [a]MP is melting point, [b]BP is boiling point and [c]Log Kowis logarithmic octanol-water coefficient

The common characteristics of PAHs include high boiling and melting points (Table 4.1) as a result of their solid nature, low vapour pressure and low water solubility (Masih et al.2012). Solubility ranges from highly insoluble (e.g. benzo[ghi]perylene, 0.0026 mg/L) to slightly soluble (e.g. naphthalene, 31 mg/L), and vapour pressures range from highly volatile (naphthalene) to relatively non-volatile (dibenzo[ah]anthracene). The latter two characteristics of these compounds tend to decrease with increasing number of rings and molecular weight. On contrary, with the increase in molecular weight, the resistance to oxidation and reduction processes increases (Masih et al. 2012). Aqueous solubility of PAHs decreases with the increase in the number of rings (Masih et al. 2010). PAHs manifest also several functions, like light sensitivity, conductivity, heat resistance, emit ability, physiological action and corrosion resistance (Akyüz and Çabuk 2010). The PAHs with each aromatic structure have a unique UV spectrum, and therefore, each isomer has a distinct absorbance spectrum. This feature of PAHs is extremely useful in their identification. Most PAHs are also fluorescent and emit characteristic wavelengths on excitation.

PAHs are highly hydrophobic as indicated by their high logarithmic octanol-water partition coefficients (i.e. log *Kow* of 3.37–6.75) and low aqueous solubility (Table 4.1). The hydrophobicity increases with increasing molecular size, while aqueous solubilities decreases from two- and three-ring compounds to the five- and six-ring PAH compounds. PAHs are also known to be carcinogenic and genotoxic in nature. The IARC has listed 15 PAHs, including 6 among the 16 USEPA enlisted PAHs to be the human carcinogens based on evidence in animal models (National Toxicology Program 2001). To assess the relative toxicity of PAH-contaminated materials, the IARC and USEPA used toxic equivalency factor and potency number (USEPA 1993; Nisbet and Lagoy 1992) respectively, to calculate their average toxicity as presented in Table 4.2. Benzo[a]pyrene has been given the value ‘1’ that serves as the model for other PAHs being rated. However, it was criticized because of ignoring the interactions among mixture PAH constituents and oversimplifies their integrated toxicity (Goldstein et al. 1998; Reeves et al. 2001). The USEPA classified seven PAHs as group B2 ‘probable human carcinogens’ (USEPA 1993). PAHs exhibit long half-lives that range from 3 weeks for the basic naphthalene up to 300 weeks for benzo[a]pyrene in aerobic sediments. Toxic equivalency factors (TEF) that are proposed for rating the relative genotoxicity of PAHs are depicted in Table 4.2, along with potency factors. These factors can be used to establish an average toxicity of a contaminated substance based on measured concentrations of an

Table 4.2 Toxic equivalency factor (TEF) and carcinogenic potential of different PAHs

PAHs	CAS-No.	Genotoxicity	IARC classification	TEF
Naphthalene	91-20-3	Negative	2B	0.001
Acenaphthylene	208-96	Questionable	Not evaluated	0.001
Acenaphthene	83-32-9	Questionable	3	0.001
Fluorene	86-73-7	Negative	3	0.001
Anthracene	120-12-7	Negative	3	0.01
Phenanthrene	5801-8	Questionable	3	0.001
Fluoranthene	206-44-0	Positive	3	0.001
Pyrene	129-00-0	Questionable	3	0.001
Chrysene	219-01-9	Positive	2B	0.01
Benz[*a*]anthracene	56-55-3	Positive	2B	0.1
Benzo[*b*]fluoranthene	205-99-2	Positive	2B	0.1
Benzo[*k*]fluoranthene	207-08-9	Positive	2B	0.1
Benzo[*a*]pyrene	50-32-8	Positive	1	1
Dibenz[*a,h*]anthracene	53-70-3	Positive	2A	1
Indeno[1,2,3-c,d]pyrene	193-39-5	Positive	2B	0.1
Benzo[*g,h,i*]perylene	191-24-2	Positive	3	0.01

[a] WHO Classification, 1998. International Program on Chemical Safety and Environmental Health Criteria 202, Selected Non-Heterocyclic and PAHs

[b] IARC Classification Group 1: The substance is a human carcinogen. Group 2A: The substance is a probable carcinogen to human beings. Group 2B: The substance is a possible carcinogen to human beings. Group 3: The substance is not classified

[c] TEF for selected PAHs based on toxicity of benzo[a]pyrene

individual contaminant and the relevant factor for each. This approach simplifies the estimation of toxicity of a complex mixture (Goldstein et al.1998; Reeves et al. 2001). Exposure of human beings to PAHs from contaminated sources is much relevant for LMW PAHs (Smith et al. 1991; Padma et al. 1998; Villholth 1999), and exposure to carcinogenic PAHs usually occurs through skin contact, inhalation of airborne dust, ingestion of particles or bioaccumulation in the food chain (Mayer et al. 1996; Hussain et al. 1998; National Toxicology Program 2001; Sverdrup et al. 2002).

4.3 Distribution and Source of PAHs

Polycyclic aromatic hydrocarbons are found in water, air, soil and sediments (Yu et al. 2005; Chadhain et al. 2006; Muckian et al. 2007; Peng et al. 2008). The PAHs or their intermediates are released into the environment through natural like forest fires, volcanic eruptions and anthropogenic activities, such as petrochemical industries, coal, transportation, waste incineration and agriculture. They are found in all types of environment and, therefore, are cosmopolitan in distribution (Mueller et al. 1996; Kurteeva et al. 2006). Coal is known as a rich source of PAHs and other organic contaminants as well. PAHs are also released from incomplete combustion of coal, pyrolysis, cooking, creosote, aluminium production, cement and asphalt (Belis et al. 2011; Guo et al. 2011). Pyrogenic, petrogenic and biogenic sources are the main three sources of PAHs (Laflamme and Hite 1978; Haritash and Kaushik 2009).

4.3.1 Pyrogenic Sources

Pyrogenic PAHs are formed from incomplete combustion of organic matter like wood and coal. When organic matter is exposed to high temperature at low oxygen or no oxygen conditions, pyrogenic PAHs are formed. The destructive distillation of coal, which occurs unintentionally into coal tar and coke, or the thermal breakdown of petroleum-based products into lighter hydrocarbons is a pyrolytic process (Eisler 1987; Haritash and Kaushik 2009). Furthermore, the other unintentional processes occur during the incomplete combustion of fossils, forest fires, waste incarnation, fireplaces, motor vehicle emissions and fuel oils in heating systems. PAHs, such as naphthalene, phenanthrene, fluoranthene, anthracene and benzoic[a]pyrene (Bap), are produced due to pyrogenic processes. The pyrogenic processes occur at high temperatures of about 350 °C to more than 1200 °C. However, PAHs can be also formed at low temperatures as low as 100–150°C over millions of years (Seo et al. 2009).

4.3.2 Petrogenic Sources of PAHs

Alkylated PAHs, like alkyl naphthalene and alkyl phenanthrene, are the examples of petrogenic PAHs that are derived from petroleum products. These PAHs are synthesized from the carbon compounds located in deep earth formed under thermal effects. They are found in rift zones, effusive rocks and mineral oils (Renzi and Peirong 1991). The PAHs formed during maturation of crude oil, coal tar production, catalytic cracking in the petroleum industries and other processes are called petrogenic PAHs. In addition, some other sources of petrogenic PAHs are oil spills, storage tank leaks, motor oil and the accumulation of small releases of gasoline and substances associated with transportation. Petrogenic PAHs enter into the soil and landscapes during weathering of rocks, through oil spills and from railways treated with creosote (Kohler and Künniger 2003, Tsibart and Gennediev 2013).

4.3.3 Biogenic Sources of PAHs

These PAHs are the products of biotransformation, synthesized by some microorganisms, algae and macrophytes or formed by degradation of vegetative matter. The formation of PAHs can occur either through natural ways or anthropogenic ways. They are present on surface of leaves, cuticles and microbial lipids (Labana et al. 2007). Aromatic amino acids, lignin compounds or its derivatives are some examples of biogenic PAHs (Seo et al. 2009). The wood from tropical forests has been reported to contain PAHs like naphthalene, phenanthrene and perylene (Wilcke 2007; Tsibart and Gennediev 2013).

4.4 Fate of PAHs in the Environment

The organic pollutants especially PAHs can enter the environment through different industrial activities including oil exploration (Rogge et al. 1997), processing of coal (Chmielewski et al. 2003), petroleum refineries timber treatments (Robinson and Anderson 2007) and gas works (Cofield et al. 2008). PAHs are found in soil, air, water and biological systems. They are widespread in distribution due to their physicochemical properties (Gao and Zhou 2004). The processes like volatilization, chemical oxidation, photooxidation, bioaccumulation and microbial biotransformation play a pivotal role in the fate of PAHs and other organic pollutants present in the environment. The transfer and turnover of LMW PAHs is more rapid than that of heavier PAHs because of their molecular weight and ring structures. The LMW PAHs that are semi-volatile in nature exist as vapours in the atmosphere and are susceptible to various atmospheric degradation processes. Contrarily, high-molecular-weight PAHs are associated primarily with particles in atmosphere and water, thus less available for degradation. Moreover, PAHs adsorbed on to soil or sediments may be transported to long distances, thus are found everywhere in the environment (Wilson and Jones 1993).

4.4.1 PAHs in the Atmosphere

Atmosphere is the major inhabitant of the PAHs that are released mainly because of incomplete combustion of fossils. In atmosphere, the PAHs are seen in two different phases, gaseous phase and a solid phase associated with particulates; at temperatures 100–150 °C, they tend to condense onto particles. Urban environment is having greater concentration of PAHs as a result of emission from industries than rural ones. The atmosphere with high PAHs concentrations is one of the pathways of many compounds into soil, sediments, water and other biological resources. The partitioning of PAHs into gaseous and particulate phases depends on the vapour pressure of a PAH involved (Wania and Mackay 1996). At ambient temperature, gaseous state is dominant for low-molecular-weight PAHs, while the PAHs with high molecular weight, PAHs are mainly associated with aerosol and particulate matter (ECPACWG 2001). The atmosphere is dominated by PAHs, like fluoranthene, phenanthrene and pyrene (Arey and Atkinson 2003). Moreover, soil organic matter is thought to be an important factor that controls the fate and transport of the hydrophobic organic pollutants in soil and sediments (Haung et al. 2003). Climatic factor is an important factor, which regulates soil organic matter (Alvarez and Lavado 1998). Under the influence of several factors and conditions, such as moisture, temperature, precipitation and microbial activity, the soil organic matter is fractioned and degraded into various organic fractions (Yamashita et al. 2006).

4.5 PAHs in Sediment

PAH compounds occur in sediments and due to low aqueous solubility and hydrophobic nature; they tend to accumulate more in soils and sediments than in water (Peng et al. 2008). Once incorporated in sediments, PAHs become slightly immobile due to their non-polar structures and highly hydrophobic nature, which inhibit their dissolution in water. In a sediment, the concentrations of PAH compounds can range from 1 μg kg^{-1} to many g kg^{-1} levels. However, it depends on the proximity of area to PAH sources, like municipalities, industries and on water currents. In rural areas, the PAHs sorbet to atmospheric particles can settle on the surface of lakes, streams and oceans by dry or wet deposition. A report from North America has revealed that the total PAH concentration in marine sediments usually ranges from 2.17 to 170,000 ng g^{-1} sediment (Latimer and Zheng 2003). They are also affected by air currents and regulated by the direction of wind. Meanwhile, PAHs are not totally insoluble, especially low-molecular-weight PAHs, small amount of which may dissolve and become bioavailable (Dong et al. 2012).

4.5.1 PAHs in Soil

PAHs are strongly adsorbed to soil organic matter and making them least available for degradation (Wild and Jones 1995). PAHs are highly resistant and can last for a long period of time and pose a significant threat to mankind and the environment. The low-molecular-weight PAHs, such as naphthalene, are relatively water soluble and are partly lost through volatilization, leaching and degradation like processes, but high-molecular-weight PAHs with three or more than three fused rings, due to their hydrophobicity adhere to fine particles and dissolved organic matter in aquatic environment making them less available for degradation (Miller and Olejnik 2001). With the increase in the number of rings in a PAH molecule, the effect of sorption also increases due to higher lipophilicity. The various physicochemical properties of PAHs, such as low vapour pressure, low water solubility and high partition coefficients, for *n*-octanol-water (log K*ow*) play a significant role in determining the fate and transport of PAHs in the environment (Canadian Centre for Occupational Health and Safety 1998). The factors, including temperature, pH and moisture and oxygen concentration, also play a pivotal role in the fate of PAHs (Weissenfels et al. 1992). Changes to the molecular structures of PAHs due to environmental modifications may result in changes in mobility, toxicity and chemical characteristics possibly rendering the molecule to bind to soil components or destruction of the molecule via biotransformation (Mueller et al. 1996). The degradation of organic contaminants in soil decreases with time (Allard et al. 2000). On the one hand, sorption and aging limit affects the degrading ability of the compounds. However, processes like this reduce the toxicity of contaminants, on the other hand, by lowering the uptake of available fraction of contaminants by living organisms (Alexander 1995).

4.5.2 PAHs in Water

PAHs are commonly found contaminants present in the freshwater ecosystems and enter the water courses through run-off and pollution of rivers and lakes by municipal wastewater, industrial effluents, and particulate matter deposition and from oil spills. They are found in low concentrations in waters as they have low aqueous solubility and adsorb to particulate matter in water bodies (Yuan et al. 2001).

4.5.3 PAHs in Plants

In plants, PAHs accumulate by atmospheric deposition and uptake through the above-ground parts, since they are lipophilic in nature and can accumulate in plants particularly in membrane bilayers (Duxbury et al. 1997). Plants growing in places with high PAH concentrations in the air or soil have high bioconcentrations of PAHs

(Jones et al. 1989). PAHs from contaminated soils also enter the plants through roots and are translocated to other parts as well. Plants also accumulate organic compounds through aerial deposition on the leaves (Thomas et al. 1998). PAH concentrations in plant tissues in nonindustrialized regions are low that range from 50 to 80 µg kg-1 (Edwards 1986), although it depends on plant species, type of PAH and other environmental factors (Salanitro et al. 1997). The vegetation of urban areas has higher PAHs levels than rural areas (Juhasz and Naidu 2000a, b).

4.5.4 Environmental Hazards of PAHs

PAHs are found throughout the environment, and the USEPA has listed 16 priority PAHs as hazardous pollutants due to their toxicity to humans, other organisms and the ecosystem (Lampi et al. 2006). They are potential cytotoxic and mutagenic for the mankind and other organisms due to their properties (Ashok et al. 1995; Habe and Omori 2003). The skin is the major route for absorption that contributes 75% of the total PAHs absorbed. The rate of absorption of PAHs is faster because of high biomagnification potential in the food chain. PAHs accumulate in the living organisms after entering the aquatic food chain. PAHs and their oxidative metabolites are found in different samples, including industrial wastewater, drinking water, municipal waste and rainwater (Sabate et al. 2001; Jamroz et al. 2003). Since, PAHs and their derivatives are toxic and carcinogenic, therefore, they are harmful to both mankind and ecosystem. PAHs exert adverse effects on terrestrial invertebrates, such as tumours, problems related to immunity, reproduction and development when present in high concentrations. Mammals absorb PAHs through various routes like inhalation, ingestion and dermal contact (Beyer et al. 2010; Dong et al. 2012; Veltman et al. 2011). The combustion products from coal were the first recognized chemical carcinogens. In 1775, the cancer in humans was reported by Percival Pott from the coal soot in chimney sweepers in London, and in 1875, coal tar workers in Germany were also diagnosed with cancers. A study carried on animals lead to the discovery of carcinogenic benzo(a)pyrene (BaP), in 1930s (Brown and Thornton 1957;). The mutagenic and carcinogenic potential of a PAH compound is related to its structural complexity; the more complex a compound is, the more toxic it will be. In general, the higher the number of aromatic rings in a PAH compound, the greater is the toxicity (Cerniglia 1992). PAHs ranging from two-ring low-molecular-weight naphthalene to seven-ring high-molecular-weight coronene are of serious concern. PAHs, such as naphthalene (Nap), fluorene (Fle), phenanthrene (Phe) and anthracene (Ant), exert severe effects, including acute toxicity to various organisms, while some HMW PAHs of four- to seven-ring structure are recognized as carcinogenic, genotoxic and tumour producing (Sims and Overcash 1983; Nylund et al. 1992). Generally, HMW PAHs are highly toxic and hydrophobic and persist for longer periods in the environment (Cerniglia 1992).

Food stuffs may also contain different PAHs in varying quantities during exposure to high temperatures. Studies have shown that PAHs are also found in fats, oil and cereals. Furthermore, PAHs distributed in soil possess serious threat to mankind as they enter the food chain. Thus, PAH-polluted soils are important sources and of serious concern for mankind (Tao et al. 2006).

4.5.5 *Effect of PAHs on Humans*

PAHs and their metabolites are carcinogenic, mutagenic and toxic to higher organisms, including human beings (Samanta et al. 2002). Many PAHs are classified as probable human carcinogens and exert deleterious effects and tumorigenic activity in mammals including humans (Cavalieri and Rogan 1995; Yu 2002) and fishes (De Maagd and Vethaak 1998). The acute toxicity, high bioaccumulation rate, persistence and cosmopolitan distribution make these PAHs of a global concern. Humans are exposed to various PAHs from natural and anthropogenic sources daily. However, exposure to a PAH is occupational. Usually human beings encounter PAHs by exposure to either air or dust, which is the primary source of exposure. The primary sources include emission from transportation, incomplete combustion of fossils, cigarette smoke, coal, coal tar and waste incineration. PAHs are hydrophobic and lipophilic compounds, which makes them permeable to cellular membranes. They are readily absorbed to tissues of mammals and remain in the body for longer time periods. Metabolism of PAHs occurs in all the tissues inside the body by various cofactors and enzymes. The metabolism of PAHs has been extensively studied, which leads to understanding of PAH metabolism. According to the USEPA, benzo[a]pyrene, due to its extreme carcinogenic potential, is recognized as the most dangerous pollutant among all PAHs. It is also a component part of smoke from cigarettes, regarded as a potential carcinogenic compound in animals and humans as well (Dell'ommo and Lauwerys 1993). It has been extensively studied and considered as a model for metabolism of PAHs. Benzo[a]pyrene metabolism is initiated by microsomal cytochrome P-450 systems. The initial breakdown of benzo[a]pyrene produce arene oxides, which get rearranged to phenols and undergo hydration to produce trans-dihydrodiols, by microsomal epoxide hydrolase, or react covalently with glutathione, either spontaneously or catalysed by enzyme cytosolic glutathione-S-transferases (IARC 1983). PAHs have high solubility to lipids, thus are quickly absorbed to gastrointestinal tract of human beings (Gibson and Subramanian 1984).

PAHs are of great environmental concern, which can enter humans either through ingestion, inhalation or dermal contact. They are associated with various types of cancers, such as skin, lung, mouth, pharynx, pancreatic cancer, etc. (Hecht 2002; Yu and Campiglia 2005; Doyle et al. 2008). PAHs can also block DNA replication by the formation of DNA-PAH stable and depurinating adducts, which induces nucleotide excision repair activities within the cells (Cavalieri et al. 2005; Khan and Chakravarti 2005; Todorovic et al. 2005). Another toxic effect of the PAHs includes the perturbation of homeostasis as a result of cell communication (Trosko and Upham 2005). Epidemiological studies have suggested that contact with PAHs possess high risk of cancers in human beings. Studies have showed that PAHs have a role in the disruption of the contact inhibition in liver epithelial cell model. The carcinogenicity of PAHs is attributed to few of their metabolic intermediates, like phthalates and epoxides or interaction with other chemical compounds (Guo et al. 2011). Numerous studies have revealed their role in tumours due to transactivation of the aryl hydrocarbon receptors (AhR) that deregulates cell proliferation in the epithelial cells. Meanwhile, the DNA-PAH adducts may activate cell defence mechanisms, which can further modify the proliferative behaviour of cells (Chramostova et al. 2004).

Naphthalene, a simple and basic PAH, is the most studied PAH for its toxic effects and serves as a model for the study of toxicity. It is readily absorbed in the tissues of the kidney, liver and the lungs, therefore manifesting its toxicity. It is also an inhibitor of mitochondrial respiration and can lead to haemolytic anaemia as well (Samanta et al. 2002). In addition, various ophthalmological changes were observed in workers associated with the naphthalene industries (Mastrangela et al. 1996; Falahatpisheh et al. 2001; ATSDR 2005). Some of the PAHs are known genotoxic and cause cytogenetic damages and form stable DNA adducts. A tricyclic PAH, phenanthrene, is found in high concentrations in sediments and soil (Coral and Karagoz 2005). It is a mild human allergen and photosensitizer and cause chromosomal aberrations. It has been found associated with tumour induction in mammals (Weis et al. 1998; Coral and Karagoz 2005). Fluoranthene has been found in mixtures of PAHs, which can cause neurological, immunological and respiratory disorders (Rice et al. 1984; Chaudhry 1994; Šepič et al. 2003;Kweon et al. 2007).

PAHs are lipophilic in nature and readily absorbed into the gastrointestinal tracts of mammals (Cerniglia 1984). They are considered as genotoxic, when activated by enzyme mammalian cytochrome P450 monooxygenase, which then oxidizes the aromatic ring to form intermediates like epoxides and diol-epoxides (Harvey 1996) that demonstrate carcinogenicity (Goldman et al. 2001). There is very limited knowledge available for PAHs, like acenaphthene, fluorene and fluoranthene, regarding their toxicity in mammals. Meanwhile, the toxicity of benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h) anthracene and indeno(1,2,3-c,d)pyrene has been extensively studied, and enough experimental evidence for their carcinogenic nature is available (Liu et al. 2001).

Moreover, PAHs are mutagenic, carcinogenic and teratogenic in nature along with their potential endocrine-disrupting properties and tumour initiation (Lee and Hosomi 2001). The relative acute toxicity of PAHs is measured by LD50 values, i.e. the lethal dose tested in 50% of the population. Although PAHs are considered as carcinogenic, those not considered to be genotoxic until mammalian enzymes are activated by reactive epoxides and quinones. The enzyme cytochrome P450 monooxygenase responsible for degradation of PAHs is mostly found in fungi, which oxidize the aromatic rings forming epoxide and diol-epoxide reactive intermediates. The genotoxic effects of PAHs come into play through oxidation caused by cytochrome P450 enzymes and form intermediates, such as epoxides and diol-epoxides (Harvey 1996). During the oxidation processes, the reactive intermediates combine with the DNA, undergo oxidation or hydrolysis and form stable covalent DNA adducts, causing mutation that may lead to tumours (Bamforth and Singleton 2005b).

These toxic compounds also exert adverse noncancerous respiratory effects including breathing problems, chest pain, bloody vomiting and throat irritation in humans (Gupta et al. 1993). They are considered as the risk factors involved in the development of atherosclerosis, which includes arterial smooth muscle cell proliferation, lipid accumulation, cellular necrosis and collagen synthesis. It is well-documented that benzopyrene affects the collagen secretion and enhances cytotoxicity (Stavenow and Pessah-Rasmussen 1988).

In humans, PAHs have been reported to cause gastrointestinal toxicity, and consumption of anthracene-containing laxatives increases the risk of colon and rectum cancers in humans (Badiali et al. 1985). It is well known that PAHs cause adverse immunological effects as well. It has been found that humoral immunity suppressed in the workers exposed to PAHs like benzo[a]pyrene (Szczeklik et al. 1994). Moreover, it also inhibits the production of T-cell-dependent antibodies by lymphocytes (Blanton et al. 1986). The information related to reproductive effects due to PAHs in humans is very limited. However, the effect of benzo[a]pyrene related to reproduction has been reported, i.e. causing neurological deformities in the foetus, resorptions and sterility and malformations in foetuses. Some other PAHs, like dibenz[a,h]anthracene and chrysene, produced lethal effects in foetus and initiate liver tumours (Buening et al. 1979).

4.5.6 Effect of PAHs on Animals

A wide range of studies conducted on animals suggested the carcinogenic potency of certain PAHs like benz[a]anthracene, dibenz[a,h]anthracene and benzo[a]pyrene (McCormick et al. 1981). Pyrene, anthracene, benzo[e]pyrene and benz[a]anthracene are reported to induce hyperplasia of the tracheal epithelium. Meanwhile, pyrene can also cause serious mucociliary hyperplasia. Almost all the PAHs have induced acute or subacute inflammation, fibrosis and hyalinization, when exposed to prolonged time periods (Topping et al. 1978). PAHs can interfere with enzyme activities in the intestinal mucosa of some animals, thereby can produce reactive intermediates causing tissue injuries. (Badiali et al. 1985). PAHs have shown adverse haematological effects; a study has shown that when a single dose of benzo[a]pyrene was given to mice, it caused cellular depletion, prominent hemosiderosis, small spleen and follicles with large lymphocytes, ultimately leading to death of an organism (Shubik and Porta 1957). They also affect proliferating tissues like blood-forming elements and bone marrow.

Severe effects in animals were observed after oral, intra-peritoneal or subcutaneous administration of several PAHs. Injuries caused to liver are among the prominent and severe effects seen in animals after exposure to PAHs. Further, induction of aldehyde dehydrogenase and carboxylesterase activity, preneoplastic hepatocytes, increased liver weight and stimulation of hepatic regeneration are some of the major observed problems in organisms exposed to PAHs (Danz et al. 1991). Reduction in thymic glucocorticoid receptors in rats was observed after exposure to benzo[a]pyrene (Csaba et al. 1991). PAHs may exert toxic effects on the renal and endocrine system, based on available studies in animals. Interstitial lymphocytic infiltrates or fibrosis and renal tubular regeneration are some effects observed in female mice after the administration of fluoranthene (EPA 1988).

The stable DNA adduct formation has been observed in mice skin after their exposure to B[a]P compared to internal organs, which indicates the skin tumours could surpass internal tumours after dermal exposure (Talaska et al. 1996). The exposure of fish larvae to B[a]P, pyrene or phenanthrene can cause the developmental defects by inhibiting Na/K-ATPase and Ca_2-ATPase activity (Li et al. 2011). Histopathological and reproduction-related problems, death of fish embryos and changes in the community structures are also reported (Peterson et al. 2003). Exposure to PAHs, such as phenanthrene increasing fibrosis in sea urchin gonads, is well documented, which includes augmentation of collagen and huge appearance of the connective tissues (Schäfer and Köhler 2009).

4.5.7 *Effect of PAHs on Plants*

Plants may absorb PAHs through their roots in soil and are translocated to the above-ground parts. The low-molecular-weight hydrocarbons may inhibit the growth and development of plants. Furthermore, physicochemical properties of aromatic hydrocarbons lead to the reduction in nutrients and water absorption of plants from the soil (Kirk et al. 2005; Nie et al. 2011). Alternatively, the rate of uptake is generally governed by aqueous solubility, concentration and their physicochemical state and type of soil. Besides intrinsic toxicity, PAHs also exhibit photo-induced toxicity towards the plants and other living organisms (Kagan et al. 1989; Krylov et al. 1997; Pelletier et al. 1997; Swartz et al. 1997; Mezey et al. 1998a, b). The photoinduction process is regarded as the basic mechanism of PAH toxicity to plants. Plants exhibit various responses towards PAHs; plant sensitivity for PAHs is improved by heavy metals co-contamination. Certain plants contain defence mechanisms that can protect them against toxic PAH effects. Also, some plants can synthesize PAHs that may act as growth regulators (Beyer et al. 2010). Considering the toxic effects of PAHs in the environment, their bioavailability is important. Intact PAHs have low aqueous solubility and can adsorb onto sediment particles in aqueous environments, which results in low accessibility to some aquatic plants and animals (Basu and Saxena 1978; Lampi et al. 2006).

Studies have showed that plant height and biomass of vetiver were reduced in soil contaminated with crude oil (Brandt et al. 2006). Growth and biomass of two plants, i.e. *Brachiaria decumbens* and *Penicillium notatum*, declined significantly when grown in soil contaminated with 5% diesel oil (Mezzarri et al. 2011). The oil, because of high aromatic content, was considered as medium to high toxic to different plant species. Generally, 1% of grease and oil in soil is considered as a practical threshold, after which petroleum-based hydrocarbons (PHC) become detrimental to plants (Reis 1996). However, the range of tolerance to different concentrations of PHC varies in different plant species.

The volatile PAHs, fluoranthene and phenanthrene, with a high vapour phase component in air are subjected to air-leaf exchange process moving towards the equilibrium with time. Plants respond rapidly and are highly sensitive to fluoranthene and phenanthrene (Kummerová et al. 2006). PAHs show high bioaccumulation potential and exhibit adverse effects on algae. PAHs may induce the generation of reactive oxygen species in the photosynthetic apparatus like that of the herbicide paraquat (Oguntimehin et al. 2007). A study conducted on different grasses showed that mixtures of PAHs affected the plants, which exhibited reduced shoot and root length. However, there was not a significant effect observed in the seed germination (Reynoso-Cuevas et al. 2008).

4.6 Bioremediation Strategies for PAHs

The term remediation is generally related with the environment, which means the removal of toxic contaminants from the different environment samples, such as air, groundwater, soil, sediments and water surfaces for the well-being of mankind and environment. PAHs can undergo various natural processes, such as adsorption, photolysis, volatilization, chemical oxidation, leaching, bioaccumulation and biodegradation after entering the environment (Ashok et al. 1995; Nadarajah et al. 2002). Each of the above processes affects PAHs in different manners. PAHs have a unique structure, physicochemical and biological properties, which play a significant role in their persistence. Even though there are various chemical and physical technologies available used for remediation of theses contaminants, they are not effective either due to high cost, or in some cases, instead of diminishing from the environment, the contaminants transfer from one state to another (Haritash and Kaushik 2009). However, bioremediation is considered as a promising process for remediation of such pollutants among all other processes. The mechanism of transformation of toxic contaminants to less toxic or nontoxic forms via bioremediation has an advantage over other physicochemical techniques (Mehrasbi et al. 2003; Mehdi and Giti 2008). Bioremediation aims to detoxify the toxic pollutants in the environment by microbial degradation process. The degradation mainly includes organic and defined as the use of microbes to remove pollutants from water, soil and sediments (Gogoi et al. 2003). A characteristic feature of bioremediation is that it takes place in open environments, with a wide variety of organisms present there. Prokaryotes are referred as the main decomposers of organic pollutants in an ecosystem. Bacterial enzymes digest the organic contaminants and make them readily available for absorption. Bacteria, especially those capable of degrading organic pollutants, play a central role in bioremediation. Other organisms, such as protozoa and fungi, also affect the process of bioremediation.

Remediation is generally based on the assessment of human health and associated ecological risks. Soil bioremediation depends on desorption of a pollutant from solid to liquid phase. Bioremediation process is limited by several factors, such as oxygen, nutrients, lack of bioavailability, pH, temperature, etc. The hydrophobicity of the pollutants is an important factor that regulates their persistence in the environment; in general, they tend to adsorb strongly to soil particles because of low bioavailability and accumulate in the food chain (Mollea et al. 2005).

The process can be enhanced by the help of various applications to remove the pollutants from the environment. The treatment of pollutants by microbes is an efficient practice towards a healthier environment (Gogoi et al. 2003; Van Gestel et al. 2003). In a bioremediation process, microbes degrade the toxic compounds. However, rate of biodegradation of a pollutant in can be affected by several factors in soil like type of microorganism, temperature, pH, moisture, oxygen, nutrients, soil type and concentration of the pollutant (Semple et al. 2001; Ghazali et al. 2004).

Bioremediation is also defined as the conversion of chemical compounds into energy, biomass and biological waste products by living beings especially microbes (Killham 1994). Microbial biodegradation is considered as the major degradation process for PAHs in nature, and the structure of a PAH compound is important for biodegradation. HMW PAHs with three or more rings pose serious challenges to biodegradation. This is because of their low aqueous solubility and greater affinity to organic solvents, which limits their bioavailability to microorganisms (Krell et al. 2013). Surfactant-mediated bioremediation is a potential biodegradation technique for least soluble hydrocarbons, such as PAHs (Bustamante et al. 2012). It is the regulation of some physicochemical properties that aids the bioremediation of pollutants. This includes adjusting physicochemical parameters like oxygen, nitrogen, phosphorus, temperature and pH. The concentration of a PAH compound is an important factor for achieving a successful bioremediation process. High concentrations of PAHs may be toxic to microorganisms; therefore, the suggested concentration for bioremediation is around 5%. Due to low water solubility and hydrophobicity of PAHs, they are not easily biodegraded and bioaccumulated in the environment after entering the food chain. Thus, PAHs in the environment pose a significant threat to mankind. Several PAHs contain Bay, K and L regions. These regions, after undergoing metabolism, produce highly reactive epoxide intermediates (Fig. 4.2).

Microorganisms are versatile organisms, which epitomize half the biomass of our globe and try to adapt with the changing environment. PAH-degrading microbes are found ubiquitously in the environment. The contaminated sediments and soils should be screened for the diversity of microorganisms with PAH degradation potential. On the other hand, bacteria with an innate property of PAH degradation as well as genetically modified microbes should be used in a bioremediation process (Mangwani et al. 2013).

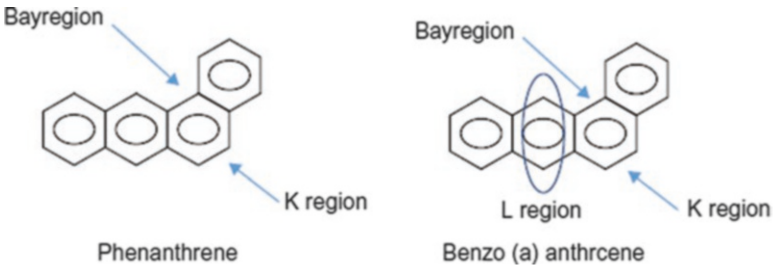


Fig. 4.2 Metabolically active regions of PAHs degradation

4.6.1 Bacteria Degrading PAHs

The main ways of dissipation of PAH compounds in the environment are sorption, leaching, chemical oxidation, photooxidation, volatilization and biodegradation. Even though there are various physicochemical processes, however, microbial biodegradation is considered as the promising process for dissipation of PAHs (Cerniglia 1992; Yuan et al. 2002). The fate of PAHs and other organic pollutants in the environment is determined by both biotic and abiotic processes, such as chemical oxidation, photooxidation, volatilization, bioaccumulation and biotransformation. Biodegradation of PAHs is receiving more attention as being an environmentally friendly process. Some microbes can utilize PAHs as a source of energy, degrade them to water and carbon dioxide or transform to other nontoxic or less toxic substances (Viñas et al. 2002; Jiménez et al. 2006; Santos et al. 2008; Perelo 2010). The ability of bacteria to degrade PAHs depends mainly on bioavailability of these compounds that decreases with the increase in the number of rings and degree of alkylation (Johnsen et al. 2005).

There is a vast diversity of microorganisms, mostly bacteria, which carry out the bioremediation of these PAH pollutants. Bacteria with PAH-degrading potential are relatively easier to find in PAH-contaminated environments. This is because the PAH-degrading bacteria include various genera, where representatives are from the genus *Proteobacteria* and *Mycobacterium*. Recently, the diversity of PAH-degrading bacteria has been credited to horizontal gene transfer partly and to recombination events. Studies on bioremediation of PAHs has led to the isolation of fast-growing species of mycobacteria with the PAH-degrading ability. Numerous bacteria, such as *Alcaligenes denitrificans, Mycobacterium* sp., *Rhodococcus* sp. and *Pseudomonas* sp., that metabolize PAHs have been isolated from various sources. A variety of bacteria have been reported that can degrade some PAHs and convert them to CO_2 and different metabolic intermediates. Studies have revealed several naphthalene-degrading microorganisms, such as *Alcaligenes denitrificans*, *Bacillus cereus*, *Bacillus* sp., *Corynebacterium venale*, *Cyclotrophicus* sp., *Moraxella* sp., *Mycobacterium* sp., *Pseudomonas cepacia*, *P. fluorescens*, *P. putida, P. testosteroni*, *P. vesicularis*, *Rhodococcus* sp., *Streptomyces* sp. And *Vibrio* sp., isolated and examined for mineralization (Samanta et al. 2001). Efficient phenanthrene-degrading bacteria such as *Aeromonas* sp., *Alcaligenes denitrificans*, *A. faecalis*, *Arthrobacter polychromogenes*, *Beijerinckia* sp., *Flavobacterium* sp., *Micrococcus* sp., *Mycobacterium* sp., *Nocardia* sp., *Pseudomonas paucimobilis*, *P. putida*, *Rhodococcus* sp., *Streptomyces* sp. and *Vibrio* sp. have been reported in a study (Samanta et al. 1999).

Reports have shown that bacteria with phenanthrene-degrading ability were isolated and screened from contaminated sites. Several PAH-degrading bacteria have been isolated from both aerobic and anaerobic environments, like marine sediments and sewage sludges (Coates et al. 1997). The major groups of anaerobic bacteria with PAH biodegrading capability are *Acidovorax* sp., *Bordetella* sp., *Desulfitobacterium dehalogenans*, *D. acetonicum, D. oleovorans*, *Desulfuromonas michiganensis*, *Desulfovibrio* sp., *G. metallireducens Pseudomonas* sp., *Sphingomonas* sp., *Variovorax* sp. and *Veillonella alkalescens* (Zhang and Bennet 2005; Jiang et al. 2009).

Cébron and Norini (2008) found various Gram-negative bacterial species from various genera, such as *Alcaligenes, Burkholderia*, *Comamonas, Polaromonas, Pseudomonas, Ralstonia* and *Sphingomonas* with PAH-degrading ability, and the Gram-positive PAH-degrading strains such as *Rhodococcus* and *Terrabacter.*

A study conducted in Fujian Province in China that reported 53 PAH-degrading bacterial strains, obtained from the mangrove sediments, includes 14 strains of phenanthrene, 13 strains of benzo[a]pyrene (Bap),13 strains of pyrene and 13 strains of mixed PAHs (phenanthrene + pyrene + bap) degrading bacteria. All the isolated bacteria were identified by 16S rDNA molecular sequencing (HuiJie et al. 2011).

Thapa et al. (2012) suggested different bacterial species can be applied for removing petroleum hydrocarbon pollutants, including PAHs from soil. They have reported the bacteria, which can degrade petroleum-based products, include *Aeromonas, Arthrobacter, Acinetobacter, Bacilli, Beijerinckia, Corynebacterium, Cyanobacteria*, *Moraxella, Mycobacteria, Modococci, Nocardia, Pseudomonas* and *Streptomyces.* Enriched bacterial culture for degradation of various PAHs has been used from sediments in the Grand Calumet River of Northwestern Indiana (Dean Ross 2003). A *Mycobacterium flavescens* strain was reported using pyrene as carbon and energy source, while another *Rhodococcus* sp. was isolated in a medium supplemented with anthracene. A sediment assay system was developed for bioremediation and suggested both the strains were able to remove the PAHs significantly from the sediments at optimum conditions.

Studies have reported most PAH-degrading microorganisms belong to the genera *Pseudomonas* and *Sphingomonas*. However, there are other bacteria from various genera, such as *Alcaligenes*, *Bacillus Mycobacterium* and *Rhodococcus* and fungi (Guo et al. 2010). PAH-degrading bacteria, belonging to genera *Burkholderia, Mycobacterium, Pseudomonas* and *Sphingomonas*, are dominant over others**.** Among which a large proportion of bacteria belong to the *Sphingomonas* (Johnsen et al. 2002).

4.6.2 Diversity of PAH Metabolism

Bacteria metabolize a diverse group of organic contaminants and microbial biodegradation of PAHs is considered as the principal process for the removal of PAHs from contaminated environments (Prince 1993; Sutherland et al. 1995). Both aerobic and anaerobic degradation pathways are well known for most of the LMW PAHs. As PAHs are stable organic compounds, therefore, the degradation occurs by oxidation under aerobic and anaerobic conditions. Anaerobic degradation of PAHs is very low compared to that of aerobic. Thus, the aerobic metabolism of PAHs has received more attention. The aerobic biodegradation starts with the attack on the aromatic ring of a PAH molecule by enzyme dioxygenase with the formation of cis-dihydrodiol. It is followed by the conversion into a dehydroxylated derivative by enzyme dehydrogenase. Then, the ring cleavage results in the subsequent formation of intermediates of TCA (Samanta et al. 2002; Chauhan et al. 2008). This can be further metabolized to water and carbon dioxide via catechols. The aerobic biodegradation of low-molecular-weight PAHs, including naphthalene, anthracene and phenanthrene, has been extensively studied revealing that numerous Gram-negative bacterial species of genera *Burkholderia, Comamonas, Pseudomonas* and *Sphingomonas* are able to grow using these hydrocarbons as a source of carbon and energy (Cerniglia 1992). Abundant research is also available on the characterization and purification of the enzymes and genes involved (Sanseverino et al. 1993). However, studies have reported the ability of Gram-positive nocardia forms, like *Nocardia, Mycobacterium* and *Rhodococcus* species, to degrade PAHs with three or more rings (Kanaly and Harayama 2010). An overview of naphthalene metabolism is presented in Fig. 4.3 that serves as a model for studying the metabolism of a large group of PAHs (Parales et al. 1998). Naphthalene is converted to cis-1, 2 dihydroxy-1, 2-dihydro-naphthalene. It is then converted to 1,2 dihydroxy naphthalene (Cerniglia 1984; Mrozik et al. 2003). Naphthalene cis-dihydrodiol dehydrogenase enzyme requires electron acceptor in the form of NAD^+ for catalysis. It is followed by the conversion of naphthalene cis-dihydrodiol dehydrogenase to cis-2-hydroxybenzyl pyruvate. A series of reactions occur where dehydrogenases convert cis-2-hydroxybenzyl pyruvate to salicylate and pyruvate. Salicylate is oxidized to catechol by enzyme salicylate hydroxylase, resulting in ortho or meta fission. Moreover, the complete degradation of other PAHs like acenaphthene and acenaphthylene has been also reported in different studies (Komatsu et al. 1993). Further, the partial degradation of some LMW PAHs may occur also with the production of hydroxy-aromatics or hydroxy-aromatic acids (Cerniglia 1992). The use of HMW PAHs, like pyrene, fluoranthene, chrysene, benzo[a]pyrene, dibenzo[a,h]anthracene and coronene as sole source of carbon and energy, is well-documented by researchers (Weissenfels et al. 1991; Bolddrin et al. 1993; Caldini et al. 1995). Partial degradation of these PAHs forms hydroxylated polyaromatic acids as end products (Mahaffey et al. 1988; Roper and Pfaender 2001).

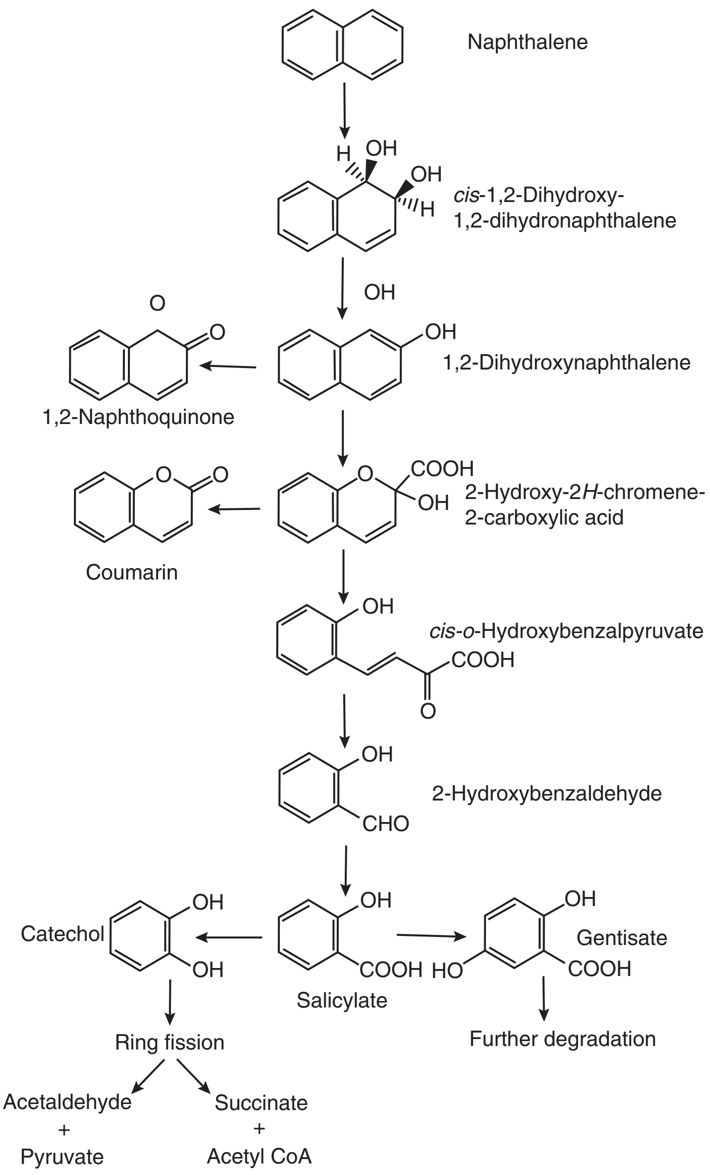


Fig. 4.3 Schematic biodegradation pathway of naphthalene M'rassi et al. (2015)

4.7 Various Factors Influencing the Bioremediation of PAHs

PAHs are hydrophobic compounds with relatively low aqueous solubility. Their low water solubility makes it tough for a living system to use them as an energy source. Meanwhile, the environment harbours a large microbial diversity with the bacteria playing a central role that can efficiently degrade PAHs. However, there are several physicochemical and other factors, such as temperature, pH, oxygen, nutrients, plasmids and chemotaxis that affect the rate of degradation. The understanding of these factors is important for designing an effective bioremediation strategy for the bioremediation of these toxic compounds.

4.7.1 Bioavailability

Bioavailability is defined as the accessibility of a chemical compound for its biological accumulation and probable toxicity (Alexander 2000). It is the effect of biological and physicochemical factors on the biodegradation rate of a contaminant. It is among the important factors that determines the fate of PAHs pollutants in the environment. The treatment of sediment and soils containing highly hydrophobic organic pollutants through bioremediation depends greatly on the bioavailability of the pollutants (Mueller et al. 1996). PAH are highly hydrophobic contaminants with low water solubility and low accessibility to microbes (Miller and Bartha 1989) and are least bioavailable (Straube et al. 2003). Due to their high molecular weight and low water solubility, they are resistant to breakdown and persist for a prolonged time in the environment. The bioavailability of a compound is determined by the mass transfer rate relative to intrinsic activity of the microbial cells. PAHs may adsorb strongly to soils due to their hydrophobic nature and low solubility in water that makes them persistent in the environment and unavailable for chemical, physical and biological degradation (Semple et al. 2003). The prolonged presence of PAHs in the environment results in irreversible sorption that leads to low biological and chemical extractability of the PAHs. This is known as the ‘ageing’ of a pollutant (Hatzinger and Alexander 1995). The solubility of a PAH compound decreases with the increase in the ring structure and molecular weight that diminishes the availability of a compound for the microbial metabolism (Fewson 1988). The use of surfactants in increasing the solubility and biodegradation of PAHs is considered as a solution to problem of PAHs persistence. Recently, studies have shown the effects of surfactants on the biodegradation of PAHs (Laha and Luthy 1991; Bury and Miller 1993). They contain both hydrophobic and hydrophilic groups; therefore, it can get access to hydrophilic microbial cells by solubilizing the hydrophobic PAHs. PAHs may be released from the mineral surfaces and organic matter by the application of surfactants. Many microorganisms are reported to produce biosurfactants, which can be helpful in the desorption of PAHs from the soil (Makkar and Rockne 2003). One of the important advantages of using biosurfactants is that they do not produce micelles, which encapsulate PAHs and prevent their microbial access. Moreover, they are less toxic to the indigenous microbes (Makkar and Rockne 2003). Emulsan, peptidolipid, rhamnolipid and sophorolipids are some biosurfactants produced by various microbes that can enhance bioavailability of PAH compounds, thereby, degradation rate (Hamme et al. 2003). Rhamnolipid biosurfactants, found in *Pseudomonas aeruginosa* biofilm matrix, exhibit various surface activities, which are supposed to help information of water channels in mature biofilm, biofilm dispersion and microcolony formation (Boles et al. 2004). They can easily diffuse hydrophobic constituents, make them bioavailable and can be useful for oil recovery and bioremediation of oil spills. Furthermore, it is suggested that some microbes can absorb PAHs directly from surfactant micelles (Stringfellow and Aitken 1994). Several studies have been carried out, which propose that surfactants can enhance PAH biodegradation rates (Rouse et al. 1994; Tiehm 1994; Liu et al. 1995; Tsomides et al. 1995), while some other reports also suggested that their application may be negligible or even harmful (Tsomides et al. 1995; Hu et al. 2006).

4.7.2 Temperature

Temperature is another major factor that determines the microbial biodegradation capability of PAHs. As a rule of thumb, solubility of PAH compounds increases with the increasing temperature that sequentially increases the bioavailability of the PAH compounds (Margesin and Schinner 2001). At high temperature, the bioavailability, solubility, distribution and diffusion rate of PAHs increase, thereby enhancing the rate of biodegradation (Margesin and Schinner 2001). Microbial degradation also increases at high temperature due to high enzymatic activity (Atlas 1981). However, increasing temperatures decreases the oxygen solubility, which may decrease aerobic biodegradation rate in the environment(Margesin and Schinner 2001) and disturb the biodegradation of PAHs by changing their physical and chemical composition (Leahy and Colwel 1990; Lakshmi et al. 2013). The optimum temperature for bioremediation of PAHs may vary within the site, depending on the range of contamination and the metabolism of the prevailing microbes (Siron et al. 1995; Margesin and Schinner 2001; Lau et al. 2003; Roberto et al. 2006; Viamajala et al. 2007). Contaminated sites cannot have an optimal temperature during the year for the successful bioremediation of a contaminant. In contrast, the concentration of oxygen in water declines at high temperatures, which can reduce the metabolic activity of aerobic microbes. Therefore, most studies use mesophilic conditions to achieve a high bioavailability with a significant microbial activity (Lau et al. 2003). Moreover, the volatilization of short-chain alkanes reduces, and their aqueous solubility increases at low temperatures that delays the biodegradation process (Atlas and Bartha 1972).

4.7.3 pH

The hydrogen ion concentration (pH) also plays an important role in the growth and metabolism of microorganisms. Monitoring the pH and regulating it is very critical in order to achieve the optimal growth of indigenous PAH-degrading microbes. The pollutants present can also affect the pH of contaminated sites, thus affecting the

PAH-degrading ability of the indigenous microorganisms under the very low or high pH conditions (Leahy and Colwell 1990). Soil pH varies from 2.5 in mine spoils to 11.0 in alkaline deserts and tailings. However, pH does not show any significant variation in aquatic environments (Leahy and Colwell 1990). Hence, the characterization of the indigenous PAH-degrading microbes for the optimum pH at a site is necessary. The pH of the contaminated sites must be adjusted in most of the bioremediation practices by the addition of lime and other substances (Alexander 1995). However, several PAH-degrading bacteria have been reported from environments that deviate from neutral pH. This may be the reason that indigenous microorganisms tolerate the PAH toxicity and possess in situ bioremediation potential of PAHs during suboptimal pH conditions (Bamforth and Singleton 2005a, b).

4.7.4 Pressure

Sediments, groundwater and deep oil fields are under excessive pressure (Margesin and Schinner 2001). Studies have shown the effect of pressure on PAHs biodegradation is restricted to the deep-sea environments. Samples collected from the Atlantic Ocean at a depth of 4940 meter inhabit PAH-utilizing microbial populations. Studies have revealed that microbial degradation increases significantly at 500 atm pressure and ambient temperature of 20 °C compared to 1 atm pressure at 20 °C (Schwarz et al. 1974). Limited knowledge is available regarding the ability of barophiles to degrade petroleum hydrocarbons at high pressure (Margesin and Schinner 2001).

4.7.5 Oxygen

Bioremediation of PAHs takes place in both aerobic and anaerobic conditions, depending on the nature of the indigenous microbes present in a site. However, bioremediation of PAHs in the presence of oxygen is most favourable by microbes, as both the monooxygenases and dioxygenases use oxygen in the initial breakdown of the ring structure of a PAH, and is quicker in completing a bioremediation process (Boyd et al. 2005; Trably and Patureau 2006). This is because the aerobic microbes are easy to culture, and the study compared to that of anaerobic microbes and the aerobic biodegradation is higher than that of the anaerobic (Rockne and Strand 1998). Moreover, in situ microbial communities can be easily stimulated by the application of hydrogen peroxide, perchlorate (Coates et al. 1999) and sodium nitrate (Bewley and Webb 2001). Meanwhile, bioremediation of the surface contamination may also be promoted by mixing or tilling of soil or water samples. Although relatively slow, some reports suggest that anaerobic bioremediation is turning more important as most of the PAHs are hydrophobic and affiliated with anaerobic environmental matrix. For improving PAHs bioremediation, further research and development of anaerobic degradation is needed. Some studies suggested that anaerobic PAHs biodegradation might be comparable to those under aerobic and denitrifying conditions (McNally et al. 1998). However, there are several drawbacks associated with anaerobic bioremediation which dominate the advantages of the process because of the following: (a) All the environments do not inhabit anaerobic microbes, (Coates et al. 1997); (b) the nature and type of the soil surface affect the anaerobic biodegradation. As electron acceptors, like nitrate, iron III and sulphate, are reduced during respiration (Stumm and Morgan 1981), the reduction of iron III to iron II and the release of phosphate from iron phosphate complexes are harmful to the environment. (c) These reducing conditions increase the pH, which results in the solubilization of carbonate minerals and release of trace metals (Ponnamperuma 1972). Therefore, a clear understanding and research on anaerobic biodegradation is needed before it is explored on a large scale in an in situ bioremediation.

4.7.6 Salinity

The rate of mineralization of PAHs, like naphthalene and phenanthrene, in soil and sediments is positively correlated to salinity. Studies have shown that correlation declines with the increase in salinity. Oceans and estuaries have high level of salts, and some waters and soils also have little high salinity that may be detrimental to microflora with PAH-degrading ability. However, there are various reports of bacteria from salt-rich habitats involved in the biodegradation (Atlas and Busdosh 1976). There is very little information available on the effects of salinity on microbial biodegradation of hydrocarbons. A report on soil containing salt in high quantities revealed that hydrocarbon metabolism rate declines with increase in salinity in the range of 3.3 to 28.4%. This may be due to the reduction in the microbial metabolic rates in high salt concentration soils (Leahy and Colwell 1990).

4.7.7 Nutrients

The nutrient availability is the additional rate-determining factor for effective bioremediation of PAHs. Since large diversity of microbes is present in different environments, still they cannot be there in the exact numbers required for bioremediation of a site. Their growth and metabolic activities must be stimulated by the addition of required nutrients. Nutrients are generally categorized as organic and inorganic sources. The inorganic is further divided into macronutrients and micronutrients. Macronutrients, including phosphorus (P), nitrogen (N), potassium (K), hydrogen (H) or oxygen (O), are important for metabolism of a microbial cell and consequently affect their growth (Bamforth and Singleton 2005a, b). Micronutrients, like cobalt (Co),copper (Cu), chlorine (Cl), iron (Fe), manganese (Mn), nickel (Ni), molybdenum(Mo) and zinc (Zn), are also required but in low quantities (Breedveld and Sparrevik 2000). Carbon is the major essential element of all living beings that constitutes about 95% of the weight of cells, needed in large quantities than nitrogen, hydrogen and oxygen. Along with the carbon source, they require numerous mineral elements, like P, N, K and Fe, for their normal growth and metabolism. Thus, the addition of nutrients in deprived nutrient content sites is mandatory for stimulating the growth of indigenous microbes to enhance the bioremediation (Atagana et al. 2003). These nutrients primarily act as the building blocks of life and let microorganisms to form the required enzymes required for the breakdown of contaminants. Sites contaminated with hydrocarbons especially PAHs can quickly become depleted in inorganic nutrients (Bamforth and Singleton 2005a, b). Therefore, the ratios of C/N or C/P will be higher at these sites that limit microbial biodegradation process and are an important factor in determining the biodegradation rates. The most frequently limiting nutrients for biodegradation of PAHs are N, P and K. However, adjustments can be done by the addition of urea-phosphate, ammonium or phosphate salt and also with N, P, K fertilizers (Fulthorpe and Wyndham 1989; Carter et al. 2010). The availability of nutrients like phosphorus and nitrogen has evidenced to be the limiting factor in biodegradation of hydrocarbons in seawater (Atlas and Bartha 1972), estuarine water (Jamison et al. 1975), freshwater lakes (Ward and Brock 1978) and sediments (Walker and Colwell 1974). Significant increase in the rate of microbial biodegradation was reported in the impacted groundwater of a laboratory site in California, when N, P and K were added in a ratio of 1:1:4 (Hwang et al. 1994). The requirement of N and P for a usual bioremediation process has been estimated to be in the ratio of C: N: P = 100:15:3 (Zitrides 1978), 120:10:1 (Alexander 1997), or 100:10:1 (Leys et al. 2005). Supplementation of inorganic nutrients, like N and to some extent P, may enhance the biodegradation rate of PAHs (Walworth and Reynolds 1995; Braddock et al. 1997). Poor biodegradation of petroleum hydrocarbon has been found in marine environments because of low phosphorous and nitrogen levels (Floodgate 1984). Moreover, higher nutrient availability can also hinder the bioremediation of contaminants (Chaillan et al. 2006). Several studies have shown the adverse effects of excessive nutrients on biodegradation of organic contaminants like PAHs (Carmichael and Pfaender 1997; Chaîneau et al. 2005). Thus, it is necessary to have a thorough understanding of nutrient levels of the contaminated sites before supplying additional nutrients for a successful bioremediation process.

4.7.8 Concentration of PAHs

The concentration of PAHs influences the uptake and mineralization rate of these compounds (Cai and Xun 2002). Higher concentrations of aromatic hydrocarbons inhibit the biodegradation usually by limiting nutrients or oxygen or because of their toxic effects (Rahman et al. 2002). The concentration of PAHs is important for two reasons, i.e. toxicity and induction. They are lipophilic in nature and may accumulate in the environment and membrane lipid bilayer of microbes. The adverse effects may be disrupting the membrane structures that cause leakage of vital cell constituents and destroy membrane-based energy producing processes, such as dissipation of electrical potential and pH gradients, or membrane protein inhibition (Sikkema et al. 1995). The higher the concentration of a PAH contaminant, the more organisms will be affected by their toxic effects. On the other hand, some pollutants are only degraded when their levels are above certain concentrations. This may be due to the enzymes involved in a process which are formed and active only when the substrate, its metabolites or possibly closely related molecules are present at a certain concentration (Chen and Aitken 1999).

4.7.9 Soil Microbial Community

Pollution caused due to a wide variety of industrial pollutants has now become a serious threat to the ecosystem (Jain et al. 2005). The environments harbour a large diversity of PAH-degrading microbes with different substrate ranges and metabolic pathways. Generally, the indigenous microbial populations in polluted environments have the capacity for PAH degradation. Thus, it is necessary to explore the community structure and changes associated with it during a bioremediation processes to enhance the microbial processes and optimizing the environmental conditions. Microbes can degrade PAHs partially or completely. During bioremediation, metabolic diversity of microbes degrades toxic pollutants (Seo et al. 2009). Like other living beings, microbes need nutrients, carbon and energy sources for their survival and multiplication. Such organisms can break down organic pollutants to acquire nutrients and energy, by converting them into simple compounds, water, carbon dioxide and other harmless substances (Seo et al. 2009). A time interval, called acclimation period, lag period or adaptation phase, comes before the degradation of a compound like PAHs. It varies from hours to months and depends on the concentration of a compound. The length of acclimation period is influenced by various factors like pH, temperature, aeration and concentration of N and P. The environments that are previously exposed to the pollutants may reduce the acclimation period and enhance the degradation rates. However, environments which never have been affected by a pollutant may have an insignificant microbial population with degrading potential. Thus, the inoculation with microbial species able to destroy the chemicals and to tolerate the specific environmental conditions may be highly beneficial and could enhance the rate of degradation (Grosser et al. 1991; Forsyth 1995; Vogel 1996). However, the population of bacteria declines rapidly after introduction, and their growth is poor probably due to competition with the indigenous microbial population and lack of adaptation to changing environmental conditions.

4.7.10 Chemotaxis

The movement of an organism in response to a source of nutrient or chemical gradient is known as chemotaxis (Paul et al. 2005). Chemotaxis enhances the bioavailability of xenobiotic pollutants such as PAHs to microorganisms. Microbes can sense the xenobiotic compounds that adsorbed onto soil particles and swim towards them, thereby overcoming the mass transfer limitations in a bioremediation process. Chemotaxis plays a vital role in finding the optimal conditions of growth for a bacterium after exposure to such pollutants during limited carbon or energy conditions. In several situations, chemotaxis also governs biofilm formation that directs bacteria to swim towards hydrophobic contaminants, which act as a carbon or energy source, followed by surface attachment through flagella (Pratt and Kolter 1999). There is a clear indication of connection between chemotaxis and biodegradation of organic pollutants that can be enhanced significantly by exploiting the chemotactic responses of bacteria. Studies have revealed that PAHs like naphthalene act as chemoattractant for bacteria (Law and Aitken 2003).

4.7.11 Surfactants

Surfactants are reported to improve the solubility of organic pollutants like PAHs (Aronstein et al. 1991; Tiehm et al. 1997). It is said that surfactants can enhance the mobility and surface area available for a microbial cell contact with hydrocarbons (Banat 1995). Studies have shown that surfactants increase the bioavailability of hydrophobic PAHs and stimulate their biodegradation subsequently (Lantz et al. 1995).

4.8 Conclusion

Anthropogenic activities coupled with industrialization have resulted in widespread pollution of the environment. Many organic contaminants, such as PAHs; polychlorinated aromatic compounds; and nitrogen-containing aromatic compounds are produced that are resistant to degradation and pose a significant threat to both the ecosystem and mankind. They are carcinogenic and mutagenic in nature, and no body part remains unaffected that ultimately can result in the death of an organism. Decontamination of sites polluted with PAHs is a quite difficult task. It is necessary to have a clear understanding of the different degradation processes involved in PAHs removal. Studies have provided the necessary information regarding the persistence and toxicity of PAHs. Different remediation strategies have been adopted to combat pollution attributed to these persistent pollutants. However, bioremediation is an attractive and promising technology for the remediation of such contaminated sites due to its eco-friendly and cost-effective nature. In the last few decades, bioremediation of the xenobiotic compounds has received a considerable attention from the scientific community. It depends upon the different environmental factors, type of microbes and nature and structure of a compound that is being degraded. Thus, to achieve the successful remediation of the target pollutants, factors responsible need to be addressed and explored. Microbial diversity seems to be a prominent resource, and several bacterial species from different environments have been reported with PAH-degrading capability. Acclimatization of the bacterial species could play a pivotal role for enhancing the rate of degradation. Exposing the microorganisms to high levels of contaminants may result in their genetic adaptability sometimes that is responsible for high rate of removal. Further, there is great progress in bioremediation studies of PAHs, and new biochemical pathways have been elucidated with novel ideas of biotransformation of these toxic compounds. Diverse groups of microbes have been reported with PAHs catabolic potentials. Many enzymes associated with PAH degradation have also been reported, but there is still limited information available. The progress in molecular approaches employed in studying catabolism of organic contaminants has contributed significantly in understanding the eco-physiology and biochemistry of PAH-degrading microbes. However, a more detailed research is required in the future for determining the actual mechanism and aspects of PAH mineralization in the contaminated environments. Further, a very scarce knowledge is available about the transmembrane trafficking of PAHs and their metabolites. Several transporters that help in transporting PAHs have been found in microbes, but by now not a single has been purified and characterized. There are several physicochemical and other factors that affect bioremediation. Adjustment of factors like pH, temperature, nutrient availability, oxygen concentration and bioavailability may increase the rate of degradation of PAHs. Meanwhile, biosurfactants can enhance the bioavailability of organic contaminants secreted by various microbes. Some microbes also exhibit chemotaxis towards pollutants that can degradation of organic pollutants. It is also worth to mention that organic amendments can affect the indigenous microbial populations and efficacy of bioremediation of PAHs in contaminated environments.

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Chapter 5
Threats and Risks of Contamination Load on Different Biota

Hilal Ahmad Ganaie

5.1 Introduction

The place in which an organism lives is known as its habitat. The habitat of an organism gets polluted by means of various ways (Bhat et al. 2017). Firstly, by applying pesticides to the agricultural land to destroy the pests (Bhat et al. 2018), these pesticides then found their way into the lakes and rivers by means of the run-off from the agricultural lands. Secondly, due to the industrial revolution, various heavy metals come out of these industries in the form of industrial waste and found its way in the aquatic ecosystem, thereby affecting the aquatic life directly and the humans indirectly.

5.2 Pesticide Pollution

Pesticides are defined as compound substances used on agricultural land, in private nurseries, along railways and in other open areas or gardens (Grube et al. 2011). As the world's population grows at an alarming rate, it has therefore become essential to protect crops by using pesticides to meet the increased demand for food. Despite the fact that agricultural products have increased several times due to pesticides, their accumulation in the food chain poses a risk for many animals, including mammals, since pesticides also have negative effects (Lozowicka et al. 2014). The pesticide applied to crops enters the surrounding environment through different destinations. After applying the pesticide, some remains in agricultural land, while others end up in the surrounding soil, air and water (Malone et al. 2004). These

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pesticides not only have the ability to stay in the surrounding environment but can move long distances such as organic compounds. Pesticide deposits in soil and water are hazards to the earth, and these have been called carcinogens. In this way, the unreasonable use of these pesticides has presented real dangers for human well-being over the past 50 years (Ouyang et al. 2016). Due to the use of pesticides to control pests since the mid-nineteenth century, there has been a significant release of these toxic compounds into the environment. Their serious use has led to pollution of the earth in this way, presenting dangerous impacts on food security, water resources and even on living organisms.

The pesticides and herbicides widely used to control pests and grasses are chemicals used in agriculture. As their definition indicates that they are toxic in nature, this has been validated by finding their bioactive molecules in different animals, plants and fungal species. The use of these pesticides is therefore regulated in European countries due to their toxicity. Since pesticides have different solubility and polarity in water, they can therefore have different ways of entering the surrounding water bodies after their application in agricultural fields. One of the most common routes for these pesticides in the case of agricultural land surface water is after irrigation and after precipitation. According to Abrantes et al. (2006), pesticides influence the biotic architecture of aquatic ecosystems, forcing them to go from a less cloudy stage to a very cloudy stage because of their harmful effects on macrophytes or zooplankton.

Humans are responsible for both point and diffuse contamination through pesticides, herbicides and mild-smelling polycyclic hydrocarbons (PAHs). Surface water contaminated with these toxic chemical pesticides is linked to human activities in the area. Since pesticides and herbicides are closely related to agriculture, it is therefore certain that the cultivated land near or around lakes will have a high intensity of these toxic compounds. In fact, it has been observed that the concentration of nutrients in surface water in a particular area is related to land use in that areas, while the concentration of polycyclic aromatic hydrocarbons is in wetlands. In contrast, areas very far from the water, such as industries, thermal power plants and remote urban areas, and diffuse sources of pollution are also linked to these toxic compounds because they have been detected in aquatic ecosystems.

The fate of these toxic pesticides in the environment is different and can be characterized by various complex processes. Their fate is different depending on the different components of ecosystems such as soil, plants, air, surface water and groundwater. As we focus on sustainable development, the misuse of these pesticides is one of the most alarming challenges for the ecosystem. The small amount of pesticide sprayed on the crops reached the target (only 1%). Persistence of pesticides in the environment for an extended period of time only occurs due to their accidental release which may be due to leaks from pipes, discharges, spills and underground soaking tanks. Therefore, it is necessary to properly monitor and verify the condition of the soil, water and air for contamination for better management of pesticides.

The use of pesticides has an imperative role in modern agricultural practices in order to save agricultural production from the destruction of pests. Modern pesticides are not only reliable, but they also have a great ability to protect crops from pests. Global consumption of this pesticide has been estimated at around 5 billion kilograms per year. This enormous consumption can have serious threats to biodiversity, non-target organisms and the food chain, which therefore represent threats to human health and the environment. The rural areas of the creative nations are very threatened. Zhang et al. (2011) reported that 3 million get suffered from the ill effects of the pesticides, and about 25 million farmers get the negative effects of these pesticides, which accounts for about 180,000 deaths every year. These huge overruns occur in light of off-base observations and guidelines and lack of learning and training among farmers.

5.3 Threats to Biodiversity by Pesticides

Owing to the unrestrained use of pesticides on agricultural land, one cannot monitor the threats that are associated with these toxins. It is therefore the need of the hour to assess the impacts of pesticides on the population of water and land flora, fauna and birds. Predators and raptors are legitimately influenced due to the accumulation of pesticides in trophic levels, which is more worrying. Pesticides are also applied to control weeds and other insects that feed on higher organisms. For example, the spraying of fungicides, herbicides and insecticides is responsible for the decline in the population of certain rare bird and animal species.

5.4 Threats to Aquatic Biodiversity

Pesticides can find their way to surface water in different ways; they can enter by drift, run-off and leakage through the ground or directly into surface water after their application to control mosquitoes. The water contaminated with these toxic pesticides poses a huge hazard to water life. Contaminated water affects marine vegetation, which decreases the dissolved oxygen content of the stream, which can lead to biochemical and behavioural variations in fish abundance. Some reports have found the presence of lawn care pesticides in surface water and in a variety of water bodies such as streams, ponds and lakes. Pesticides reach aquatic ecosystems after their application to agricultural land and harm aquatic life, including fish and other non-target animals. In aquatic ecosystems, these toxic chemicals not only harm fish but also interrelate in the midst of destructive algal blooms that act as stressors. Due to extreme utilization of pesticide, the population of different fish species has fallen to a noticeable range (Scholz et al. 2012). Animals in the aquatic ecosystem are exposed in three different ways (Helfrich et al. 2009):

- Dermal: the pesticide is engrossed openly throughout the skin.
- Inhalation: the chemical can be taken by the process of respiration.

- Oral: the pesticide enters the body by drinking the contaminated product, the water.

Aquatic plants provide about 80% dissolved oxygen for the survival of marine living. As a result of destroying the marine plants by applying the herbicides, the levels of the oxygen dissolved in the aquatic system will reduce and lead to the hypoxia condition, which will then cause heavy damage to the fishes living there (Helfrich et al. 2009). Surface water contains higher levels of pesticides than groundwater due to run-off from surface agricultural land and contamination from sprays (Anon 1993). Pesticides enter groundwater through drainage of degraded surface water, inappropriate transfer of pesticides and spills and accidental spills.

Aquatic life is severely damaged due to the washing of these toxic chemicals from agricultural land into these aquatic ecosystems (lakes, ponds and rivers). The pesticide, atrazine, has been found to be not only toxic to certain fish but also in some way to damage the resistant method “immune system” of amphibians (Forson and Storfer 2006; Rohr et al. 2008). Surface water contaminated with pesticides has harmful effects on amphibians due to their overexploitation and loss of habitat. The carbaryl pesticide class has been found lethal to a few terrestrial and aquatic creatures, while the herbicide glyphosate is an agent responsible for significant deaths of amphibians, including their larvae (Relyea 2005). The population structure of plankton and algae populations have been found to be modified due to the low quantity of the pesticide, malathion. The change in the population structure of these snowboarders has affected the population density of amphibians (Relyea and Hoverman 2008). Last but not least, pesticides, endosulfan and chlorpyrifos, also cause damage to amphibians.

5.5 Terrestrial Biodiversity Threatened

Pesticides have an impact on terrestrial biodiversity by killing non-target plants. Phenoxy herbicides volatilize, causing injury to in close proximity vegetation and bushes (Dreistadt et al. 1994). The vulnerability of plants to disease is increased by the herbicidal glyphosate and also reduces the quality of seeds. The devastating effects taking place to output of non-target crops, innate plant community and flora and fauna are found even in the presence of minimum dose of pesticides, sulfonylureas, sulphonamides and imidazolinones. The life of terrestrial animals is also not immune to these pesticides. With the continuous spraying of broad spectrum insecticides, for example, carbamates, organophosphates and pyrethroids, the abundance of many beneficial insects has decreased considerably. The insect population was found higher on organic farms than on non-organic farms. Honeybees are affected when the above pesticides are applied to crops. Neonicotinoid insecticides such as clothianidin and imidacloprid are toxic to bees. The foraging behaviour and learning ability of bees is reduced even at low doses of imidacloprid. The unexpected disappearance of bumblebees at the start of the twenty-first century was the greatest destruction triggered by the use of neonicotinoids. This disappearance of honeybees was a notable concern for subsistence activities, since 1/3 of the food generation is based on honeybees for pollination. A significant proportion of neonicotinoid pesticides have been reported in honey from commercial hives.

The use of pesticides has also decreased bird populations to around 20–25% since preagricultural times. When these pesticides accumulate in the tissues of these birds, they die. One of the famous examples of bird decline is that of the bald eagle in the United States because of their long exposure to DDT and its components. Fungicides kill earthworms on which birds and mammals feed, thereby indirectly declining their populations. Some of the pesticides which are in the form of grains are mistakenly eaten up by the birds as grains of food. The organophosphate insecticides are very toxic to the birds. Even at a sublethal quantities of the pesticides have been proven dangerous to the nervous system of the birds and thus can change the conduct and actions of the organism (Fig. 5.1).

We can apply pesticides in a variety of ways to control pests. They can be melted or infused in dirt or can be connected in the form of granules or can be applied to seeds and can also be applied directly to the crop in the form of liquid sprays. Shortly after the application of pesticides to the target area, they disappear by various means. They can degrade, they can disperse, and they can be volatile or infiltrate into float up and groundwater, so these can be absorbed by vegetation or animals

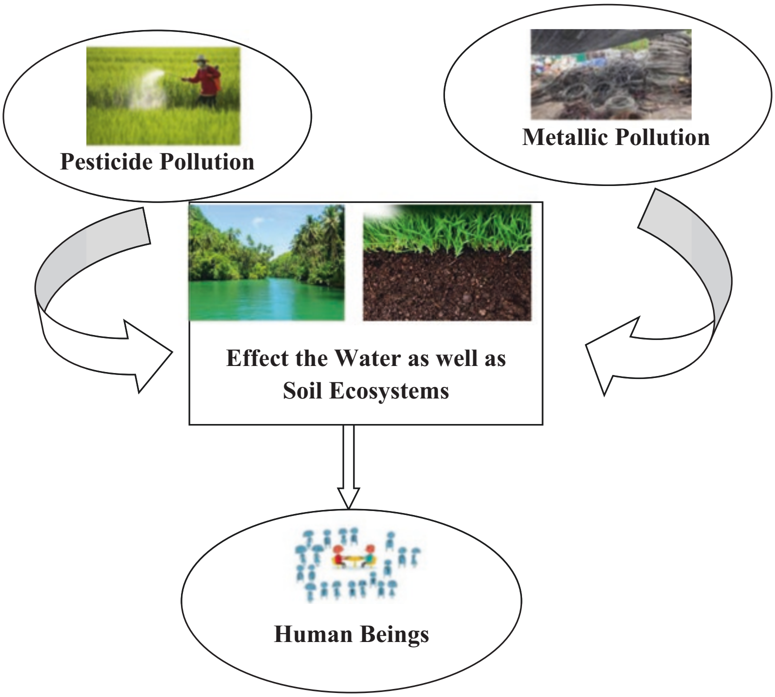

Fig. 5.1 Pesticide and metallic pollution ultimately affect the human beings

from the ground, or they can stay in the ground as such. The main concern is the leaching of these pesticides into the soil as they affect the microorganisms that live there. These microbes that live in the soil help the plant in various ways. They not only increase soil fertility but also absorb soil nutrients and help break down organic matter, thereby increasing soil fertility. In addition, these microbes play an important role in human well-being and relay plants for major needs. Consequently, the overuse of these pesticides can have dramatic consequences on these organisms, and a day may come when our soil will not be fertile and may therefore be degraded.

Among these microbes living in the soil, some bind nitrogen from the air to nitrates. Using fungicides chlorothalonil and dinitrophenyl, it has been found that the processes of nitrification and denitrification by these bacteria are disturbed (Lang and Cai 2009). The change of state from ammonia to nitrite by nitrifying microorganisms is inhibited when the herbicide triclopyr is used. The population of these microbes in the terrestrial environment is reduced by the use of a non-selective herbicide, glyphosate, and the transformation of ammonia into nitrite which is carried out by soil bacteria is inhibited by the use of pesticides, 2, 4-D. These too act as a source for significant harm to fungal diversity in the earth due to the use of trifluralin and oryzalin pesticides, as both inhibit the growth of symbiotic mycorrhizal fungi, which aid in the absorption of nutrients. Oxadiazon is well-known to decrease the quantity of fungal spores, while triclopyr is poisonous to some variety of mycorrhizal fungus. Earthworms which act as bioindicators of soil pollution have a major role in the surrounding environment, and they are used as model organisms to test the toxicity of soils. They also help to make the soil fertile. Pesticides also have their toxic effects on these tiny organisms, and the effect occurs through the pore water after contaminating the soil. Earthworm DNA is damaged after cell damage by using pesticides, glyphosate and chlorpyrifos. The food activity and viability of these organisms are affected by the pesticide glyphosates.

5.6 Metallic Pollution

Though the heavy metals have not been defined in a precise way, one finds that density is the most prominent factor in defining the heavy metal. Therefore, we can define a heavy metal as “the compound which is having a specific density more than 5g/cm^3”. The most important threat to the health of humans by the heavy metals is linked with the introduction of cadmium, arsenic, lead and mercury. The use of the heavy metals dates thousands of years for various purposes. The lead was used for building purposes etc. for 5000 years ago. In olden Rome, lead acetate was used to enhance sugar to aged wine, and a few people of Rome could have frenzied up to 1 gram of lead per day. It is said that mercury was used by the people of Rome to get relief from the pain in the teeth in infants, after which it was also used to treat the syphilis. Claude Monet used pigments of cadmium a lot in the mid-eighteenth century; nevertheless, the rarity of the metal restricted its use in artists’ resources near the beginning of the nineteenth century.

Even though the harmful things of weighty metals on health are recognized for an extensive point in time, the contact to weighty metals continues as well as increases in certain regions. For instance, Hg is still used in gold mines in several regions of Latin America. Arsenic is still universal in timber preservatives, and tetraethyl lead remnants an ordinary stabilizer to gasoline, even if these exercises have declined considerably in countries which are developed. Ever since the mid of the nineteenth century, the fabrication of weighty metals has improved sharply for more than 100 years, through associated emission into the surroundings. Heavy metal emissions to the surroundings occur through a wide range of processes and pathways, including to air (e.g. during combustion, extraction and treatment), to surface water (via the run-off and discharges from storage and transport) and into the soil (and therefore into groundwater and crops) (Singh et al. 2018). Air emission tends to be of most worry in terms of person well-being, together since the quantity concerned and the extensive dispersal and possible contact that frequently results. The emission of lead is mostly associated to street transportation and is therefore more evenly distributed in air. The emission of cadmium is mainly related by way of nonferrous metallurgy as well as combustion of the fuel, while the spatial allocation of anthropogenic emission of mercury mainly reflects the intensity of consumption of coal in diverse regions.

The inhabitants can be open to the elements that are harmful, and the elements may be substance, bodily and organic agents present in the atmosphere, foodstuff, stream or earth, yet contact does not only react from the occurrence of a destructive instrument in the surroundings. The explanation statement in the description of the exhibition is get in touch with (Berglund et al. 2001). It is important to mention that there should be a firm contact between the harmful metal and the external of the body of human beings, may it be the respiratory tract, opening of the mouth or the dermal surface. The term “exposure” is frequently defined as a “function of concentration and time”. Thus, it can be illustrated an occasion when there occurs a contact between the external body of the humans and the environment in which the contaminant is present with a specific concentration during the time interval (NRC 1991). On the need for the contact to happen, there must be the coexistence of both the humans and the contaminant.

5.7 Cadmium (Occurrence and Exposure)

Cd is found obviously in ores along with copper, zinc and lead. The compounds of Cd are widely used in polyvinyl chloride products, in alloys and now recently in Ni-Cd rechargeable batteries as stabilizers. The tinny Cd has been mainly used as an anti-corrosion agent (cadmination). It is present in the phosphate fertilizers as a pollutant. Though the use of Cd in Europe has reduced to a large extent, its use for the production of various items has considerably increased in the twentieth century. The products made from Cd are not recycled back but are rather dumped along with the wastes produced in the homes. In this way, their contamination in the environment has increased.

The sources from which Cd is released include both the natural and anthropogenic sources. The various sources increase their emission from the industries and also by applying the fertilizers and other sewage on the agrarian lands. This leads to the contamination of the soil and aquatic environments. As a result, the Cd uptake by the plants and vegetables gets increased. The absorption of Cd is enhanced, while the pH of the top soil is low down ((Jarup et al. 1998). The main source by which humans get exposed to Cd is smoking. It has been shown that the levels of the Cd in the blood of smokers are higher than the non-smokers. The smoking increases a little bit to the body Cd load. Natural monitor of cadmium in the general people has revealed that smoke can direct to a major add in blood cadmium (B-Cd) level, the concentrations in smokers being on standard 4–5 times upper than in non-smokers (Jarup et al. 1998). In spite of the facts of contact to ecological tobacco smoulder (Hossn et al. 2001), it most likely contributes small to the whole body cadmium load.

Foodstuff is the major basis of cadmium contact in the universal non-smoking inhabitants of most country (WHO 1992). Cadmium is there in most food, but the amount varies significantly, and the person intake also varies significantly, owing to difference in consumption behaviour (Jarup et al. 1998). Women usually use less cadmium, owing to their inferior liveliness expenditure than men. The gastrointestinal assimilation of cadmium can be prejudiced by dietary factors, such as status of iron (Flanagan et al. 1978).

Blood cadmium usually reflects present contact, other than lifetime body burden (Jarup et al. 1983). The concentration of cadmium in urine (U-Cd) is mainly influenced by the body load, U-Cd being proportional to the renal concentration. The smokers and inhabitants existing in infected areas are having elevated urinary cadmium concentrations, smokers having approximately two times as elevated concentrations as those who do not smoke (Jarup et al. 1998).

5.8 Health Effects of Cadmium

Inhalation of vapours or cadmium particles may be serious, and though sharp pulmonary effects and loss of life are uncommon, irregular cases still happen (Seidal et al. 1993; Barbee and Prince 1999). The introduction to cadmium can be reason to damage the kidneys. The primary symptom of kidney injury is often tubular dysfunction, which is evident from the fact that little molecular weight proteins or enzymes are passed away with the urine (Jarup et al. 1998). The damage to the kidney tubules has been found to be reversible (Hotz et al. 1999); however, there is devastating proof that tubular damage induced by cadmium is certainly irreversible.

The World Health Organization (1992) approximates that urinary flow of 10 nmol/mmol of creatinine would compose a “critical limit”, under which no kidney damage can happen. On the other hand, World Health Organization has intended that about 10% of people who are having the above-mentioned concentration in the kidney suffer from tubular lesions. Various information has from the time shown that damage to the kidney in addition to/or else bone effects with lower levels of renal cadmium are likely to occur. European studies have exposed signs of cadmium-induced renal damage in the common inhabitants when the levels of cadmium are approximately 2–3 μg Cd/g creatinine in urine (Buchet et al. 1990; Jarup et al. 2000).

Early tubular injury may develop into extra harsh kidney harm, and as early as 1950, it was reported that some workers exposed to cadmium had developed a reduced glomerular filtration rate (Friberg 1950).

"This has been confirmed in subsequent studies of workers who have been exposed to occupational exposure (Bernard et al. 1992; Jarup et al. 1995)". An excessive danger of kidney sand, probably linked to the increase in the excretion of calcium in the urine after tubular injury, has been revealed in various studies (Jarup et al. 1998). "A link between cadmium exposure and chronic renal failure (end stage renal disease (ESRD)) has recently been demonstrated (Hellstrom et al. 2001)". By means of a registry of patients treated for uraemia, researchers set up a twofold risk of ESRD in people that live near factories (<2 km) that emit industrial cadmium, as well as in professionally exposed employees.

High long-standing exposure to cadmium can be a source of skeletal harm, initially reported in Japan, where "itai-itai" (ahi-ahi) (a disease that occurs when osteoporosis and osteomalacia combine together) was reported in the 1950s. The exposure was caused by cadmium-contaminated water used to irrigate local rice fields. A few studies exterior to Japan include the similar results as reported in Japan (Jarup et al. 1998). Recent records have emerged in current years signifying that comparatively little disclosure to cadmium can also lead to damage of the skeletal system, as is evident by stumpy density of mineral in bones (osteoporosis) and bone breakages (Staessen et al. 1993; Alfven et al. 2000; Nordberg et al. 2002). "Animal studies have suggested that cadmium may be a risk factor for cardiovascular disease, but human studies have not been able to confirm this". A study in Japan, however, depicted an excessive danger of cardiovascular death in people who were open to the elements of cadmium and showed symptoms of tubular renal injury as compared to people who were devoid of renal injury (Nishijo et al. 1995).

"IARC has classified cadmium as a carcinogen for humans (group I) based on sufficient evidence in humans and laboratory animals (IARC 1993)". However, IARC distinguished that the evaluation was based on some lung cancer studies in professionally populations who were exposed, frequently by way of incomplete disclosure records and devoid of the possibility of considering the potential confusion due to smoking and additional related exposure (e.g. arsenic and nickel). "Cadmium has been associated with prostate cancer, but positive and negative studies have been published. Initial data indicated a link between cadmium exposure and kidney cancer (Colonel 1976)". Subsequent research was not in a position to corroborate this clearly, except a huge multicentre study depicted an excessive general (borderline) hazard of kidney cell carcinoma, even if a negative dose-response association does not corroborate a fundamental relationship (Mandel et al. 1995). Moreover, a multicentre population-based study of kidney cell carcinomas demonstrated an excessive danger in relation to the occupational exposure of humans (Pesch et al. 2000). ‘In summing up, the proof of cadmium as a carcinogen is feeble enough for humans, especially following oral contact. Hence, a categorization of Cd as “probably carcinogenic to humans” (IARC 2A group) would be more suitable. This wrapping up too satisfies the CE categorization of a few Cd compounds’.

5.9 Mercury (Occurrence and Exposure)

“Cinnabar consisting of mercury” (HgS) was used in primitive cave paintings for red colours, and metallic mercury was identified in olden Greece, where (with white lead) this was used as a cosmetic to improve the skin. In medicine, in addition to using the aforementioned mercury as a remedy for syphilis, the compounds of mercury have been used too as diuretics [calomel (Hg_2Cl_2)], and the mercury amalgam is still used to fill the teeth in many countries (WHO 1991). “Metallic mercury is used in thermometers, barometers and blood pressure instruments. An important use of mercury is in the chlor-alkali industry, in the electrochemical chlorine production process, in which mercury is used as an electrode”. The profession most open to the elements of mercury is dental employees. In the 1970s, their concentration in the atmosphere of a few dental offices reached 20 $\mu g/m^3$, however as followed by the level had usually fall to about a tenth of these amounts. Inorganic mercury is transformed into organic mercury, for example, methylmercury, that is very constant and accumulates in the food chain. “Until the 1970s, methylmercury was often used to control seed mushrooms. The general population is mainly exposed to mercury through food, with fish representing an important source of exposure to methylmercury (WHO 1990) and dental amalgams”. A number of investigational studies have revealed that vapours of mercury are unconfined from amalgams and that the rate at which they are released may rise with chewing (Sallsten et al. 1996). Mercury in the urine is mainly linked to (relatively recent) revelation of inorganic compounds, while mercury in the blood can be used to recognize contact to methylmercury. Numerous investigations have found a link between the quantity of fillings of the teeth and surfaces of amalgam with the mercury content in person’s autopsy tissue, in addition to blood samples, plasma and urine (WHO 1991). Mercury in the hair can be used to guess long-standing contact; however, possible pollution can create the explanation not easy.

5.9.1 Health Effects of Inorganic Mercury

“Acute exposure to mercury can damage the lungs. Chronic intoxication is characterized by neurological and psychological symptoms, such as tremors, personality changes, restlessness, anxiety, sleep disorders and depression. Symptoms are reversible after stopping exposure”. Due to the blood-brain barrier, there is not any harm to the central nervous system connected to the exposure of mercury which is inorganic. Metallic mercury can be a reason for renal injury, and this damage can be stopped if the exposure of the mercury is closed. This was also feasible to spot proteinuria at comparatively low levels of professional disclosure.

"Metallic mercury is an allergen that can cause contact dermatitis and amalgam mercury can cause oral lichen. It was feared that the mercury contained in the amalgams could cause several symptoms". However, this so-called "amalgam disease" is contentious, and even though a few writers argue that the symptoms are relieved after extracting the dental amalgams (Lindh et al. 2002), there is not any methodical proof to hold up the fact (Langworth et al. 2002).

5.9.2 Health Effects of Organic Mercury

Methylmercury poisoning has a latency of at least 1 month after severe revelation, and the main signs are related to damage to the nerve structure (Weiss et al. 2002). The first signs are paraesthesia and deadness of feet and hands. Afterwards the problems of coordination and concentric narrowing of the visual field may increase, in addition to hearing signs. Elevated dosage can cause mortality, generally 2–4 weeks following the beginning of signs and symptoms. The disaster with Minamata in Japan in the 1950s was caused by methylmercury poisoning of fish infected by the release of mercury in the surrounding sea. In the early 1970s, more than 10,000 people in Iraq were poisoned by eating bread baked with mercury-contaminated cereals, and several thousand people died from poisoning. On the other hand, the common inhabitants do not counter considerable fitness risks associated with introduction to methylmercury, by the exclusion of some groups with elevated consumption of the fish meat.

"The hypothesis is that a high intake of mercury through fish consumption increases the risk of cardiovascular disease (Salonen et al. 1995)". A current case-control research evaluated the combined involvement of levels of mercury in nail trimmings and levels of docosahexaenoic acid in adipose tissue with the danger of a first heart attack in humans (Guallar et al. 2002). The levels of mercury in patients were 15% higher than in controls (95% CI, 5–25%), and the corrected probability ratio for myocardial infarction linked with the highest mercury quintile compared to the lowest mercury quintile was 2.16 (95% CI 1, 09–4.29; P for trend = 0.006). "Another recent case-control study investigated the association between mercury levels in the toenails and the risk of coronary heart disease in health professionals with no history of cardiovascular disease". The levels of mercury were considerably interrelated with consumption of fish, and the average level of mercury was elevated in dentists than in non-dentists. At that time when extra danger factors for coronary heart illness were restricted, the levels of mercury were not considerably linked to the danger of coronary heart disease (Yoshizawa et al. 2002). These intriguing conflicting results should be followed by other research in other likewise population to the exposure of organic mercury.

5.10 Lead (Occurrence and Exposure)

The common inhabitants are exposed to food and air lead in approximately the same extent. Previously, lead in food came from cooking utensils used for cooking and storage, and lead acetate was previously used to sweeten the port. Over the past century, lead emissions into the atmosphere have contaminated our surroundings, more than 50% of gasoline lead emissions. However, "in recent decades, lead emissions in developed countries have declined dramatically due to the introduction of unleaded gasoline. Therefore, blood lead levels in the general population have decreased".

Professional revelation to inorganic lead occurs in foundries and mines, in addition to the welding of lead-painted metal and in factories of battery. Small or modest exposures may occur in the glass manufacturing industry. Elevated levels of lead into the atmosphere can contaminate regions near mines of lead and smelters. Lead suspended in the air can be deposited in soil and water and reaches people through the food chain.

The lungs can absorb nearly 50% of the inorganic lead by means of inhalation.

Adults absorb 10 to 15% of lead from food, while kids can take up to 50% in the gastrointestinal tract. Lead in the blood is connected to RBCs, and their exclusion is time-consuming and mainly through the urine. Lead accumulates in the bare bones and is gradually released from the compartments of the body. The half-life period of lead in the blood is nearly 4 weeks, while in bones the half-life is 20–30 years (WHO 1995).

"In adults, inorganic lead does not penetrate the blood-brain barrier, while this barrier is less developed in children. The high gastrointestinal absorption and the permeable blood-brain barrier make children particularly susceptible to lead exposure and subsequent brain damage. Organic lead compounds enter the membranes of the body and cells. Tetramethyl lead and tetraethyl lead easily penetrate the skin. These compounds can also cross the blood-brain barrier in adults, and thus adults can suffer from lead encephalopathy linked to acute poisoning by organic lead compounds" (Rashid et al. 2019).

5.10.1 Effects of Lead on Health

The signs and symptoms of severe lead poisoning are headaches, abdominal pain, irritability and a variety of signs of the nervous system. Lead encephalopathy is characterized by insomnia and restlessness. The children might be influenced by behavioural problems, learning difficulties and attentiveness. In harsh cases of lead encephalopathy, the exaggerated being can experience confusion, acute psychosis and loss of consciousness. "People who have been exposed to lead for a long time may experience memory problems, longer reaction times and reduced understanding. People with an average blood concentration of less than 3 μmol/l may show signs of peripheral nerve disorders with reduced nerve conduction velocity and reduced skin sensitivity". If the neuropathy is rigorous, the injury may be everlasting. The classic image contains a line of dark blue lead sulphide with a gingival edge. In less severe cases, the most obvious sign of lead poisoning is an interruption of haemoglobin synthesis, and prolonged exposure to lead can cause anaemia. Latest investigation has exposed that prolonged exposure to low intensity lead in children can also lead to reduced intellectual capacity.

"It is known that acute exposure to lead causes proximal tubular kidney damage. Prolonged exposure to lead can also cause kidney damage and, in a recent investigation by Egyptian police, urinary excretion of NAG has been positively correlated with the duration of lead exposure from exhaust gas, automobiles (Rashid et al. 2019), lead and lead nails (Mortada et al. 2001)".

In spite of intense efforts to describe the association between the body's lead load and blood pressure or other effects on the cardiovascular system, no causal relationship has been demonstrated in humans (WHO 1995). With the help of regularly collected mortality rates (1981–1996), statistical data on hospital episodes from 1992 to 1995 and mandatory reports to the Health and Safety Manager (RIDDOR), one death case and 83 cases were identified in hospital (Elliott et al. 1999). The authors found that hospitalizations and death from lead poisoning were rare in England but that there were still cases and that some were related to significant morbidity. Blood lead levels in younger children with 10 μg/dl have so far been considered acceptable, but recent data indicate that potential toxicological effects of lead may occur at expected exposure levels. There are also indications that some genetic and environmental factors may raise the destructive effects of lead on neuronal growth, producing a few infants extra susceptible to neurotoxicity (Lidsky and Schneider 2003). The IARC classifies lead as a "possible human carcinogen" based on adequate human and animal statistics in 1987. Ever since then, some researches have been published, where general tests for lead as a carcinogen are so weak, most candidates are likely to have gliomas and lung and stomach cancer (Steenland and Boffetta 2000).

5.11 Arsenic (Occurrence and Exposure)

"Arsenic is a widely distributed metalloid found in rock, soil, water and air. Inorganic arsenic is found in groundwater used for drinking in several countries around the world (for example, Bangladesh, Chile and China), while organic arsenic compounds (such as arsenobetaine) are found mainly in fish, which can therefore lead to human exposure (WHO 2001)". Non-ferrous metal smelting and energy production from fossil fuels are the two main industrial processes that lead to arsenic contamination of air, water and soil, with smelting activities being the largest single anthropogenic source of air pollution (Chilvers and Peterson 1987). "Other sources of contamination are the manufacture and use of arsenical pesticides and wood preservatives. The EU DG Environment working group concluded that there had been significant reductions in arsenic emissions to air in several European Union member states in the 1980s total arsenic emissions to air in the Member States were estimated at 575 tonnes". In 1996, the total expected release of arsenic to atmosphere in the United Kingdom was 50 tonnes. Air concentrations in rural areas range from <1 to 4 ng/m^3, while concentrations in cities can reach 200 ng/m^3. Much higher concentrations (>1000 ng/m^3) have been measured near industrial sources. Concentrations in water are generally <10 µg/l, although higher concentrations may occur near anthropogenic sources. Levels in soils generally range from 1 to 40 mg/kg, but the application of pesticides and waste disposal can result in much higher concentrations (WHO 2001).

"The general population's exposure to arsenic is mainly through the consumption of food and drinking water. Food is the most important source, but in some areas, arsenic in drinking water is an important source of exposure to inorganic arsenic. Contaminated soils such as mine tailings are also a potential source of exposure to arsenic (WHO 2001)". The assimilation of arsenic in the air particles is extremely reliant on the size and solubility of the particles. Soluble arsenic compounds are simply assimilated from the gut. On the other hand, inorganic arsenic is largely methylated in humans, and the metabolites are released from the body in the form of urine (WHO 2001).

"Arsenic (or metabolite) concentrations in the blood, hair, nails and urine have been used as exposure biomarkers. Arsenic in hair and nails can be a useful indicator of past arsenic exposure, if care is taken to avoid external arsenic contamination of the samples. The metabolites specified in the urine expressed as inorganic arsenic or as the sum of the metabolites (inorganic arsenic + MMA + DMA) are generally the best estimates of the recent dose of arsenic. However, the consumption of certain seafood can disturb the estimation of exposure to inorganic arsenic and should therefore be avoided before urine collection (WHO 2001)".

5.11.1 Effects of Arsenic on Health

Inorganic arsenic is extremely poisonous, and consuming huge amounts leads to symptoms in the gastrointestinal tract, harsh turbulence of the cardiovascular and "central nervous systems" (CNS) and possibly fatality. The persons who may survive show a large number of disorders such as depletion of bone marrow, hepatomegaly, haemolysis, melanosis, encephalopathy and polyneuropathy. Intake of inorganic arsenic can stimulate peripheral vascular disease which, in its severe type, leads to festering changes.

The people who are exposed to arsenic by means of the water they drink present an excessive danger of death from cancer in the bladder, lung and kidney; this danger can be high with higher doses or exposure. As a result, the skin is also affected by showing cancer-like diseases and some lesions in it, for instance hyperkeratosis as well as changes in pigmentation.

The latest "WHO assessment (WHO 2001) concludes that exposure to arsenic via drinking water is causally linked to cancer of the lungs, kidneys, bladder and skin, the latter being preceded by directly observable precancerous lesions. Uncertainties in estimating past exposures are significant when evaluating exposure-response relationships, but it would appear that arsenic concentration in drinking water approximately 100 μg/L can cause cancer at these sites and as precursors of skin cancer levels of 50 to 100 μg/L".

5.12 Conclusion

Current information designate that harmful exposure to cadmium might happen at introduction levels lower than predictable, mostly in the shape of injury to the renal tube but also to bones and fracture to bones. Several citizens in Europe by now go beyond these levels of introduction, and the scope is very small for large groups. Therefore, it is appropriate to take measures to diminish introduction to cadmium in the common inhabitants so as to reduce the danger of unfavourable health effects. The common people does not face a considerable risks to the health due to methylmercury, though some groups which consume large amounts of fish might reach blood levels allied with a little danger of damage to the nervous system in adults. Since there is a risk for the particular fetus, pregnant women should stay away from high consumption of assured fish, such as shark, swordfish and tuna. In particular, fish, such as pike, pike perch and perch, originating from contaminated fresh water, should be avoided in particular. "The safety of dental amalgams has been discussed and it has been claimed that amalgam mercury can cause various diseases, but to date no studies have been conducted to demonstrate the association between amalgam fillings and poor health. Children are particularly vulnerable to lead exposure. Blood levels in children should be reduced to values previously considered acceptable, with recent data indicating that the neurotoxic effects of lead may occur at exposure levels lower than expected". Even though lead in gasoline has decreased significantly in recent decades, falling introduction to the environment, it is necessary to eliminate the remaining use of lead additives in fuel. The use of paints which are based on lead ought to be suspended, and lead must not be used in food containers. In particular, the community must know glass containers for food that can filter lead from food.

Long-standing introduction to arsenic in drinking water is mostly linked to amplified dangers of cancer to the skin, however also to certain extra types of cancers and other lesions of the skin such as hyperkeratosis and changes in pigmentation. Professional introduction to arsenic, above all by breathing, is causally linked with cancer of the lung.

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Chapter 6
Mechanisms and Importance of Phytoremediation

Fernanda Maria Policarpo Tonelli, Flávia Cristina Policarpo Tonelli, Núbia Alexandre de Melo Nunes, and Moline Severino Lemos

6.1 Introduction

Sustainability principles are essential to be respected when human beings interact with different environs; otherwise, anthropogenic actions can cause damage to living forms and also pollute air, water, and soil with organic and/or inorganic pollutants product of mine exploitation; industrial wastes from the production of fabrics, medicines, and paints; exploitation of offshore oil/petroleum; pesticides' use; etc. (Jafari et al. 2013; Bhat et al. 2017; Barrios-Estrada et al. 2018; Carpenter 2018; Bilal et al. 2019; Mendes et al. 2019; Pesantes et al. 2019; Pu et al. 2019; Rosculete et al. 2019; Vázquez-Luna and Cuevas-Díaz 2019; Zhang et al. 2019).

Some of these contaminants, known as persistent contaminants, are even more damaging due to the fact that they may last for a very long time without transformations on contaminated environs, posing as threats for generations (Bhat et al. 2018; Mushtaq et al. 2018). Aromatic molecules, for example, are hardly ever easily degraded, persisting on the polluted sites (Parrilli et al. 2010). Others can bioaccumulate in some organisms, reaching high levels and presenting high risk of causing chronic poisoning to the organism or to an organism that eats the first one. Pharmaceuticals, for example, when thrown in water, such as in rivers, can bioaccumulate in zooplankton (Xie et al. 2017), algae (Vannini et al. 2011), mussels (Maruya et al. 2014), fish (Du et al. 2012), among others. There are also pollutants

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that can do both. Heavy metals, for example, are highly toxic (being able to poison, induce cancer, cause death) and persistent contaminants that may accumulate in living organisms, performing trophic level transfer in food chain (Jaishankar et al. 2014; Jacob et al. 2018; Ali et al. 2019; Rashid et al. 2019; Mehmood et al. 2019).

Therefore, it is necessary that strategies capable of restoring polluted environs be developed. Polluted water causes concern worldwide once it is essential that water of good quality can be offered to human beings to live healthy. However, conventional methods of water treatment (such as reverse osmosis) might present some important disadvantages to be performed in large scale as elevated costs and generation of toxic waste (Dasgupta et al. 2015; Albering et al. 2016; Bilal et al. 2018).

Among the new strategies developed are the ones related to bioremediation: methods that use biological agents to clean up contaminated environs (Strong and Burgess 2008). The use of plants in these strategies originated the phytoremediation, and there are also researchers that consider the microbes associated to plants as part of this remediation's concept (He et al. 2020). Phytoremediation can be performed through different mechanisms, depending on plant, polluted environ, and contaminant characteristics (Panesar et al. 2019).

This chapter will address the phytoremediation as a strategic method to deal with polluted environs in an attempt to restore them, also highlighting the mechanisms by which plant species can remediate.

6.2 Phytoremediation of Polluted Environs

Phytoremediation is a remedial approach that allows in situ recovery of polluted environs in a sustained way, and some mechanisms (such as rhizofiltration) also allow ex situ remediation (Panesar et al. 2019; Bhat et al. 2018). There are some plant species that can remediate various types of pollutants, inorganic (such as radioactive isotopes, phosphates, heavy metals, nitrates) or organic (such as dyes, pesticides, fuels) (Dushenkov 2000; Horne 2000; Nwoko and Egunjobi 2002; Nwoko et al. 2004; Okeke et al. 2004; Singh et al. 2018); *Eichhornia crassipes* (water hyacinth), for example, can remediate dyes, phosphate, heavy metals, and radioactive isotopes (Jayaweera and Kasturiarachchi 2004; Nie et al. 2015; Thapa et al. 2016; Priya and Selvan 2017).

Phytoremediation can be performed through different mechanisms, depending on plant and contaminant characteristics. Phytostabilization, phytovolatilization, and mechanisms involving pollutant sequestration are commonly the ones used by plants to remediate inorganic pollutants, while organic ones are commonly phytoremediated by phyto- and rhizodegradation (Nwoko 2010).

Remediation promoted by plant species can suffer interference by the presence of other plant species and microorganism (especially in phytodegradation, a process in which microorganisms associated to plant's roots take part). *Eupatorium* *odoratum* extract at low concentration, for example, can attenuate formaldehyde toxic effects over *E. crassipes*, enhancing phytoremediation (Gong et al. 2018). Especially when dealing with mixed pollutants, phytoremediation can also be improved by the participation of plant growth-promoting rhizobacteria and plant endophytes (including bacteria and fungi) in a process known as microbe-assisted phytoremediation (He et al. 2020).

It is also important to mention that not only microorganism and the presence of other plant species can affect the phytoremediation efficiency. The pH of the area to be remediated, the composition regarding pollutants (if it is mixed in contaminants that need to be remediated), the presence of fertilizers if it is related to soil remediation, and the presence of chelators can impact the results obtained (Rostami and Azhdarpoor 2019; Xu et al. 2019, Yu et al. 2019; He et al. 2020).

Especially when it comes to remediating heavy metals, biochar is an interesting tool. It is produced from various kinds of biomass through pyrolysis and carbon sequestration (Woolf et al. 2010), also regulating soil pH and reducing plants' stress caused by contaminants (Kiran and Prasad 2019). Biochars could, for example, increase *Ricinus communis* Pb tolerance to sustain phytoremediation, helping the plant to deal with oxidative stress (producing more antioxidant enzymes) and improve nutrient intake as same as plant growth (Kiran ans Prasad 2019).

Phytoremediation presents itself as an advantageous strategy to restore environs from pollution once it presents low initial investment requisition and is an auto-sustained process well accepted as a feasible and safe remediation strategy (Muthusaravanan et al. 2018).

There are various mechanisms of phytoremediation and various plant species available to be used in this kind of procedure. Depending on the type of pollutant and the type of environment that is to be recovered through remediation, certain species and mechanisms are more suitable.

6.3 Mechanisms of Phytoremediation

Phytoremediation of contaminated environs can occur by different mechanisms (Fig. 6.1 and 6.2) and involving different plant species (Table 6.1). Each mechanism of phytoremediation possesses its peculiarities regarding the type of environment in which they can remedy more efficiently and which is the main type of pollutant they can deal with and involving different plant species that receive or not help from microorganisms during the process.

The main types of mechanisms of phytoremediation – phytohydraulic control, phytoaccumulation, phytodegradation, phytostabilization, phytovolatilization, rhizofiltration, and rhizodegradation – are revisited in this chapter.

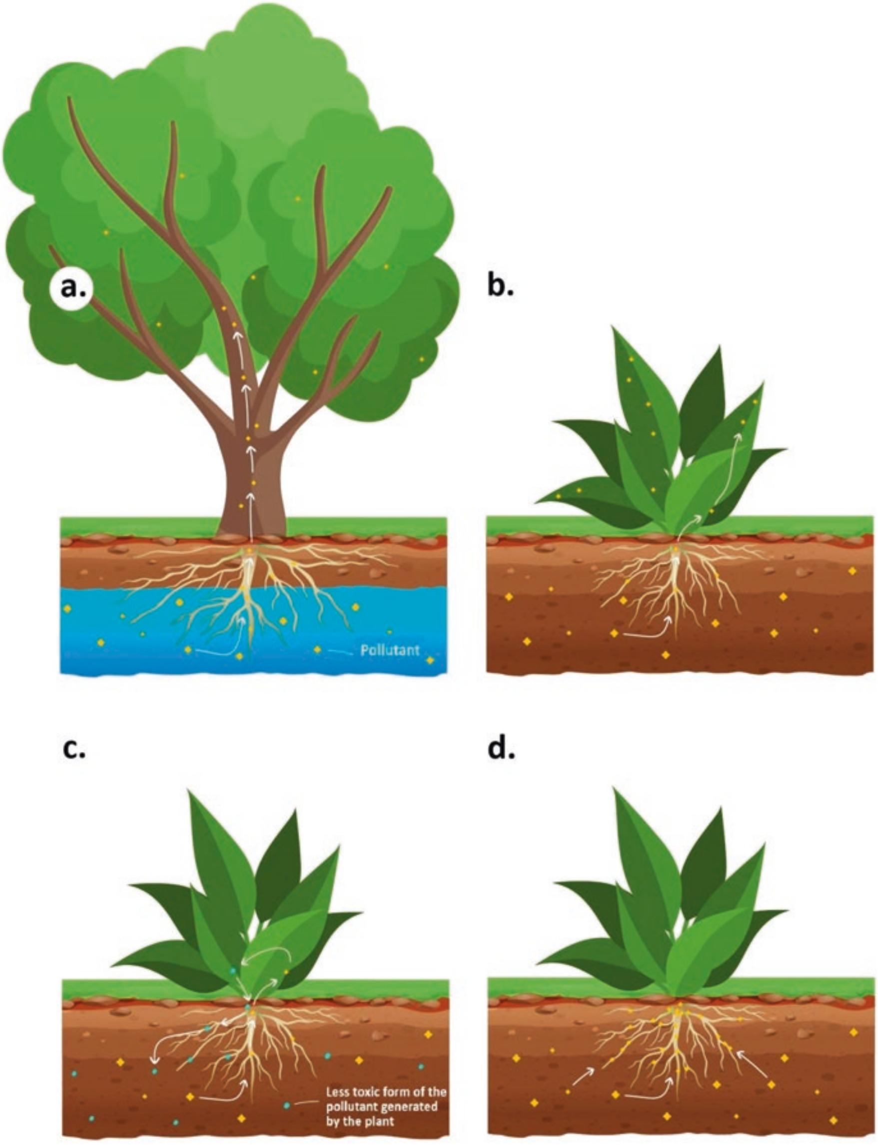

Fig. 6.1 Phytoremediation mechanisms: (**a**) phytohydraulic control; (**b**) phytoaccumulation; (**c**) phytodegradation; (**d**) phytostabilization

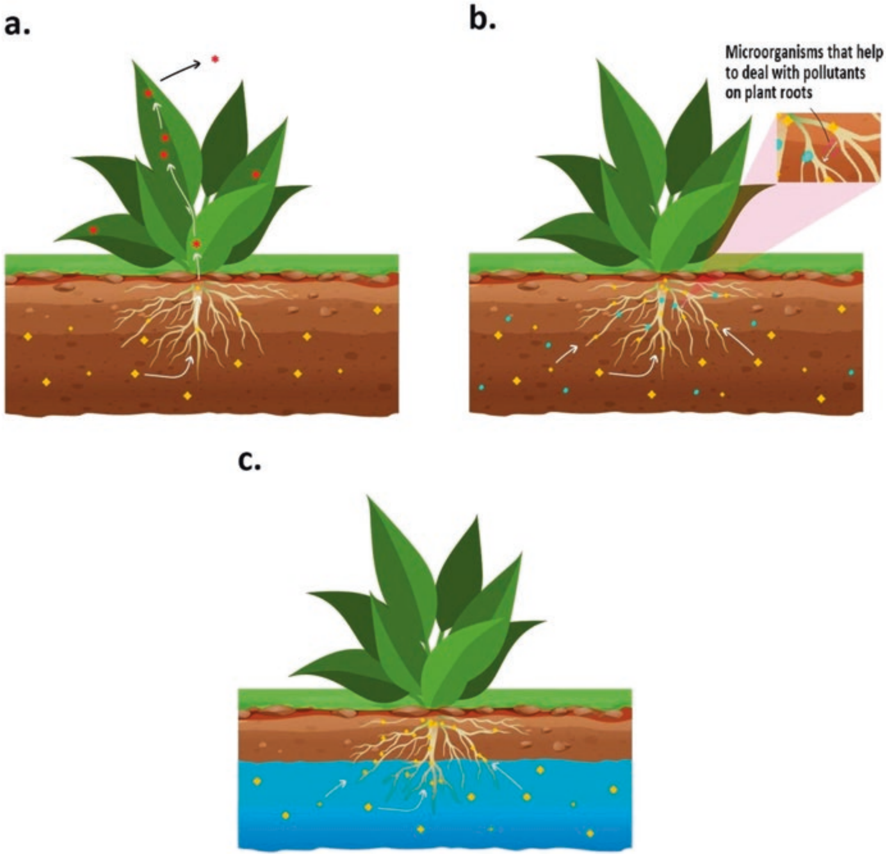

Fig. 6.2 Phytoremediation mechanisms: (**a**) phytovolatilization; (**b**) rhizodegradation; and (**c**) rhizofiltration

6.4 Phytohydraulic Control

The hydraulic control is a kind of indirect phytoremediation strategy especially regarding to groundwater and involving tree species (Fig. 6.1a) (Khalifa and Alkhalf 2018). It consists in a method by which plants act as natural pumps contributing to regulate groundwater's cycle/movement: roots take up water from groundwater, plants can use this or return it into the environment (through transpiration), and then this water can be condensed to return to the groundwater after raining. If, however, the groundwater contains pollutants, the hydraulic control can help to control, limit, and diminish migration or even clean up the area, removing contaminants among the water mass taken up and sometimes phytotransforming them (Ahlfeld and Heidari 1994; Muthusaravanan et al. 2018). The most interesting species to perform this kind of remediation are plants with large root mass and that can release a considerable part of the water taken up into the environment, in other words, species

Table 6.1 Examples of plant species suitable for phytoremediation

Plant species	Favorite remediation mechanism	Pollutant	Reference
Polygonum punctatum	Hydraulic control	Perchlorates	Susarla et al. (2000)
Nymphaea odorata	Hydraulic control	Perchlorates	Susarla et al. (2000)
Allenrolfea occidentalis	Hydraulic control	Perchlorates	Susarla et al. (2000)
Vetiveria zizanioides	Phytoaccumulation	Polycyclic aromatic hydrocarbons	Un Nisa and Rashid (2015)
Cyperus rotundus	Phytoaccumulation	Cadmium and chromium	Subhasini and Swamy (2014)
Brassica juncea	Phytoaccumulation	Copper, lead, and nickel	Singh and Sinha (2005)
Centella asiatica	Phytoaccumulation	Copper	Mokhtar et al. (2011)
Eichhornia crassipes	Phytoaccumulation	Copper	Mokhtar et al. (2011)
Arabidopsis thaliana	Phytoaccumulation	Cesium	Adams et al. (2017)
Chromolaena odorata	Phytodegradation	Sodium dodecyl sulfate	Gong et al. (2019)
Eichhornia crassipes	Phytodegradation	Malathion, ethion	Xia and Ma (2006)
Scirpus grossus	Phytodegradation	Petroleum hydrocarbon	Al-Baldawi et al. (2015)
Myriophyllum aquaticum	Phytodegradation	Trinitrotoluene	Rajakaruna et al. (2006)
Senna multijuga and peat	Phytostabilization	Copper	De Marco et al. (2017)
Festuca rubra	Phytostabilization	Copper	Radziemska et al. (2017)
Osmanthus fragrans, Ligustrum vicaryi, Cinnamomum camphora, Loropetalum chinense, and *Euonymus japonicus*	Phytostabilization	Cadmium	Zeng et al. (2018)
Typha latifolia	Phytovolatilization	Selenium	LeDuc and Terry (2005)
Brassica juncea	Phytovolatilization	Mercury	Moreno et al. (2008)
Populus deltoides and *Populus nigra*	Phytovolatilization	Perchloroethylene	James et al. (2009)
Pistia stratiotes	Rhizofiltration	Iron, chromium, lead, and copper	Galal et al. (2018)
Arundo donax	Rhizofiltration	Copper	Oustriere et al. (2017)

(continued)

Table 6.1 (continued)

Plant species	Favorite remediation mechanism	Pollutant	Reference
Phragmites australis	Rhizofiltration	Uranium	Wang and Dudel (2017) and Wang and Dudel (2018)
Phleum pratense	Rhizofiltration	137 cesium	Mikheev et al. (2017)
Sesbania cannabina	Rhizodegradation	Petroleum hydrocarbons	Maqbool et al. (2012)
Medicago sativa	Rhizodegradation	Hydrocarbons from oily sludge	Bano et al. (2015)
Sorghum x drummondii	Rhizodegradation	Polycyclic aromatic hydrocarbons	Dominguez et al. (2019)

that can transpire large volumes of water, influencing the existing water balance. These species remove a great amount of polluted groundwater and reduce infiltration/leaching of contaminants back to the water table (Etim 2012). In *Populus* gender there are species that are considered high-transpiring ones (Hirsh et al. 2003). Some genotypes from the species *Populus nigra* L., for example, are suitable to perform this kind of remediation. The Spanish genotype can generate organisms with low water use efficiency and high capacity to use hydraulic control to remediate, possessing a high transpiration rate and a large root system (Bogeat-Triboulot et al. 2019).

6.5 Phytoaccumulation

This mechanism of phytoremediation is also called phytoextraction (Fig. 6.1b). It consists in removing contaminants, especially inorganic ones, without destroying them, from polluted spots, primarily from soil (Ahalya and Ramachandra 2006), and concentrating them in plant parts (commonly shoots or leaves) (Rashid et al. 2014; Muthusaravanan et al. 2018). The pollutants, such as heavy metals (Kamal et al. 2004), are captured by the plant among water and nutrients from polluted spots and stored by plants. When it comes to heavy metals, for example, plants' capacity to store them in a large amount depends upon the rate through which roots can uptake the metal, rate of its internal translocation to shoots, how well plant cells can tolerate increasing concentration of the pollutant without experiencing cytotoxicity, and bioavailability of the heavy metal in rhizosphere (Etim 2012). There are organisms, known as hyperaccumulators, that store high amounts of pollutants, being suitable to be used to remediate environs. When it comes to copper, for example, these organisms can store more than 1000 μg from this metal to 1 g of dry plant. The hyperaccumulator *Calendula officinalis* could tolerate high soil concentrations of copper, and at 300 mg/kg of this metal in soil samples, the plant species could accumulate this pollutant in leaf at 4675 µg/g and in root at 3995 µg/g. Antioxidant enzymes such as superoxide dismutase and catalase helped the plant to deal with Cu stress, making high accumulation rates possible (Goswami and Das 2016).

6.6 Phytodegradation

Through this mechanism, also known as phytotransformation (Fig. 6.1c), plants can not only uptake especially organic pollutants but also promote their breakdown into less complex substances by plant's metabolic pathways or by special enzymes produced by plants to perform this role (Newman and Reynolds 2004; Trap et al. 2005). Pollutant's characteristics such as hydrophobicity influence on the remediation efficiency once it interferes on uptake efficiency, as same as contaminants' concentration on the spot and plant phytochemical properties (Etim 2012). Pharmaceuticals are an increasingly concerning problem when it comes to environs' pollution by persistent and biologically active contaminants. In this way, phytoremediation strategies are being developed to deal with this challenging issue. *Phragmites australis*, a wetland plant, could uptake and transform Ibuprofen using enzymes such as cytochrome P450 monooxygenase; the pollutant was degraded in hydroxy-, 1,2-dihydroxy-, carboxy-, and glucopyranosyloxy-hydroxy-Ibuprofen versions (He et al. 2017).

6.7 Phytostabilization

Contaminants can be immobilized, having their soil migration limited, by this remediation mechanism, reducing their bioavailability and consequently their damaging risks. Through this strategy (Fig. 6.1d), the pollutants do not enter vegetative parts of plants, being kept in rhizosphere (Berti and Cunningham 2000; Mendez and Maier 2008; Muthusaravanan et al. 2018). It is a very useful remediation technique to ecological restoration of polluted spots such as mine areas. *Erica australis* could efficiently sequestrate in root cortex toxic elements such as Cd, Cu, Pb, and S and could also tolerate extreme acidic condition, being suitable for remediation of areas containing mine wastes. This plant species also presented interesting characteristic of favoring the reestablishment of vegetation, improving the survival capacity of plant species less tolerant, such as *Nerium oleander* (Monaci et al. 2019). If inorganic soil amendments are added to the sample to be remediated, it can improve the capacity of some plant species to promote remediation; limestone could improve Cu, Ni, and Cd phytostabilization performed by *Festuca rubra* (Radziemska et al. 2019). The presence of organic matter such as manure-based compost or biomass product after pyrolysis (known as biochar) (Saletnik et al. 2019) could help to immobilize the pollutants such as metallic ones (Cd and Zn) by corn plants (Sigua et al. 2019). Microorganisms can also improve plants' ability to promote phytostabilization of pollutants. The fungi *Funneliformis mosseae* could improve *Robinia pseudoacacia* Pb phytostabilization by helping to immobilize the pollutant and could also attenuate its toxicity to roots (Huang et al. 2019).

6.8 Phytovolatilization

This mechanism of phytoremediation consists in plants uptaking contaminants from polluted areas, generally converting them to a less toxic form, and then releasing them to the atmosphere as volatile products from leaves or stems, in a process known as direct phytovolatilization (Fig. 6.2a), or from roots – the indirect type of phytovolatilization (Limmer and Burken 2016). However, it is also possible that the form released by plants to the atmosphere still possesses a concerning toxicity to living forms, so it is essential to first analyze if a certain pollutant would be suitable for phytovolatilization without provoking additional damage. This mechanism of phytoremediation should be avoided to remediate, for example, samples polluted with arsenic and mercury by *Pteris vittata*, once the final products (dimethyl selenide and mercuric oxide) generated by the plant are also toxic (Sakakibara et al. 2010). Species from *Populus* and *Salix* gender are commonly used in this kind of strategy due to their characteristic of uptaking contaminants very well and also *Brassica juncea* and *Arabidopsis thaliana* that possess the ability to convert heavy metal pollutants into volatile forms (Pulford and Watson, 2003; Ghosh and Singh 2005). Trichloroethylene could be remediated by *Eucalyptus sideroxylon* through phytovolatilization from the leaves and roots (soil) in Travis and Fairchild Air Force Bases, California (Doucette et al. 2013).

6.9 Rhizodegradation

Through this mechanism (Fig. 6.2b), plant species can degrade organic contaminants working together with microorganisms associated to plant's roots, which have their development/growth stimulated by metabolites (e.g., amino acids and growth factors) released by these plants in rhizosphere (Dominguez et al. 2019). *Hylotelephium spectabile* could help to deal with petroleum hydrocarbons' pollution mainly through rhizodegradation (maximum rate of 53.3%), which was optimized by inducing the presence of microorganism with capacity to degrade these pollutants and with high salt tolerance (*Alcanivorax* and *Bacteroidetes*). Compared to the control group, the plants involved in promoting remediation increased their gene copy number of genes related to petroleum hydrocarbons' degradation up to 14.44 times (Cheng et al. 2019).

6.10 Rhizofiltration

This mechanism of phytoremediation (Fig. 6.2c) is similar to phytoaccumulation/phytoextraction: pollutants, through biotic or abiotic process, are absorbed by plant's roots or hold on tightly to this plant part (Panesar et al. 2019). However, rhizofiltration focus on remediating polluted groundwater (mainly with metallic contaminants), while phytoaccumulation/phytoextraction is applied mainly to polluted soil (Ahalya and Ramachandra 2006). Plants that will be used to perform this type of remediation are grown hydroponically and not in soil and can perform in situ or ex situ remediation (Mikheev et al. 2017; Tiwari et al. 2019). Within 24 h of experiment, *Helianthus annuus* could remove, through rhizofiltration, 80% of the uranium present in contaminated water from groundwater and laboratory solution samples, offering final concentrations that were under the drinking water limit; *Phaseolus vulgaris* presented the capacity of removing 60–80% of the contaminant, and both species offered a root's capacity of removing this contaminant superior than 500 mg/kg (Lee and Yang 2010).

6.11 GMPs and Phytoremediation

As previously discussed in this chapter, there are plant species naturally capable of promoting environs' remediation. However, depending upon pollutant concentration and toxicity mechanism, the stress induced in the vegetal can limit the success of the phytoremediation or even induce plant's death (Tiwari and Lata 2018).

Genetic manipulation arises as a tool to allow DNA manipulation, for example, to improve plant's resistance to pollutants to phytoremediate them, to improve the efficiency of plants' previous ability to remediate, and to convert a vegetal that was not able to remediate into an organism that can perform this process (Prasad 2019).

To generate a transgenic plant, the most popular methodology involves the use of organisms from *Agrobacterium* gender (*Agrobacterium rhizogenes* or more commonly *Agrobacterium tumefaciens* (Cunningham et al. 2018)).

It is common, for example, strategies that use genes from plants that possess a high capacity to deal well with pollutants, to generate a genetically modified plant (GMP) with an improved phytoremediation potential. The gene that codifies a selenocysteine methyltransferase could be obtained from *Astragalus bisulcatus* (a plant species that can hyperaccumulate selenium) and inserted into *Brassica juncea*'s DNA to enable it to remediate the pollution caused by this element (LeDuc et al. 2004). The MT2 coding sequence from *Sedum alfredii* could reprogram *N. tabacum* to tolerate better and accumulate larger amounts of the pollutant copper (Zhang et al. 2014).

Bacterial genes can also be used in the generation of a GMP. The *atzA* gene from *Pseudomonas* sp. after being inserted in *Medicago sativa* and *N. tabacum* (tobacco plant) could allow the production of the enzyme atrazine chlorohydrolase, allowing the transgenic to efficiently remediate the pollution caused by the pesticide atrazine (Wang et al. 2005). *Enterobacter cloacae NfsI* gene when inserted into tobacco plants' DNA led to the production of a nitroreductase that allowed remediation of sample polluted with 2,4,6-trinitrotoluene (TNT) (Hannink et al. 2007). The gene of a nitroreductase from *Escherichia coli* allowed a similar effect on the genetically modified *Arabidopsis thaliana* (Kurumata et al. 2005). Other gene from *E. cloacae* (*Onr* gene) allowed nitroglycerin's remediation to be performed by transgenic *N. tabacum* (French et al., 1999). *Rhodococcus rhodochorus*' *XplA* and *XplB* genes allowed *Arabidopsis thaliana* to remediate 1,3,5-trinitro-1,3,5-triazine (Jackson et al. 2007). Transgenic tobacco plants expressing *Pseudomonas putida* genes *CzcB* or *CzcA* could efficiently accumulate more Cd in the roots than wild-type plants (Nesler et al., 2017). The gene *copC* from *Pseudomonas fluorescens* was used to generate transgenic tobacco hairy roots, converting these organisms into copper hyperaccumulators that could deal well with the stress induced by the heavy metal (Pérez-Palacios et al. 2017). Genes *nfsI*, *xplA*, and *xplB* from bacteria allowed *Pascopyrum smithii* to remediate, respectively, the explosives 2, 4, 6-trinitrotoluene and hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine (*xplA* and *xplB*) (Zhang et al. 2018).

Human genes such as *CYP2E1* could also be used to generate transgenic *Arabidopsis thaliana*, capable of remediating samples polluted with trichloroethylene and ethylene dibromide (Doty et al., 2000). *CYP1A1*, *CYP2B6*, and *CYP2C19* genes allowed *Oryza sativa* to phytoremediate the pesticides atrazine, metolachlor, and simazine (Kawahigashi et al. 2006).

The genes used to generate transgenic plants to perform phytoremediation can also be sequences from the same species to generate autotransgenic organisms that will overexpress the transgene. Autotransgenic potato designed to overexpress StDREB transcription factors could deal more efficiently with Cd pollution (Charfeddine et al. 2017).

6.12 Conclusion

Phytoremediation is an interesting strategy to remediate polluted environs containing pollutants from diverse chemical nature, organic or inorganic. It can be performed through different mechanisms such as phytohydraulic control, phytoaccumulation, phytodegradation, phytostabilization, phytovolatilization, rhizofiltration, and rhizodegradation. The process' efficiency depends upon some plants characteristics, the area to be remediated, and the contaminant to be remediated. Strategies such as using biochar and microorganisms can favor the aimed results to be achieved. Besides presenting advantageous characteristics intrinsic to the remediation involving plants, phytoremediation may also benefit from generation of genetically modified plants with enhanced remediation capacity, converting even plants that normally cannot remediate in organisms able to clean up contaminated environments.

6.13 Futures Perspectives

It is expected that bioremediation protocols continue to be proposed involving the use of plant species and also strategies to improve the remediation capacity. However, when these strategies involve recombinant DNA technology, it is also expected a special concern regarding safety of these modified organisms' use in the field.

It is also expected that phytoremediation limitations, such as incomplete remediation; roots' size that does not allow cleaning deep inside aquifers; species that can hyperaccumulate but do not degrade pollutants, presenting a risk of food chain contamination with high level of pollutants; the necessity of large areas under controlled situation for field studies; and the risk of converting into air pollution the contaminants remediated through phytovolatilization, can be successfully surpassed.

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Chapter 7
Role of Soil Biota and Associated Threats

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7.1 Introduction

The diverse and complex biological communities are in the soil due to their elevated physiochemical heterogeneity, species phonology, and microclimatic features, which encourage the growth and preservation of a vast number of niches (Tiedje et al. 2001; Ettema and Wardle 2002). In addition to microbial diversity (Ramirez et al. 2018), soil contains a wide range of higher taxa that include vertebrates, insects (root-feeding), and nematodes (Bardgett and Van der Putten 2014). Species of organisms that exist in soil have been identified into microflora, mesofauna, microfauna, and macrofauna (Fig. 7.1), but it is the larger organisms (macrofauna) which have got more attention as compared to smaller organisms despite their greater diversity.

Tiedje et al. (2001) confirmed that millions of fungi and bacteria have been identified and their metabolic mechanism was known in fertile surface soils and only around 0.1% of microbial taxa were cultured (Torsvik et al. 1994). Biota of soil

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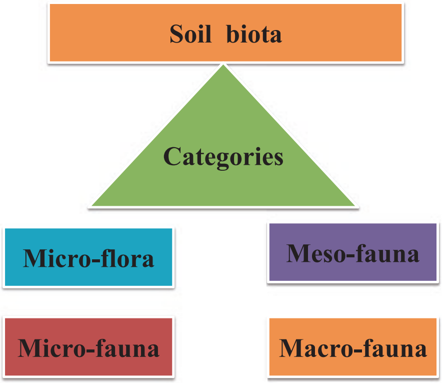

Fig. 7.1 Classification of soil organisms

imparts a significant contribution in the ecological services that include nutrient capture (NC), physical structure of soil (Jego et al. 2001; Jouquet et al. 2006), and plant dynamics (Forey et al. 2011), with a synergistic effect on crop production. Biota of soil is an important element of agro-ecosystem (Van der Heijden et al. 2008: Murray et al. 2009) and plant dynamics (Brussaard et al. 1997). Several researchers have reported that microorganisms as well as soil-dwelling animals are engaged in signaling processes that lead to agro-ecosystem integrity and promote crop production (Sanon et al. 2009; Endlweber et al. 2011). Soil macrofauna also take part as a vital player in altering soil structure by bio-turbation and biogenic systemic growth (Brussard et al. 1997; Lavelle and Spain 2001). Earthworms, ants, and termites affect the nutrient and soil water balance by altering the whole soil environment (Lavelle et al. 1997a, b). The overall economic benefits of biological diversity of soil to ecosystem services was estimated at 1.5 quadrillion US dollars (Pimental et al. 1997). In recent publications, global budgets for carbon (Nielsen et al. 2010), quality of water (Cardinale 2011), nutrient retention and supply (Wagg et al. 2014), and greenhouse gases (Pritchard 2011) have been shown to be affected by biodiversity. Soil species are an integral part of the soil (Hole 1981), greatly affecting the properties of soil, for example, aeration, hydrology, and gaseous components, all of them are important for fundamental production and decomposition of agro-wastes. Nearly about 90% of decomposition is carried by bacteria and fungi (Swift and Anderson 1993). Due to the presence of extracellular enzymes in the fungi, they can decompose all forms of organic substances, decompose soil constituents, and thus regulate the carbon and nutrient equilibrium. A positive effect has been seen on nutritional value of plants (most notably sugar and nitrogen content) in the agricultural field due to the presence of all the soil species (Godschalx et al. 2015; Brunner et al. 2015; Ryalls et al. 2016). The growth of soil species may get affected in the field due to secondary plant resistance metabolites present in the soil that play a part in the palatability of host plants (Wurst et al. 2008; Megías and Müller 2010). The plant defense mechanism is influenced by interactions with soil organisms that lead to increased plant immunity from subsequent antagonist attacks (Pieterse et al. 2014). This phenomenon is better identified as induced systemic resistance (ISR) and thus in the field can offer a vital contribution in interactions between plants and insects (Saravanakumar et al. 2008; Prabhukarthikeyan et al. 2014). The conservation of soil biota for sustainable agriculture and other ecological services is of utmost need. The various practices for the management of agriculture, for instance, tilling of soil, crop rotation, use of pesticides and fertilizers, irrigation, etc., have potential to affect the abundance and biodiversity of biodiversity of soil (Baker 1998). Natural and man-made activities can also change physicochemical and biologic characteristics of soil which in the long run can affect the output of land (Buger and Zedaker 1993; Gupta and Malik 1996). Thus, enriching the soil quality and health is necessary not only for land managers but also for someone who cherishes a glass of clean water or has access to a constant and ample food supply.

7.2 Soil Biota/Biodiversity

Microbes of soils are a major component of terrestrial ecosystems because of their immense role in the interaction with other organisms as well as in the nutrient cycling (Dengler et al. 2014). However, the role of biota is not well known below the surface of soil (Wall et al. 2010). Diversity in soil is very high, and it has been reported that up to 1 billion cells of bacteria, 200 m fungal hyphae, and a broad array of arthropods, nematodes, and worms are present in 1 gm of soil (Roesch et al. 2007; Bardgett 2005). This huge and unseen diversity supports aboveground diversity and contributes to the total terrestrial biomass (Fierer et al. 2009; Wardle et al. 2004). The biodiversity of soil as compared to various other ecosystems of earth is less known. The reason may be due to scarcity of taxonomic knowledge, lack of accessibility and technical challenges of soils, and the micro size of the vast majority of soil organisms (Bardgett 2002; Wardle 2002). Bacterial abundance is especially extensive, with thousands to millions of genomes (species replacement) in just a few grams of soil with higher power of regeneration in less time (Torsvik et al. 1990; Gans et al. 2005). The soil biodiversity doesn't only pertain to microbes but also to several faunal species which include other diverse groups of nematodes, earthworms, mites, etc. (Brussaard et al. 1997; Wall 2004). The widespread abundance of soils led to the presumption that there was a great functional redundancy among soil species (Andren et al. 1999; Setala et al. 2005). Bloemers et al. (1997) reported that 89 species of nematodes were identified from 1 Cameroon forest soil core and from 582 cm^2 grassland soil, 159 mite species were identified (St John et al. 2006). The biota of soil has large functional redundancies due to vast extent of the species wealth of soil (Andren et al. 1999; Seta et al. 2005), and it also varies in terms of habitat. Schouten et al. (2002) reported that in sandy soils, bacteria and earthworms constitute 81% and 13% of live biomass of soil, respectively, while in clay soils the soil biota consists of 77% and 22%, respectively, and the rest of proportion of biota consists of nematodes, enchytraeids, collembols, and mites. Nonetheless, recent analyses of organic milk farms on sandy soils have shown that

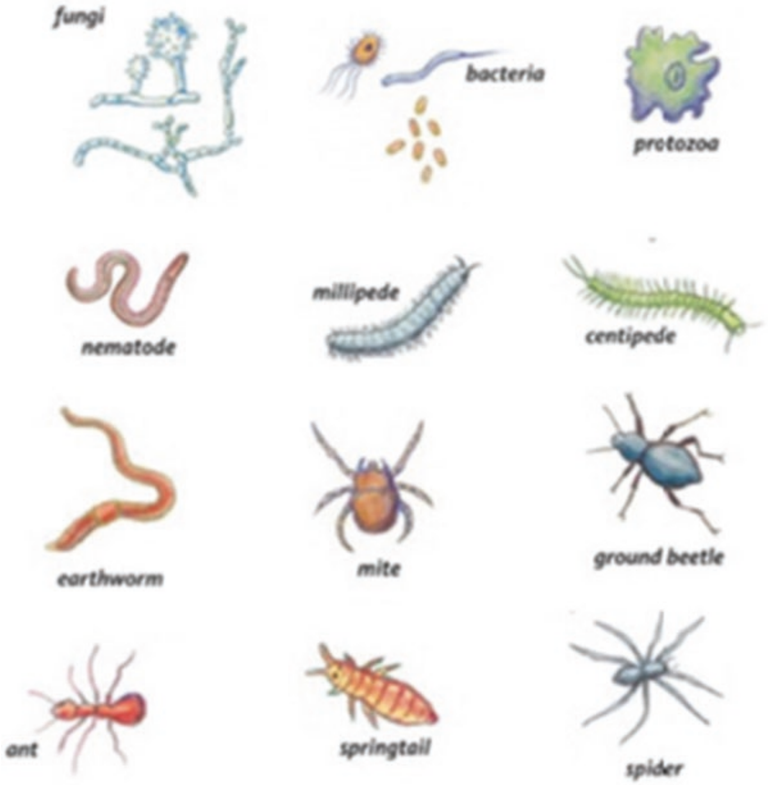

Fig. 7.2 Different organisms present in the soil

fungi constitute about 22 percent of the total biomass of microbes (De Vries et al. 2007). Despite decades of soil biological research and the use of different sample techniques, value of biomass and average abundance of invertebrates present in soil remain extremely difficult to obtain. Major work has been done in temperate woodland soils, while other ecological zones that include tropical or other land uses, like forestry, have been taken into account very less. The soil biota (Fig. 7.2) can be sub divided in different classes on the basis of size such as microflora, microfauna, mesofauna, and macrofauna (Swift et al. 1979) (Table 7.1).

7.3 Role of Soil Biota

Soil biota plays immensely important roles (Fig. 7.3) as discussed and given below.

Table 7.1 Major soil biota groups on the basis of size

S.No	Major group	Examples	Size
1.	Microflora	Bacteria, archaea, and fungi	Very small
2.	Microfauna	Protozoa, ciliates, and nematodes	<200 μm
3.	Mesofauna	Mites, collembola, and enchytraeids	100 μm–2 mm
4.	Macrofauna	Termites, ants, root herbivorous insects, and earthworms	> 2 mm

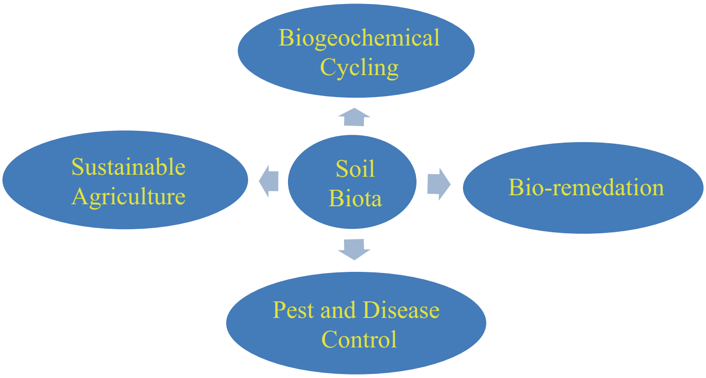

Fig. 7.3 Roles played by soil biota

7.3.1 *Sustainable Agriculture*

The twenty-first century is a major challenge for agricultural farmers and scientists. World population is growing fast and currently at a rate of 1.14% per year and is estimated to reach 9.5 billion by 2050, so to feed such a huge population, they have to produce sufficient nutritious food (UN 2013). The agricultural production has improved tremendously since the Green Revolution because of the use of inorganic fertilizers (Dotaniya and Kushwah 2013; Dotaniya et al. 2014), but this speed of yield cannot be maintained for long because of reduction of soil organic matter, changing climatic conditions, and withdrawal of nutrients from the soil (Meena et al. 2016 a, b). The presence of low amount of organic substances in soil leads to low rate of nutrient conversion and as a result low availability of nutrients to plants (Omar et al. 2017; Kushwah et al. 2014). Similarly, soils where high amounts of chemical fertilizers and pesticides are used have less fertility and potential for crop production (Dotaniya et al. 2016). This chemical management of agricultural ecosystems has destroyed natural habitations (Foley et al. 2005) and also biota of soil (Tsiafouli et al. 2015). Various other problems like decreased water and air quality, diseases, and pest outbreaks have also been reported (Zhang et al. 2007; Kremen and Miles 2012). Because of these well-recognized effects of modern agriculture and global changes, it is very important to move toward sustainable agriculture ways so as to produce enough nutritious foodstuffs (Koohafkan et al. 2011; Bommarco et al. 2013). In order to enhance quality and yield of agro-ecosystems, the utility of fungal diversity of soil has been developed as a novel and promising way in plant development that might be described as "the Second Green Revolution" (Bagyaraj and Ashwin 2017). Fungi play a significant role in decomposing organic substances and bringing nutrients for plant growth. As bio-agents they have a vital contribution in the protection of plants from the attack of pathogenic microbes (Frac et al. 2015). Plant residues left in the soil are broken down by these microorganisms to form nutrients in available state so that plants can very easily assimilate them (Meena et al. 2016b; Dotaniya et al. 2015). The bacterial and fungal diversity in the soil can be increased by adding organic matter which inturn may rupture cell walls of pathogenic fungi, thereby increasing the suppressiveness of soil against plant pathogens. Using these soil-borne fungi can be a best substitute to chemical fungicides that destroy both beneficial and harmful fungi. In horticultural and agricultural soils, the arbuscular mycorrhizal fungi (AMF) are the most vital group of valuable microorganisms (Smith and Read 2008; Bhat et al. 2017). Different experimental works have shown that crop outputs of many plants have improved significantly by inoculating with AMF (Thilagar and Bagyaraj 2015; Khanday et al. 2016; Bagyaraj and Ashwin 2017). The main impacts of AMF symbiosis include soil structure perfection, nutrient cycling enhancement, plant root enhancement, improvement in low-mobility ion intake, and improvement in plant tolerance to stresses (Azcon-Aguilar and Barea 1997). Many antagonistic fungi like *Glomus* sp. or *Trichoderma* sp. can be used to control diseases in crops (Dawidziuk et al. 2016). There are some microbes which produce growth promoters such as auxins, abscisic acid, gibberellins, or ethylene which improve plant growth (Arshad and Fraankenberger 1998; Jiang et al. 2012). Soil pests are often maintained at low levels by predatory insects and spiders living in soil by attacking soil-dwelling pests (Lundgren and Fergen 2014); therefore, these soil-borne organisms reduce the need of chemical pesticides. Soil biota especially microorganisms have the capability to transform atmospheric nitrogen to easily available form for consumption by plants to increase their growth and yield (Zehr et al. 2003; Philippot and Germon 2005). Microbial enzymes secreted by soil microflora are the key drivers of nutrient mineralization and transformation as they convert or decompose inorganic and organic forms of matter into the form that can be consumed by plants easily (Pankhurst et al. 1995; Dotaniya et al. 2017). These enzymes are very vital as they contribute in maintaining soil fertility and health as well as in protecting environment via pollutant degradation (Gianfreda and Rao 2014; Stirling et al. 2017). When nitrogenous inorganic fertilizers are added to the soil, only about 50% of nitrogen is consumed by crops, while a huge portion of it remains unused and is lost via gas emissions and leaching (Smil 1999; Liu et al. 2010). A number of environmental problems are caused by these nutrient losses like water pollution, eutrophication, global warming, and loss of biodiversity (Schlesinger 2009; Galloway et al. 2003). Several investigations have found a positive result of AMF on nitrogen and phosphorus nutrition. These fungi can also decrease phosphorus (Asghari et al. 2005) and nitrogen (Asghari and Cavagnaro 2012) losses via leaching. Thus, our crop and soil management practices should focus on maintenance of soil organic matter, reduction on pesticide and fertilizer use, maintenance on soil fertility and soil biota. Thus, one of the primary strategies for achieving sustainable agriculture is the conservation of soil biodiversity, which is very vital to maintain soil health and productivity.

7.3.2 Pest and Disease Control

Annually, huge losses to the crops occur due to soil pests and diseases worldwide. Diseases and pests are kept under check by healthy and diverse food web via several mechanisms that include antibiosis, predation, and competition (Susilo et al. 2004). The crop productivity is less due to more vulnerability to pests and diseases in the nutrient-poor soils. As reported by Lendzemo et al. (2005), in Northern Cameroon, sorghum and maize were grown in *Striga hermonthica*-infested soils; utilizing AMF (*Gigaspora margarita* and *Glomus clarum*), the *S. hermonthica* emergence was reduced by 30–50% and biomass by 40–63%, and this was probably because of better nutrition, which leads to better resistance of healthy plants to pests and diseases. AMF are the largest genus of protective microorganisms in horticultural and agricultural soils (Smith and Read 2008). Inoculation with these fungi has reported significant increase in the output of many crops (Thilagar and Bagyaraj 2015; Bagyaraj and Ashwin 2017). The symbiotic association of AMF with plants helps in promoting nutrient cycling, improving the soil structure, improving stress resistance, rooting improvement, and overall development as well as the use of low-mobility ions and increased plant population diversity (Azcón-Aguilar and Barea 1997). The microbial flora-rich soils not only help to prevent the loss by diseases, pests, and weeds but also improve certain biologic functions related to the environment (Wall and Virginia 2000). Because of the involvement of mycorrhizal fungi, the plant growth is influenced by mutualism, pathogenicity, and availability and cycling of nutrients (Wagg et al. 2014; Hannula et al. 2017). The soil-borne plant health issues can be reflected by the presence of these three soil organism classes which include root rots, plant-parasitic nematodes, and white grubs. In order to stay alive in the conditions of soil, strong defense mechanisms develop over time due to a wide variety of microbes and their release of toxins; thus, the white grubs and other soil pests proved to be hard to control (Jackson 2003). Biologic management of *Costelytra zealandica* (grass grub) was particularly effective because the bacterial entomopathogens *Serratia entomophila* were highly host-specific (Jackson et al. 1992; Hurst et al. 2004). To plant-parasitic nematodes, several types of microbial antagonists including actinomycetes, endophytic fungi, nematophatic fungi, and the bacteria have been found (Dong and Zhang 2006; Bhatti et al. 2017). The intensity of galling of roots and replication of *Meloidogyne incognita* (a root-knot nematode) have been shown to be significantly reduced by inoculation with AMF of the genus *Glomus*, and the same has been found with *G. mosseae* in banana (Jaizme-Vega et al. 1997), *G. fasciculatum* in tomato (Bagyaraj et al. 1979), and *G. viscosum*, *G. mosseae*, or *G. intraradices* in olive plants (Castillo et al. 2006). Presence of rich rhizospheric microbial flora in soil regulates health and overall development as plants secrete secondary metabolites which perform numerous functions in the root zone. Exudates vitamins, amino acids, organic acids, and hydrates can be chemo-attracting agents that are capable of metabolizing nutrients as well as permit the growth of population (Bertin et al. 2003; Bais et al. 2006). Additional exudates, including flavonoids, particularly phenotropic derivatives attract rhizobic bacterial species, for instance, *Rhizobium*, *Sinorhizobium*, *Allorhizobium*, *Bradyrhizobium*, and *Mesorhizobium* (Hernández-Salmerón et al. 2013). In addition, certain exudates, such as phenotypes and terpenoids, form part of the plant protection system, which has an effective antifungal and antibacterial ability. Furthermore, some volatile radically emitted compounds have been identified recently as plant defenders like *Pseudomonas fluorescens* which suppress the take-all wheat disease caused by *Gaeumannomyces graminis* and black-red tobacco developed by *Thielaviopsis basicola*, in addition to induced cucumber root diseases produced by *Pythium ultimum* (Laville et al. 1992) and sugar beet damping disease produced by *P. ultimum* and *Rhizoctonia solani* (Andersen et al. 2003). The bio-control capabilities of these strains rely on rapid colonization of roots, antibiotic development, and stimulation of systemic resistance in the plant or unique interaction with fungal pathogenicity factors (Haas and Défago 2005). Therefore, under unfavourable circumstances, rhizosphere microbiome and other soil biota may exert a considerable effect on plant growth, health, and survival; in this sense, rhizosphere biota can be considered as an inherent mechanism for plant survival and has coevolved with plants.

7.3.3 Bioremediation of Pollutants or Toxins (Pesticides and Heavy Metals)

As a result of human activity, a large number of pollutants and contaminants are added to the environment. Pesticides and heavy metals are among such contaminants released into the environment due to the wide applicability of such chemicals and other industrial pollutants. Such chemical substances have been identified as chronic toxic substances by their poor biodegradability (Tayade et al. 2013). Continuous use of these pesticides has led to the disappearance of beneficial species in the soil environment. In addition to contaminating the ecosystem, including the vegetation, pesticide residues often damage beneficial species such as earthworms, bees, mice, plants, and natural degradation that would otherwise have helped prevent dangerous pests (Singh et al. 2014). Detrimental effects of pollutants on soil microbiota can be directly related to biodiversity loss and to activities such as nutrient recycling. The microbial activity is also significantly reduced by the presence of heavy metals such as zinc (Zn), mercury (Hg), cadmium (Cd), and chlorinated materials such as PCBs and DDT in polluted sites (Su et al. 2014). Millions of dollars will be needed to clean the contaminated soil manually by excavating and disposing it in protected areas. The number of physical and chemical techniques has been developed for remediating polluted soils. But they are very expensive and have negative effects on soil biodiversity as well. Bioremediation is one of the ways in which infected environment is treated by nature (Dada et al. 2015) and includes the use of living organisms to eliminate or detoxify toxins in the ecosystem (Gupta et al. 2006; Rahimi et al. 2012).

7.3.3.1 Microbial Bioremediation

Methodology of biodegradation is commonly used in soil management of xenobiotics such as synthetic chemicals, heavy metals, PAHs, etc., and due to its low cost and being environmentally friendly, it is used in many countries (Enrica 1994; Ritmann et al. 1988). The breakdown of pesticides results in the decay of parent compounds and leads to generation of water and carbon dioxide, and during this cycle, bacteria get energy from degradation products (Bhat et al. 2018; Mushtaq et al. 2018). For the intent of pesticide degradation, it is extremely essential to manage environmental conditions and the correct microbial community within the site of contamination (Chishti et al. 2013). A strain *Sphingobium japonicum* is used for degradation of hexachlorocyclohexane, a chlorinated pesticide. Similarly pesticide lindane 20 mg/L is completely degraded in 10 hours by strain (*Sphingobium japonicum LZ-2*) (Liu et al. 2007). In 20 days with an initial dose of 50 mg/L in mineral salt media, 69% imidacloprid degradation and 86% metribuzin degradation can be obtainable via *Burkholderia cepacia* strain CH-9 (Madhuban et al. 2011). Cho et al. (2009) have stated that organophosphate fermentation process can degrade organophosphorus from lactic acid bacteria. Highly efficient bacterial strain enterobacteria can kill many other pesticides, including bifenthrin, cypermethrin, etc. (Lio and Xie 2009; Shafi et al. 2018). Furthermore, the use of the organophosphate pesticide degradation (Sabdono and Radjasa 2008) is achieved by bacterial strains, e.g., *Bacillus*, *Actinobacteria*, and *L-proteobacteria*. In reduced salt water, the bacterium *Bacillus thuringiensis* effectively degrades malathion. The bacterial growth rises up to 105-fold by adding yeast and glucose and within a month degrades 99% malathion. The fungal strains, such as *Fusarium oxysporum*, *Lentinula edodes*, *Penicillium brevicompactum*, and *Lecanicillium saksenae*, have also great scope in the degradation of pesticides like terbuthylazine, difenoconazole, and pendimethalin and have been reported as helpful organisms for the breakdown of pesticides (Hai et al. 2012). *Pseudomonas* is the most effective bacterial genus to degrade venomous chemicals according to Abo-Amer (2012). In another investigation three strains of pseudomonas were evaluated for biodegradation of aroclor herbicide 1242 by Vasquez and Reyes (2002) and they found that these bacteria have a strong degrading potential, respectively 99.8, 89.4 and 98.4, in their degradation levels. Another experiment has demonstrated the efficacy of *Rhodococcus* sp. bacteria in the degradation of nitrated triazines and reported that the herbicide atrazine has been transformed into nitrite (30%), ammonia (10%), formaldehyde (27%), and nitrous oxide (3.2%) by microbial action (Fournier et al. 2002).

A variety of metabolic and redox functions are carried out by essential micronutrients like calcium (Ca), zinc (Zn), copper (Cu), chromium (Cr), and nickel (Ni), but their higher concentration can suppress their activity or kill microbes in soil. Heavy metals like mercury (Hg), selenium (Se), chromium (Cr), arsenic (As), and uranium (U) have been reported to be degraded by microbes. Some important microbes like *Agrobacterium*, *Arthrobacter*, *Enterobacter*, and *Pseudomonas aeruginosa*, *Chlorella vulgaris,* etc. have great potential in reducing metals (Ramasamy and Banu 2007). Sulfur-reducing bacteria, namely, *Desulfuromonas* spp., and iron-reducing bacteria (Fe) like *Geobacter* spp. have been found to reduce toxic metals. The bacterium that absorbs sulfur is purely anaerobic and gram-negative and totally oxidizes organic acid to carbon dioxide.

7.3.3.2 Bioremediation by Earthworms (Vermiremediation)

Vermiremediation is a process by which earthworms are used to clean up toxicants from the soil environment. Various studies have revealed the ability of worms to carry soil bioremediation (Contreras- Ramos et al. 2006; Ceccanti et al. 2006). A number of studies have reported that earthworms efficiently biodegrade or bioaccumulate broad range of toxicants like heavy metals, pesticides, and polycyclic aromatic hydrocarbons from the soil (Pattnaik and Reddy 2011; Dada 2015). Soils and sites polluted with hydrocarbons can be remediated by vermiremediation in an ecofriendly and cost-effective manner in just few days to months (Njoku et al. 2016). The mechanical activity of earthworms together with biotic (burrowing, ingestion) and abiotic processes and subsequent growth enhancement of microorganisms helps in remediation process (Azedah and Zaeabi 2015). The effect of earthworm species *Lumbricus rubellus* on the degradation of spiked polyaromatic hydrocarbons phenanthrene and fluoranthene (100 ug/kg of soil) was studied, and it was observed that both PAHs were lost at a faster rate in earthworm-amended soils than the non-earthworm soils (Ma and Imerzeel 1995). PAHs were also found to be degraded by *Eisenia fetida*, and it was observed that the concentration of anthracene reduced by 2-fold and benzo(a)pyrene by 1.4-fold and phenanthrene was totally removed after the addition of worms (Contreas –Ramos et al. 2006).

7.3.4 Role in Biogeochemical Cycling

The biogeochemical cycles highlight the intertwined role played by living and nonliving components of the environment for the supply of essential molecules necessary for the reproduction and development of life forms. During the extensive evolutionary course, archaea and bacteria have developed mechanisms essential for recycling of almost all complex natural molecules into atomic constituents vital for the sustenance of higher living organisms. Decomposition process and transformation of elements have been greatly focused due to their key role in the biogeochemical cycles particularly N, P, and C (Swift et al. 1979a, b; Coleman et al. 2004).

7.3.4.1 Nitrogen and Phosphorus Cycling

The nutrient recycling is a critical ecological function essential for the survival of life forms on the earth. Micro-symbionts have exerted well-recognized direct positive effects on the yield of crop by increasing plant access to nutrients such as phosphorus by arbuscular mycorrhizal fungi and nitrogen via biological nitrogen fixation by bacteria present in soil (e.g., *Rhizobium*) (Giller 2001; Smith and Read 1997). Nitrogen is vital for the growth of plants and frequently acts a key limiting factor in the agricultural yield. Biological nitrogen fixation may play a crucial part in supplying nitrogen inputs to the budget of crop systems. Numerous organisms that exist in agro-systems are capable of fixing nitrogen at varied rates, but the maximum estimate shown by symbiotic biological nitrogen fixation may be 400 kg N/ha/yr. For instance, the symbiotic association between *Azolla* and *Anabaena* can supply nearly 76 kg N/ha/yr. by deriving at least 1/3 of the contributed nitrogen from the air via biological nitrogen fixation and as a result make up a significant fraction of nitrogen required for rice (Ladha and Reddy 2003). Fungi and bacteria contribute nitrogen directly by mineralizing and immobilizing nutrients. The contribution of bacteria in the mineralization of nitrogen ranges from 20 to 140 kg N/ha/yr. (De Ruiter et al. 1993). However, fungi in comparison to bacteria contribute for lower mineralization of nitrogen, i.e., from 1 to 24 kg N/ha/yr., but this low nitrogen supply is compensated to a certain extent by symbiotic association of mycorrhizae with plants. For instance, the effects of mycorrhizal species on biomass and phosphorus levels of shoot in grass species such as *Festuca* and *Bromus* have been positively measured (Van der Heijden et al. 1998). Protozoa as well as nematodes indirectly affect the cycling process of nutrients by foraging on biomass of soil microbiota and excreting nutrient-enriched waste. Macro- and mesofauna also directly affect recycling of nutrients by breaking down and transporting inorganic and organic substances while indirectly controlling the population and activating the activities of microbes. Deficiency of phosphorus also acts a common constraint in crop yield. Soil organisms directly influence the acquisition of phosphorus by mycorrhiza. Arbuscular mycorrhizal fungi boost the acquisition of phosphorus by plant via exploring huge volumes of soil with hyphal system (Jakobsen et al. 1992). The studies on symbiotic efficacy on three dissimilar species of arbuscular mycorrhizal fungi (*Glomus macrocarpum*, *Glomus fasciculatum*, and *Glomus intraradices*) and sorghum showed that in *G. macrocarpum*, the colonization of roots is twofold and length of hyphae ten times higher than *G. fasciculatum* and *G. intraradices* that leads to over five times higher intake of phosphorus by *sorghum* (Marshner 1995). The drastically higher growth and rate of survival of plants colonized by arbuscular mycorrhizal fungi make these plants as potential candidates for rehabilitating degraded soils, as a result of which the inoculation of arbuscular mycorrhizal fungi has become a crucial entrance point for restoring the yield of soils (Requena et al. 2001; Allen et al. 2005).

7.3.4.2 Carbon Cycle

Soils are enormously rich in species and store around 80% of worldwide terrestrial carbon. In the dynamics of carbon, soil biota plays a very important role. Presently there is very much attention toward carbon cycling because of its relationship with climate change (Heimann and Reichstein, 2008; Chapin et al. 2009), and soils are of prime importance as approximately 80% carbon is present there (IPCC 2000, 2007) and are main sites for decomposition of organic matter. Microorganisms present in soil are key drivers in plant material decomposition as they produce enzymes responsible for degrading recalcitrant substances like lignin (Masai et al. 2007). Some other organisms like termites and worms have also been reported to play a very vital role in organic matter decomposition (Bignell and Eggleton 2000; Milcu et al. 2008). Besides direct effects of soil organisms on carbon cycling, there are also indirect interactions which affect carbon cycling because of large diversity of soil organisms (Wardle 2006). For example, cellulose which is a recalcitrant compound is broken down by some saprophytic fungal species into simpler substances which are metabolized by other fungal species which cannot degrade cellulose, thereby facilitating larger fungal diversity and quicker decomposition (Tiunov and Scheu 2005; Wardle 2006). Hence, cycling of all essential nutrients is very vital as absence or low level of any nutrient can reduce overall productivity. In most ecological systems, the growth of plants entirely depends on the nutrients that are recycled by soil microorganisms. It is also known as the internal recycling. In most of the ecosystems, all nutrients necessary for plant growth are recycled by microbial litter decomposition (Van der Heijden et al. 2008), thereby suggesting that many ecosystems entirely depend on internal nutrient cycling.

7.4 Threats to Soil Biota

Throughout the globe, degradation of terrestrial ecosystem is a serious problem. In the last few decades, the pollution load of soil has improved because of unsystematic use of fertilizers and pesticides. Every year tons of inorganic chemicals are added to the soil to boost its fertility for the sustenance of food production. Farmers usually don’t care about the negative effects of fertilizers on beneficial soil organisms and use excess amounts of fertilizers to produce more yields without following general recommendations. The extensive application of fertilizers and insecticides in farming has increased concern about soil pollution throughout the world (Garcia et al. 2011; De Silva et al. 2010; Santos et al. 2011). Majority of pesticides are harmful not only to target species but also to non-target species because of physiological and structural similarities between pests and non-pest species (Walker et al. 2010; Santos et al. 2010). Agricultural intensification particularly the application of pesticides often leads to reduction in biodiversity (Hole et al. 2005), but the effect of pesticides especially on the soil biota is not very clear. Various organisms of soil are at high risk to these changes (Parrent et al. 2006; Briones et al. 2007). However, the vulnerability of soil biota to global changes as well as soil biota data is poorly known, meaning the degree of impact on potential soil biota cannot be understood surely. Nonetheless, various studies have shown that soil biodiversity has changed because of anthropogenic effects and suggest that soil biodiversity will also likely change in the future. For example, a 99.9% reduction in bacterial genome richness was observed in metal-polluted soil and the number of different genomes decreased from about ten million to 1000 in ten (10) grams of soil (Gans et al. 2005). Likewise, a number of studies in agricultural systems have shown decrease in soil biodiversity associated with higher intensity of management activities (Eggleton et al. 2002; Adl et al. 2006). Some other factors which have been found responsible for change in soil species composition or richness include global warming, habitat degradation, soil moisture content, exotic plant species, etc. (Hanski et al. 2007; Batten et al. 2008). Agricultural activities like plowing, insecticide and fertilizer use, irrigation, and crop rotation have led to degradation in physiochemical and biological properties of soil (Edwards 1984; Lee 1985) and are also linked with reduction in soil biodiversity abundance and richness including earthworms and other invertebrates. The production and addition of harmful pollutants like heavy metals, pesticides, and fertilizers has increased because of rapid industrialization. Due to their high toxicity and accumulation in the environment, heavy metal contamination is one of the main environmental issues and potent dangers to soil organisms including human beings (Chen et al. 2005; Blaylock et al. 1997). Numerous studies have reported that high level of heavy metals in the soil leads to higher mortality of earthworms (Jamshidi and Golchin 2013). Earthworms are key soil organisms playing an important role in soil aeration, water infiltration, and mixing of soil and also act as an essential source of food for higher tropic level organisms like birds, moles, etc. (Edwards and Bohlen 1996; Lavelle et al. 2006). Due to the contact of pesticides to earthworms, they are not able to carry out their significant and vital functions in the soil ecosystems (Rathore and Nollet 2012). Mostly it is the epigeic and anecic species of earthworms which are affected by the application of pesticides because of their occurrence on the upper surface of soil (Singh et al. 2016). Acid rain is another type of ecological pollutant which is responsible for the loss of soil biota and may also reduce the metabolic activity of soil microbial population (Wang et al. 2014). The various factors that pose immense threat to soil biodiversity are shown in Fig. 7.4.

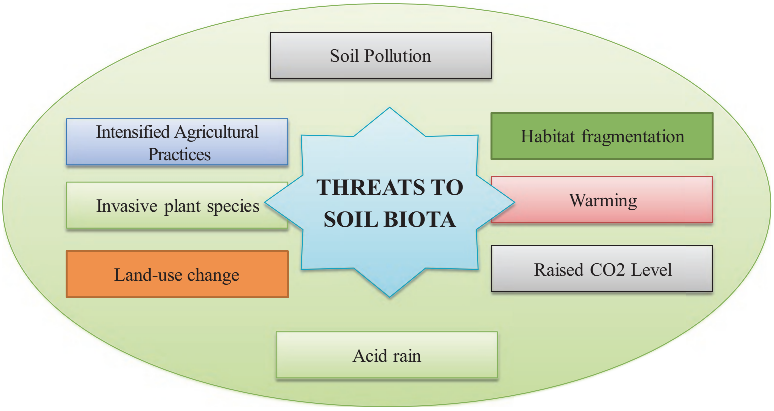

Fig. 7.4 Factors that pose threats to soil biota

7.5 Conclusion

Though soil biota constitutes a small proportion of the entire soil, their existence and activities are very crucial for the formation and modification of physiochemical properties of soil. The diversity and number of organisms inhabiting soil are huge as compared to other habitation of earth; however, the population characterization and dynamics is yet in the infancy stage. Soil biota regulates numerous pedologic processes especially those associated with mineralization of organic substances and nutrient turnover. The diverse organisms of soil offer a broad array of ecological services that are not only vital for the sustainable functioning of all ecosystems (natural and managed) but also an essential resource for the sustainable management of agro-ecosystems. Numerous factors that include type of soil, agro-practices, pH, land use, temperature, etc. may take part as critical role players in modulating the micro- and macrofauna diversity of soil. The intensification of agriculture frequently degrades soil conditions that results in the decline of species abundance. As a result of reduction in ecosystem biodiversity, the services offered by organism present in soil are halted, and sustainable existence of mankind is threatened.

Hence, it can be concluded that for the sustainability of mankind, soil biota is very vital and appropriate steps are required to be taken for its management, so that we and our upcoming generations can continuously benefit from the endless services provided by soil biota.

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Chapter 8
Viability of In Situ and Ex Situ Bioremediation Approaches for Degradation of Noxious Substances in Stressed Environs

Monica Butnariu and Alina Butu

8.1 Background

The soil is represented by the layer from the surface of the earth's crust consisting of mineral particles, organic matter, water, air, and living organisms. The process of soil formation (pedogenesis) takes place under the influence of pedogenic factors: climate, microorganisms (MOs), vegetation, and relief. By its position, nature, and role, soil is a component of the biosphere resulted at interference between the biotic and abiotic environment, representing a specific area of concentration of living organisms, their energy, products of metabolism, and decomposition.

The organisms (plants, animals, MOs) and the soils are intertwined and interconditioned in complicated ecological systems which are changing according to the dynamics and physical characteristics of the physical-geographical environment.

The energy reserves and biophilic elements accumulated over thousands of years in the soil-formation process highlight the extremely high importance of organic matter and secondary minerals for soil fertility. The loss of humus and secondary minerals, due to unreasonable exploitation (soil depletion, erosion by water and wind), is also disastrous for agriculture in any environmental conditions would be practiced, as well as for many components of the biosphere (Wu et al. 2019a, b).

Soil pollution is any activity that produces the disturbance of the normal functioning of the soil as a support and living environment within the natural or anthropized ecosystems.

Soil is the place where all the noxious substances (NSs), dusts in the air, toxic gases transformed by rain into the atmosphere meet, so the soil is most exposed to

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the negative effects of these substances. The infiltration waters impregnate the soil with NSs, driving them deeper; the polluted rivers infect the flooded or irrigated surfaces; almost all the solid residues are deposited by agglomeration or only accidentally thrown on the ground.

Soils with associated MOs play the role of an absorbent, purifier, and neutralizer of all organic wastes and residues. Due to this function of soils within the biosphere, mankind has relied on such a long period of time on the "self-purification of nature" against the wastes and residues produced by the ever-growing population and the development of the industry and released in the environment.

The soil-organism ecosystem is one of the most important mechanisms in the formation, stability, and productivity of the biosphere (Scholz-Starke et al. 2013).

However, the development of industry, agriculture, transport, and urbanization in the last 100–150 years has begun to disturb the normal functioning of the soil-plant-animal system. World soil resources are limited qualitatively and quantitatively; currently over 70% of soils require improvements of different kinds.

But the situation becomes even more alarming, since in the development process of human society, in the last 75–100 years, the area of agricultural land has been considerably reduced. It would seem that it is not necessary to give special importance to this phenomenon if the soil cover is considered only as a resource for obtaining agricultural and forestry products. But the concern stems from the fact that the possible changes in the global balance of oxygen and carbon dioxide, the decrease of the reserves of clean biological water, and the eutrophication of the lakes require to pay even more attention to the soil as part of the biosphere.

From the existing data, it turns out that in the course of history, mankind has lost about 2 million hectares of land. Therefore, the problem of preventing and combating soil pollution involves the coordination of an special importance both from the point of view of the world agri-food production and the production of plant raw materials as well as of the spatial reduction, directly or indirectly, and especially of the normal functioning of the biosphere.

Permanent growth of agricultural production requires the adequate protection of the cultivated plants. The losses caused to agriculture worldwide by various harmful organisms amount to 35–40% of the crops annually (Kulmatiski 2018).

Therefore, it is necessary to resort – within the means of combating harmful organisms to plants – to NSs. Leaving aside the positive aspect of the use of these, NSs are toxic substances, substances that after entering into the body, in a relatively high dose, once or several times, in a very short period, or in small doses repeated for a long time, causes, transient or permanent, impairment of one or more functions, impairments that can go to complete annihilation or lead to death.

In the process of control, NSs go through different pathways in the ecosystem. Ideally, the NSs used will run out once the intended purpose is achieved.

In fact, it is known that from a pesticide only 3% of the total activates, the rest of about 97% is lost, it reaches in soil, on plants and other organisms of the agroecosystem. The extremely large quantity unused from the point of view of control creates all the known ecological problems, hence the need to ensure the greatest possible availability of NSs.

Given the multiple and still unpredictable risks of using NSs in plant production, increasing attention has been paid to the elaboration and introduction into practice of plant production of methods to combat diseases and pests with as small as possible risk of pollution or even without pollution (Guan et al. 2018).

The natural rain has a pH of 5.65 due to the natural CO_2 from the atmosphere. Through pollution, the pH value can fall to 4. In this case, the potential acid rain would be due to nitrogen oxides. Although the NSs eventually are evacuated to high altitude, the dispersion in the atmosphere is made in several days, during which photochemical reactions take place and the oxides turn into acids. Acid rains have an effect on the soil, on the one hand, its washing of nutrients and, on the other, the reduction of pH.

In the type of pollution with agricultural vegetable wastes and residues, all the SCs are included by the disorderly storage or simply by the accidental disposal of vegetable waste and residues – including straw and corn stalks left in the field over winter.

Although they have a more or less accidental character, however, it is necessary that, like harmful situations that remove from the economic circuit the lands by pollution to the environment, to be avoided (Wu et al. 2016).

The extension of the irrigation system through channels in which it is not possible to level the water flow leads to the prolonged excess of moisture in the soil, chemical, and biochemical processes take place, which lead to the appearance of the phenomenon of gleization – by raising the level of groundwater and pseudogleization under the influence of excess of river water.

Under these conditions, besides the lack of oxygen, a series of toxic compounds appear that inhibit the life of the soil and the nutrition of the plants, causing losses of harvest.

Especially on these lands, there is a phenomenon of compacting or settling the soil due to the execution of the agricultural works with heavy machines, the increase in the number of passage with machines and other equipment, the execution of the works in conditions of inadequate humidity, and the lack of adequate crop rotation with the predominance of the stubble crops. Because of this, the productive capacity of the soil is affected by the destruction of the structure, the reduction of the aeration and the permeability, the impairment of the water and thermal regime, and the regulation of the soil nutrition regime, all of which constitute a phenomenon of soil pollution (Zheng et al. 2019).

The intensity of this phenomenon depends on the soil structure, the lack of organic matter, climatic conditions, cultivated plants, and the degree of development of the plants when the roots reach the compact layer. Each compulsory restoration work also contains a chapter on the distribution of arable land by plow resistance categories and the distribution of arable land according to the loosening requirements.

For example, on the sandy lands, it is not necessary to deep loosening, in contrast to the other categories of lands, with a clay texture; it is necessary to loosening to 35–45 cm for breaking the plow sole. Crust formation is a particularly a widespread phenomenon.

In the case of clayey soils and those with a high content of fine sand, these processes lead to a considerable diminution of the stability of the structural aggregates that, under the action of unfavorable external factors, easily dissolve, forming crust. One of the external agents of the formation of the crust is the rain, to which, in the case of irrigated soils, the irrigation by spray increases the effect (Jensen et al. 2017).

The superficial crust has a negative impact on the productive capacity of the soil stagnating or preventing all the germination of the seeds and the emergence of the plants, modifying the water circuit, so easy to remove, by a suitable superficial work of the soil, but which, if it persists, can have important economic consequences.

Within the processes of bioremediation, the role of MOs consists in the genesis of oil deposits as well as in the microbiological biodegradation of hydrocarbon residues from different habitats (soil, water, etc.) (Reinecke et al. 2016).

As they can be used in the deposits of hydrocarbon-SCs, MOs are of particular ecological importance. In this regard, it has been observed that many MOs have the ability to use hydrocarbons both in the gaseous state and in the liquid and solid state in the aliphatic, aromatic and asphaltic series, which they use as a source of carbon and energy series and asphalt as carbon and energy source.

The process of remediation of hydrocarbon-SCs by biological processes is known as bioremediation. Bioremediation is achieved through indigenous or specially created MOs introduced into the polluted soil (Panchenko et al. 2018).

This can be prevented by associating them with natural fertilizers or alternating their use. The most important impact on human health and the environment is nitrogen and phosphorus fertilizers. The nitrites from the soil is leached and carried into the water of the springs and from there they reach the human body, being transformed into nitrogen that enters the blood, disrupting the intracellular respiration (Bore et al. 2017).

The increasing of the concentrations of nitrogenous fertilizers used results in their growth concentration in plant tissues.

The phosphorus accumulated in soil and water in high doses can inhibit the vital processes of plants: phosphoric anhydride in the soil, over a certain limit, can lead to a deficiency of zinc by immobilizing it and implicitly by reducing crops (Ahmed et al. 2017).

Irrigation systems also changes the ecological balance of the soil, affecting the conversion process which can leads to the decrease of the productive potential (according to Table 8.1).

For good soil productivity, it is necessary to combine the mineral fertilizers with the organic ones, or alternate their administration, so that the organic fertilizers are administered at least every 3–4 years. Increased amounts of chemical fertilizers increasingly reduce the organic components and humus in the soil. This has the effect of deteriorating the pedological structure, thus contributing to the decline of the clay-humic absorbent complex in the soil (Cui et al. 2019).

Most NSs, non-biodegradable, are concentrated along the trophic chains, being toxic to plants and animals, and pests become resistant to their action, creating new synthetic substances that are efficient but more toxic to the environment. In order to

Table 8.1 Problems related to the impact of irrigation and drainage systems and mitigation measures

The impact	Improvement measures
Affect downstream ecosystems due to hydrological changes	There are designated surfaces, which will be administered by environmental protection institutions or organizations, for floodable areas, wetlands, drainage of surplus water, etc.
Water ponding	Ensure proper drainage
Increased acidity	Regulation and management of irrigation and drainage systems so as to ensure efficient circulation and distribution of water
Increased alkalinity	Proper maintenance of canal systems to prevent water ponding, including removal of mud, and vegetation
Increased salinity	Providing drainage including water collection in reservoirs to ensure water evaporation or drainage to other aquatic basins
Avoid contamination with NSs	Irrigation water quality monitoring
Changing water quality due to return water from irrigation	Establishment of areas for the accumulation of salinized water and the construction of separate channels for the circulation of these waters
Reducing biodiversity in the landscaped area	The functioning of the systems will take into account the needs from downstream of the dams. To facilitate the protection and the presence of the fauna and flora specific to the area

reduce the negative effects that may occur when using NSs, to avoid pesticide residue pollution of plants, soil, water, and other components of agroecosystems, it is necessary to respect the technologies of application and the careful supervision of the users and the service providers of these products (Brunet et al. 2011).

8.2 Anthropogenic Salinization of Soils

It consists of two distinct processes: salinization consisting of the accumulation in soil of soluble salts in concentrations greater than 0.1% for chlorides (NaCl, KCl, $CaCl_2$, $MgCl_2$) and 0.15% for sulfates (Na_2SO_4, K_2SO_4, $MgSO_4$ and partially $CaSO_4$) and carbonates and bicarbonates (Na_2CO_3, $NaHCO_3$, K_2CO_3, $Ca(HCO_3)_2$).

The salts come from the surface waters or from the highly mineralized groundwater, and their accumulation in the soil is due to a dry climate and a depression and accumulative relief. The result of these accumulations is the appearance of the salinization horizon on the soil profile, a horizon that is called saline if it exceeds 1% of the concentration of chlorinic salts and 1.5% when sulfatic salinization.

Alkalization is the accumulation of sodium ions in the colloidal complex of the soil and the increase of the sodium carbonate content. The sodium ion maintains colloidal dispersion and promotes the migration of colloids from the top of the profile. The result of this phenomenon is the emergence of an extremely permeable argillic horizon, plastic, and adherent in a wet state (Litalien and Zeeb 2020).

Sodium carbonate in the colloidal complex increases the alkalinity of the solution leading to high pH values. The sodium content of the colloidal complex with values between 5% and 15% forms the alkalization horizon.

These processes occur naturally in the soil profile (Wu et al. 2019a, b).

The problem arises when there are soils with saline or alkaline potential, which under the conditions of improper irrigation management and exploitation become saline and alkaline. The presence of salts in the upper part of the soil profile is due to the capillary ascension from a groundwater, surface deposits, updating of saliferous layers through surface erosion. The low efficiency of irrigation leads to the raising of the water level, and the absence of drainage works and the presence of restrictions in application lead to the accumulation of salts. For example, an annual application of 1000 mm of good-quality irrigation water, with a content of only 250 mg/L, will bring to the soil an additional 2500 kg of salts for each irrigated hectare. This problem is solved by an additional supply of washing water that will fill the aquifer layer, and under the conditions of natural drainage, it will not cause capillary ascension. However, most of the times the natural drainage does not cope with these operations and it is necessary to perform the artificial drainage works. Thus, we identify two functions of drainage (Merchán et al. 2015).

Firstly, the main function of maintaining the air-water regime under optimal conditions, and secondly, for the arid and semiarid areas, it maintains a favorable balance also for the salt regime in the root layer.

Large amounts of exchangeable sodium can also accumulate under the conditions when sodium is present in major concentrations in irrigation water. For the saline soils, the measures adopted must reduce to tolerable limits of the soluble salts in the plants, and the alkaline soils require the elimination of the excess sodium from the colloidal complex, the saline – alkaline soils requiring both types of interventions (Timpano et al. 2018).

The adverse effects of the excess of salts manifest on the plant due to the toxicity of some ions, the increase in the osmotic pressure of the cells, and also the worsening of the hydrophysical, chemical, and biological properties of the soil.

8.3 Elements Involved in the Bioremediation Process

One of the elements involved in the bioremediation process is the polluting agent, in our case the oil-contaminated soil. It is biodegraded by soil microbial activity. The rate of biodegradation of NSs by MOs is influenced by certain factors such as: nutrients, soil type, humidity, temperature, pH, type, and metabolism of MOs. The nutrients needed for cell development are nitrogen, phosphorus, potassium, sulfur, magnesium, calcium, manganese, iron, zinc, copper, and other microelements. In order for the biological activity to proceed under optimal conditions and to ensure the nutrient requirement, the C:N:P ratio should be approximately 100:10:1. The development of MOs is also influenced by humidity, the optimum range being between 25% and 85%, as water ensures the transport of nutrients, promotes enzymatic catalysis, and maintains the osmotic pressure of the cells.

Temperature influences the microbial activity in the soil. The biodegradation rate is low at low temperatures, so that in cold climates the bioremediation process may be inefficient during the cold periods of the year if the bioremediation is not carried out in a controlled climate. As a general rule, low temperatures delay the volatilization rate of low molecular weight hydrocarbons, some of which are toxic to MOs. Also, in cold regions, the degradation rates are much lower and, consequently, less suitable for removing the crude oil from the environment (Birgander et al. 2018).

Soil pH influences the solubility and availability of many soil constituents, affecting the biological activity of MOs. The pH should be between optimal values in the range: 5.5–8.5. Another very important element in the biodegradation of hydrocarbons is the concentration of oxygen, which influences the microbial activity in the soil.

Depending on the oxygen content of the soil, the degradation processes can be aerobic or anaerobic. Biodegradation of crude oil is particularly active in aerobic process, which is explainable because all known biochemical pathways function with the participation of oxygenase and molecular oxygen. Researchers have highlighted the importance of oxygen required for oxidation reactions of biodegradation, establishing that 3–4 mg of oxygen is required for complete oxidation of 1 ml of hydrocarbon (Zhou et al. 2017).

It is recommended the residual oxygen concentration greater than 1 mg/L in the aqueous phase and in the gaseous phase not to fall below 2–4% (volumetric percent). The biodegradation process results in CO_2, H_2O, as well as non-toxic substances harmless to the environment.

8.4 Advantages and Disadvantages of Bioremediation

The most important advantages of bioremediation are the following:

- Bioremediation, being a natural process, is perceived as a possible treatment process on contaminated materials, such as hydrocarbon-contaminated soil. MOs have the ability to degrade a large number of NSs, and as a result of their activity, the result is harmless to the environment. Another advantage of bioremediation is the fact that this process can be carried out on the spot, without causing major interruptions in the activity (Ma et al. 2018a, b).
- The operating costs are lower than in the case of other conventional processes applied (washing, incineration, thermal desorption).
- In order to increase the efficiency of the biodegradation process, hydrogen peroxide inoculation can be used. Waste disposal issues are eliminated.

Some of the disadvantages of bioremediation are:

- Bioremediation is limited to biodegradable compounds only.

- It is difficult to extrapolate from laboratory conditions to large scale (field). Bioremediation does not work too well on compact, clay soils where oxygen or nutrients are difficult to enter in the area to be treated (Touceda-González et al. 2017).

The bioremediation process takes a much longer period than other treatments, such as excavation or soil incineration. The properties of MOs involved in the bioremediation of hydrocarbon-SCs are known from the main conditions that MOs must meet in the processes of biodegradation of crude oil:

- To intensive and rapidly degrade a large range of petroleum compounds
- To be genetically stable and can be conserved and cultivated without undergoing essential changes
- Not to cause toxic effects and not to be pathogenic
- Can be used in combination with other active MOs, to ensure the degradation of different types of hydrocarbons
- To reproduce itself rapidly
- To multiply in natural environments

The possible negative effects of MOs on oil hydrocarbons are listed:

- Alteration of the crude oil from the tanks associated with the decrease of the normal density and with other unwanted modifications
- Occurrence of unpleasant odors and modification of the physicochemical properties of mineral oils used as lubricants or cooling agents
- Discoloring of refining products
- Production of explosive mixtures in kerosene or gasoline storage tanks, by the formation of a mixture of methane and H_2, resulting from the decomposition of kerosene in contact with water
- Decrease in the octane number of kerosene and gasoline used in aeronautics (Kinley et al. 2016)

The MOs that participate in the process of biodegradation of hydrocarbons are: bacteria, fungi, yeasts, as well as algae. But the most important groups are bacteria and fungi.

Aerobic bacteria are mainly used from bacterium domain (*Achromobacter* sp., *Acinetobacter* sp., *Actinomyces* sp., *Alcaligenes* sp., *Arthrobacter* sp., *Bacillus* sp., *Brevibacterium* sp., *Corynebacterium* sp., *Flavobacterium* sp., *Micrococcus* sp., *Mycobacterium* sp., *Nocardia* sp., *Pseudomonas* sp., *Spirillum* sp., *Serratia* sp., *Rhodococcus* sp., *Vibrio* sp.), followed by the anaerobic ones (*Geobacter metallireducens*, *Thauera aromatica*, *Desulfococcus multivorans*, *Clostridium* sp., *Desulfobacterium cetonicum*).

Fungi that are of particular importance in hydrocarbon degradation belong to the following genera: *Alternaria*, *Apergillus*, *Cephalosporium*, *Cladosporium*, *Fusarium*, *Graphium*, *Geotrichum*, *Mucor*, *Penicillium*, *Rhizopus*, *Trichoderma*.

In very general terms, bioremediation (biotechnologies for the decontamination and remediation of polluted soils) can be defined as a treatment technique with the help of MOs or plants that can degrade contaminating or polluting substrates with toxic character, transforming them into non-toxic substances for the environment (Siciliano et al. 2016).

In other words, bioremediation is the elimination, mitigation, or transformation of polluting substances, using biological processes, in order to minimize the effects of NSs on human health or the environment (Turker et al. 2016).

The living organisms participating in the bioremediation process can ingest and degrade the organic substances and use it as a source of food and energy or they can degrade these substances, obtaining non-toxic final compounds, but which they do not use in the growth and development process (Shafi et al. 2018). Overall, the bioremediation process can be regarded as a system in which the active part is represented by living organisms (MOs, plants) that act on the NSs, which represent the passive or static part of the system (Liang et al. 2016).

The living part of the system can be represented by lower and higher organisms. Among the lower organisms, in addition to bacteria with biodegradative properties, yeasts and filamentous fungi can also be mentioned.

All of these MOs form the biomass of the system, which is the force that puts the whole assembly in motion and has a dynamic character. In the category of higher organisms enter the leguminous plants, cereals, trees and shrubs, water plants, etc. The concept of bioremediation does not yet have a unanimously accepted framework. In the broadest sense, bioremediation refers to the modification of the properties of some compounds determined by the biological activity of some MOs or plants. These processes most often affect organic materials but do not exclude inorganic ones. In general, a certain organic substance cannot be completely degraded by a single species of MOs.

Usually, the microbial attack is initiated by a species that possesses extracellular enzymes required for a first cleavage of the complex structure, and then, as the degradation progresses, other species of MOs intervene and further metabolize the intermediates resulting from the activity of initial degradation.

The remediation methods can be classified according to their place of application and the nature of the processes being performed (according to Fig. 8.1).

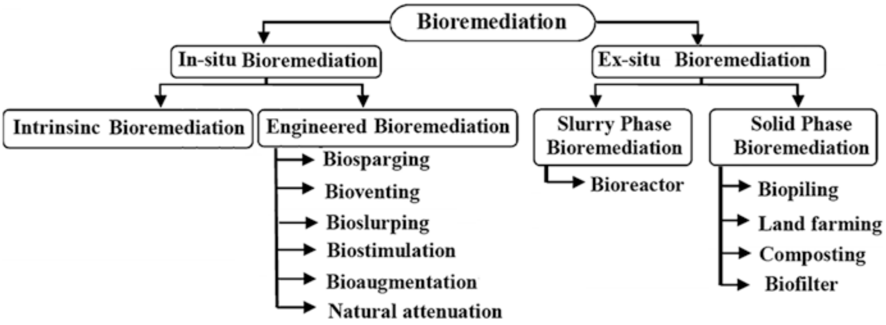

Fig. 8.1 Schematic representation of in situ and ex situ bioremediation methods

Thus, according to the first criterion, ex situ and in situ processes are distinguished. Ex situ treatment methods require the mobilization of contaminated soil followed by its treatment either on the same site (on-site remediation) or in a specialized off-site soil treatment facility (off-site remediation). In situ treatment methods are carried out directly in the contaminated site, without the need to mobilize soil from the site (de Jesus et al. 2015).

8.5 Soil Remediation Technologies, Applied In Situ

8.5.1 Biological Remediation of Soils In Situ

Starting from the degradation activities of the MOs, numerous depollution technologies have been developed, which are generically included in the term of bioremediation and which have applicability both for the decontamination of a terrestrial substrate and of an aquifer.

Bioremediation is a waste management technique that involves the use of biological organisms (MOs, plants, etc.) for cleaning soil and polluted water. This technique consists of adding materials to polluted environments in order to cause the natural biodegradation process to accelerate (Evans et al. 2019).

Bioremediation is therefore the use of living organisms to improve the ecological status of a polluted or degraded substrate (area, soil, aquifer, etc.) or to bring it to better quality parameters, which are harmful to life, or to restore it to its unpolluted state.

Bioremediation is a modern technology for treating NSs that uses biological factors to convert certain chemicals into less harmful/dangerous final forms, ideally to CO_2 and H_2O, which are non-toxic and released into the environment without altering substantially the balance of ecosystems.

Bioremediation is based on the ability of some chemical compounds to be biodegraded by stimulating the growth of certain microbial agents that use NSs as a source of food and energy. NSs that are treated by bioremediation include oil and other petroleum products, solvents, and NSs (Balseiro-Romero et al. 2019).

Bioremediation technologies include processes with a high degree of complexity, which require knowledge from different fields, because the processes require: knowledge of the mechanisms of biodegradation of the polluting substance, knowledge of the effect of the polluting substance and its behavior in the polluted environment, establishing the species of MOs that can realize metabolism of the respective NSs solids; can be performed on site, permanent waste disposal (limiting compliance problems for waste landfills), positive from the point of view of public acceptance, minimal disruption of the site, eliminates transport costs. It can be combined with other treatment technologies.

Disadvantages of bioremediation:

- Long duration for the applied treatment.
- It is necessary not to prevent NSs- MOs contact.

- It may increase the mobility of NSs in the soil due to the circulation of aqueous solutions through the soil profile.
- Due to the circulation of aqueous solutions, pollution of the underground groundwater can occur, which subsequently requires treatment operations.
- High concentrations of heavy metals and long carbon chain hydrocarbons can be toxic to the MOs used.

The principles are common to a number of methods named in various ways:

- Bioremediation
- Biostimulation
- Bioventing;
- Biosparging
- Bioaugmentation

In the practice of bioremediation, several concepts are used, respectively different terms that reflect the bioremediation process, depending on the type of action of the MOs involved in the bioremediation process: biodegradation, biostimulation, bio-augmentation (bio-amplification), bioremediation (Levakov et al. 2019).

Biotechnologies play an important role in the process of treating SCs. As with any microbial process, optimizing environmental conditions in bioremediation is an important objective as microbiological, physiological, and biochemical activities are directed towards biodegradation of compounds that have polluted the area.

Depending on the multitude of factors that act, the activity of MOs is variable, both from the biological point of view (the alternation of the vegetative phases with the latency phases), as well as from the point of view of the metabolic and nutritional activities.

Many soil MOs have the ability to use gaseous, solid, and liquid hydrocarbons from the aliphatic and aromatic series as the sole source of carbon and energy, decomposing them into compounds of lower molecular weight, or even carbon dioxide and water.

Changes of these parameters beyond the optimum values can change the rate of microbial growth, as well as the substrates concerned, and can cause premature termination and failure of the bioremediation process.

Widespread in natural environments and sometimes numerically significant, active MOs attack different compounds such as: petroleum, kerosene, mineral oils, paraffin, lighting gas, wells, natural and synthetic rubber, cooling oils, asphalt surfaces, pipes, and also electrical cables which are protected from corrosion using paraffin impregnated materials, elastomers, or different hydrocarbon derivatives (Li et al. 2019).

Present in soil, in fresh and marine waters, and in some sediments, in a wide range of environmental conditions, these MOs have the ability to synthesize a wide spectrum of enzymes that ensure the degradation of individual hydrocarbons and the potential for removal or conversion of crude oil from the environment.

While in unpolluted ecosystems the number of MOs using hydrocarbons may represent only 0.1% of the total, in polluted ones it can reach up to 100% of the number of viable MOs.

This is due to the fact that in environments with high levels of pollution, there is a change in the composition in microbial species, those sensitive to NSs being eliminated. The biodegradation potential may also be limited by the toxicity of the NSs.

Some species may develop cellular defense systems, which allows them to tolerate high concentrations of toxic NSs.

The concept of biodegradation actually implies a cooperation of the processes of decomposition of some natural or synthetic constituents, by activating strains of specialized MOs, natural or introduced into that environment, resulting in useful or non-toxic final products in terms of environmental impact.

Therefore, biodegradation involves the breakdown of a toxic compound or substance, under the action of MOs.

Biostimulation is the method by which the populations of MOs, natural or introduced into the soil, are stimulated by the addition of nutrients in order to target the microbial activity in the soil in the direction of the proposed purpose for the decontamination of the polluted area.

This practice ensures the increase of speed of the natural remediation processes, achievable by changing some environmental parameters: humidity, pH, O_2 concentration.

Biorestoration is the restoration of the original state or of a state close to the original one by the use of living MOs. Taking into account the place where the depollution is carried out, the bioremediation can be done in situ or ex situ.

In situ bioremediation means treating the affected habitats on the spot (in this case the soils). In situ bioremediation (ISB) is the use of MOs to degrade NSs on site (“in situ”) for the purpose of producing non-hazardous final compounds.

The effectiveness of in situ bioremediation is good under certain conditions:

- High soil moisture 25–85%
- Relatively neutral soil pH 6.5–8.5
- Relatively high temperature 15–45 °C

The advantages of in situ bioremediation:

- Less expensive technique because contaminated groundwater and soil can be treated simultaneously, which is a cost advantage
- More efficient than standard pumping and treatment methods for treating aquifers and soils contaminated with chlorinated solvents, petroleum hydrocarbons, heavy metals
- The relatively undisturbed site, as this method allows the soil to be treated without its excavation and transportation
- Complete destruction of NSs
- Lower risks for workers on site
- Lower costs for installation and operation
- Generating a lower amount of gaseous emissions and waste

Ex situ bioremediation means treating SCs outside their natural site, in the laboratory, in experimental, bioreactor models, where favorable conditions for increasing the efficiency of controlled degradation of NSs can be created (Hara et al. 2019).

The choice of an “in situ” or “ex situ” remediation solution depends on the nature of the pollution and the conditions of each site: “ex situ” treatments are preferable if a quick fix is needed and the NSs migration process to a sensitive receiver is prevented (such as an aquifer used for drinking purposes).

There are technologies that are suitable for both “in situ” and “ex situ” application, depending on the conditions of the site, the availability of necessary materials, and costs (Wang et al. 2017).

Soil remediation technologies that can be applied in situ are the following: bioaugmentation; bioventing; biosparging; phytoremediation; soil washing.

Bio-augmentation (bio-amplification) is the method by which specific living organisms are added to a site or material to achieve a desired bioremediation effect. It is a sensitive method, as MOs specialized in the decontamination of certain toxic compounds/NSs are injected (Mahbub et al. 2017).

Bio-augmentation of a soil usually involves the percolation or injection of groundwater or non-contaminated water mixed with nutrients and saturated with dissolved oxygen.

Sometimes acclimatized MOs (bio-augmentation) and/or other oxygen sources such as hydrogen peroxide can be added. Irrigation by spray infiltration is regularly used in shallow SCs and injection wells for deep SCs.

The increase of oxygen can be achieved either by bubbling air under the water mass or circulating oxygenated water throughout the groundwater in the contaminated area. Air bubbling under the water mass increases the oxygen concentration in the groundwater and increases the rate of biological degradation of organic NSs by naturally occurring MOs.

The procedure is not difficult and the implementation of injection wells is not so expensive, which makes this bioremediation technology successful (Chang et al. 2015).

Bio-augmentation can be applied for decontamination of polluted sites with volatile organic compounds (VOCs) – benzene, formaldehyde – and non-halogenated semi-volatiles (SVOCs) – phthalates, bisphenols, fuels (Ouyang et al. 2006).

Limitations of bio-augmentation:

- Nature of the substrate: a heterogeneous substrate (clay) will not facilitate the penetration of the washing solution, so that areas with high permeability will be more quickly decontaminated.
- Nitrate injection into the groundwater is very strict as there are vulnerable areas established for nitrate pollution of groundwater,
- Air bubbling increases pressure in unsaturated areas, vapors can accumulate in basins that are generally low-pressure areas.

8.5.1.1 Bioventing

Soil vapor extraction technologies have been efficiently used to reduce concentrations of volatile organic compounds (VOCs) and certain semi-volatile organic compounds (SCOVs) resulting from underground storage tanks for petroleum products.

Extraction of vapors from the soil is generally more successful when applied to more volatile petroleum products such as gasoline. Diesel, oils, and kerosene, which are less volatile than gasoline, are not easy to treat by vapor extraction technologies, but may be suitable for bioventing removal (García Frutos et al. 2010).

An important indicator of a constituent's volatility is the constant defined by Henry's law.

The constant of Henry's law is the partition coefficient that refers to the concentration of a constituent dissolved in water, to its partial pressure in vapor phase under equilibrium conditions. This describes the relative tendency for a dissolved constituent to strike a balance between the vapor phase and the dissolved phase.

Therefore, Henry's constant law is a measure of the degree to which constituents that are dissolved in soil moisture (or groundwater) will pass into vapor state to be removed by vapor extraction processes (Werner et al. 1997).

Usually vapor extraction procedures are not successful when applied for the extraction of lubricating oils, which are non-volatile, but these oils can be removed by bioventilation.

Soil vapor extraction is a well-known and efficient technology when applied to permeable soils, but it does not have the same efficiency in impervious soils, especially those containing significant amounts of mud and clay. This bioventing technique works as a closed loop, through a process of recirculating the hot air in the unsaturated area.

As there are no external emissions, no clearance is required. The hot air emitted by a blower is injected directly into the waterproof soil, which produces desiccation of the soil (humidity drop). It is known that the permeability of the soil is dependent on its degree of humidity. From the dry soil, its volatile organic compounds are easily desorbed and are collected through a conventional soil vapor extraction system (Magalhães et al. 2009).

The vapors from the soil extraction system pass through an active carbon system and will be recycled through the blower.

The compressive heat of the air flowing through the blower creates the warm air that is introduced back into the contaminated area, the treatment area.

The advantage of the closed vapor extraction system through this recirculation loop is that the dehydrated soils are much more permeable.

Bioventing is a technology that stimulates the natural in situ biodegradation of any aerobic degradable compound by providing oxygen to MOs existing in the soil. In contrast to the extraction of vapors by aspiration, bioventing uses weak air flows to provide sufficient oxygen only to support microbial activity. Oxygen is most often applied by direct injection into the residual NSs in the soil (Lee et al. 2006).

Applicability:

- Is a decontamination technology with medium- and long-term effect
- Remediation of soils contaminated with petroleum hydrocarbons, non-chlorinated solvents, NSs, wood preservatives, and other organic compounds

Limitations:

- The vapors can be collected in basins within the radius of influence of the air injection probes, which determines the need for air extraction near the structure. It is necessary to monitor the waste gases on the surface of the soil.
- Soil moisture is a limiting factor of biodegradation and implicitly determines the efficiency of bioventing (Mihopoulos et al. 2002).

8.5.1.2 Biosparging

The technology involves injecting air or oxygen through a contaminated soil/aquifer to remove volatile organic compounds (VOCs) and semi-volatile compounds (SCOVs) through volatilization.

The injected air helps to wash the NSs in the unsaturated area for treatment. It is a rehabilitation technique, in which air is injected into the saturated area to stimulate native MOs. The injected air vaporizes the retained NSs into the soil capillaries, mobilizing them towards the surface. In their upward path, NSs are degraded by aeration-stimulated biomass and nutrient intake. The principle of this procedure is the injection of pressurized air into the contaminated underground environment, which causes intense vaporization of NSs with volatile properties (Machackova et al. 2012).

The resulting toxic vapors are still inhaled by a venting plant. Pressurized air is introduced through a drill or injection well, provided at the bottom with a perforated section that is shorter than the perforated section corresponding to the drill or suction well.

Applicability:

- The NSs that can be eliminated by sparging are volatile and semi-volatile organic compounds (benzene, toluene, xylene, gasoline, chlorinated solvents).
- For extending the range of NSs removal by sparging, the clean air is replaced with a mixture of air–ozone or air–oxygenated water.

Limitations:

- During the operation, it is difficult to appreciate the treated volume, its configuration, and the efficiency of the depollution process (Kao et al. 2008).

8.5.1.3 Phytoremediation

The phytoremediation technique refers to botanical bioremediation and involves the use of plants for the decontamination of soils, water, and air. It is a technology that can be applied to both organic and inorganic NSs (metals in particular) present in soil, water, or air (Bhat et al. 2018).

The idea of using metal-accumulating plants, for selective removal and recycling of excess metals in the environment, was introduced around the 1980s, gained special interest in the 1990s, and has been increasingly examined as a practical, less expensive technology compared to the conventional methods of replacing or washing SCs.

In most studies of contamination with petroleum products, grasses and legumes have been considered suitable because of their potential for phytoremediation of contaminated sites (Pettit et al. 2018a, b).

Their advantage is the highly developed fibrous root system, which explores a large volume of soil. In addition, legumes could have an advantage over non-leguminous plants in the phytoremediation process due to their ability to fix nitrogen, thus not competing with MOs and other plants for limited amounts of nitrogen assimilable from oil-contaminated soil.

Phytoremediation of elemental NSs involves multiple processes: extraction, translocation of toxic cations or oxyanions into the supraterrestrial tissues, conversion of the elements into roots for the penetration of the polluted area.

Phytodegradation represents the assimilation of NSs by the roots of the plants and their transfer/accumulation into roots, trunks, and leaves. Advanced biodegradation of the rhizosphere occurs in the soil surrounding the plant roots.

The natural substances released from the roots provide the nutrient MOs, which increase their biological activity (Pettit et al. 2018a, b).

The roots of the plants loosen the soil and then die leaving paths for water circulation and ventilation. Phytoextraction involves the cultivation of one or more species of hyperaccumulating plants, to which the best development conditions are created to ensure a maximum plant mass, in order to be able to extract, accumulate, and remove as much NSs (usually heavy metals).

Phytodegradation involves the metabolization of NSs in plant tissues. Plants produce enzymes such as dehalogenase and oxygenase that help catalyze degradation (Pettit et al. 2018a, b).

Physiological processes that take place in the plant during phytoremediation are described below.

Phytostabilization is a phenomenon of the plant's production of chemical compounds that serve to immobilize NSs at the contact of the roots with the soil.

This technique can be used to restore the vegetation to the places where the natural vegetation is missing due to the high concentrations of heavy metals in the surface or due to the physical degradation of the surface materials.

Tolerant species can be used to restore the vegetation of the area, while decreasing the potential for migration of NSs under the influence of wind and water erosion and of leaching to groundwater (erosion and sanding are common on land without vegetation) (Gerhardt et al. 2017).

Phytovolatilization occurs in plants that absorb water containing organic NSs and release NSs into the atmosphere through the leaves. Plants can also release chemical bonds from organic NSs and release the resulting products into the atmosphere.

Some authors propose the concomitant use of chemical amendments (calcium carbonate, phosphates, iron and manganese oxides, zeolites) to transform NSs into inaccessible and stable forms (Limmer and Burken 2016).

Applicability:

- It is suitable for the decontamination caused by organic NSs.
- It showed the possibility of generating less secondary residues, associated with the minimum disturbance of the environment.
- It demonstrated the ability to leave the soil in place and in conditions useful for the next treatment.

Limitations:

- The depth of the treatment area is determined by the plants used in phytoremediation; in most cases, this process can be used on shallow soils.
- The time required for phytoremediation is long, being a relatively slow process.
- High concentrations of hazardous substances can be toxic to plants.
- Transferring the NSs from the soil to the air, or they can be mobilized in groundwater or assimilated by animals.
- Is not effective for highly adsorbed NSs (Arnold et al. 2007).

8.5.2 Chemical Remediation of Soils, In Situ

The chemical purification procedures are based on the elimination of NSs from the soil or the annihilation of the toxic character by oxidation-reduction and exchange reactions.

8.5.2.1 Soil Washing

It is a method used to eliminate the residual phase of immobilized NSs in the soil matrix. The washing principle consists in separating NSs from the soil and transferring them in liquid or gaseous phase, under the action of water and mechanical energy.

Soil washing “in situ” allows the extraction of NSs from the soil without excavating it. The method is applied in the case of permeable soils and is based on a system of infiltration into the soil of the washing water which has the effect of solubilization of the NSs, followed by the collection downstream and the pumping on the surface of the water carrying NSs.

On the surface, the water is subjected to a decontamination process, after which it can be re-introduced into the soil (Wadgaonkar et al. 2018).

The soil from the surface of the polluted area is sprayed with clean water or a diluted solution containing washing reagents (dispersing agents, surfactants).

Applicability:

- It is used with good results for sandy, gravel, or stone soils and for high granulation materials resulting from soil sealing.
- It can wash organic NSs, soluble inorganic NSs, heavy metals.

Limitations:

- Not applicable for soils containing clay or humus; requires an additional stage of separation of NSs (solubilization, precipitation and filtration, etc.) (Safa and Mehrasbi 2019)

8.5.2.2 Extraction of Pollutants by Solubilization

The removal of NSs from the soil by extraction with the help of organic solvents, acids, or bases is an efficient procedure that is successfully applied internationally. By the method of extraction of the NSs, this process is similar to the washing procedure described above.

The extraction of NSs with the help of organic solvents is carried out in treatment plants off-site or even on-site. The NSs that can be extracted in this way are pesticides, aromatic, polycyclic hydrocarbons, and heavy hydrocarbons. Extraction with the help of acids and bases can be achieved directly by introducing the solution into the contaminated soil.

The NSs extracted with the help of acids and bases are heavy metals and cyanides, amines, phenols, etc. (Eljack and Hussam 2014).

Decontamination is frequently performed by using hydrochloric acid, sulfuric acid, and nitric acid and sodium hydroxide.

8.5.2.3 Thermal Remediation of Soils, In Situ

The degradation of the NSs by thermal method is especially applicable to the ones of organic nature, considering the final products of their degradation: CO_2 and H_2O, but the methods of thermal remediation are mainly applicable “ex situ.”

In situ thermal treatment includes many methods and combinations of different techniques for applying heat to polluted soils. The heat can destroy or volatilize organic chemicals, and the gases are extracted through collection wells for capture and cleaning in a treatment unit (Xu et al. 2019).

The most important methods of thermal decontamination are steam injection and vitrification.

8.5.2.4 Steam Injection

The aim is to remobilize some NSs and turn them into a form that is easier to recover. By steam injection, the volatile organic compounds vaporize, thus accelerating their recovery.

This technology includes the steam generating plant, the steam injection wells, collection wells, and condensation treatment plant. Steam depollution involves almost complete recovery of the NSs, immediately after the steam has penetrated the entire polluted area. By heating the soil, the volatile organic compounds vaporize, thus accelerating their recovery, but also the semi-volatile organic compounds.

The solubility in water is influenced by temperature, increasing the temperature causing the solubility to increase and therefore increasing the NSs concentration in water, thus increasing the depollution rate by pumping (Nilsson et al. 2011).

Adsorption is an exothermic reaction and thus an increase in temperature usually reduces the adsorption.

8.5.2.5 Vitrification

The process consists of melting the soil at high temperatures and transforming it, after cooling, into a glass material, inert and chemically stable. Vitrification is a thermal process, but it can also be included in the stabilization and inertia processes, if viewed through the objective pursued.

The vitrification of the soil is obtained by introducing into the contaminated area four electrodes arranged in the square and fed to a source of electricity.

Because the soil in the dry state is not a conductor of electricity, a layer of graphite sheets and fried glass is placed on the surface of the electrodes. This layer has the role of starting and activating the thermal reaction from the soil.

The contaminated area is subjected to temperatures of about 2000 °C. At such temperatures, the soil composed predominantly of aluminosilicates is transformed into glass, in which all the compounds present are melted or vaporized.

As the melted zone expands, it incorporates non-volatile elements, while organic products are destroyed by pyrolysis (Celary and Sobik-Szołtysek 2014).

Above the area being decontaminated, a lid is installed, provided with a suction mouth of the gases resulting during the reaction. These gases are treated separately, depending on the specific NSs in their composition. After the completion of the chemical reaction and after cooling the molten material, it is in a stable state being chemically inert and devoid of leachable elements. It is very similar, in terms of stability, with a granite.

Applicability:

- This process of in situ decontamination of polluted soils is applied in the laboratory and pilot phase.

Limitations:

- The transformation of the soil into a sterile, impermeable rock, without agricultural value
- The risk of causing a migration of NSs outside the contaminated area, due to the high temperatures used in the process
- The high cost of decontamination, generated by the need to ensure significant energy potential (Xiao et al. 2008)

8.6 Soil Remediation Technologies, Applied Ex Situ

8.6.1 Biological Remediation of Ex Situ Soils

8.6.1.1 Ex Situ Bioremediation

The advantages of "ex situ" bioremediation: They allow to a greater extent the supervision of the conditions in which the process is carried out; make NSs more easily accessible for destruction or disposal; they allow more accessible control of emissions and waste resulting from remediation. The main disadvantages of the "ex situ" treatments are: the need for excavation of the land and possibly of transport and repeated handling of the excavated material; some treatments may alter the structure and composition of the soil layer or rocks and thus limit their reuse.

For example, aggressive treatment such as incineration alters soil composition, structure and fertility, and even geotechnical properties of rocks (Guillen Ferrari et al. 2019).

Soil bioremediation technologies that can be applied ex situ are the following: bioreactors and biopiles.

8.6.1.2 Bioreactors

Bioreactors are systems designed in which NSs are degraded, in a specific environment, with the help of MOs.

Bioreactor treatment involves the introduction of polluted soils, conditioned in the form of sludge, into a reactor, equipped with agitation and aeration systems.

The excavated soils first need an adequate mechanical preparation such as homogenization and shredding. The soil is placed in a reactor with a soil/liquid nutrient medium ratio that allows the formation of a soil suspension.

The soil particles are mixed and held in suspension in a liquid nutrient environment under a permanent flow of compressed air that promotes homogenization and oxygenation of the soil suspension. A liquid/solid separation follows, the liquid phase being subjected to the treatment of dissolved NSs (Lopez-Echartea et al. 2019).

Applicability:

- Rapid and relatively complete removal of polluted components
- Provides optimal conditions for conducting and conducting the biodegradation process (pH, temperature, humidity, nutrient addition, reaction time, etc.).

Limitations:

- High cost of transport and the need for excavation and soil preparation

8.6.1.3 Biopiles

Biopile treatment requires excavated soils to be mixed with amendments and placed in treatment areas that include infiltration water collection systems and aeration systems.

Biopile technologies, also known as biocells, or compost piles, are used to reduce the concentrations of petroleum constituents in excavated soils through biodegradation.

This technology involves the collection of SCs in piles (or “cells”), as well as stimulating the activity of aerobic MOs in the soil through aeration and/or the addition of minerals, nutrients, and moisture. Biopiles are similar to landfarms in that both are engineered systems that work on the surface soil and use oxygen, generally from the air, to stimulate the growth and reproduction of aerobic bacteria, which, in turn, degrades the oil constituents adsorbed on the soil (Kim et al. 2018).

While in the “landfarms” procedure aeration is done by plowing or plowing, biopiles involve forcing the air to move by injection or extraction through the slots of pipes placed along each pile. The uniformity of the air flow is an essential condition in maintaining an optimum balance in the case of aeration of a soil by the biopile method, a condition ensured by the use of the vertical ventilation system. The treatment area will generally be covered or kept with a waterproof liner to minimize the risk of NSs leakage on uncontaminated soil.

Limitations:

- It is necessary to excavate contaminated soil.
- It is necessary to test the degree of treatment in order to determine the biodegradability of the NSs, to ensure an adequate oxygenation and nutrient requirements.
- Being a static process, the treatment, respectively the decontamination can be non-uniform, compared to the processes that require periodic mixing.
- The risk of partial dispersion of NSs during evacuation, loading, transport, and unloading works (Roland et al. 2008).

8.6.1.4 Land Farming

The method of land farming is to deposit soil contaminated with organic products, often of petroleum origin, on a surface prepared in advance.

The deposit is made in a layer of reduced thickness (several tens of centimeters) on well isolated areas, to protect the basement from any risk of infiltration. This technique has been used for many years in the management and disposal of oil sludge and other waste from oil refineries through excavation maneuvers.

The equipment used is the typical one used in agricultural operations. These agricultural activities on cultivated land have the role of increasing the microbial degradation of dangerous compounds (Neu et al. 2020).

As a basic rule, the higher the molecular weight of the NSs (i.e., the more rings in a polycyclic aromatic hydrocarbon), the slower the rate of degradation.

The effectiveness of this technique depends on the NSs characteristics, soil characteristics, and land availability.

Therefore, these parameters must be determined firstly, and consequently the suitability of the land farming technique for a certain contaminated site can be evaluated. If these parameters are less optimal, the land farming process can be used provided there are certain operational adjustments, such as changes in soil pH.

Applicability:

- It is one of the simplest treatment techniques that does not require advanced skills to function effectively.
- It is suitable for the decontamination of most of the petroleum constituents, whether they are volatile, such as gasoline, semi-volatile (diesel), or non-volatile (oil for heating).

Limitations:

- It is not a suitable technique for residential areas,
- The conditions that influence the biodegradation of the NSs (temperature, rainwater) cannot be controlled, which prolong the completion time of the remediation.
- Volatile NSs, such as solvents, need to be treated beforehand because they could evaporate into the atmosphere and cause pollution (Azubuike et al. 2016).

8.6.2 Ex Situ Chemical Remediation of Soil

Ex situ chemical remediation of soils involves the operation of excavating contaminated soil and transporting it to a treatment unit/area, which entails additional costs incurred by these operations. However, this type of remedy is feasible from a cost point of view, since the degree of decontamination can be controlled (Wu et al. 2019a, b).

The basic chemical methods that can be applied ex situ are: soil washing, chemical immobilization, extraction with various solvents, chemical oxidation, etc. The principles of these methods have been described in the chapter on in situ chemical remediation.

Thermal Remediation of Ex Situ Soils

The most common method of remediation by ex situ thermal procedures of a contaminated soil is incineration. Incineration of soil pollutants burning of NSs as a means of polluting SCs is a more expensive process than desorption because working temperatures exceed 1000 °C to ensure the destruction of organic NSs and to obtain the final products of CO_2 and H_2O degradation. In the case of soil contamination with polychlorinated biphenyls (PCB) products when burning them, the same problems appear as when burning household residues: dioxins and furans (PCDD and PCDF – carcinogens) (O'Brien et al. 2017).

The soil incineration plant must be provided with deoxygenation columns and electrofilters for retaining heavy metals, similar to those made when cleaning the flue gases of the household waste (Kucharski et al. 2005).

The loss of NSs by combustion is accompanied by the destruction of the organic components of the soil so that after decontamination the soil is no longer suitable for agricultural uses.

8.7 Conclusions and Recommendations

Due to the different physicochemical properties of the NSs as well as due to the hydrogeological particularities of each site, the systems and techniques adopted for remediation of the sites affected by the pollution are addressed to each case and refer only to a certain class of NSs. In these conditions, the implementation in a particular site of a depollution solution used in other cases must be preceded by a correct assessment of the degree of contamination and the particularities of the contaminated soil through a series of physicochemical, hydrogeological, and microbiological studies as well as of experimental studies to determine the viability of the solution for the given situation.

Analyzing the advantages and limitations of soil remediation processes polluted with organic compounds, it appears that both ex situ remediation processes and in situ chemical treatment processes (applied independently) are costly and more unsustainable in terms of maintaining/recovering functions quickly. On the other hand, the processes of natural attenuation or stimulated bioremediation have the disadvantage of a much too long remediation time (years/decades depending on the particularities of the NSs and the degree of pollution). Therefore, combining chemical and biological remediation processes in situ can lead to the overcoming constraints connected to cost, time, and sustainability that may occur for each technology applied separately.

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Chapter 9
Bioremediation: A Viable Approach for Degradation of Petroleum Hydrocarbon

Monica Butnariu and Marian Butu

9.1 Background

Soils contaminated with diesel or benzine are much harder to treat than more volatile petroleum hydrocarbons (PHCs), e.g., specific contaminants that are components, such as BTEX (benzene, ethylbenzene, toluene and xylene), n–hexane, jet fuels, fuel oils, and mineral-based crankcase oil, gasoline. The harmful effects of PHCs on the environment can be diverse: some aromatic and polyaromatic compounds have shown carcinogenic effect, being toxic or mutagenic, benzene for example; having carcinogenic effect even upon absorption through the skin; inhalation of vapors can lead to nausea, acute toxic reactions, liver disease, or teratogenic effects; some compounds can affect the taste and smell, so that their presence in surface and groundwater, even in small quantities, makes them no longer suitable for consumption; volatile compounds can form flammable or explosive mixtures with oxygen from air (Waters et al. 2017).

Figure 9.1 shows some structures of some PHCs (aliphatic hydrocarbons, cyclic and polycyclic aromatic hydrocarbons from PHCs).

Most of the chemicals in the category of harmful pollutants are nonpolar organic compounds; as a result they are hydrophobic, with extremely low solubility in water; they are lipophilic, which causes the accumulation in the fatty tissues of organisms. Due to the phenomenon of bioaccumulation and bio-amplification, the concentration of harmful pollutants can be much higher in the tissues of organisms at the end of the trophic chains (species of fish, mammals, birds, and humans) than the concentration in the environment (even 70,000 times higher).

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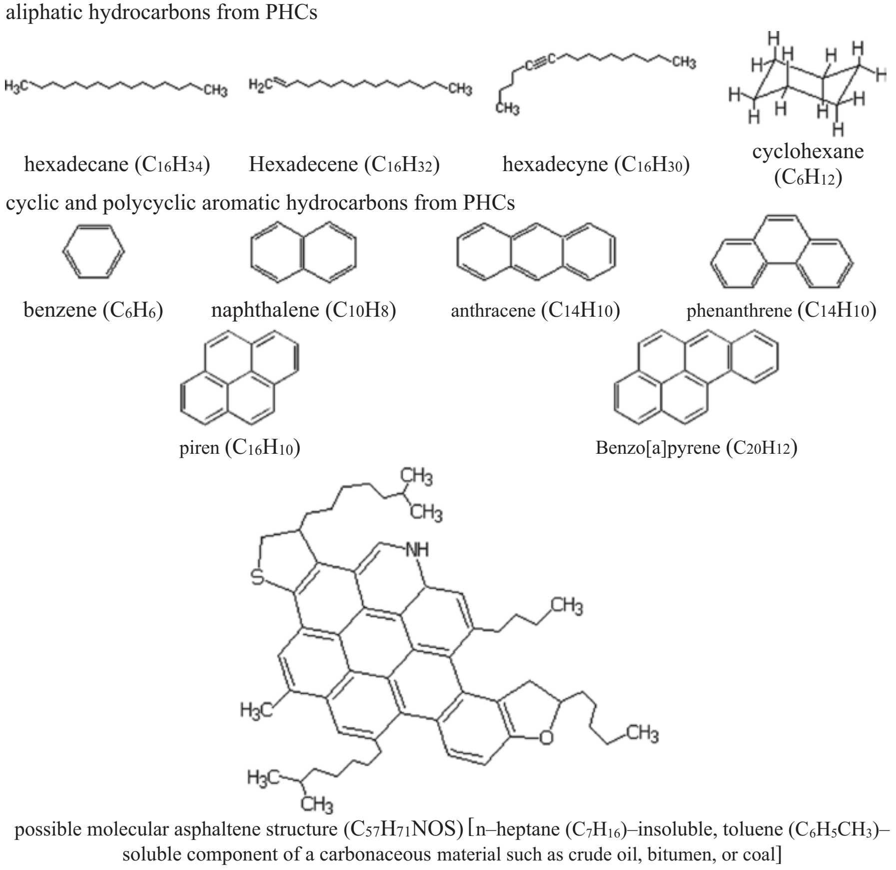

Fig. 9.1 The chemical structure of some PHCs representatives

In the literature, most studies address the assessment of artificially contaminated soils with individual pollutants. The in situ washing technology of the soil, in which the oxidant is introduced in the washing solution (chemical oxidation in situ), coupled with the electrokinetic process (EKOSF), was evaluated. EKOSF was made using different oxidants, sodium hypochlorite (NaOCI), permanganate ($KMnO_4$), and sodium persulfate ($Na_2S_2O_8$), which were transported from the electrode chambers into the solid matrix sections under the action of the electric field. Initially, the soil was characterized and several ex situ experiments were performed to determine the relationship between the pollutants present in the soil and the key process parameters and to evaluate the efficiency of each oxidant in the PHCs degradation process present in the soil. Sensitive soils include all soils in residential and recreational areas, soils used for agricultural purposes and soils in undeveloped areas. Less-sensitive soils include all soils for commercial and industrial use and land areas that will have such use in the near future. The toxicity of oil and petroleum products (PHCs) falls into two categories: immediate and long term. The immediate one is caused by the saturated hydrocarbons which in high concentrations cause the death of organisms. Aromatic hydrocarbons are the most toxic, and olefinic hydrocarbons have intermediate toxicity between saturated and aromatic ones.

Long-term toxicity is caused by the interference between hydrocarbons and soil components dissolved in water, interference with numerous chemical messengers, with the role of nutrition and reproduction of many aquatic organisms, leading to ecological imbalances (Errington et al. 2018a, b). The profile distribution of the pollutant is dependent on the amount of pollutant, the characteristics of the pollutant, the terrain configuration, the soil characteristics, and the dwell time. In soils with poorly permeable or impermeable horizons, an area of pollutant concentration appears above them, because of its heterogeneous polydisperse body properties, the soil acts as a chromatographic column. The components of the oil are retained especially in the upper horizons, and the film water that accompanies the oil in various proportions, with higher density and less viscous, penetrates faster in the lower horizons. Volatile PHCs fractions containing 6–7 carbon atoms in the molecule are volatilized, and nonvolatile hydrocarbons tend to concentrate and solidify. With the passage of time, the process of redistributing the oil components on the soil profile is accentuated, with a tar and asphalt retention taking place.

Oil stains lead to an imbalance of the C:N ratio in all spots with oil stains, as fresh oil is essentially a mixture of C and H. This causes a deficiency of N in soils soaked in oil, which slows the growth of bacteria and use of carbon sources. In addition, deficiencies of N and different nutrients such as phosphorus can limit the growth rate in soils soaked in oil. In addition, high concentrations of biodegradable organic products in the upper horizon of agricultural soils lower oxygen reserves in the soil and reduce the rate of oxygen diffusion into deeper layers.

PHCs pollutants tend to persist in the soil until remedial measures, involving the application of nutrients, are used, because O and N are limiting factors for all types of oil degradation. The contradiction between the tendency of concentration and bioaccessibility for a soil contaminant can be explained by the stronger, almost irreversible sorption by Fe and Al oxides or silicate clays, or by chemical complexation with organic matter. In addition, the contaminant molecules can become physically isolated in three ways.

First, the contaminant molecules can be trapped in the soil nanopores, the ends of pore spaces from 1 to 100 nm in diameter. These pores, inside the humus and the clay colloids, are large enough to house the contaminant molecules, but too small for the entry of bacteria or even extracellular enzymes that would otherwise be capable of attacking the contaminant. Second, the contaminant molecules can diffuse into the pores; they can be absorbed into the solid structure of the humus particles, where, again, they are no longer exposed to living cells or their enzymes. Third, the contaminant molecules may become buried, or occluded, beneath the precipitated mineral layer, and isolated again from biological interactions. The PHCs pollutant molecules trapped in either of these mechanisms can offer a reduced risk of environmental mobility or biological toxicity even if their total soil concentration remains high. Due to this aging process, some researchers believe that environmental cleanliness standards need to be based more on the measured bioaccessibility of the contaminant than on their total concentration.

The term remediation covers: measures to eliminate or reduce pollution (decontamination measures) and measures to prevent or reduce the spread of pollutants in a safe manner, without removing pollutants (encapsulation measures).

Among the methods of treating soils contaminated with PHCs are:

- Physical immobilization: sealing, treatment barriers, hydraulic locking, and stabilization and inerting
- Biological methods: natural attenuation, phytoremediation (hydraulic control, phytoextraction or phytoaccumulation, phytodegradation or phytotransformation, rhizodegradation, phytostabilization, phytovolatilization and phytostimulation), bioremediation, and alternative systems of bioremediation (bioreactor, land-based treatment, composting, and bio-oxidation systems in soil piles)
- Chemical methods: photo-oxidation, dehalogenation, chemical extraction, oxidation, reduction, dechlorination, precipitation, and microbial fuel cell
- Physicochemical methods: excavation, pumping, washing, flotation, biosparging, venting, electrokinetic extraction, electroacoustic decontamination, washing and applying electromagnetic waves, and passive absorption on polymers
- Thermal methods: incineration, pyrolysis, thermal desorption, vitrification and microwave treatment

The treatment techniques that meet the requirements are selected and then evaluated on the basis of nine mandatory criteria: complete protection of human health and the environment; compliance with the relevant applicable or relevant requirements; long-term and permanent efficiency; reducing toxicity, mobility, or volume; short-term efficiency; implementability; cost (Errington et al. 2018a, b); state acceptance; and community acceptance.

9.2 Treatments Can Be Performed In Situ or Ex Situ

The main advantage of in situ treatment is that it allows the soil to be treated without being excavated and transported. In situ treatments generally require longer periods of time and are less certain about the uniformity of the treatment due to the variability of soil characteristics under unverified conditions.

In situ bioremediation refers to the biological treatment of contaminated soil without excavation prior to treatment. In situ technologies can be cheaper, create less dust, and result in lower losses of contaminants in the environment compared to ex situ technologies. It is also possible to treat larger volumes of soil at a given time. In situ techniques can be slower, harder to drive, and are more efficient in places with permeable soils (sandy or coated).

Ex situ treatments (including application on agricultural land, composting, soil-based bioremediation, and sludge bioremediation) using soil work, continuous digging, or mixing of sludge, to apply oxygen and nutrients, and is performance in the training bed or reactor.

The researches that have been developed worldwide have had the major objective to develop simple, economically efficient, rapid methods of decontamination, which will ensure by applying them in situ blocking the migration of pollutants underground, destroying the pollutant, and restoring the natural environment.

Bioremediation technology includes biostimulation (stimulation of viable native microbial populations), bioaugmentation (artificial introduction of viable microbial populations), bioaccumulation (in living cells), biosorption (in dead microbial biomass), phytoremediation (with plants), and rjizo-remediation (through interaction between plants and microorganisms).

Rhizo-remediation, which is the most evolved process of bioremediation, involves the removal of specific contaminants from the residual products from the contaminated sites through the mutual interaction of the plant roots and the suitable microbial flora.

Bioremediation efficiency is often a function of the microbial population and how they can be enriched and maintained in the environment. Strategies for cheap in situ bioremediation of oil-contaminated soils include stimulation of indigenous MOs by stimulation with nutrients (biostimulation) and/or by inoculation with enriched microbial mixture cultures in soil (bioaugmentation).

Biodegradation has proven to be suitable for: PHCs such as diesel, light liquid fuel, gasoline, lamp oil, mineral oils, benzene, toluene, xylene, etc. wastes from oil production, sludge, and oil residues; organic products and residues from the basic chemical industry (alcohols, acetone, phenols, aldehydes, and other solvents); and complex compounds such as polycyclic aromatic hydrocarbons and pesticides.

During the biodegradation treatment, we have to keep track of physical factors (characteristics of the polluted environment: permeability, porosity, granulometry, structure, texture, etc., the presence of O_2, humidity, temperature, pH, adherence of the pollutant to soil particles or sediments), chemical factors (nature and the concentration of the pollutant, the degree of toxicity of the pollutant, the solubility of the pollutant, the bioaccessibility of the pollutant, the presence or absence of a co-substrate, the salinity of the environment, the presence of accessible nutrients, the organic content in the environment, the biodegradability of the pollutant), and the biological factors (the density of indigenous MOs capable of degrading). Bioremediation is the creation and maintenance of a favorable environment for MOs, some indigenous others nonindigenous, to use soil contaminants as a carbon source. The most important factors influencing the biodegradation process are:

- Addition of surfactants, carriers
- Quantity and quality of the contaminant
- The biodegradation capacity of the indigenous microflora
- The characteristics of the polluted soil (pH, humidity, texture, structure, content in nutrients, aeration, temperature, biological activity, etc.)
- The presence of nutrients essential for the growth of MOs and especially the ratio between P and N
- The type of MOs presents in the polluted environment and so on

Bioremediation of oil-contaminated soils is an efficient, safe, economically feasible technique, environmentally friendly, a versatile or complementary alternative to physicochemical treatments although the bioaccessibility of hydrophobic organic compounds for MOs can be a limiting factor during biodegradation processes.

Bioremediation can be organized on the spot, the residues are permanently eliminated, it is very economically efficient, nondestructive or with a minimum of destruction, relatively uncomplicated in implementation, it requires nonspecialized equipment, the risks associated with long-term liability related to the remains of the contamination are eliminated, it eliminates transportation costs and liability for debris removal, can be coupled with other treatment techniques, and can be extremely effective in removing recalcitrant PHCs (new synthetic compounds that are slowly biodegradable or nonbiodegradable are known as recalcitrant compounds) (Fuentes et al. 2014). Bioremediation techniques are used to treat contaminated soils, contaminated waters, sludge, and aquifer materials. The choice of the most suitable processes for a specific place depends on the physical–chemical environment, the desired final results, and the economic conditions.

Disadvantages of bioremediation include the following: design criteria for high-efficiency remediation are site specific and may require extensive monitoring, some chemicals cannot be bioremediated, contaminant toxicity, the level of scientific knowledge, potential production of unknown by-products, and perceived as a technology with no contingencies.

In order to improve the low-moderate soils polluted with oil, the following improvement works are required: removals of excess oil; amendments, scarification, deep plowing, organic ameliorative fertilization, mineral fertilization with NPK (biostimulation), with the increase of the nitrogen weight in order to reduce the C:N ratio; o treatments with selected MOs (bioaugmentation); o preparation of the germinating bed and sowing of plants with large seeds (maize, peas, etc.) (Sturla Lompré et al. 2018).

9.2.1 Methods to Stimulate Bioremediation

Biostimulation is a method of stimulating the activity of indigenous populations of MOs for remediation of contaminated soil. The term “enhanced bioremediation” encompasses a large number of technologies that differ with respect to their inputs. These technologies may involve the addition of electron acceptors or electron donors to stimulate the natural development of microbial populations (biostimulation) or may introduce specific MOs to improve the biodegradation of target compounds (biostimulation). The efficiency of biodegradation of PHCs in soils is limited by many factors (e.g., types of MOs, nutrients, oxygen, and contaminant concentration). Therefore, rates of pollutant degradation can be improved by adding nutrients, oxygen, and primary substrates to contaminated systems. These can increase the populations of indigenous MOs and thus improve the efficiency of pollutant biodegradation (Liu et al. 2019).

Among the methods of stimulation of bioremediation are: the use of inoculum of MOs, the use of fertilizers, the application of absorbents, the amendment, the works of the soil, the use of plants, and stimulation with surfactants. Experiments were organized in the reactor where the efficiency of the addition of nutrients, oxygenated water, and molasses from sugar cane were pursued; washing the soil with a biodegradable surfactant (Simple Green SG); and pretreatment of soil by Felton-type oxidation for bioremediation of oil-contaminated soils.

The native MOs dominant in oil-contaminated soils after each treatment process were determined by polymerase chain reaction, gel electrophoresis gradient determination, and nucleotide sequence analysis. The results show that approximately 32–56% of the total PHCs were removed (the initial concentration was 5000 mg/kg) from the reactor by adding nutrients and molasses from the sugar cane (1000 mg/L), with 9% from PHCs removed from the control reactor maintained under untreated conditions, after 120 days of incubation.

The addition of sugar cane molasses produced the growth of the population of MOs and therefore the rate of PHCs degradation improved. The results also show that about 61% of the removed PHCs was observed in the reactor in which H_2O_2 (100 mg/L) and nutrients were added after 120 days of incubation. This indicates that the addition of the reduced concentrations of H_2O_2 (100 mg/L) will result in the desorption of PHCs from the soil particles and the increase of dissolved oxygen and thus the efficiency of the bioremediation in the reactor (Hou et al. 2019).

9.2.2 Removal of Excess Petroleum Hydrocarbons

It is necessary that the first intervention in the event of accidental oil pollution consists in the fastest removal of hydrocarbons from the surface of the soil to reduce the depth of penetration into the soil. Collection gutters for pollutant and small pits to concentrate the pollutant will be executed so that it can be collected with the help of suction systems in a tank and transported to a treatment station (Zhu et al. 2005).

9.2.3 Application of Absorbents

The use of absorbents has several main objectives: the absorption of oil and its retention on the surface of the soil in order to be collected and sent to a recovery and treatment station; the retention of oil in order to prevent the penetration of the soil profile and in this way make the remediation process difficult; preventing the formation of an impermeable film on the surface of the soil; stimulating the multiplication of MOs involved in bioremediation; regulating the aerohydric regime of the soil; source of nutrients and water. Some absorbers are made from Sphagnum peat and have an absorption capacity of 10–14 times its weight. Such an absorbent (Nature Sorb) absorbs and encapsulates, almost instantly, the PHCs in the plant cells of the dehydrated peat muscle. In parallel, a biochemical process of breaking the chemical bonds of hydrocarbons begins by the enzymes produced by the bacterial flora existing in soil and water. In the presence of oxygen, a minimum temperature of 10–12 °C, and humidity, the biodegradation process normally proceeds (Paulauskiene 2018).

Biogenic elements such as nitrogen, phosphorus, and potassium stimulate this process. Other experts recommend to apply immediately after pollution, absorbents in the form of carpets, barriers, rollers, pillows, linings, gloves (metasorb, sorbx, sorbs 2), which preferentially absorb oil and other hydrocarbons but do not absorb water-based liquids.

After soaking with oil, these absorbent materials are taken to an oil extraction and treatment plant. This reduces the risk of deeper soil pollution, which would make it difficult to remedy. The use of absorber (AbsE) has been tested to stimulate biodegradation by promoting the development of bacteria and increasing the rate of biodegradability of PHCs. AbsE is composed of 10 naturals cellulose fibers mixed with nutrients to activate MOs. AbsE is obtained from plant fibers and cellulose waste, all treated and additivated. The studies were carried out on a cambic chernozem with vegetation polluted with 5% and 10% of crude oil, inoculated and not inoculated with selected bacteria and treated with various doses of AbsE.

The bacteria selected were: *Pseudomonas*, *Mycobacterium*, *Arthrobacter globiformis*, and *Bacilus megaterium*. The best results in the bioremediation process of the oil-contaminated soil were obtained in the variants that received the maximum absorbent dose (30 t/ha in the case of 10% oil pollution and 15 t/ha in the case of 5% oil pollution) accompanied by the application of bacterial inoculum. The bacterial inoculum led to a 5% reduction in the total hydrocarbon concentration, so in the polluted variant with 5% oil, the decrease was 12% in the case of treatment with 7.5 t/ha AbsE, and in the treated versions with 7.5 t/ha AbsE with inoculum, decrease in total hydrocarbon concentration was 17% after 90 days from pollution. In the case of 10% oil pollution, the level of the oil residue after 90 days decreased by 20% in the case of treatment with 15 t/ha AbsE and by 25% in the case of treatment with 15 t/ha AbsE plus the bacterial inoculum (Ram et al. 2019).

The research carried out on a soil (with vegetation) contaminated with 3% crude oil in which peat and zeba were absorbed in different doses, basic fertilization with $N_{200}P_{200}K_{200}$ and liquid fertilizers based on humic substances extracted from KH lignite (fertilizer containing potassium humate with microelements), fertilizer 1 (potassium humate in NPK and magnesium matrix, with nitrogen in amide form), fertilizer 2 (fertilizer containing potassium bytes in an NPK matrix with microelements and 4% monosaccharides, where nitrogen is in amide form), and fertilizer 3 (fertilizer containing potassium peroxide in an NPK matrix with microelements and 8% monosaccharides, in which nitrogen is in amide form) led to best results in the bioremediation process on a nonabsorbent basis were obtained in the variants fertilized with fertilizer 1 (potassium humate in NPK and magnesium matrix, with nitrogen in the form amide) where PHCs values decreased by 47% within 45 days of treatment; the process of bioremediation against the use of peat as an absorber at a dose of 16 t/ha was carried out with the highest intensity in the variants in which fertilizers of the type 2 (fertilizer containing potassium in a micro-element NPK matrix with microelements were applied and 8% monosaccharides in which nitrogen is in amide form) and bacterial inoculum, the PHCs values being reduced by 50% after 45 days after treatment; against the background of using the peat as an absorbent, of the fertilizers best behaved fertilizer; against the application of 16 kg/ha absorbent the most effective variant of bioremediation was shown to be the one in which it was fertilized and bacterial inoculum was applied, where the content in PHCs was reduced by 57% after 45 days after treatment; against the application of at a dose of 32 kg/ha the best results in the bioremediation process are obtained by applying the fertilizer at a dose of 11,650 l/ha + 64 kg/ha glucose, in which the PHCs level decreases by 58% after 45 days from the application of the treatment and 60 days from the oil pollution.

Under the conditions of nonuse of an absorbent, the greatest number of bacteria was determined in the variants where mineral fertilizers were applied in the dose of $N_{200}P_{200}K_{200}$ together with the bacterial inoculum.

The application of the bacterial inoculum together with the fertilizer (fertilizer containing potassium humate in an NPK matrix with microelements and 4% monosaccharides, in which the nitrogen is in amide form) in the bioremediation process led to the increase of the soil content in mobile potassium (Karppinen et al. 2017). Some researchers recommend the application of superabsorbent polymer in the amount of 1000 kg/ha to absorb the residual oil that remains after collecting the oil layer/film, in order to prevent its infiltration into the soil profile and subject them to the degradation process. Polymers are catenary-type combinations with large molecular mass, which respect a common formation principle which consists in repeating, along the macromolecular chain, a minimal group of atoms called a structural unit. These units are identical or similar in composition to the monomers from which the polymers were (or could have been) synthesized. The number of structural units included in a macromolecular chain represents the degree of polymerization of the polymer. Polymers can be water soluble or water insoluble.

Polyelectrolytes are polymers whose monomer units possess ionized or ionizable groups. In aqueous solution, the polyelectrolytes dissociate into polyvalent macroions (polyions) and a large number of small ions of opposite-counterions (Cartmill et al. 2014).

Depending on the nature of the ionizable groups, the polyelectrolytes can be classified into:

- Polyacids or anionic polyelectrolytes, which possess as a functional group the carboxylic group – COOH, the sulfonic group – SO_3H, or the phosphoric group – PO_3H
- Cationic polybases or polyelectrolytes, having as functional group the amine group – NH_2, the imine group> NH, the quaternary ammonium group – NH_4, etc.
- Amphoteric polyampholytes or polyelectrolytes, which have both acidic groups (carboxylic, sulfonic, phosphoric, etc.) and basic groups (amines, ammonium, etc.) on the macromolecular chain

Polyelectrolytes are useful as soil conditioning agents. Improvement of the physical, chemical, and biological characteristics of the soil creates conditions for the intensification of the bioremediation processes (Wrede et al. 2012). Amendment with activated carbon resulted in a dramatic reduction in PHCs concentration in the aqueous solution and the bioaccessibility of pollutants for diverse estuarine biota such as *Macona balthica* mollusk, *Hinia reticulata* gastropod, and *Nereis diversicolor* polychaete. Potential obstacles to the successful application of this technique include dirt from active coal by dissolving organic matter in sediments and slowing the transfer of pollutant mass to active coal under field conditions. Biodegradation and stabilization can become competitive processes when carbonaceous material is added, by reducing the free concentrations in the solution and reducing the accessibility of pollutants to degrading MOs. If the pollutants are biodegradable, the addition of sorbent materials may prevent them from decomposing, but if they are not rapidly biodegradated, sorbent amendment may be an effective alternative method for reducing environmental risk (Zhen et al. 2019).

Bioremediation and amendment with activated carbon (AC) were compared as remediation strategies for sediments in the Tyne River containing 16.4 ± 7.3 μg/g PHCs and approximately 5% carbon particles from the total sediment weight. Unamended, amended with nutrients (biostimulated), and amended with nutrients and *Pseudomonas putida* (bioaugmentation) inside the sediments failed to show a significant decrease in the total concentrations of PHCs in the sediment after a period of 1 month. The passive polyethylene samples were incorporated for 21 days in this sediment for the purpose of measuring the accessible portion of PHCs and the accumulation of passive polyethylene 4.70 ± 0.25, 12.43 ± 1.78, and 23.49 ± 2.73 μg PHCs s/g PE from unaltered, biostimulated, and biodocumented material. The higher uptake of PHCs by the samples with activated polyethylene under biostimulation and bioaugmented conditions coincides with the slowing down of the target phenanthrene in the free sediment filtrate from these experiments compared to the unamended variant filtrate (Varjani and Upasani 2019).

Analysis of the microbial community revealed changes in the bacterial community followed directly by the addition of nutrients, but the addition of the *P. putida* community failed to establish itself. Addition of 2% activated carbon to the weight of the dry sediment reduces the PHCs uptake of PE (passive polyethylene) samples to 0.28 ± 0.01 μg PHCs /g PE, more than 90% reduction compared to unamended variant (Zhang et al. 2013).

9.2.4 Amending

For the normal development of the physicochemical processes involved in the degradation of the oil and the stimulation of the activity of MOs, especially of bacteria, it is recommended that the corresponding amendments be applied on acid and basic soils. To improve the reaction of acid soils, it is recommended to apply limestone-based amendments, the dose being determined according to the formula:

$$\mathrm{DCA}\left(\mathrm{t/ha}\right)=\mathrm{SBi}\left(\mathbf{100}/\boldsymbol{Vi}-\mathbf{1}\right)1.5\left(\mathbf{100}/\mathbf{NPA}\right)$$

DCA – dose of calcareous amendments;
SBi – the sum of the initial exchange bases;
Vi – the degree of saturation in bases calculated with hydrolytic acidity;
NPA – the neutralization power of the amendment in $CaCO_3$.

This formula is used in the elaboration of agrochemical recommendations and aims to bring pH values in the range 6.5–7.3, optimal for plant growth and for the normal development of the physicochemical processes involved in oil degradation and the activity of MOs, especially bacteria. In the case of saline and alkaline soils, the dose of the amendment is calculated taking into account the content of the soil in exchangeable Na, the alkalinity given by Na carbonates, the cation exchange capacity, and the acidification value of the amendment. The sodium in the complex is removed until a balanced Na/Ca ratio is achieved according to the needs of the cultivated plants. This ratio corresponds to the time when the soil contains only 5% exchangeable Na of T. Practically, it has been shown that a satisfactory improvement is obtained even when the soil contains up to 10–12% exchangeable Na of T (Liu et al. 2018). The dose of amendment is expressed in $CaSO_4 \cdot 2H_2O$ (gypsum). The following relationships can be used for calculation:

$$\text{Dose of } \mathrm{CaSO_4{\cdot}2H_2O}\left(\mathrm{t/ha}\right)=0.086\left(\mathrm{b}-\mathrm{T^C}/100-\mathrm{d}\right)+\mathrm{H{\cdot}Wv}$$

in which:

b – soil content in exchangeable Na (me/100 g soil)
T – soil cation exchange capacity (me/100 g soil)
c – the percentage of exchangeable Na that can remain in the soil (5–12%)
d – alkalinity due to carbonate and bicarbonate of Na (me/100 g soil)
H – the depth of the plowing layer that improves (cm)
Wv – the volumetric weight of the soil (t/m3) having the values: 1.3–1.7 in the alluvial soils; 1.3–1.5 on sandy soils; 1.5–1.75 on heavy soils; 1.55–1.65 in swamp; 0.086 – coefficient of transformation of the milliequivalents of convertible Na into g $CaSO_4 \cdot 2H_2O$

$$\text{Dose of } \mathrm{CaSO_4{\cdot}2H_2O}\left(\mathrm{t/ha}\right)=\mathrm{a}\left(\mathrm{b}-\mathrm{T^C}/100-\mathrm{d}\right)$$

in which: “a” is the acidification value of the amendment, the size of which varies as follows: 1.00 for gypsum; 1.25 for phosphogips; 0.38 for concentrated sulfuric acid; 0.18 in elemental sulphur; 0.58 at $CaCO_3$. In this formula, the amendment dose is calculated for a 100 mm thick soil layer (Kai et al. 2018).

9.2.5 Soil Works

The homogenization of the soil profile is a work that aims to create optimal conditions under the relationship of soil–water relations and water circulation. This is done by successive plows, at different depths, realizing the most intense mixing of soil horizons, diminishing and combating the negative influences of pollutants on the profile. There is also a horizontal dilution of the pollutant and the provision of 14 aerobic conditions in the polluted area to stimulate the bioremediation process (Yao et al. 2018). It has been recommended to scrape the soils with high porosity, with low aeration porosity, in order to improve the aerohydrous conditions in the soil. The scarification will be carried out at a depth of 60 cm, and the distance between the active organs will be 1 m. The optimum time for execution is when the soil has humidity of 60–80% of the active humidity range. The work is performed perpendicular to the drying channel or the natural emissary. On certain polluted soils and with salt water, it is also recommended to perform mole drainage. Fertilization and soil work increased the diesel losses in the soil by 55% compared to the initial level (soil polluted with 5% oil over a depth of 15 cm) compared to 24% in the unfertilized and untreated control.

The accessibility of the terminal acceptors of suitable electrons (e.g., oxygen, nitrates, iron, manganese, sulfates) more than the single nutrients will be a factor that determines the expanding of biodegradation. Soil works provided oxygen and nitrogen fertilization provided nitrates. Fertilization, works and bioaugmentation increased the percentage of biodegradation up to 89% and registered an increase of 34% compared to bioremediation only with fertilizers and works and by 58% compared to the untreated control (Khudur et al. 2019).

9.2.6 Stimulation with Surfactants

Surfactants, surface active agents, are synthetic organic chemicals having a polar (hydrophilic) and a nonpolar (hydrophobic) portion. They are usually classified as anionic, cationic, amphoteric, and nonionic. Surfactants are used in the formulation of synthetic detergents for personal or household cleaning, as dispersants and emulsifiers, for different industrial uses, and as an ingredient or additives with potential multiscope in food, mining, oil, and textiles. Some nonionic surfactants, such as alcohol ethoxylate and ethoxylated alkylamino, are used as pesticide adjuvants (Li et al. 2018). Increased use of these compounds leads to increased dispersal in the environment. For this reason, they are seen as a source of pollution and carefully controlled. Using surfactants to improve the restoration of highly polluted soils is a forerunner of high-efficiency remediation technologies.

The surfactant improves soil washing, a process that generates high toxicity effluents, usually including potentially hazardous chemicals extracted from contaminated sites. In particular, where surfactants are present, processes such as bioremediation, ultrasonic irradiation, advanced oxidation, activated carbon, and the biological membrane reactor are applied (Liu et al. 2016a, b).

There are two types of surfactants: synthetic and biosurfactants. The application of surfactants or emulsifying agents can cause a decrease in interphase tension and an increase in the solubility of hydrocarbons (Liu et al. 2016a, b). The sorption of surfactants by soil particles depends on the type of surfactant, the properties of the soil, and the amount and structure of the clay in the soil. Biosurfactants (surfactants with properties to increase microbial activity) have characteristics superior to synthetic surfactants such as absence of toxicity, biodegradability, and efficacy at extreme values of temperature, pH, and salinity. In addition, biosurfactants can be produced from cheap raw materials. Adding surfactants enhances the efficiency of processes in sludge bioreactors by increasing the rate of mass transfer of contaminants into the aqueous phase, thus increasing the contact of contaminants with the soil microbial population and improving their biodegradation. There are, however, cases when the application of biosurfactants is not effective because the culture of MOs produces sufficient biosurfactants (Li et al. 2016).

Research has shown that after 14 days after soil pollution with 5% crude oil, PHCs values in the improved variants begin to decrease compared to the untreated pollutant variant, where decontamination in the soil was achieved through natural attenuation processes. After 21 days, it becomes obvious that when the soil was conditioned with the higher dose of AbsE, i.e., 0.5% (100 g/vessel), and inoculated with selected bacteria, the rate of disappearance of the pollutant from the soil was much higher, compared to the other experimental variants, the results having a high degree of statistical assurance. In the case of variants in which the soil was polluted with 10% oil, a relatively slow rate of oil degradation was found in the interval between 30 and 300 days. The significance of this long period of slowing down of the processes of biodegradation of PHCs, in the case of the excessively polluted soil with oil, may be the difficulty of adapting the biodegradating MOs, both indigenous and those introduced by adding bacterial inoculum, after the excessive pollution.

Relatively few works related to the simultaneous treatment of hydrocarbons and surfactants include wastewater from soil washing. With all these technological approaches, flocculation–coagulation processes are suitable methods for treating wastewater generated in the field, on site, without requiring expensive equipment and in a small space, with high efficiency at a very low price. Flocculation–coagulation was used to treat municipal and industrial wastewater, with medium and high load of organic material. The amount of wastewater generated in the process can be highly variable, but a proportion of 3–5 l of water per kg of washed soil is produced. This is of course dependent on many factors such as the initial oil hydrocarbon concentration, the type and amount of surfactants used, the soil texture, the energy supplied to the washing system, etc.

At the end of the washing process, the generated wastewater must be deposited in a drainage system, or discharged into the natural watercourses, so it is compulsory to treat the contaminated stream up to the levels required by the legislative framework (Li et al. 2019). Applying surfactants in contaminated soils can potentially reduce interphase tension, increase the solubility and bioaccessibility of

PHCs, and thus facilitate their biodegradation. The addition of synthetic surfactants in the environment contaminated with PHCs has been studied as a way in which their inhibitory effects of biodegradation have been recognized, especially at concentrations above the critical micellar concentrations. The potential benefit of biodegradable surfactants includes their unusual structural diversity, which can lead to unique properties, economically efficient production, and their biodegradability (Cheng et al. 2019).

9.2.7 Use of Plants

The combined effect of plant growth and different microbial strains on improving the bioremediation of soil contaminated with PHCs was studied. Raygras (*Lolium perenne*) was planted and microbial strains were used as both simple and mixed agents. The results show that combining the raygras with the mixture of *Bacillus subtilis*, *Sphingobacterium multivolume*, *Acinetobacter radioresystems*, *Rhodococcus erythropolis*, and *Pseudomonas fluorescens* microbial strains gave the best results with a 58% degradation rate after 162 days.

Fractional analysis of PHCs gives indications that the degradation of saturated hydrocarbons appears to be more intense at the combination of MOs and raygras; the degradation of polar fractions is more intense through phytoremediation, and the aromatic fractions have been further degraded by microbiological remediation. Higher polyphenol oxidase activity occurs in all applied treatments (compared to control), but lower dehydrogenase activity was found in microbiological remediation processes.

The number of degrading MOs was higher in the rhizosphere of the alfalfa (*Medicago sativa* L.) and the alpine meadow-grass (*Poa alpina* L.), than in the mass of the soil where they grew in the soil amended with organic contaminants. The number of pyrene-degrading MOs was significantly higher in the thick rhizosphere (*Cynodon dactilon* cv. Guymon) compared to soil mass. The number of total hydrocarbons degrading MOs was lower in the soil without vegetation compared to the soils with vegetation (Teng et al. 2011). It has been reported that the number of PHCs-degrading MOs per gram of dry soil was 100 times higher in treatment with vegetation than in treatment without vegetation. The number of MOs that degrade hydrocarbons, alkanes, and PHCs per gram of soil was significantly higher in the rhizosphere of the Sudan grass (*Sorgum sudanenese*) compared to the soil outside the rhizosphere in the six doses of N used. Sudan grass grew for 7 weeks in soil with a PHCs level of 16.6 g PHCs/kg soil (Kirkpatrick et al. 2006). Nitrogen was added based on PHCs C:N total ratios (PHCs–C:TN) ranging from 44: 1 to 11: 1. The presence of Sudan grass led to significantly more total hydrocarbon and alkane degrading MOs per vessel when grown in the fine soil with an 11: 1 ratio (inorganic nitrogen) PHCs–C:TN compared to higher ratios PHCs–C:TN (carbon from total PHCs: nitrogen from total nitrogen added). The soil outside the rhizosphere in the Sudan grass vegetation vessels did not contain a number of contaminants degrading

MOs significantly different per gram of soil than in the plant less vessel. Increased doses of N stimulated the growth of the roots of Sudan grass which led to the increase of the potential for degradation in the contaminated soil due to the influence of the rhizosphere (Hou et al. 2019).

The results demonstrate the importance of the rhizosphere in increasing the potential for contaminant biodegradation. For efficient phytoremediation, additional doses of nitrogen will be sufficient to optimize plant growth and maximize the number and activity of contaminant-degrading MOs. A positive correlation between the reduction of PHCs and n-hexadecane and the number of degrading MOs has been reported by other studies (Chaturvedi et al. 2019).

9.2.8 Use of Microorganism Inoculum

The experiments of inoculation with specific MOs aim to intensify certain biological processes in the soil, being shown that enrichment of the polluted soil with these selected MOs intensifies the initiation and the development of biodegradation. For this reason, bioremediation technologies have been developed which involve: knowledge of ways to optimize the conditions of biodegradation, behavior and effects of chemicals introduced into the soil on the ecosystem, and selection of MOs with superior degradative abilities (Meyer et al. 2012). MOs that are capable of degrading xenobiotic substances are generally present in polluted environments, but natural biodegradation occurs at very low rates. The application of bacterial biopreparations is the main technological link in the process of bioremediation of soils contaminated with biodegradable compounds, as is the case of PHCs (Dos Santos and Maranho 2018). Treatment of 10% oil-contaminated brown luvosoil, with an inoculation of bacterial strains of the genera *Bacillus*, *Arthrobacter*, *Pseudomonas*, *Mycobacterium*, *Micrococcus*, *Escherichia*, and *Streptomyces*, selected from oil-polluted soils, led to the following conclusions: significantly increases the total number of bacteria and microfungus in the variants treated with the inoculum compared with the untreated control; during the dry summer, usually July and August, the number of bacteria is reduced, so also the biodegradation activity, which requires the application of irrigation; significantly increased the taxonomic diversity of microorganism species in the variants treated with the inoculum, especially in years 2 and 3 after pollution; in the last experimental year, there was a net differentiation in terms of the number of bacteria in the inoculated versus noninoculated variants ($14.4–33.3 \cdot 10^6$/g dry soil compared to $5.3–9 \cdot 10^6$/g dry soil); after 3 years after treatment, the level of pollution became insignificant (Hou et al. 2019). Numerous heterotrophic MOs in soil, both bacteria and fungi, are able to use crude oil as an energy source for cell growth and development. Some MOs, especially bacterial species from the genera *Bacillus*, *Pseudomonas*, and *Acinetobacter*, were tested on a soil contaminated with crude oil from India and found to be most effective in decontamination; it was a species of the genus *Bacillus*, achieving a rate of biodegradability of 59%, followed by species of the genera *Acinetobacter* 37% and

Pseudomonas 35%. Great progress has been made in biodegradation of oil-contaminated soils and in decreasing their level of toxicity, up to the ability to support plant growth. In all cases, biodegradation is effective only within certain pollutant concentrations. If a certain limit of the pollutant concentration in the environment is exceeded, the MOs may remain at the periphery of the contaminated area or may be destroyed due to the high toxicity of the pollutant (Aguelmous et al. 2018). Microbial cultures must have the ability to adapt to environmental conditions and survive in the presence of other MOs. Most studies based on inoculation with selected MOs are carried out by inoculating filamentous fungi in polluted soil, which have the ability to biodegrade polynuclear aromatic hydrocarbons with up to four nuclei.

Inoculation technology with selected MOs is used in particular for the degradation of pure compounds. Various studies have investigated the use of exogenous bacteria or groups of bacteria. This method is called bioaugmentation and involves the selection of microbial strains for their ability to degrade the contaminants and add them to a particular place (Kotoky et al. 2018). Were examined nine highly adapted, commercially available microbial strains. Their results indicated that commercial products do not adapt quickly to the environment in which they were exposed. Therefore, the efficiency of the adapted microbial strains was severely limited. In fact, the conclusion showed that indigenous bacteria have sufficient potential for degradation if they are provided with the proper conditions and nutrients. Eight cultures of commercial bacteria were tested on PHCs brought daily to North Alaska in closed laboratory reactors. It was concluded that indigenous bacterial populations already present in crude oil were the first to be responsible for biodegradation.

They applied *Bacillus pumilus* MVSV3 (*Bp* MVSV3) on two plots of land polluted with PHCs and found an increase in the degree of decontamination from 53% to 76% compared to the method of “land farming.” The addition of *Bp* MVSV3 leads to stimulation of microbial activity, evidenced by both increased respiration and the number of bacteria. After 6 months of treatment with *Bp* MVSV3, the value of aromatic hydrocarbons decreased from 37 mg/L to 2 mg/L. Research carried out in the vegetation house showed that by applying a bacterial inoculum consisting of three strains belonging to the genus *Pseudomonas* and two strains belonging to the genus *Arthrobacter*, the content of PHCs in the soil was significantly reduced, their level decreasing from 3% to 1.99% (33%) in only 26 days. The application of bacterial biopreparations has been appreciated as being the main technological link in the bioremediation of hydrocarbon-polluted soil (Hemala et al. 2014). In order to streamline the action of this link, the biopreparations were made using 19 bacterial strains isolated from the polluted soil subjected to decontamination, as well as strains composed of bacterial species isolated from various polluted sites with crude oil, subjected to selection and laboratory tested for biodegradability of crude oil.

Bacterial polyculture mainly contained representatives of the genera: *Pseudomonas* sp., *Escherichia*, *Micrococcus*, *Bacillus megaterium*, *Bacillus subtilis*, *Arthrobacter* sp., and *Streptomyces*. The inoculum was used to stimulate the biodegradation process by composting and applying it on the oil-contaminated farmland after the oil shell was removed. After 7 months, the rate of disappearance of the pollutant was 17.3% for the untreated control, 36.5% for the treatments with bacterial biopreparations, and 42.3% for the application of microbial biopreparations with $N_{200}P_{100}K_{100}$. In the variants treated with the bacterial inoculum, mineral fertilizers with NPK, and superabsorbent polymers, the disappearance rate of the pollutant was 71.2% (Varma et al. 2017). Contamination of fresh oil reduced the number of actinomycetes, fungi, and MOs that break down cellulose and increased the number of bacteria that are isolated on pepton and starch. Between the quantity of hydrocarbons and bacteria in the genetic horizons of the soil there is a close regression relation. It is often the case that bioaugmentation (inoculation with MOs) of contaminated soils to be applied during bioremediation strategies in an attempt to improve both the rate of contaminant degradation and the final concentrations (Ugochukwu et al. 2013). Both the addition of single strains and of the consortium of MOs in contaminated soils usually produce low added values in terms of degradative ability compared to indigenous soil MOs, which are often only limitations in the degradative capacities of the contaminant due to the suboptimal soil condition (Table 9.1).

The promotion of indigenous MOs is therefore the first target and will lead to the optimization and improvement of both biotic and abiotic conditions; what the rams can improve (Kim and Lee 2012). If the soil is polluted with both PHCs residues and salt water, the bioremediation measures are combined with appropriate desalination measures, i.e., arrangements for washing the salts on the soil profile and capturing the washing water in a drainage system to be purified prior to discharge into the outlet. The optimal environmental conditions required for oil degradation are: soil pH 6.5–8.0, humidity 30–90%, oxygen content 10–40%, temperature 20–30 °C, and nutrient ratio C:N: P = 100: 10: 1. Soils treated with *Acinetobacter* sp. A–3 allowed better germination and growth of bean seedlings, showed a better plant length, weight, and chlorophyll content in leaves. This shows that *Acinetobacter* sp. A–3 was capable of reducing the phytotoxicity of oil by biodegradation. It has been shown that many researchers have put complete mineralization of PHCs on the account of a consortium of MOs rather than a strain.

To assume that only a strain of bacteria is responsible for decomposition would mean ignoring biochemical relationships that are well established in microbiology. Studies have shown cooperation between two strains that were able to degrade pollutants. Other researchers have found that a mixture of bacterial cultures is responsible for the processes of decomposition. It was concluded that a consortium of bacteria is responsible for pollutant degradation. The complete degradation of some contaminants is due to the aerobic and anaerobic microbial communities. In part, this is because soil and groundwater are contaminated with a mixture of compounds more often than with pure substances (Mujumdar et al. 2019). The efficacy of *Bacillus subtilis* DM4 and *Pseudomonas aeruginosa* M and NM strains isolated from oil-contaminated soil samples from North-East India for the bioremediation of fresh oil in soil and stirring vials was compared. These bacterial strains can use fresh PHCs as their sole source of carbon and energy. Bioaugmentation of the PHCs-contaminated pilot with *P. aeruginosa* M and NM in consortium with

Table 9.1 Limitations of aerobic bioremediation and the main effects of the debris that minimize these limitations

No.	Limitations of bioremediation	Creating displacement/shelter channels	Ingestion, digestion, and excretion	Coprolite
1.	Lack of oxygen, anaerobic conditions	*		
2.	Soil heterogeneity	*	*	
3.	Compact soil	*	*	
4.	Improper ratio C:N		*	*
5.	Insufficiency of accessible nutrients		*	*
6.	Reduced accessibility of related residues		*	
7.	Presence, number, and activity of degrading MOs	*	*	*
8.	Contaminant concentration too low to induce catabolic ability			
9.	Toxic levels of contaminants, or presence of contaminants that restrict the induction of catabolic ability			
10.	Temperature			
11.	pH			*
12.	Improper humidity conditions	*		

* Effects

B. subtilis strains significantly reduced PHCs levels in treated soil compared to untreated control soil at the end of 120 days of experience. *P. aeruginosa* strains were more effective than strains of *B subtilis* in reducing PHCs content in the environment. The strains of *B. subtilis* DM-04 and *P. aeruginosa* M and NM can be effective in in situ bioremediation. Mixed microbial cultures have degraded Louisiana crude oil both in closed vials and in large basins with seawater.

In field simulation studies, the application of a mixed microbial culture to an oil film produced a measurable decrease in the thickness and quantity of the film on the water surface. The initial rate of removal of oil by MOs was at least twice the rate of evaporation. The highest oil removal rates occurred during the initial period of growth (Wang et al. 2019). This has been attributed to the use of n-paraffins less than C15. The number of cells indicated that sown cells preferentially remain at the oil–water interface during the entire experimental period. Studies in closed vials have shown a clear metabolic preference for the use of hydrocarbons by microbial cultures for saturated paraffins. Oxidation rates of saturated paraffin were directly dependent on incubation temperature. The highest oxidation rates of saturated paraffin appeared during the initial growth periods when n-paraffins lower than C18 were used. The range of use of n-paraffins was between C12 and C30. Aromatic and naphthenic compounds do not appear to be metabolized. Within bioremediation, it is often necessary to improve and maintain moisture, oxygen, and nutrient levels and to ensure their homogeneous distribution over time, especially if it is necessary for bioremediation to be applied to the soil depth, if the soil is compacted, or rich in clay.

Although they are time consuming, intensive labor and expensive methods can be used to help the optimize these variables, there may be cheap inputs to solve this problem (Al-Dhabaan 2019). The earthworms move through the soil, where they make shelters (shelters being species-specific) acting as entry points to, and preferential pathways for, the movement of water and particles and the flow of nutrients and aeration. In addition, the occurrence of coprolites and thus of ingested and digested soil leading to a positive effect on the soil environment, as the mechanical fragmentation of soil particles (Sun et al. 2019) the forces applied to soil particles as they cross the gut remodel and reorganized them. For example, it was noted that the earthworms (*Eisenia fetida*) reduced by digestion the particles of organic matter larger than 2000 μm with values between 97% and 27% (200–2000 μm), while it was observed that the earthworms (*Millsinia anomala*) divided the organic matter from the soil causing a reduction in size by 25–30%. Such research underscores the major role of earthworms in the fragmentation of soil litter in aggregates with smaller sizes. It has been hypothesized that there is potential for earthworms to contribute to the disposal of organic contaminants associated with the soil. In addition, such activities have been shown to increase the size of the soil organic matter surface, which will have the role of exposing the fractionated material to interaction with MOs, leading to an increase in the potential for contaminant degradation.

Fractions of organic matter processed by digestion and excretion have positive effects on soil structure and soil environment. These include increasing soil porosity, increasing oxygenation, water retention, improving soil fertility by accelerating the decomposition of organic matter, and improving nutrient accessibility (Zhou et al. 2019).

Although the process is dependent on the species of earthworms, it is known that earthworms interact with soil MOs (fungi, bacteria, and actinomycetes) in three broad spatial directions (lining the shelters, coprolites, and gut or bowels). For example, mucus and coprolites deposited on the walls of shelters and other sources of organic carbon transferred through shelter systems promote the growth and distribution of MOs in shelters, while mucus, urine, and glucose can lead to microbial biomass growth. This is relevant, because the increase in microbial biomass is related to the increase of microbial catabolic activity, related to the potential increase of bioaccessibility due to the action of the earthworms on the soil through gut (Martinkosky et al. 2017) which may increase the potential for loss of microbial compounds through mineralization.

The higher number of MOs, the diversity and the activity are also known to be related to the passage of MOs through the intestines. The earthworms intestines, as well as the promotion and the stimulation of the dormant flora from the intestines, however, are in very close relation with the passage time through the intestine (Ekperusi and Aigbodion 2015). Importantly, the growth of the microflora is associated with the intestine, which is thus excreted into the environment by the coprolites of the earthworms and by the microbiological adhesion to the skin of the earthworms, while the mechanisms of transit and dispersion are associated with the flow of water which also helps in the subsequent dissipation of MOs. Such actions are clearly relevant to any phytoremediation methodology that wants the spatial incorporation of MOs capable of degrading organic contaminants.

9.3 Application of Fertilizers

Ameliorative fertilization is the action of restoration and appreciable growth of the fertility of the soils that have lost this property due to various causes. It aims, first of all, to raise to an optimum level, from an agrochemical point of view, and in a limited period of time, the content in nutrients and implicitly of the ratio C:N. Mineral fertilization is absolutely necessary in the case of oil pollution, due to the insufficient nitrogen in the soil found in abnormal relationships with the organic carbon brought by hydrocarbons (C:N ratio too high).

It is desirable to apply both nitrogen and phosphorus so that the C/N/P ratio of 300/10/1–100/10/1 is achieved, but without applying in doses greater values than 200 kg/ha N to avoid unnecessary wasting loss and toxicity to MOs. To achieve and maintain the balance of nutrients in the soil, to create conditions for rapid multiplication of MOs, doses of 200 kg/ha N, 100 kg/ha P and 100 kg/ha K were applied, and the results of the bioremediation process were very good on the chernozem. In order to carry out the physicochemical processes involved in oil degradation and stimulate the activity of MOs in good conditions, some researchers recommend: amending the soil with calcium carbonate to bring the pH to values above 6.5; annual application of mineral fertilizers all over the area, in the dose of $N_{200}P_{100}K_{100}$; plow at 15–30 cm depending on the thickness of soil horizon, for breaking the oil film and diluting the pollutant in a larger mass of soil; the annual organic fertilization with 150 t/ha of semi-fermented manure (Chen et al. 2019), by uniform application throughout the polluted surface and its immediate incorporation into the soil.

9.3.1 Application of Bacterial Inoculum

Organic fertilization of hydrocarbon-polluted soils is essential in the bioremediation process. The role of organic fertilizer is multiple:

- It has a high capacity of cation exchange and adsorption, which makes it absorb (fix) a large quantity of crude oil, preventing percolation into the depth and being able to break any oil film installed on the surface of the soil after pollution.
- It is a source of nutrients for plants and soil MOs.
- It is a source of various MOs, which can be involved in oil degradation and stimulate soil biological activity.
- It increases the resistance of plants to the content of salts in the soil.
- It allows better aeration of the soil, so it stimulates the decomposition process, which is more intense under aerobic conditions.
- It improves soil aerohydric regime and all physicochemical parameters.

Contaminated land has priority at organic fertilization. In vegetation vessel experiments, it was concluded that a concentration of 220 N, 110 P, and 110 K mg/kg soil is suitable for growing vetiver (*Vetiveria zizanioides* (L.) Nash) on soil contaminated with 5% PHCs.

In biostimulation methods, additional nutrients for oil hydrocarbon degradation were usually directed to the addition of nitrogen and phosphorus, or other organic or mineral fertilizers. Because carbon is a major constituent of oil, its traditional role in bioremediation research has typically watched as an index to determine the amount of N and P needed to be added to reach the optimal C:N:P ratio. More recently, the role of carbon supplementation in biodegradation of contaminants has been investigated through the use of molasses from sugar cane, surfactants, glucose, urban sludge, or composting (Nwankwegu et al. 2016).

9.3.2 Species of Microorganisms Identified in the Degradation of Certain Hydrocarbons

Bioremediation uses live MOs, primary MOs, to degrade contaminants from the environment into less toxic forms. MOs may be native to the contaminated area or may be isolated elsewhere and brought to the contaminated area. For bioremediation to be effective, MOs must enzymatically attack pollutants and convert them to less toxic products. This process often involves manipulating environmental parameters to allow microbial growth so that degradation occurs at a higher rate. The *Achromobacter* genus has been successfully used in the degradation of carbazole (Farajzadeh and Karbalaei Heidari 2012) and phenanthrene degradation (*Achromobacter xylosoxidans*) (Hou et al. 2018). Within the genus *Bacillus*, the following species are noted: *Bacillus firmus* – strain APIS272 is capable of completely degrading acenaphthylene, anthracene, and benzofluoranthene and reducing concentrations of naphthalene, dibenzoanthracene, and indenopyrene. *Bacillus licheniformis* – strain APIS473 is capable of completely degrading only anthracene, while the rest of the hydrocarbons only reduces the concentration. *Bacillus subtilis* – strain SBS526 completely degrades acenaphthene, anthracene, and benzofluoranthene and reduces the concentration of naphthalene, indenopyrene, and toluene. *Bacillus pumilus* has been shown to be the most efficient in the process of biodegradation of hydrocarbons, with a degradation of 86.94%. The genus *Brevibacterium* isolated from Nigerian soils degraded 40% of the hydrocarbons in 12 days. *Mycobacterium* species that have the ability to biodegrade hydrocarbons are *M. lacticola, M. luteum, M. phlei, M. rubrum*, and the last three species listed degrade gasoline, petroleum, and paraffin (Cheung and Kinkle 2001). Within the genus *Pseudomonas* we notice: *Pseudomonas alkaligenes* – strain DAFS311 which completely degrades naphthalene, benzofluoranthene, and indenopyrene and reduces the concentrations of anthracene, benzoanthracene, and benzoperylene, and *Pseudomonas putida*, which has the ability to degrade organic solvents such as toluene or naphthalene.

In the case of fungi, results were obtained regarding the biodegradation capacity of hydrocarbons, some strains of the genera *Aspergillus*, *Penicillium*, *Paecilomyces*, and *Fusarium*. We were able to identify the genus *Penicillium*, which had the ability to degrade 90% phenanthrene and 75% acenaphthylene and fluoren (Kozlovsky et al. 2020).

Studies have shown the ability of *Cladosporium resinae* species to degrade aliphatic hydrocarbons. *Rhizopus* genus includes filamentous fungi, found in soil, fruits, vegetables, and old bread. The genus has been isolated and studied from the point of view of the biodegradation capacity of hydrocarbons, obtaining satisfactory results (Balaji et al. 2014). Biodegradation occurs in several stages and is not the result of a single specific organism; usually it acts synergistically with several strains of MOs. In this regard, the synergistic phenomenon between *Nocardia* and *Pseudomonas* is described, which in combination are capable of degrading cyclohexane: *Nocardia* by the use of cyclohexane produces intermediate compounds, which are taken over by *Pseudomonas*. *Pseudomonas* produces the growth factors (mainly biotin) needed for the growth of *Nocardia* bacteria. Research was carried out on the development of a consortium of bacteria and fungi.

From the experiments it has been observed that *Penicillium* and *Rhodococcus* have been shown to be very effective in degrading polycyclic aromatic hydrocarbons, while *Rhodococcus* with *Aspergillus terreus* did not have synergistic relationships (Yi et al. 2011).

Bioremediation has been defined as “the activity of adding materials to the contaminated environment to produce an acceleration of the natural biodegradation process.” This technology is based on the premise that a high percentage of the oil components is readily biodegradable in nature. The success of the bioremediation depends on the ability to establish and maintain the conditions that favor the increase of speed of biodegradation of crude oil in the contaminated environment. Biodegradation is a particularly important mechanism for removing nonvolatile components of crude oil from the environment. This is a relatively slow process and may take months or years for MOs to degrade a significant fraction of the oil spilled in soil. Factors to be considered when deciding on the type of soil remediation include: the type of oil; the total concentration of PHCs in the soil; salinity; the existence of a microbial population capable of degrading pollutants; soil type; the age of pollution; pH; temperature; humidity; nutrients; the presence of oxygen; microelements (Akbari and Ghoshal 2015).

Organo-mineral fertilizers, having in their composition natural organic and/or synthetic polymers associated with different mineral salts, which besides providing the deficient elements in the nutrition of plants also have qualities of improvement of some properties of the soil, are relatively new products used in agriculture and remediation of degraded soils. They were created and developed, in particular, as a result of the need for improvement of sandy, luvic, degraded soils, as well as of other soils with low humus content, under the intensive development of agriculture, as well as for the improvement of soils contaminated with products, organic, or heavy metals. There are numerous references in the recent specialized literature on the effects of humic substances, as well as their salts, extracted from different natural sources (lignite, leonardite, oxidized lower carbons, peat, compost, lignosulfonates, polysaccharides, etc.) on plant growth and development as well as modification by their application of the bioavailability of the nutrients in the soil (Sui et al. 2014).

There are numerous studies that describe the positive relationships between the content of humic substances in soil or applied extraradicular and the yield and quality of agricultural production, as follows:

- Plant metabolism is improved due to the high availability of various minerals present in humic molecules. When suitable humic substances are present in the soil, the need for NPK fertilizer to be applied is reduced. The application of liquid or solid humic products to the soil dramatically improves the efficiency of classical fertilizers and plant metabolism. Also, foliar application of mixtures of liquid humic fertilizers reduces the need for fertilization doses.
- Humic and fulvic acids stimulate the growth and development of plant roots. In the controlled experiments in which these acids were applied, an increase of the roots by 20–50% was observed compared with the roots of the untreated plants.
- Foliar fertilizers containing humic and fulvic acids intensify the metabolism of the plant immediately after application. By this the photosynthesis in the leaves intensifies and the synthesized sugars are quickly transported to the root and released into its rhizosphere. These substances eliminated by the root provide the nutrients to the MOs in the soil that live on its surface. Active MOs synthesize the substances needed for the plant in the growth process.
- Humic and fulvic acids have a direct effect on the plant cell membrane. Thus, humic acid molecules influence the permeability of the cell membrane resulting in the intensification of electronic transport and the exchange of minerals required in specific metabolic processes.
- Humic substances increase the production of adenosine triphosphate (ATP) in plant cells.
- Humic and fulvic acids play the role of growth hormones by inhibiting the Indole-3-Acetic Acid (IAA) oxidase enzyme.
- Carbon-containing compounds from humic substances are an important source of energy and mineral elements for soil organisms that ensure microbiological activity (algae, ferments, bacteria, fungi, nematodes, mycorrizae, actinomycetes, protozoa, and small animals).
- Humus has the role of improving the soil's ability to retain water. Humic and fulvic acids present in the soil bind to the clay molecules and form stable organic-clay complexes that retain an amount of water of approx. 4–7 times their weight. This water retained in the soil can be released to the roots of plants during periods of drought. At the same time, the rate of evaporation of water and soil temperature is stabilized by humic substances.
- Humic substances buffer the pH of the soil and are key components of a friable (noncompact) soil structure, which allows gas to enter and infiltrate water (Koshlaf and Ball 2017).

Among the current techniques for remediation of contaminated soils, the techniques in which the treatment is performed locally, without excavation, either by extracting the pollutant or by degrading or fixing it in the soil should be highlighted, these being known as in situ techniques. This group also includes electroremediation or electrokinetic remediation. Soil electrokinetic remediation is a developing technology, consisting of the movement and entrainment of contaminants, mainly by electromigration of ionic species and by electroosmosis. It is a relatively safe method and easy to implement, which can be applied to different types of soils and a wide variety of pollutants that are organic, inorganic, or with a mixed composition. Despite the proven efficacy of this technique, there are some limitations in particular due to PHCs properties. These compounds are hydrophobic, have low water solubility, and are resistant to degradation. On the other hand, advanced oxidation processes, which are based on the reactivity of species with high oxidation potential, appear as an efficient alternative for degradation of such pollutants. Of these, the Fenton process is a very interesting option, as we can deduct from the large number of manuscripts dealing with this topic. However, there are some limitations that need to be addressed. One of the main problems of the homogeneous electro-Fenton process is the generation of sludge, rich in iron, at the end of the process, and the need to complete this reagent throughout the remediation process, which can be an environmental problem and may entail additional costs. However, as has already been investigated and demonstrated in a number of studies, this problem can be avoided by using heterogeneous catalysts (Huguenot et al. 2015). Electrochemical oxidation of organic compounds during electro-Fenton treatment is strongly influenced by the nature of the electrode material. Many researchers have already investigated the effect and properties of different types of anodes. Since the generation of the main oxidant (H_2O_2) occurs by reducing the oxygen at the cathode, it is important to evaluate the electrode materials that favor this reaction. In addition, another major drawback of the electro-Fenton process is the high energy consumption. Thus, in recent years, by combining different technologies, the energy consumption has been reduced and an efficient alternative has been ensured, minimizing or even eliminating some disadvantages of the individually applied remediation processes, by coupling them (Ouriache et al. 2019). Although the electro-Fenton oxidation process has been considered one of the most efficient in eliminating different pollutants, given that it is not always possible to apply this treatment and considering that it may be more expensive compared to other technologies, it is necessary an in-depth study aimed at improving the process and identifying those technologies that can lead to an increase in the efficiency of the decontamination process, which are economically feasible and do not present the risk of secondary pollution.

9.4 Technological Recommendations

Digging holes for the rapid collection of PHCs spread on the ground and transporting them to a treatment and recovery station. Application of 16 t/ha peat to absorb the remaining oil and limit its penetration into the soil, to aerate the soil and to stimulate the development of hydrocarbon degrading MOs. Collecting the peat soaked with oil and transmitting it to a treatment station.

Loosening by plowing the soil to a depth of 25 cm to ensure aeration of the soil. If the quantity of oil is large, the work will be repeated every 2–3 months. The following ventilation work can be done using the harrows. If the soil is acidic or basic, it is recommended to apply amendments and incorporate them into the soil. Scarification of heavily soiled soils, with low aeration porosity, in order to improve aerohydrous conditions in the soil. The scarification will be carried out at a depth of 60 cm, and the distance between the active organs will be 1 m.

The optimum time for execution is when the soil has a humidity of 60–80% of the active humidity range. The work is executed perpendicular to the drying channel or the natural emitter. On certain polluted soils and with salt water, it is also recommended to perform mole drainage. Absorber is applied at a dose of 32 kg/ha to keep water in the soil and thus stimulate the multiplication of degrading MOs. Microbial polyculture selected from the fields contaminated with hydrocarbons is applied. Bacterial polyculture mainly contained representatives of the genera: *Pseudomonas* sp., *Escherichia*, *Micrococcus*, *Bacillus megaterium*, *Bacillus subtilis*, *Arthrobacter* sp., and *Streptomyces*, which have been shown to be involved in the breakdown of hydrocarbons. Fertilization is done with 150 t/ha composted fermented manure. It will be applied as homogeneously as possible on the polluted land.

Garbage ensures not only better aeration of the soil, but also a great diversity of MOs participating in the bioremediation process, breaks the oil film, retains the hydrocarbons on the surface of the soil where the area is more aerated, and most are lost through volatilization, which assures a very large range of macro- and micronutrients accessible to plants, stimulates water retention in the soil, soil structuring, and improves all soil physical parameters. It is fertilized with mineral fertilizers. Very good results were obtained by applying $N_{200}P_{200}K_{200}$. But the recommendations differ with the concrete characteristics of the soil. Very good results provided the liquid fertilizers based on humic acid at a dose of 650 l/ha. Of these, the fertilizer (potassium humate in an NPK matrix with microelements and 8% monosaccharides or 100 g/l glucose applied at a dose of 650 l/ha + 64 kg/ha glucose) against the application of absorber in the dose of 32 kg/ha, in which the PHCs level decreased by 58% 60 days after oil pollution, is considered to be a favorable alternative for bioremediation. The land could be cultivated with maize, *Lolium perenne*, sunflower, alfalfa, barley, oats, *Lolium multiflorum*, mixtures of grasses and legumes, etc.

The analysis of the degradation of the main compounds identified can lead to a better knowledge of the degradation of the different types of hydrocarbons. Stabilizing the pH value (buffer capacity) associated with the addition of a complexing agent has been shown to be necessary in situ treatment, so as to facilitate the availability of metals, avoid precipitation in the soil, and favor the transport of hydrogen peroxide agents. The EK–Fenton process was successfully coupled with selected surfactants and used to achieve in situ decontamination of historically polluted soils.

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Chapter 10
Application of Macrophytes for Remediation of Wastewater in Constructed Wetlands

Syeed Mudasir, Shah Ishfaq, Ruqia Bhat, Gousia Jeelani, Shabeena Farooq, Shah Fouziya, and Baba Uqab

10.1 Introduction

Wastewater is posing serious environmental problems in urban areas, particularly in underdeveloped countries (Ajibade et al. 2013; Bhat et al. 2017). The proper treatment of wastewater, both municipal and industrial, is a method of environmental management (Bhat et al. 2018a, b) that aims to avoid any sort of pollution to receiving waters by reducing the organic load and recovery of nutrients (Queiroz et al. 2019).

In small-scale industries, conventional methods of treating the effluents are rarely used due to operational, economical, and regulation issues. Operations like activated sludge process, membrane bioreactors, etc. are not viable for smaller industries when located in rural areas (Wu et al. 2015). Wastewater management and treatment technology, thus, needs to be suitable and sustainable (Ajibade et al. 2014). It also needs to consider cost-effectiveness, ease of operation and maintenance, and high efficiency in removing both organic matter and heavy metals. The removal of unwanted components in wastewater can be done by processes like sedimentation, precipitation, filtration, adsorption, microbial application, and

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phytoremediation (Hammer 1989), which is the most effective one among all the strategies in constructed wetland (CW) technologies.

10.2 Wastewater Treatment Technologies

The availability of water is a global concern due to increasing demand and increase in population, industrial expansion, unsustainable agricultural practices and climate change as well as inadequate water resources. For example, the Middle east, south and central Asia, Southern USA, South Europe, and North Africa (Almuktar et al. 2018). Due to this shortage of water throughout the globe, alternative non-conventional sources play an important role in meeting the requisite demands of water. Among these, wastewater has been a viable alternative for fulfilling the water demand (Bichai et al. 2012; Noori et al. 2014; Almuktar and Scholz 2015; Almuktar et al. 2015a, b; Almuktar and Scholz 2016a, b).

Discharge of wastewater directly into fresh water resources poses a threat to human health (Khurana and Pritpal 2012). Hence, to reduce its impact it needs to be treated. According to FAO, wastewater water treatment and recycling can potentially provide sufficient quantities of fresh water in coming decades (FAO 2003). To harness the wastewater, a suitable economical and rapid treatment technology needs to be developed against the conventional one (Kumar et al. 2012).

10.3 Conventional Technologies

These technologies involve mainly the usage of modern instrumentation for the removal of the chemicals from the wastewater. These treatment technologies include low to high end techniques for the wastewater treatment, with varying removal efficiencies. The sewage treatment plants (STPs) are one of the technologies that are being used for decades now. Reverse osmosis (RO) is one of such high end techniques used for the treatment of the wastewater. Although these technologies have high efficiencies in treating wastewater, these are not preferable at many places due to certain factors like high installation and operational costs, difficult operations, maintenance costs, trained personnel, etc., which become limiting factors while opting for such techniques in the treatment of wastewater.

10.4 Emerging Technologies Using Plants

The use of plants for the removal/uptake of chemical toxicants from the wastewater and from contaminated soils is called as phytoremediation (Bhat et al. 2018a, b). It is an emerging technology which involves the use of specialized plants for waste removal from natural ecosystems, like terrestrial ecosystems, aquatic ecosystems, wetlands, etc. These specialized plants are known as hyperaccumulators, as they can uptake such chemicals from the media, in which they grow, many times more than other plants. Nowadays, hybrid plant species are developed to increase the efficiency of the plants selected for the removal of wastes from wastewaters.

A constructed wetland (Fig. 10.1) is an artificially maintained wetland used to treat wastewaters from municipal or industrial sources, including gray-water or storm-water runoff. They are designed to remove water quality constituents like organic matter, suspended solids (SS), nutrients (e.g., nitrogen and phosphorus), heavy metals, etc. Phytoremediation strategy, using the constructed wetlands (CWs) technology, is the most effective technology used today. Various macrophytes have been used to treat wastewaters in the constructed wetlands, so as to reduce the waste concentration in the wastewater as per norms (Table 10.1), before the wastewater finally discharges into other water bodies.

Different macrophytes show varying waste removal efficiencies, which is a function of various parameters and is calculated as given by the following formula:

$$\text{Removal efficiency}\left(\%\right)=\frac{\left(\text{Influent concentration}-\text{Effluent concentration}\right)}{\text{Influent concentration}}\times 100$$

Based on previous studies, the variation in waste removal percentage may be related to differences in the selected macrophyte species and density, wastewater type, media, loading rates, retention times, temperature, other climatic conditions, design, and size of the experimental setups (Tanner et al. 2012). Based on previous studies, most of the plants used in effective constructed wetlands are either weeds or aquatic plants, possessing higher growth rates than others, which is an important criterion in effective phytoremediation.

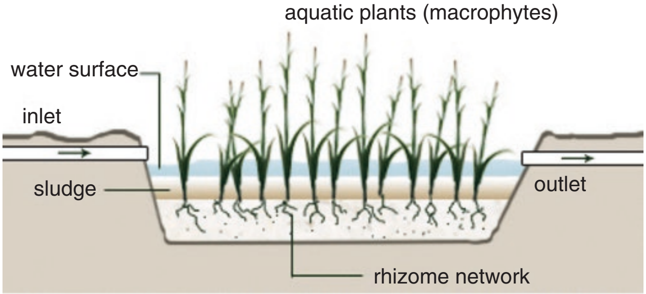

Fig. 10.1 A constructed wetland (free-water surface constructed wetland). (Onyango et al. 2009)

Table 10.1 Recommended standard for the safe disposal of treated wastewater (Adams 1989)

		WHO standards	
S. no.	Parameter	Desirable limits	Maximum permissible limits
1.	pH (at 20 °C)	7.0–8.9	6.5–9.5
2.	Turbidity (NTU)	5.0	5.0
3.	Nitrite (mg/L)	10	50
4.	Nitrate (mg/L)	0.2	3
5.	Sulfate (mg/L)	250	500
6.	Odor	Unobjectionable	Unobjectionable
7.	Taste	Unobjectionable	Unobjectionable

10.5 Classification of Constructed Wetlands (CWs)

The constructed wetlands are classified generally on three main factors: water level in the system (surface and sub-surface flow); macrophytes; and the direction of water movement (Kadlec and Knight 1996; Nikolić et al. 2009; Langergraber et al. 2009; Hoffmann et al. 2011; Vymazal 2014). In addition, CWs may also be categorized according to their objectives into habitat creation, wastewater purification, or flood control (Vymazal 2013, 2014; Stefanakis et al. 2014).

The two main flow types of constructed wetlands (CWs) are considered to be (a) free water surface flow with substantial macrophytes along with an exposed water surface and (b) subsurface flow with no clear water surface (Kadlec and Knight 1996; Kadlec et al. 2000; Langergraber et al. 2009; Knowles et al. 2011; Nivala et al. 2012; Vymazal 2013; and Wu et al. 2014). Constructed wetlands are classified into two categories depending upon the direction of flow viz., vertical-flow and horizontal-flow types (Fig. 10.2), which together can form a hybrid system to achieve high pollutant removal (Vymazal 2013, 2014; Wu et al. 2014).

10.6 Parameters of Efficient Macrophytic Phytoremediation in Constructed Wetlands

The prerequisite parameters for the effective phytoremediation process to occur are to be kept in consideration while planning. The important parameters include macrophyte species, pH, temperature, and salinity of the target waters.

10.6.1 Macrophyte Species

A number of macrophytes have been reported to have been used in the treatment of wastewater in constructed wetlands as well as natural aquatic ecosystems (Table 10.2). While determining the utilization of any macrophyte for

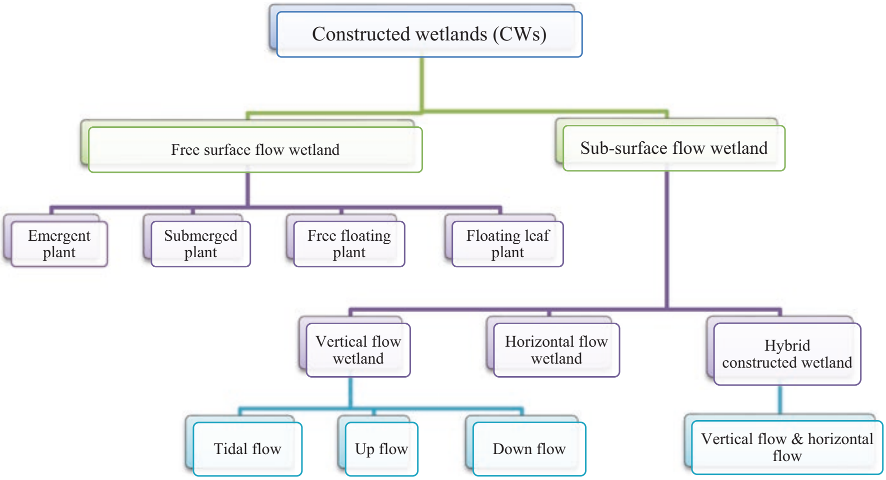

Fig. 10.2 Classification of constructed wetlands. (Almuktar 2018)

Table 10.2 List of some commonly used macrophytes for the treatment of wastewater in constructed wetlands

S. no.	Macrophyte species	Reference(s)
1.	*Phragmites australis*	Vymazal and Brezinova (2016), Ajibade and Adewumi (2017), and Vymazal (2013)
2.	*Eichhornia crassipes*	Ajibade and Adewumi (2017)
3.	*Commelina cyanea*	Ajibade and Adewumi (2017)
4.	*Ludwiga helminthorriza*	Nunez et al. (2011)
5.	*Polugonum punctatum*	Nunez et al. (2011)
6.	*Typha latifolia*	Vidayanti and Choesin (2017) and Vymazal (2013)
7.	*Colocasia esculenta*	Obi and Woke (2014)
8.	*Alocasia puber*	Thani et al. (2019)
9.	*Alocasia macrorrhiza*	Thani et al. (2019)
10.	*Pistia stratiotes*	Thani et al. (2019)
11.	*Lemna minor*	Basile et al. (2012) and Lemon et al. (2001)
12.	*Elodea canadensis*	Basile et al. (2012)
13.	*Leptodictyum riparium*	Basile et al. (2012)
14.	*Salvinia rotundifolia*	Reddy and Tucker (1985)
15.	*Wolffia borealis*	Lemon et al. (2001)
16.	*Trapa natans*	Tsuchiya and Iwakuma (1993)
17.	*Hydrocharis dubia*	Tsuchiya (1989)
18.	*Nymphaea tetragona*	Kunii and Aramaki (1992)
19.	*Spirodela polyrhiza*	Lemon et al. (2001)
20.	*Azolla micrphylla*	Mishra et al. (2016)

phytoremediation, the rate of uptake of wastewater constituents by plants and the assimilation of such chemicals (nutrients) into the macrophytic biomass are of utmost importance (Kinidi and Salleh 2017). The suitability of macrophyte for various types of wastewaters depends on the macrophytes tolerance with respect to exposure to different types of contaminants in the wastewaters. Besides, while choosing the macrophyte for a constructed wetland, it should be kept in mind that it should be locally available, tolerant to anoxic, waterlogged, and hyper-eutrophic conditions (Kadlec and Knight 1996).

10.6.2 pH of Wastewater

The pH value of wastewater does influence the efficiency of macrophytes in the remediation process. A pH value of 6–9 is reported to be the most favorable for the treatment of wastewater using macrophytes (Shah et al. 2014). El-Gendy et al. (2004), in their study, used *Lemna minor, Eichhornia crassipes*, and *Pistia stratiotes* for remediation of municipal wastewater and concluded that *Eichhornia crassipes* show maximum growth at pH 7. However, it can even withstand the pH values ranging from 4 to 10 (El-Gendy et al. 2004).

10.6.3 Temperature

Temperature variations significantly determine the efficiency of phytoremediation by macrophytes (Shah et al. 2014), because the phytoremediation potential depends upon mainly on the plant growth. It acts as one of the important environmental factors which affects the productivity of a particular macrophyte species in any natural aquatic ecosystem or any constructed wetland. Most of the macrophyte species grow between 20 and 30 °C and show retarded growth below 10 °C (Perdomo et al. 2008). However, some species do grow in cooler months, like *Centella asiatica,* which, thus, can be used to replace *Eichhornia crassipes*-based nitrogen wastewater treatment systems (Reddy and Debusk 1985).

10.6.4 Salinity

The salt stress affects the growth and reproduction of macrophytes, depending upon the difference in tolerance ranges exhibited by the macrophyte species. The tolerance of macrophytes towards salt stress affects their efficiency and performance in the treatment of wastewaters due to the reduction of total dry weight and transpiration rates at higher salinity levels and may even cause death of macrophyte species (Haller et al. 1974).

10.6.5 Availability of Oxygen

The availability of oxygen in the constructed wetlands depends mainly on the design and type of constructed wetland used. Thus, availability of oxygen will determine the fate of the reactions, whether they will be aerobic or anaerobic.

10.6.6 Design of the Constructed Wetlands (CWs)

The design of the constructed wetlands has a vital role in the treatment of wastewater. For example, the water depth in a constructed wetland has an impact of treatment efficiency of organic matter removal and has been shown that shallow water depth is better than the deep ones, mainly in terms of biochemical oxygen demand (BOD). However, for a CW meant for phytoremediation through use of macrophytes, the depth is determined by the maximum root depth of the macrophyte. Table 10.3 summarizes the specific design and operational recommendations for the treatment of wastewater in the constructed wetlands (Wu et al. 2015).

Table 10.3 Design and operational recommendations for treating wastewater using the constructed wetlands

S. no.	Parameter	Design criteria	
		FWSF CW	SSF CW
1.	Bed size (m^2)	As larger as possible	<2500
2.	Length-to-width ratio	3:1–5:1	<3:1
3.	Water depth (m)	0.3–0.5	0.4–1.6
4.	Hydraulic slope (%)	<0.5	0.5–1
5.	Hydraulic loading rate (m/day)	<0.1	<0.5
6.	Hydraulic retention time (days)	5–30	2–5
7.	Media	Natural media and industrial by-product preferred, porosity of 30–50%, particle size <20 mm, 50–200 mm for the inflow and outflow, respectively	
8.	Vegetation	Native species preferred, plant density 80% coverage	

Adapted from Wu et al. (2015)

Note: FWSF CW stands for "free water surface flow constructed wetland" and SSF CW for "subsurface flow constructed wetland"

10.6.7 Inflow Properties

The inflow qualities of the wastewater will definitely affect the use of a particular type of constructed wetland. For example, vertical flow CWs perform well in terms of nitrification of wastewater; that is why they are preferred in ammonia-nitrogen rich wastewaters and not preferred in denitrification cases. On the other hand, horizontal-flow constructed wetlands perform well in terms of denitrification and poor in nitrification. That is the reason of them being recommended for inflow wastewater with elevated nitrate-nitrogen values.

10.7 Advantages of Phytoremediation in CWs

Phytoremediation by macrophytes in constructed wetlands (CWs) are numerous, whether it is ease of operation, cost effectiveness, potential environmental risks, etc., and some of them are enlisted in Table 10.4.

Table 10.4 Advantages of phytoremediation over conventional wastewater treatment techniques

S. no.	Parameter	Conventional treatment technologies	Phytoremediation in constructed wetlands or other aquatic ecosystems
1.	Type of chemical used	Various chemicals are used (e.g., lime, chlorine gas, various electrolytes, etc.)	Notably no chemical is needed
2.	Generation of harmful by-products	Corrosive, explosive, and toxic by-products are commonly generated	No harmful by-products generated
3.	Consumption of energy	Demand large amounts of energy, based upon the treatment techniques used. Reverse osmosis is one of such techniques, which consumes large quantities of input energy	Harvest energy from sunlight
4.	Environmental risks (*if any)*	Although modern technologies are safe nowadays, still a scope of potential risks exists	No environmental risks
5.	Cost	Although quicker method of treating wastewater than phytoremediation in many cases	Comparatively cheaper and efficient technology than conventional treatment technologies
6.	Operational ease	They are not easy and require proper training and knowledge of the instruments for effective operation	They are comparatively easier to use
7.	Maintenance cost	Due to wear and tear, and other technical faults, require decent investment of money. Besides, human negligence in operation can increase such costs	Require little or minimum investment for operation as well as maintenance

10.8 Other Potential Benefits from Sustainable Waste Management Practices Like Phytoremediation Using Constructed Wetlands

Some of the potential benefits of using macrophytes in constructed wetlands by the process of phytoremediation are discussed below,

10.8.1 Biogas Production

The anaerobic digestion of organic waste (macrophytes) can be done to produce biogas, which is an environmentally clean fuel (Yadvika et al. 2004). Macrophytes, due to their high C/N ratio and high proportion of fermentable matter, can be used to generate biogas. Macrophytes such as *Trapa natans, Lemna minor, Eichhornia crassipes, Typha latifolia, Salvinia molesta*, *and Pistia stratiotes* can be decomposed easily and thus generate high biogas yield (Gunnerson and Stuckey 1986; Strom 2010; Sudhakar et al. 2013; Mathew et al. 2015; Pantawong et al. 2015).

10.8.2 Vermicomposting

Vermicompost is the nutrient-rich product of microbial degeneration of organic waste with the help of earthworms (Gajalakshmi et al. 2002). Vermicompost from the macrophyte *Eichhornia crassipes* can be used as an organic fertilizer (soil enhancer) because it is rich in nutrients (Bernal and Hernandez 2016). Vermicompost with phytoremediated aquatic macrophytes biomass is effective and environmentally friendly for sustainable agriculture (Mishra et al. 2016). Among the aquatic macrophytes used were *Azolla microphylla, Pistia stratiotes, Salvinia cucullata*, and *Salvinia molesta* (Mishra et al. 2016).

10.8.3 Biochar Production

Biochar basically comprises of carbon-rich material generated from organic waste (Kameyama et al. 2011) by means of pyrolysis technology. The pyrolysis product of *Lemna minor* can be converted into gasoline and diesel (Miranda et al. 2014).

10.8.4 Paper Making

Due to their high moisture content, many macrophytes are suitable with the aqueous characteristics of paper pulp (Asuncion 2003). Macrophytes like *Typha angustifolia, Scripus grossus*, and *Cyperus rotundus*, due to their fiber characteristics, physical properties, and chemical composition, can be used in the manufacture of paper (Bidin et al. 2015), and thus can be used to lessen the pressure of paper making from forests.

10.9 Guidelines to Consider During Decision-Making and Planning for Setting Up of Constructed Wetlands for Treatment and/or Reuse of Wastewater

Although constructed wetlands are generally efficient in treating wastewater from different sources, their effluent quality is primarily dependent on influent properties of the wastewater. As per the studies conducted so far, many guidelines/tips have been suggested for obtaining the better results and efficiencies while using any constructed wetland for the treatment of wastewater and/or its use thereof (Table 10.5).

Table 10.5 Guidelines for decision-making while using constructed wetlands for treatment of wastewater

S. no.	Particulars	Remarks
1.	Location	The location of the constructed wetland system will affect the type of wetland to be used. For instance, free water surface-flow wetlands are not recommended in cities, mainly due to the high chances of exposure of humans to pathogens
2.	Environmental conditions	Environmental conditions play an important role while constructing wetlands. For instance, at high temperatures, evapotranspiration rate will increase the salinity of the effluent. In such conditions, subsurface flow constructed wetlands (SSF CWs) are highly recommended. (However, it is noteworthy to mention that a slightly high temperature may positively affect the system behavior due to the higher activity of microorganisms resulting in higher wastewater treatment efficiencies)
3.	Longer hydraulic detention time	It helps in providing more contact time between the activated biomass and the chemicals or contaminants, leading to a better effluent quality
4.	Moderate resting time	Moderate resting time of wetlands provides the system with ample oxygen content, thus supporting the growth of microbes, and improving effluent quality
5.	Selection of suitable macrophyte	The selection of a proper macrophyte is a must, which depends upon the inflow properties and plants tolerance to the particular chemical (nutrient, heavy metals, salts, etc.) in the inflow wastewaters
6.	Inflow properties	It greatly affects the efficiency of any constructed wetland, as it is the primary factor that decides the constructed wetland type, macrophyte to be selected, hydraulic detention time to be given, etc.
7.	Depth	It depends on the selected plant root depth. However, shallow constructed wetlands are more efficient than deeper ones

10.10 Conclusion

The role of macrophytes in the phytoremediation in constructed wetlands is gaining importance day by day, as it has emerged as an eco-friendly technique. Besides, it has a lot advantages over the conventional wastewater treatment techniques. Nowadays, scientists are seeing this technique as a potential way of acquiring of metals, reclaiming of damaged wetlands, and as a viable option in water scarce areas for providing drinking water facilities during the lean months of the year in arid and semi-arid areas, areas with meager water resources.

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Chapter 11
Application of Biotechnology for Restoration of Degraded Environs

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11.1 Introduction

The anthropic action over ecosystems due to rapid industrialization/urbanization and the increase in agricultural activities and mine exploitation generated innovations, especially technological ones, that resulted in new substances that reached the environment and accumulated in organisms, causing serious damages. Among the major problems society has to face nowadays is environmental pollution (Gavrilescu et al. 2015; Fulekar and Pathak 2020).

Explosives, heavy metals, pesticides, fertilizers, oil, dyes, among other inorganic and organic substances (Guerra et al. 2018; Zhang et al. 2019), are examples of environmental pollutants. Most of them can accumulate on the polluted site, as persistent pollution, increasing the risk they represent. Pesticides, for example, can accumulate not only on the environment, but also in living organisms in polluted areas increasing the risk to the living beings (Varjani et al. 2019). Furthermore, pesticidal compounds such as azoxystrobin and atrazine can cause neurological diseases and cancer due to the damage that these molecules provoke in the DNA (Fatima et al. 2018; Singh et al. 2018; Bagazgoïtia et al. 2018). Pollution offers, besides serious health risks, a detrimental effect on ecological security (Chaoua et al. 2019; Zheng et al. 2020).

Environmental biotechnology proposes strategies that are safer and present lower costs to efficiently remediate air, water, and soil from polluted environs than the

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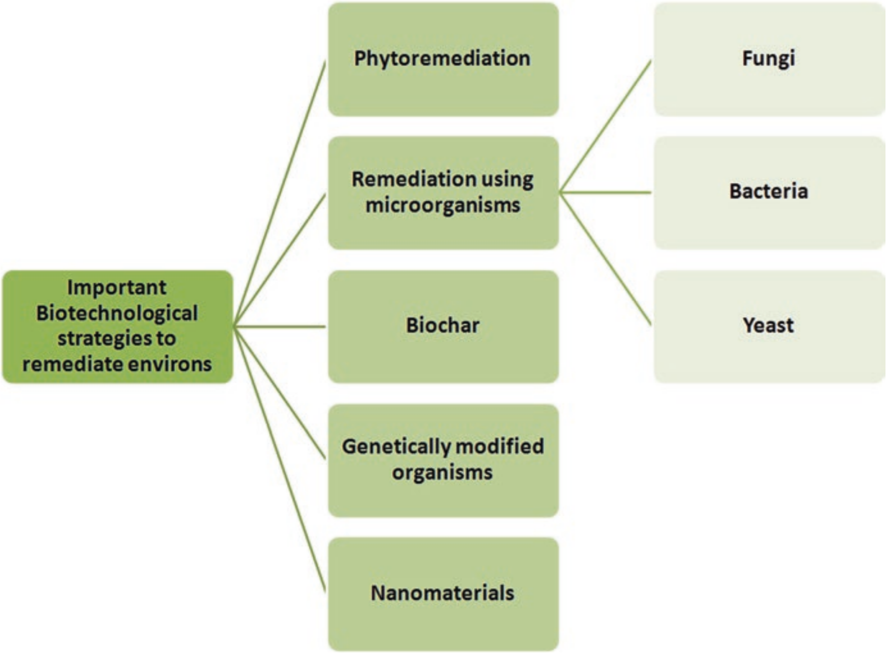

Fig. 11.1 Important biotechnological strategies that can be used to remediate environs

physicochemical treatments generally applied with this purpose (Guerra et al. 2018; Koźmińska et al. 2018; Fulekar and Pathak 2020). These strategies use living organisms, new materials, transformed biomass, or a combination of these elements (Ye et al. 2017; Gaur et al. 2018; Gong et al. 2018a, b; Jaiswal et al. 2019) (Fig. 11.1).

11.2 Strategies for Environmental Remediation

In order to remediate a contaminated environ, it is possible to apply physicochemical technologies, biological technologies, or a combination of both which generally offer the best results when it refers to mixed pollution (Ye et al. 2017).

Physicochemical technologies generally present higher costs for large-scale remediation when compared to biological technologies (Ye et al. 2017). Oxidative processes, Fenton processes, photocatalysis, plasma oxidation, ozonation, soil washing, chemical extraction, and electrokinetics are examples of these methodologies that do not depend upon living organisms to remediate (Baldissarelli et al. 2019) as same as nanomaterials.

Biological technologies, on its turn, also presents other advantages like being environmentally friendly (Azubuike et al. 2016), which helps to explain the large number of this kind of strategies proposed by different research groups. These strategies involve the use of living organisms, like microorganisms and/or plants (Strong and Burgess 2008).

In order to select which type of remediation to be performed at a polluted area, it is necessary to consider aspects like the area's characteristics, financial resources that can be apply to promote the remediation, degree and depth of pollution and contaminants characteristics such as chemical nature, and the diversity of toxic substances present (Azubuike et al. 2016).

11.3 Biotechnology as a Tool for Remediation

This chapter will focus on biotechnological strategies to restore polluted environs such as phytoremediation, the use of microorganisms to remediation, genetic manipulation of organisms (such as yeast, bacteria and plants) to optimize them to perform this function, the use of biochars, and also nanomaterials to completely mitigate or repair the damage that human actions have caused to the environment.

11.3.1 Phytoremediation

Phytoremediation is the bioremediation that uses plants (Strong and Burgess 2008) to restore, in situ, in an auto-sustained and inexpensive way polluted environs (with inorganic and/or organic contaminants), and it can be performed through different mechanisms and with different efficiencies, depending on plant, sample, and contaminant characteristics (Nwoko 2010; Muthusaravanan et al. 2018; Panesar et al. 2019). *Chrysopogon zizanioides* (vetiver grass) could remediate leachates from Italy's landfills accumulating high level of metals, but leachate composition influenced on plant growth and remediation efficiency (Fasani et al. 2019).

The mechanisms of phytoremediation include phytoaccumulation, phytodegradation, phytostabilization, phytovolatilization, rhizofiltration, rhizodegradation, and an indirect phytoremediation known as phytohydraulic control (Dzantor 2007; Abdullahi 2015; Muthusaravanan et al. 2018).

Phytoaccumulation or phytoextraction is a mechanism to remediate mainly inorganic contaminants, such as heavy metals, by extracting them from polluted environ (specially polluted soil) and accumulating in plant parts (Muthusaravanan et al. 2018). Some plant species known as hyperaccumulators can deal well with high amounts of pollutants (Lajayer et al. 2019).

Rhizofiltration is an in situ or ex situ remediation similar to phytoaccumulation/phytoextraction once pollutants are sequestrated by plant's roots (plants are grown hydroponically), but in this mechanism the main remediated sample is groundwater polluted with metallic contaminants (Panesar et al. 2019). *Arundo donax*, for example, could deal with copper pollution through rhizofiltration (Oustriere et al. 2017).

Phytostabilization also involves contaminants extraction from pollutant environs by plant's roots, but in this mechanism the contaminants are kept in rhizosphere, not entering plant's vegetative parts (Muthusaravanan et al. 2018). *Erica australis* could, through phytostabilization, deal with heavy metal and other phytotoxic contaminants soil pollution (Monaci et al. 2019).

Phytodegradation or phytotransformation allows the remediation especially of organic pollutants, converting them into fewer complexes and less toxic substances (Muthusaravanan et al. 2018). *Eichhornia crassipes* could phytodegradate the pesticides malathion and ethion (Xia and Ma 2006).

Phytovolatilization involves not only contaminants uptake and conversion into a less toxic form, but also the release of conversion back into atmosphere as a volatile substance (Limmer and Burken 2016). Through phytovolatilization, mercury pollution could be remediated by *Brassica juncea* (Moreno et al. 2008).

Rhizodegradation is a mechanism that involves microorganism's participation helping pollutants (mainly organic ones) degradation in plant's roots area (Dominguez et al. 2019). This strategy allowed the generation of a floating mat to remediate, with the aim of 10 different hydrocarbon-degrading bacteria, water polluted by oil; the plant species used were: *Phragmites australis*, *Typha domingensis*, *Leptochloa fusca*, and *Brachiaria mutica* (Afzal et al. 2019).

The phytohydraulic control is performed by tree species acting as pumps to remediate groundwater by taken up pollutants together with water through roots taking part in water cycle in nature and phytoremediating simultaneously (Khalifa and Alkhalf 2018; Muthusaravanan et al. 2018). *Polygonum punctatum*, for example, is a plant species that could, through phytohydraulic control, deal with perchlorate's pollution (Susarla et al. 2000).

Plant's capacity of remediating polluted environs can be influenced by different factors such as the presence of other living organisms nearby – plants or microorganisms (Gong et al. 2018b, 2019; Cheng et al. 2019; He et al. 2020). The arbuscular mycorrhizal fungi *Rhizophagus intraradices* reduced Cd availability in contaminated soil by promoting the proliferation of Actinobateria, allowing remediation without overloading rice plants (Chen et al. 2019).

The process efficiency can also be influenced by abiotic factors such as pollutants composition, pH, and presence of other chemicals like chelators, for example, among other conditions (Xu et al. 2019; He et al. 2020).

11.3.2 The Use of Microorganisms and the Biochemical Remediation

Biological remediation appropriates the ability that the living system has to change heavy metals and decompose organic contaminants (Zhu et al. 2012; Ye et al. 2017). Compared to some conventional technologies, such as incineration, solvent extraction, and chemical reduction in the gas phase, bioremediation is an economic and ecological process that uses microorganisms to remove contaminants from environment. In addition, this maintains ecological sustainability due to the organisms' capacity to restore soil functionality (Epelde et al. 2009; Gaur et al. 2018; Gong et al. 2018a). Arguably, chemical remediation and the disposal of contaminants constitute a risk to workers' health. Therefore, the bioremediation process is more sustainable and an alternative to physical-chemical processes (Fernando et al. 2019).

Bioremediation is a process that employs microorganisms, which can be native or cultivated, to degrade contaminants in the soil and ground water. Normally, the employed microorganisms are bacterium, filamentous fungi, and yeasts. The importance of the use of microorganisms is they change toxic compounds in harmless compounds to human and environment (Andrade et al. 2010). Since the 1980s, bioremediation strategies have been implemented for the treatment of oil-contaminated soils (Delfino and Miles 1985; Tsao et al. 1998; van der Hoek et al. 1989).

Every microorganism presents the possibility to be utilized in the bioremediation. However, few particular or engineered microorganisms are employed to properly eliminate contaminants such as *Bacillus, Corynebacterium, Staphylococcus, Streptococcus, Shigella, Alcaligenes, Acinetobacter, Escherichia, Klebsiella,* and *Enterobacter*. It is important to highlight that in the remediation of organic compounds, *Bacillus* sp. is widely used (Haritash and Kaushik 2009).

Bioremediation can affect environmental decontamination through microbiological processes in situ or ex situ (Ortiz-Hernández et al. 2018). When it comes to in situ bioremediation, the decontamination occurs without removal of the soil from the site. Conversely, in ex situ bioremediation the treatment involves unearthing of the soil from the polluted site (Parween et al. 2018).

Bioremediation technology, applied for the purpose of reducing persistent organic pollutants, relies on the technical apparatus of bioventing, biostimulation, and bioaugmentation (Gaur et al. 2018). Bioventing is a process of aerating of soil and/or water in order to enhance the in situ biodegradation of organic compounds (Hinchee and Leeson 1996; Hyman and Dupont 2001). Biostimulation modifies contaminated media in order to provide nutrition to the soil microbiota (Singh et al. 2011). Bioaugmentation is a process that adds microorganisms or any biocatalyst (gene and enzyme) in order to eliminate contaminants (Stroo et al. 2013).

Special attention has been given to the exploration of microorganisms that have the potential to restore contaminated soil with heavy metals and organic contaminants. Metal binding, extracellular chemical precipitation, valence transformation, and volatilization are some of the main mechanisms used to micro-mediation of heavy metals (Wu et al. 2010; Huang et al. 2008). The mobility and toxicity of metals as Au^{3+}, Cd^{2+}, Cu^{2+}, and Hg^{2+} was reduced by metal binding to microbial cells (Xu et al. 2012). In addition, other researches demonstrated bioremediation of metal contaminated soils by microorganisms as the study conducted by Polti and collaborators. It presents that *Streptomyces* sp. MC1 reduced Cr^{6+} in soil samples to its most stable and less toxic form (Polti et al. 2009).

Organic contaminants can be degraded by various microorganisms or their enzymes. Interestingly, some specific organic pollutants can be degraded simply to serve as sources of carbon, nitrogen, and energy for microorganisms. For example, *Pseudomonas putida*, *Pseudomonas nitroreducens,* and *Rhodotorula glutinis* have efficiently degraded phenolic compounds such as p-coumaric acid and p-hydroxybenzoic acid using these phenolic contaminants as a carbon source (Zhang et al. 2010). Also, *Pseudomonas stutzeri* OX1 showed the ability to degrade tetrachlorethylene, and the researchers attributed this degradation to the expression of toluene-xylene monooxygenase (Ryoo et al. 2000).

Effective removal of DTT, PAH, PCB by the addition of bacteria has been demonstrated in many studies. The bacteria isolated from mangrove sediments, such as *Novosphingobium* sp. PCY, *Microbacterium* sp. BPW, *Ralstonia* sp. BPH, *Alcaligenes* sp. SSK1B, and *Achromobacter* sp. SSK4, PCY, showed capacity to degrade PAHs (Wongwongsee et al. 2013). The bacterial strain *Alcaligenes faecalis* JBW4 demonstrated potential for the degradation of organochlorine pesticides (Kong et al. 2013). In addition, the study conducted by Cuozzo and collaborators demonstrated which *Streptomyces* strains degraded more than 50% of ϒ-chlordane (Cuozzo et al. 2012).

Another very versatile microorganism used in bioremediation is fungi. They degrade a wide variety of compounds, a process known as mycodegradation. Fungi have efficient degradation ability, as it has been reported on several occasions when it degrades different types of materials such as plastic and leather, among others. For instance, *Irpex lacteus* and *Pleurotus ostreatus* reduced PAH from contaminated industrial soil (Bhatt et al. 2002). It is important to highlight that fungi also contribute to the elimination of pesticides, dyes, hydrocarbons, polychlorinated biphenyls, and chlorinated and phenolic compounds through the use of different enzymes produced by them, such as laccases (Bhattacharya et al. 2012).

Fungi present interesting properties such as modifying soil permeability, ion-exchange capacity, and detoxifying contaminated soil. Several species of fungi, such as *Phanerochaete chrysosporium*, *Pleurotus ostreatus*, and *Lentinula edode*s, degrade harmful compounds using various oxidative and reducing mechanisms. It is important to mention that fungi need substrate for metabolism due to their slow growth (Gaur et al. 2018).

Other microorganisms that have a pollutant degradation capacity are microalgae and protozoa, although few are mentioned in the degradation of hydrocarbons, pesticides, and PCBs (Jain and Bajpai 2012). Like bacteria and fungi, these microorganisms can use non-chlorinated aliphatic and aromatic hydrocarbons as a source of carbon in their metabolism. Algae have the ability to degrade petroleum hydrocarbons in their less toxic form with the support of enzymes they produce (Chekroun et al. 2014). A study conducted by Tang and coworkers reported that an artificial microalgae-bacterial consortium effectively degraded hydrocarbons (Tang et al. 2010).

Many biochemical pathways of microorganisms can be involved in the process of environmental decontamination of pollutants. Various metabolic reactions can occur during the degradation process, such as hydrolysis, oxidation, and addition of oxygen to the double bond, oxidation of the amino group to the nitro group, dehalogenation, and reduction of the nitro group to the amino group, replacement of sulfur by oxygen, cleavage of the ring, and addition of the hydroxyl group to the benzene ring. It is important to mention many factors such as accessibility, bioavailability, and metabolic potential of microorganisms can influence the biodegradation of organic compounds (Gaur et al. 2018; Ortiz-Hernández et al. 2018). Besides, the mechanisms of degradation and detoxification of various classes of pollutants are widely discussed (Das and Adholeya 2012; Robinson et al. 2001; Wilson Jones 1993; Fernando et al. 2019).

Microorganisms modify the functional groups or degrade the molecular structure of the compound, leading to the formation of water, inorganic salts, and carbon dioxide. The degradation by microorganisms can be carried out under aerobic or anaerobic conditions. In aerobic conditions, it needs molecular oxygen, such as mono- and dioxigenase, to act as an electron terminal acceptor and also as a co-substrate. Differently, in anaerobic conditions, it does not need molecular oxygen; however, an electron removal group is required for an initial reducing attack. Interestingly, highly chlorinated molecules are degraded by anaerobic conditions due to difficulties in degrading them under aerobic conditions (Kot-Wasik et al. 2004; Mehboob 2010).

Through computational devices, it is possible to perceive complex metabolic pathways of biodegradation and bioremediation (Liu et al. 2018). Elimination of persistent pesticides through the use of gene editing tools and systems biology will appear as the best option.

The environment has been compromised by the indiscriminate use of synthetic pesticides. Undoubtedly, these synthetic molecules are quite varied; certainly a single bioremediation pathway may not be enough. Thus, knowledge of metabolic pathways for gene editing and application of system biology plays an essential role. This makes possible to undertake metabolic pathways and thereby keep remediation more efficient. Considerable improvements have been noted for the bioremediation of pesticides through the application of genetic tools. In addition, genomics, metagenomics, metabolomics, transcriptomics, proteomics, and biodegradation networks pave the way for pesticide bioremediation. In addition, TALEN, ZFNs, and CRISPR Cas9 are tools for gene editing to obtain the function of specific microorganisms with specific genes and enzymes responsible for the bioremediation of pesticides (Jaiswal et al. 2019).

Although the use of microorganisms in remediation has advantages, it is important to notice that there are also disadvantages: some biodegradable contaminants can be toxic in high concentrations to organisms capable of degrading them; indigenous strains may not have an intrinsic capacity to degrade pollutants, and the induction of enzymes for degradation may require pre-exposure to the contaminant; some conditions such as pH, temperature, salinity, and redox potential must be in optimum conditions for degrading strains; a threshold concentration of contaminants is usually required for growth, so low concentrations of contaminants can also be a problem (Fernando et al. 2019).

The use of microorganisms in remediation presents advantages and disadvantages. Therefore, employing different methods for remediation is a potential measure. Furthermore, the implementation of individual remediation is not easy due to the complexity of contaminating molecules in the soil. To complement each other, much research is dedicated to the effective application of physical-chemical and biological technologies in an associated way for the effectiveness of remediation processes (Ye et al. 2017).

For instance, in the soil washing process, chelators and surfactants are used to improve the extraction of heavy metals and PAHs, followed by the inoculation of bacteria to eliminate residual PAHs and restore biological function (Chen et al. 2016). A study by Sung and colleagues used pure water to eliminate dissolved metals, reducing the metal's toxicity in soil microbial degradation (Sung et al. 2011). Surprisingly, research that investigates the use of synergic of nanoparticles and microorganisms to remedy soils contaminated with hydrocarbons has been carried out (Kumari and Singh 2016).

11.3.3 Genetic Engineering and Remediation

The advances in genome elucidation, genome editing technologies, and molecular biology field, in general, highlighted genetic engineering of living being as an efficient strategy to obtain optimized organisms to perform desirable tasks such as remediating polluted environs (Zhao et al. 2017; Liu et al. 2019).

Fungi and yeast (especially the latter) possess the capacity to accumulate, precipitate, and/or change the redox state of heavy metals, being specially employed in some remediation strategies to deal with these pollutants (Ayangbenro and Babalola 2017). However, genetic modification of these organisms can optimize the results. When the metal transporter gene *EpNramp* from *Exophiala pisciphila* was expressed in yeast, it could increase Cd^{2+} sensitivity and accumulation naturally possessed by the organism (Wei et al. 2016). After being genetically modified with the coding sequence for EC20 protein (a synthetic phytochelatins), yeast presented higher capacity to accumulate Pb^{2+} and Cd^{2+} on cell wall (Fontes et al. 2015).

Bacteria are also efficient microorganisms to perform environs remediation from inorganic and/or organic pollutants, and there are several examples of genetically engineering strategies to optimize their efficiency to deal with specific target contaminants. *Acinetobacter* sp. strain BS3 could efficiently degrade crude oil substances such as aromatic hydrocarbons and n-alkanes after being genetically modified using a gene from *Pseudomonas putida* strain BNF1 that code or the production of that codifies a catechol 2, 3-dioxygenase (Xie et al. 2014). To enhance *Escherichia coli* tolerance and capacity to accumulate Cd, Cu, and Hg, researchers engineered the organism with the gene of phytochelatin synthase from *Pyrus calleryan* (Li et al. 2015). Cd biosorption could also be enhanced in *E. coli* through heterologous expression of a non-metallothioneins cadmium-binding protein from *Lentinula edodes* (Dong et al. 2019). Recalcitrant azo dyes decolorization could be performed by *Escherichia coli* DH5α and *Pseudomonas fluorescens* PfO-1 after DNA manipulation to insert the *azo*A gene (that produces azoreductase) from *Enterococcus* sp. L2. The overexpression of *azoA* gene simultaneously to the overexpression of *fdh* gene (that produced a formate dehydrogenase) from *Mycobacterium vaccae* N10 increased the efficiency of the remediation (Rathod et al. 2017).

Similarly to fungi, yeast, and bacteria, there are some plant species that can naturally deal well with pollutants present in the environs, remediating them; for example, the hyperaccumulator species from Brassicaceae family (Jafari et al. 2013). However, genetic manipulation made possible to convert non-remediating plants into organisms that can phytoremediate, and also increase natural remediation ability previously present. There are various interesting examples of genetically modified plants to perform efficient phytoremediation. *Nicotiana tabacum* could be modified to overexpress the *Elsholtzia haichowensis*'s metallothionein 1 amplifying the plant's capacity to accumulate copper in roots and increased plant's capacity to deal with the oxidative stress induced by the pollutant (Xia et al. 2012). The same species (tobacco plants) could also increase its tolerance and accumulation capacity to deal with cooper after being engineered to express the protein M2 from *Sedum alfredii* (Zhang et al. 2014). *Arabidopsis thaliana* could enhance its accumulation capacity to deal with Zn and Cd after being genetically modified to express the ZNT1 protein from *Noccaea cearulescens* (Lin et al. 2016). *Pascopyrum smithii* (the Perennial western wheatgrass generally used to re-vegetate military ranges) could be genetically manipulated to deal with explosive's pollution. Transgenic plants were modified to contain bacterial genes nfsI (confers the ability to tolerate and remediate 2,4,6-trinitrotoluene (TNT)), xplA, and xplB (confer the ability to deal with hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) pollution). Compared to wild-type plants, the transgenic ones detoxified the explosives more efficiently and dealt better with their presence and induced stress (Zhang et al. 2018).

11.3.4 Biochar

Biochar is the product of biomass' pyrolysis and is considered a multifunctional carbonaceous material due to the fact the it consists of porous solid of polycyclic aromatic compounds that can sequestrate carbon efficiently (Woolf et al. 2010; Zheng et al. 2020). There are different protocols to obtain biochar from different biomass types (Zhang et al. 2019); for example, for biochars obtained from *Saccharina japonica* macroalgae to be used to remediate cationic dyes, the washing pretreatment with biochar/water ratio at 1:10 increases adsorption capacity (Boakye et al. 2019). When it comes to producing giant reed-derived biochars to adsorb the pesticides chlorpyrifos and chlorpyrifos-methyl, the temperature is a very important parameter; higher temperatures (600 °C) offered increased adsorption capacity when compared to lower temperatures (300 °C) once it favors pores and aromatic compounds' presence enhancing sorbates capture. Pores could also be generated by treatment with low-molecular-weight organic acids (Zheng et al. 2019a).

It can be used to remediate especially environs contaminated with heavy metals (Sigua et al. 2019), but also water and soil contaminated with other inorganic pollutants or organic ones, once the large specific surface area of biochar possesses functional groups (and can also be chemically modified–functionalized to contain desirable groups) that can immobilize pollutants (reducing toxic contaminants availability) for removal (Ahmed et al. 2018; Wang et al. 2019a; Wu and Wu 2019; Yang et al. 2019; Yuan et al. 2019). Cadmium removal from soil could be performed more efficiently by sulfur-modified biochar (29.71%) than by non-modified biochar (12.54%) or sulfur-iron-modified biochar (18.53%) (Wu et al. 2019).

Organochlorine pesticides had their accessibility reduced by biochars from peanut shells and soybean straw (added at 3% w/w in contaminated soil) in rates up to 75% and 86%, respectively; sewage sludge and rice straw biochar also acted in this sense achieving reduction rates of 69% and 67%, respectively (Ali et al. 2019).

By sequestrating pollutants, biochars also help to preserve the capacity of organisms nearby to survive, avoiding their uptake of toxic contaminants. Spinach, for example, could grow better absorbing micronutrients in an optimized way in soil contaminated with nickel in the presence of rice husk biochar; when it was prepared at the temperature of 550 °C and added to calcareous soil at 2.5% w/w, it could offer a great reduction on the heavy metal toxicity to the plant species by capturing the pollutant from the environment nearby (Boostani et al. 2019).

Besides the ease of being possible to generate biochar from diverse types of raw materials, their production process also possesses low cost and the material is recyclable (Dai et al. 2019). It contributed for its large application, not only to remediate environs, but also to, for example, regulate soil pH, increase soil fertility and crop nutrient supply, provide habitat for important soil microorganisms, attenuate the stress induced by contaminants to living organism nearby contaminated areas, mitigate greenhouse gas emission (such as CO_2 and CH_4), and generate bioenergy (O'Connor et al. 2018; El-Naggar et al. 2019; Kiran and Prasad 2019; Varjani et al. 2019). And it is also possible to use the same biochar for more than one function; the phosphorus excess in wastewater discharges could be reduced to desirable levels by biochar loaded with colloidal and nanosized aluminum oxyhydroxides. This biochar, after being used for this goal achievement, could also perform the role of fertilizer, stimulating *Vigna radiata* seed germination and early development (Zheng et al. 2019b).

For each intended use, there is a more efficient raw material for the biochar's generation. Rice straw biochar could surpass sewage sludge biochar capacity to adsorb Cd^{2+} (Gao et al. 2019). In soil microbial fuel cells, petroleum hydrocarbons can occur simultaneously with electricity generation. In wood sawdust biochar, the presence of Desulfatitalea organisms increased and the charge generation efficiency was high differently from the pollutant removal efficiency that was poor; however, in chicken manure and agriculture biochars remediation, high removal efficiency was observed with the increase of development of different organisms: Actinotalea (Li et al. 2019a). Iron-biochar (with impregnation mass ratio 1:1) generated through *Acacia confusa* and *Celtis sinensis* wood waste could simultaneously remove from hydraulic fracturing high-salinity wastewater: inherent cations (K, Na, Ca, Mg, Ba and Sr), potentially toxic elements (Cu^{2+}, Cr^{6+}, Zn^{2+} and As^{5+}), 1,1,2-trichlorethane, and other organic compounds (Sun et al. 2019). The degradation of the xenobiotic antibiotic sulfamethoxazole could be achieved through a biochar-induced Fe^{3+} reduction for persulfate activation system (Wang et al. 2019b).

Considering the effects of biochars on organisms nearby, as previously mentioned for plants and microorganisms, strategies that combine phytoremediation involving microorganism and biochar can be developed. Rhizodegradation of polycyclic aromatic hydrocarbons, especially when performed in the presence of oxalic acid, can favor the presence of microorganisms associated with these pollutants remediation and efficiently deal with these contaminants in soil samples (Li et al. 2019b).

11.3.5 Nanomaterials and Remediation

Since late 1950s, nanotechnology field has made possible the development of nanomaterials (materials that, at least in one dimension, possess size ranging from 1 to 100 nanometers) with different useful characteristics and based or not in carbon when it comes to chemical constitution, to perform desirable roles. Carbon nanotubes, graphene, graphene oxide, fullerene, some quantum dots (carbon-based nanomaterials), gold nanorods, and magnetic nanoparticles (non-carbon-based nanomaterials) are relevant examples (Drexler 2004; Weiss et al. 2006; Zhang et al. 2008).

Strategic characteristics that contribute to nanomaterials' versatility are their high surface-to-volume ratio and the possibility to chemically modify their surface (functionalize) to convert them into more suitable and specific versions to perform a desirable action. For example, carbon nanomaterials, nanometal oxides, and nanocomposites can be designed/synthesized to be used in water treatment to absorb pollutants and/or present photocatalytic and antimicrobial activities (Santhosh et al. 2016; Khan and Malik 2019).

Nanoscale zero-valent iron (nZVI) can be used to remediate, at low cost and with low toxicity, especially heavy metal and organic pollutants with an efficiency that varies regarding contaminant's properties, nZVI functionalization/size (which helps to regulate aggregation and assures more stability), and environmental conditions such as pH and temperature (Jiang et al. 2018). To enhance performance, it can be combined to other elements like copper. Nanoscale valent iron–copper bimetal could be used efficiently to remove more than 99% of Cr+6 at pH 5 and 303 K from contaminated soil, in 10 min (Zhu et al. 2016). In order to avoid disruptance in local ecosystem especially when it comes to living organisms, nZVI can be associated to photo-remediation or micro-remediation. The use of nZVI at 150 mg/kg, as same as the use of beneficial rhizosphere microorganisms, could favor *Salix alba* capacity to remediate Pb, Cu, and Cd and deal with pollution-induced stress. A higher dosage (300 mg/kg) negatively impacted seedlings growth and phytoremediation (Mokarram-Kashtiban et al. 2019). To avoid the problem of iron leaching, it is also possible to reunite nZVI with biochar. Oak sawdust-derived biochar containing nZVI could remove more pollutant (nitrobenzene) than biochar or nZVI alone (Wei et al. 2019).

Magnetic nanoparticles are also suitable material for remediation. Fe_3O_4 nanoparticles could be functionalized with humic acid to be attached to oyster shell surface in order to generate a super paramagnetic and selective adsorbent capable of remediating samples polluted with Hg^{2+}, presenting a maximum absorption capacity of 141,57 mg/g (He et al. 2019).

Carbon nanotubes can efficiently remove contaminants due to large array of functionalization options and hollow structure with high surface area. Their TiO_2/SiO_2-functionalized version possesses photocatalytic properties that enable them to remediate not only heavy metals, but also organic compounds like dyes, polycyclic aromatic hydrocarbons, and pesticides (Rasheed et al. 2019). A combination of activated carbon and hydrophilic carbon nanotubes could remove fluoxetine hydrochloride from contaminated wastewater, and the composite generated by remediation process was non-toxic to zebrafish embryos (Sousa-Moura et al. 2019).

Graphene and graphene oxide are also interesting tools to deal with polluted environs (Wang et al. 2019c). A sustainable date syrup-based graphene sand hybrid could be generated to be used to remove, with good recyclability, a cationic and an anionic dye and also heavy metals (Pb^{2+} and Cd^{2+}) from contaminated water (Khan et al. 2019). Graphene oxide fibers functionalized with sodium could absorb 220 mg/g of Cs^+ in aqueous polluted samples removing this pollutant in cycles; after saturation, the nanomaterials could be washed with NaOH being regenerated and releasing the Cs^+ attached to initiate a new removal procedure (Lee et al. 2019).

As same as carbon nanotube and graphene, fullerene also possesses a structure based on carbon atoms and is a suitable material for environs remediation. Fulerene functionalized with zinc porphyrin could be attached toTiO_2 to offer an optimized photocatalytic activity to remediate phenol (by photodegradation) and methylene blue pollution in river and wastewater (Regulska et al. 2019).

Methylene blue degradation could also be achieved by using the photocatalyst green-emissive carbon quantum dots (Das et al. 2019). Quantum dots can also be generated through metals to perform remediation, due to their catalytic properties (besides the optical and electrical ones). Silver quantum dots could be used with 2D SnO_2 nanoflakes to remediate water samples contaminated with rhodamine B (Kumar et al. 2019).

Nanomaterials can also be used to generate precise sensors to pollution detection. Gold nanorod (AuNR), for example, due to its localized surface plasmon resonance extinction in the visible range, is a suitable material for the development of colorimetric sensors (Rao et al. 2019). AuNRs functionalized with poly(ethylene glycol) methyl ether thiol (mPEG-SH) followed by meso-2,3-dimercaptosuccinic acid and attached to a paper strip could detect in a fast way low concentrations of arsenic contamination in water. The presence of the pollutant could be noticed through color change (Priyadarshni et al. 2018). The capacity of signaling in surface-enhanced Raman scattering as hotspots, gold nanorods can also be used in this kind of sensors. When reunited to two-dimensional MXene, the nanomaterial contributed to the generation of a high sensitive platform to detect the presence of the pollutants rhodamine 6G, crystal violet, and malachite green (organic dyes) (Xie et al. 2019). Green-emissive carbon quantum dots could be used as fluorescent probes to detect ascorbic acid (that "turned on" the nanomaterial's fluorescence) and also Fe^{3+} (that "turned off" the nanomaterial's fluorescence) even in the presence of other metal ions (Das et al. 2019).

11.4 Conclusion

As seen in this chapter, pollution has been present in human daily life mainly due to its economic activities such as industry and agriculture. Several strategies that use biotechnology for the remediation of environments have been analyzed. Among the strategies, we can mention: the use of plants, microorganisms, biochars, nanomaterials, and also the genetic manipulation of living beings. They have already been used and contributed to depollution. It is necessary more advances to be made in the area of genetic engineering, production of new biodegradable materials and a combination of strategies for remediation. However, one should not forget the important role of the human being who, following the principles of good environmental education, must respect the environment.

11.5 Futures Perspectives

It is expected that there will be further advances in molecular biology techniques so that new microorganisms and plants can be genetically engineered and applied in environmental clean-up methods. In addition, it is essential to manufacture new types of biodegradable materials that, even if present in the environment, do not cause damage to it. Even more interesting is the application of combined techniques that contribute to non-pollution and the remediation of polluted environments. However, the relevance of human behavior and environmental education cannot be denied. The balance between human being and nature is essential for the former to make the best use of the latter's resources without destroying it. In this relationship, respect must prevail.

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Chapter 12
Role of Free-Floating Aquatic Macrophytes in Abatement of the Disturbed Environs

Zulaykha Khurshid Dijoo, Rohaya Ali, and Mehvish Hameed

12.1 Introduction

In reflection to worldwide apprehensions, water pollution is among the gravest issues faced by humanity in these contemporary times as majority of the aquatic ecosystems have been polluted by the humans (Chan 2012; Kusin et al. 2016). The reason for the rampant pollution of water bodies is ever-increasing quantities of contaminants that are dumped into the lakes, rivers, and ponds (Bhat et al. 2017, 2018a, b). Technologically advanced nations mostly contribute to the deterioration of water bodies by addition of wastes consequential from industries and modern agricultural technologies. Therefore, the issues there are largely tackled through improving wastewater management methods. While in developing countries, speedy industrial development, urbanization, and increasing population have amplified the pollution of water bodies. This unparalleled contamination of aquatic systems necessitates environmentally friendly and economical remediation techniques. On the other hand, the dearth of practical expertise, an infirm application of eco-friendly strategies, and restricted budgetary are notable challenges. The manifestation of noxious contaminants in aquatic environments results in hostile consequences to human health, aquatic life, and the environment (Kusin et al. 2016). Thus, remediation of polluted aquatic environs is as vital as of terrestrial environs.

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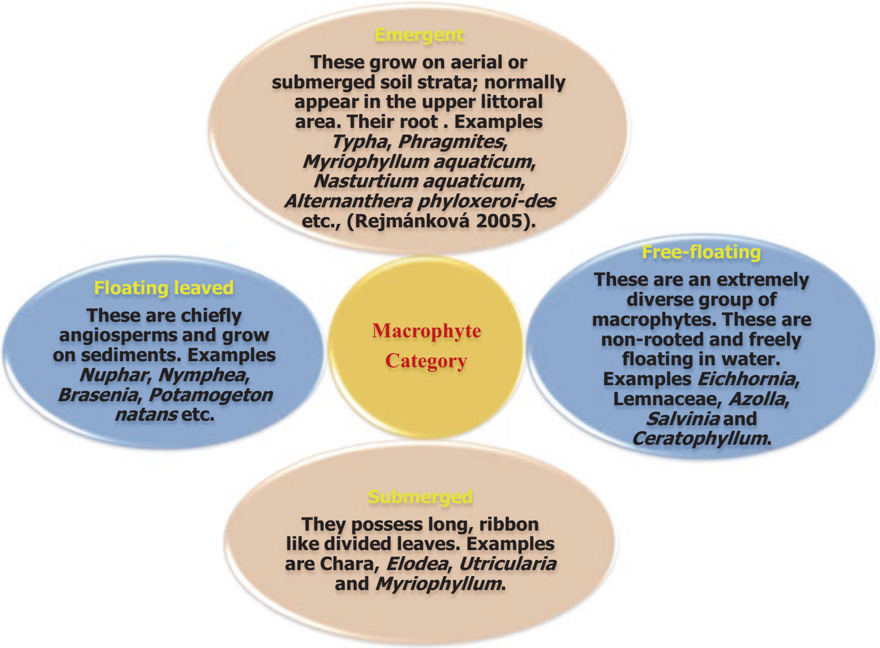
12.2 Aquatic Macrophytes

Aquatic macrophytes are crucial constituents of aquatic and wetland environments. Being producers, they are the foundation of herbivorous and detritivorus food chains. They endow food to aquatic organisms besides acting as a storehouse of organic carbon for bacteria. Their bodies act as a holding ground for periphytons, and a habitat for countless aquatic organisms (Timms and Moss 198; Dvořák 1996). Aquatic macrophytes execute a prominent role in maintenance of the water quality (Bhat et al. 2018a, b). Macrophytes regulate biogeochemical processes, water, and sediment dynamics in aquatic ecosystems. These improve the quality of water because of their capability of absorbing extremely high amounts of nutrients mainly by their roots and leaves. A pronounced deal of consideration is given to the fact that the aquatic macrophytes can be used to minimize the levels of noxious phytoplankton and nutrients like nitrogen and phosphorous from the water bodies (Steward 1970). Free-floating macrophytes like water hyacinth (*Eichhornia crassipes*), duckweed (*Lemna gibba*, *L. minor*, *Spirodela polyrhiza*), and water ferns (*Azolla caroliniana*, *A. filiculoides* and *A. pinnata*) are capable of treating contaminated water bodies (Sutton and Ornes 1975). Some macrophytes have key significance of providing food, biomass, as well as building supplies to human populations (Costanza et al. 1997; Engelhardt and Ritchie 2001; Egertson et al. 2004; Bornette and Puijalon 2011). However, death and decay of the macrophytes proliferates nutrient quantities in water bodies subsequently leading to eutrophication. Therefore, a balance between these two concurrent events is compulsory for the maintenance of the quality of aquatic environments. An accurate understanding of the functioning of aquatic macrophytes in these ecosystems is imperative for grasping the fundamental working of these ecosystems. This can prove helpful in ecosystem restoration, wastewater management, as well as in monitoring of invasive species (Lavoie 2010; Casanova 2011).

Phytoremediation is a competent green technique in which aquatic macrophytes are used for cleaning up polluted waters. Presently, aquatic macrophytes are utilized to overcome environmental issues, especially water and soil pollution. Phytoremediation of toxic pollutants in water bodies can be promptly accomplished by aquatic plants as the method comprises of biosorption plus bioaccumulation of impurities. In aquatic ecosystems, plants are either floating on the surface or inundated into the water. The free aquatic plants store impurities from the water by its roots, whereas the underwater plants amass metals by their entire body.

12.3 Classification of Macrophytes

Arber in 1920 and Sculthorpe in 1967 have categorized macrophytes into classes presented in Fig. 12.1.



Emergent
These grow on aerial or submerged soil strata; normally appear in the upper littoral area. Their root . Examples *Typha, Phragmites, Myriophyllum aquaticum, Nasturtium aquaticum, Alternanthera phyloxeroi-des* etc., (Rejmánková 2005).

Floating leaved
These are chiefly angiosperms and grow on sediments. Examples *Nuphar, Nymphea, Brasenia, Potamogeton natans* etc.

Free-floating
These are an extremely diverse group of macrophytes. These are non-rooted and freely floating in water. Examples *Eichhornia*, Lemnaceae, *Azolla, Salvinia* and *Ceratophyllum*.

Submerged
They possess long, ribbon like divided leaves. Examples are Chara, *Elodea, Utricularia* and *Myriophyllum*.

Fig. 12.1 Classification of aquatic macrophytes

12.4 Phytoremediation by Aquatic Macrophytes

Together terrestrial and aquatic plants have been utilized remarkably well for their application in phytoremediation techniques. This is because of the fact that these plant species holds a stability to purify, terminate, as well as eliminate pollutants from the polluted environs (Greger 1999). The aquatic and wetland plant species, specifically free floating, underwater (rooted), and partially rooted plants in water, have attained all-inclusive prominence due to their constructive proficiency of eliminating a multitude of pollutants ranging from heavy metals, radioactive nuclides, explosives, organic/inorganic pollutants from contaminated water bodies (Cardwell et al. 2002; Dushenkov et al. 1995; Prasad et al. 2006; Rai et al. 1995; Salt et al. 1995; Wolf et al. 1991). Some species are more efficient than others at remediation (Table 12.1).

12.5 Factors Affecting Contaminant Removal Efficiency

The essential factors regulating the fundamentals of phytoremediation are to be taken well into consideration in order to make certain that the results of the phytoremediation process are efficacious. The key factors affecting the efficiency of this process are as follows:

Table 12.1 Phytoremediation techniques (Vamerali et al. 2010; Ghosh and Singh 2005)

Phytotechnology	Mechanism involved	Contaminant	Substrate
Phytoextraction	Hyper-accretion absorption, concentration, and precipitation	Inorganics: cobalt, chromium, cadmium	Soil
		Radioactive elements: strontium, cesium, uranium, etc.	
Phytostabilization	Sorption, precipitation, and/or complexation	Inorganics: arsenic, cadmium, copper, zinc, chromium, lead, etc.	Soil, sediment, and groundwater
Phytovolatilization	Volatilization by means of leaves via transpiration	Organics/inorganics: chlorinated compounds, mercury, arsenic, selenium	Soils and groundwater
Phytotransformation	Disintegration in plants increases microbial breakdown in rhizosphere	Organics: chlorinated compounds, phenols, herbicides	Soil, groundwater (contained by rhizosphere)
		Xenobiotics	
Rhizofiltration	Rhizosphere accumulation by way of sorption, concentration besides precipitation	Organics/inorganics: cadmium, copper, nickel, zinc, as well as radioisotopes	Water

12.5.1 Species Type

The suitability of the species to be used for phytoremediation is governed by its degree of contaminant uptake. This is followed by determining the degree to which these up taken products are assimilated into the plant biomass. This generated biomass is a valuation to determine the contaminant uptake capability of the species used (Gao et al. 2003). On the other hand, tolerance limits to different contaminants contrast from species to species.

12.5.2 Salt Content

The concentration of the salts in water influences the growth and reproductive capabilities of aquatic macrophytes. The salt tolerance limits varies among various species. It governs their efficiency to remove pollutants from aquatic settings. The high salt levels cut transpiration rates as well as the total dry weight of plants. This can precede to death of these macrophytes, due to dipping in osmotic potential levels (Haller et al. 1974). Conversely, Pascale et al. (1997) detected that biomass productivity is restrained at elevated salt levels.

12.5.3 Temperature

The functioning of macrophytes fluctuates with temperature (Shah et al. 2014). It is because the growth of these macrophytes is dependent on the overall performance of the plant. Temperature is among the extremely essential ecological influences that determine the throughput of a particular macrophyte type. Maximum aquatic macrophytes are capable of growing in the temperature ranges of 20–30 °C. A temperature equal to or less than 10 °C results in the inhibition of metabolic activities of most macrophyte species (Perdomo et al. 2008). However, diverse macrophytes are feasible for cooler environments also.

12.5.4 pH

The performance of macrophytes depends upon the type of contaminant present in the medium. A pH range of 6–9 is highly favorable for the treatment of wastewaters using aquatic macrophytes (Shah et al. 2014), while this pH range may be incapable of providing suitable conditions if the environment is contaminated by heavy metals. Therefore, the pH value impacts the effectiveness of aquatic macrophytes to remove contaminants.

12.6 Potential Aquatic Macrophytes for Abatement Measures

*12.6.1 Water Hyacinth (*Eichhornia*)*

Water hyacinth is a free-floating aquatic macrophyte. It is native to South America, but presently it's prevalent in every tropical nation. *Eichhornia* genus encompasses seven species viz., *E. azurea*, *E. crasspes*, *E. diversifolia*, *E. heterosperma*, *E. natans*, *E. paniculata*, and *E. paradoxa*. The species *E. crassipes* is highly abundant owing to its higher growth rates. Yet, its vast biomass productivity, extraordinary contaminant tolerance ranges (Ebel et al. 2007), plus distinguished heavy metal and nutrient absorbing capabilities meet the requirements for its utilization in wastewater management (Ebel et al. 2007; Fang et al. 2007). Water hyacinth signifies an unswerving substitute for bioremediation in aquatic environments. However, water hyacinth's invasive nature is of utmost concern for ecologists while employing it for contaminant removal from water bodies (Giraldo and Garzon 2002). Therefore, all advantages and disadvantages of its application in phytoremediation methods should be reflected upon.

12.6.2 Duckweed

Duckweed is a minute free-floating aquatic angiosperm group without any distinctive stems or leaves. Duckweed family includes 4 genera and 34 species. These genera under duckweed are *Lemna*, *Spirodela*, *Wolffia*, and *Wolfiella*. *Lemna*, *Spirodela*, and *Wolffia* have been stated to amass arsenic from water (Zhang et al. 2009; Mkandawire et al. 2004a, b; Mkandawire and Dudel 2005; Alvarado et al. 2008 Rahman et al. 2007, 2008a, b). Therefore, these macrophytes serve a worthy choice for arsenic-polluted waters. *Salvinia natans* and *Lemna* species are reported to decrease ammonical nitrogen as well as phosphate from highly eutrophic water bodies (Cedgreen and Madsen 2002). *Lemna minor* possesses the ability to intake substantial quantities of inorganic nitrogen with its roots and fronds. Similarly, duckweed are good at removing extraordinary concentrations of nutrient specifically ammonium ions (Oron et al. 1988).

*12.6.3 Water Fern (*Azolla*)*

It is also known as mosquito or water fern; it is a tiny, free-floating fern. It is extensively dispersed in aquatic environs. It has the ability to fix atmospheric nitrogen while being in a mutualistic relation with *Anabaena*. This has made *Azolla* to be exercised as eco-friendly manure as it enhances soil fertility and has been quite useful in rice cultivation (Wagner 1997). *Azolla* possesses a pronounced ability to assimilate heavy metals like Hg, Cd, Cr, Cu, Ni, as well as Zn from water (Sela et al. 1989; Rai 2008; Rai and Tripathi 2009). Thus it can be a potential option for phytoremediation of heavy metal contaminated waters (Bennicelli et al. 2004; Arora and Saxena 2005; Rakhshaee et al. 2006). Few species of *Azolla*, i.e., *A. caroliniana*, *A. filiculoides*, and *A. pinnata*, are potent for As eradication from water.

*12.6.4 Butterfly Fern (*Salvinia*)*

Butterfly fern is a free-floating aquatic macrophyte. They are widely distributed and have high reproduction rates. These live in close association with ferns like *Azolla* and *Lemna*, thus enhancing their phytoremediation competence. *Salvinia natans* and *Salvinia minima* can be used for arsenic remediation (Hoffmann et al. 2004; Rahman et al. 2008a, b). Many members of this macrophyte family are explored for toxic metal remediation (Banerjee and Sarker 1997; Espinoza-Quinones et al. 2005; Sanchez-Galvan et al. 2008; Dhir 2009; Wolff et al. 2009).

*12.6.5 Water Lettuce (***Pistia***)*

Pistia comprises a single species, *Pistia stratiotes*. It is also known as water cabbage/lettuce. It is a widespread aquatic weed. These form mats on the surface of water and block the air–water boundary, thereby dropping dissolved oxygen content in the water column. This threatens the life of organisms living there. However, it has been reported to reduce metal concentration in the water bodies (Tewari et al. 2008; Odjegba and Fasidi 2004; Skinner et al. 2007), as well as contaminants from municipal wastes (Zimmels et al. 2006).

12.7 Contaminants Removed by Aquatic Macrophytes

12.7.1 Heavy Metals

Heavy metals account for the major class of pollutants which are competently eliminated by macrophytes. Biomass of macrophytes, both living and dead, is being utilized in elimination plus scrutinization of heavy metal (Hu et al. 2003; Kamal et al. 2004; Lee et al. 1998). Aquatic macrophytes are able to isolate heavy metals from water (Maine et al. 2001; Muarmoto and Oki 1983; Neumann et al. 1994; Sela et al. 1989; Vesk et al. 1999; Wang et al. 1996). The metal elimination is ensured by bioaccumulation or biosorption. The former signifies intake by living cells while the latter signifies intake by dead biological material (Table 12.2). The ability of free-floating macrophytes for heavy metal accumulation and elimination has been reviewed comprehensively (Chigbo et al. 1982; Lee and Hardy 1987; Wolf et al. 1991; Maine et al. 2004; Miretzky et al. 2004; Olguin et al. 2002; Sharp and Denny 1976; Vale et al. 1990; Ye et al. 2001). *E. crassipes*, *S. herzogii*, *S. minima*, *P. stratoites*, *Spirodela intermedia*, *L. minor*, and *A. pinnata* are well-known free-floating macrophytes used for scavenging heavy metals. The main site for active uptake of contaminants is through the plant roots (Gupta et al. 1994; Maine et al. 2004; Sen et al. 1987). It is then translocated to all sections of the plant, while the passive metal uptake primarily encompasses adsorption followed by the accumulation of contaminants mostly in aerial portions of the macrophyte (Maine et al. 2004). This process of hyper-accumulation and hyper-tolerance by macrophytes gives an understanding of the diverse approaches used by them for resisting metal toxicity. In several free-floating plant species like *Pistia stratoites*, metallothioneins and phytochelatins are formed while accumulating heavy metals like cadmium, mercury, lead, copper, as well as zinc (Gupta et al. 1995, 1998; Rai et al. 1995; Toetz 1971).

Table 12.2 Free-floating aquatic macrophytes for removal of heavy metals

Free-floating macrophyte Species	Heavy metal removed	Reference
Eichhornia crassipes	Chromium, copper, nickel, zinc, cadmium, mercury, silver, lead, platinum.	Muarmoto and Oki (1983), Delgado et al. (1993), Farago and Parsons (1994), Zhu et al. (1999), Vesk et al. (1999), Olguin et al. (2002), Molisani et al. (2006), and Hu et al. (2007)
Pistia stratoites	Chromium, iron, manganese, copper, and zinc	Sen et al. (1987), Chua (1998), Zayed et al. (2000), Maine et al. (2004), Miretzky et al. (2004), and Odjegba and Fasidi (2004).
Lemna trisulca	Cadmium	Huebert and Shay (1993), Zaranyika and Ndapwadza (1995), and Prasad et al. (2001)
L. gibba	Arsenic, cadmium, nickel	Zayed et al. (2000), Mkandawire et al. (2004a, b), and Mkandawire and Dudel (2005)
L. minor	Arsenic, lead, nickel, copper, chromium	Dirilgen and Inel (1994), Rahmani and Sternberg (1999), Axtell et al. (2003), Kara (2004), and Ater et al. (2006)
L. polyrhiza	Lead, zinc, nickel	Charpentier et al. (1987), and Sharma and Gaur (1995)
Azolla pinnata	Zinc, chromium	Arora et al. (2006)
A. filiculoides	Cadmium, chromium, zinc, lead, nickel	Sela et al. (1989), Zhao and Duncan (1997, 1998), Sanyahumbi et al. (1998), Benaroya et al. (2004), Bunluesin et al. (2004), and Arora et al. (2006)
Salvinia minima	Chromium, nickel, cadmium, arsenic	Srivastava et al. (1993, 1994), Olguin et al. (2002), and Hoffmann et al. (2004)
Wolffia globosa	Cadmium, chromium	Upatham et al. (2002)
Spirodela polyrhiza	Chromium, arsenic	Tripathi and Chandra (1991), Appenroth et al. (2000), and Rahman et al. (2007)

12.7.2 Radioactive Isotopes

Free-floating aquatic macrophytes have high capability to remove radioactive-nuclides from water (Abdel Malik et al. 1973; Popa et al. 2004; Sharma et al. 1997). Among these, the prominent ones are caesium, cobalt, and manganese. Duckweed group of macrophytes form a key potent set for their elimination as well as disintegration abilities of radioactive materials (Table 12.3). *Lemna minor* has higher potential for accumulating and retaining of Technetium (Tc). Tc is among the various radionuclides produced by nuclear fission of uranium besides plutonium. The intake as well as the decline of radionuclides by macrophytes is fast. The portion of polysaccharides plus lipids existing on the exterior of the cells is dynamically encompassed in the radionuclide accretion. This accumulation is also aided by the occurrence of carbonate groups existing on the macrophyte body (Popa et al. 2006).

Table 12.3 Aquatic plant species prospective of accumulating radioactive nuclides

Free-floating macrophyte species	Radioactive nuclide	Reference
Lemna minor (Common Duckweed)	Lanthanum, cobalt, and technetium	Hattnik et al. (2000), Wolterbeek (2001), Weltje et al. (2000), and Popa et al. (2006)
L. gibba (gibbous duckweed)	Cobalt, caesium	El-Shinawy and Abdel Malik (1980)
Azallo filiculoides (water fern)	Caesium and cobalt	Popa et al. (2004)
Ceratophyllum demersum (hornwort)	Caesium, cobalt, and strontium	El Shinawy and Abdel-Malik (1980), Abdel malik et al. (1973), Shokod'Ko et al. (1992), and Bolsunovskiĭ et al. (2002)

Table 12.4 Free-floating aquatic macrophyte which can be useful in removing/accumulating mentioned organic pollutants

Free-floating macrophyte	Contaminant	Reference
E. crassipes	Ethion, dicofol, cyhalothrin, pentachlorophenol	Roy and Hanninen (1994) and Xia et al. (2002a, b)
L. gibba	Phenol, 2,4,5-TCP	Hafez et al. (1998) and Sharma et al. (1997)
L. minor	2,4,5-TCP, halogenated phenol	Tront and Saunders (2006) and Tront et al. (2007)
Spirodela oligorrhiza	Organophosphorus compounds, organochlorine compounds, and chlorobenzenes	Gobas et al. (1991), Wolf et al. (1991), Rice et al. (1997), and Gao et al. (2000)

12.7.3 Organic Pollutants

Free-floating aquatic macrophytes have the ability to remove, isolate, as well as transfer organic pollutants (Day and Saunders 2004; Larsen et al. 2005; Tripathi et al. 1996). The ability of intake as well as accretion of organophosphorus, organochlorine compounds, as well as chlorobenzeneh has been reviewed broadly (Gao et al. 2000; Gobas et al. 1991; Rice et al. 1997; Windham et al. 2001). The quantity of organic contaminants isolated by macrophytes varies with the species, its tissue biochemical, as well as physicochemical characteristics (Table 12.4).

12.7.4 Inorganic Contaminants

Free floating aquatic macrophytes are able to eliminate a good proportion of nutrient contents from wastewaters (Madsen and Cedergreen 2002). The species found useful in this regard are *Ceratophyllum demersum* and Ei*chhornia crassipes*. These species have successfully eliminated nutrients like N and P from hydroponic systems and microcosms (Madsen and Cedergreen 2002; Sinha et al. 2002). The nitrogen up taken by macrophytes is assimilated in the form of ammonium as well as nitrate (Sinha et al. 2002). The roots and leaves uptake relatively greater quantities of inorganic N and P (Madsen and Cedergreen 2002).

12.8 Conclusion

Phytoremediation of polluted waters by using free-floating aquatic macrophyte is an advantageous alternative. Various free-floating macrophytes are being used for the remediation of numerous contaminants from aquatic environs. Water hyacinth (*E. crassipes*), duckweed (*Lemna*, *Spirodela* and *Wolffia*), water fern (*Azolla* spp.), *Hydrilla* (*H. verticillata*) and water cresses (*N. officinale*, *N. microphyllum*) have been recommended for phytoremediation because of their ability for elimination of diverse contaminants from aquatic ecosystems. Numerous studies have reported that using these free-floating macrophytes is a worthy choice to cleanse contaminated water. However, managing and discarding of used macrophytes is a challenging task for the efficacious execution of phytoremediation expertise.

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Chapter 13
Genetically Modified Microbes as Biofertilizers

Rohaya Ali, Khurshid Dijoo Zulaykha, and Nasreena Sajjad

13.1 Introduction to Biotechnology

Biotechnology is a divergent and multidisciplinary field of biology. Biotechnology is basically the utilization of biological substances like microbes or cellular constituents in a controlled manner for the advantage of mankind. In other words, biotechnology is an integrated utilization of biochemistry, microbiology, and engineering knowledge for the utilization of microbes, cultured cells, or tissues to their best (Okeno et al. 2012). In the past, people exploited microbes for production of cheese, bread production, or brewing alcohol; even if the process of fermentation was not tacit, comprehensively human beings have sustained their search for enhancing the natural potential of microbes and making them competent for novel methods. At present, the application of biotechnology is highly complicated. Now, scientists can manipulate living organisms and transfer genetic matter among them, producing transgenic organisms. The present significance of biotechnology is largely in the area of biomedicine and agriculture. Present methods permit the construction of novel and enhanced food. Novel vaccines and antibiotics have been produced against various diseases like AIDS, cancer, and many hereditary diseases. Biotechnology is also used in the area of biofuel production, mining, and pollution control (Fig. 13.1). Genetically modified microbes and plants are utilized to remove toxic chemicals from oil spoil spills or industrial effluents (Chen et al. 2007).

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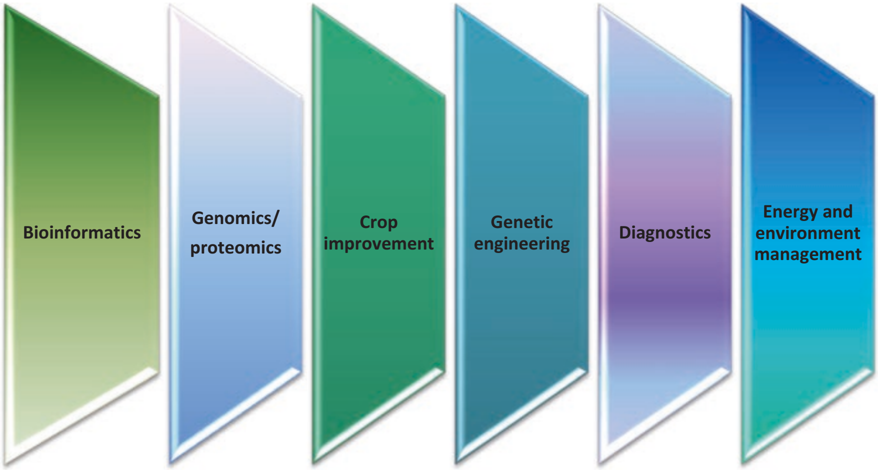

Fig. 13.1 Role of biotechnology for sustainable development

Besides, improved superiority of life there exists countless and exhilarating opportunities in various other fields of biotechnology (e.g., green, red, or white biotechnology).

Green biotechnology is a vital field of contemporary biotechnology. Its foundation is on the crop enhancement and manufacture of new crop products (McAllister et al. 2012). It comprises three major areas which include: plant tissue culture, plant genetic engineering, and plant molecular marker-assisted breeding. Plant tissue culture involves the production of the whole plant or part of it under laboratory conditions. Its main advantage is the quick manufacture of plant materials like citrus fruits, banana, etc. On the other hand, plant genetic engineering involves the introduction of beneficial genes from one living organism to other (Dana et al. 2006). This generates improved varieties of crops with enhanced production (Brookes and Barfoot 2009). In case of plant molecular marker-assisted breeding, molecular markers (specific short sequences of DNA) are accountable for a preferred attribute. Thus, improved properties like disease resistance can be achieved (Horvath et al. 2012).

White biotechnology is concerned with industries. It utilizes enzymes, bacteria, yeast, or molds to produce valuable products. It results in the manufacture of wide range of bioproducts like vitamins, antibiotics, detergents, etc. (Beuno et al. 2016).

Red biotechnology is concerned with medical biotechnology. It involves genetic manipulation of organisms to create antibiotics. Herein, the human body's own tools are utilized to eliminate the pathogens. It is of immense significance in the conventional drug discovery and also aids in improving the potential for cure, anticipation, and analysis of diseases (Becker et al. 2008).

13.2 Biofertilizers

Chemical fertilizers quickly perk up the development and yield of crops and are hence gaining fame around the world. Conversely, extensive use of such fertilizers causes serious ecological problems. Nitrate leaching and contamination of ground water are due to increased exploitation of fertilizers. Inorganic fertilizers like calcium nitrate, ammonium chloride, and sodium nitrate produce greenhouse gases that results in pollution. Elevated levels of greenhouse gases and heavy metal uptake by plants are major causes of environmental damage. Eutrophication of freshwater is also due to chemical fertilizers. Furthermore, chemical fertilizers can eradicate the advantageous microbial or insect community of the soil (Liu and Golden 2002). Fortunately, nature has bestowed the soil with a variety of microbes with specific mechanisms to overcome this challenge. This mechanism besides maintaining soil quality also works in tandem with plants as an element of the ecosystem. Such mechanism is what constitutes "biofertlizers" (Khosro and Yousef 2012). Biofertilizers constitute a central part of green agriculture. Biofertilizers contain proficient strains of microbes, organic products, and departed and rotten parts of plants which supply nutrients to soil. It progressively elevates crop yield by means of enhancing soil fertility. They change the unavailable form of nutrients to the accessible form by escalating the population of microbes in the rhizosphere (Leonardo et al. 2006). Microbes are accountable for delivering soluble nutrients to crops. These are helpful in a variety of ways that include solubilization of plant nutrients (like phosphorus, sulfur, etc.) and fixing of atmospheric nitrogen (Fig. 13.2). They also encourage the formation of growth-promoting phytohormones like cytokinins and auxins. They also defend the plant against various abiotic and biotic stresses (Mitragotri et al. 2014; Chang and Yang 2009).

Biofertilizers aid plants in accessing the nutrient present in its surroundings. The microbes frequently employed as the biofertilizers include *Rhizobium*, *Azotobacter*, *Anbaena* (nitrogen fixers), *Pseudomonas putida*, mycorrhizal fungi, etc. Likewise, phytohormone/auxin-producing bacteria could also be utilized as biofertilizers (Somasegaran and Springer 1994). These microbes enhance growth and development in plants. The grievance from agriculturalists regarding the effectiveness of biofertilizer is their improper storage and the larger time period between field application and production (Youssef and Eissa 2014). This restricts their employment due to compatibility and constancy issues under diverse soil environments. For this reason, improved shelf life is the basis for the popularization of biofertilizers (Adesemoye and Kloepper 2009).

Currently, a variety of marketable biofertilizers are obtainable and a variety of mechanisms have been formulated to guarantee maximum viability of the microbes used in such formulations (Bhattacharyya and Jha 2012). These strategies include: optimization of biofertilizer formulation, usage of thermo-resistant or drought-resistant and genetically modified strains, and employment of liquid biofertilizers.

For dexterity, a carrier substance is utilized as a vehicle for the microbes which are to be used as biofertilizers. Carrier substances include clay, vermiculite, peat, seed, lignite powder, rice bran, charcoal, etc. For enhanced shelf life of biofertilizer

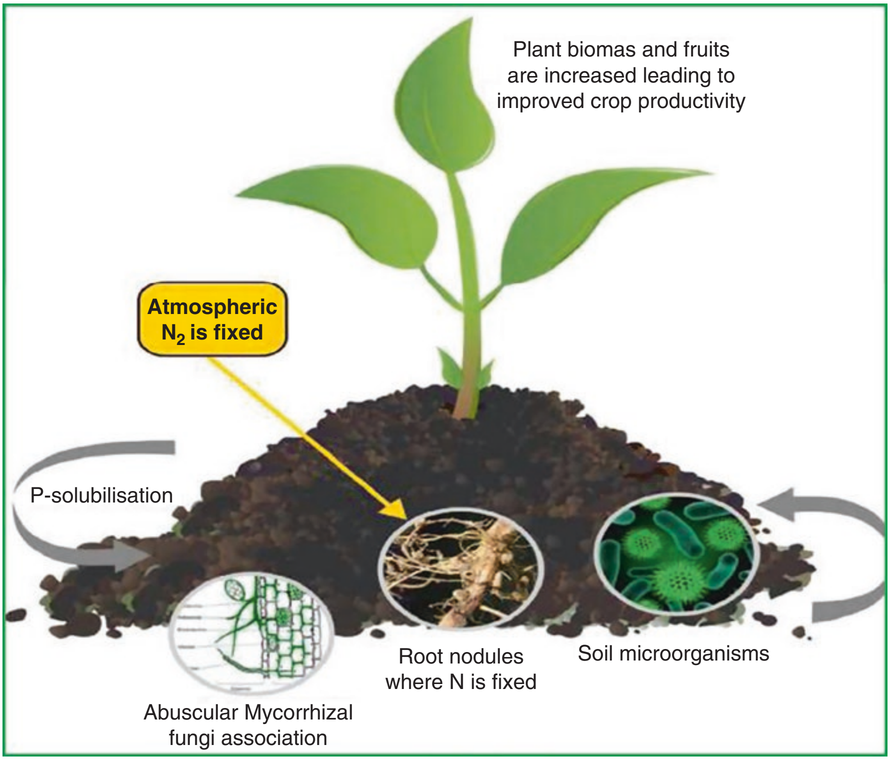

Fig. 13.2 Biofertilizer technology utilizes plant-microbe interactions in influencing plant growth and development. (Raimi et al. Cogent Food & Agriculture 2017)

formulation, a combination of these carriers is employed. Likewise, pre-sterilization of carriers is done to enhance the shelf life of microbes (Wani et al. 2013). Liquid biofertilizer formulation is an important aspect to improve shelf life. These formulations enclose an adequate amount of cell protectants and nutrients that are responsible for the extended shelf life of biofertilizers. Besides, these formulations can endure huge temperature range (Santos et al. 2012).

Biofertilizers got commercialized with the launch of “Nitrogin” by Hiltner and Nobbe. This preparation was for legumes. Later microbial inoculants for legumes were made like “Alnit.” It proved advantageous for the development of non-leguminous plants. These bacteria were recognized to be local ammonifiers. Discovery of *Azotobacter* and *Clostridium* developed a new field for investigating economical bacterial fertilizers (Goswami et al. 2014). The rhizosphere of these plants contains a range of species of soil bacteria that enhance plant growth by numerous ways. Such bacteria are jointly known as plant growth-promoting rhizobacteria (PGPR). One of the ways is through fixing of atmospheric nitrogen which enhances the accessibility of exploitable form of nitrogen in the rhizosphere. They also promote symbiosis between plants and microorganisms (Mfilinge et al. 2014). In general, the benefits of biofertilizers in agriculture can be summed up in Fig. 13.3.

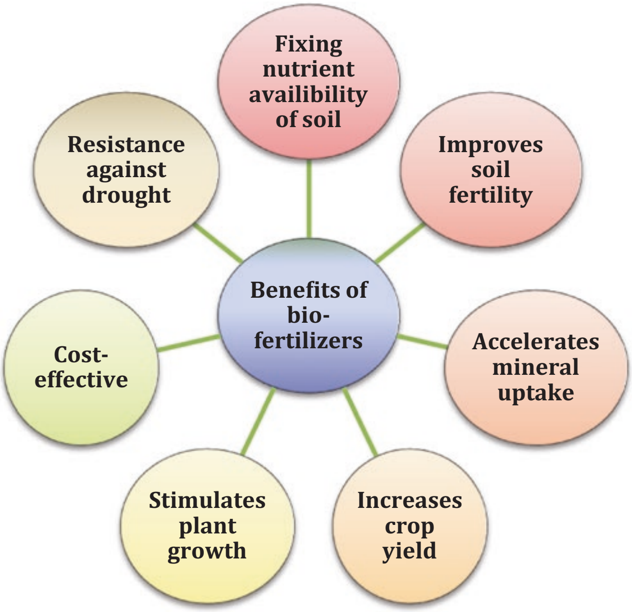

Fig. 13.3 Benefits of biofertilizers

13.3 Categorization of Biofertilizers

Biofertilizers are categorized into various types on the basis of microorganisms they contain (Chun–Li et al. 2014). The different types of biofertilizers are discussed below.

13.3.1 Symbiotic Biofertilizers

Symbiotic microbes infect root tissues and form new structures. In many cases, the application of molecular biology tools allows the discovery of the genes and signals concerned with the positive interaction between the microorganism and the plants (Raja 2013). The main symbiosis relating to agricultural application as biofertilizers is considered below.

13.3.1.1 Rhizobia

Rhizobium is an illustration of a symbiotic association colonizing legume roots and fixes the atmospheric nitrogen. It has capability to fix atmospheric nitrogen in leguminous and non-leguminous plants. The different genus and species inhabiting legumes root nodules are usually referred to as rhizobia. These involve alpha-proteobacterias, such as *Rhizobium*, *Bradyrhizobium*, *Sinorhizobium*, *Mezorrhizobium*, *Azorhizobium*, *Allorhizobium*, *Agrobacterium*, and beta-proteobacteria, such as Burkholderia. The best model describing the interaction between rhizobia and legume roots includes flavonoids/isoflavonoids molecules released by the plants which induce bacterial genes and hence trigger the synthesis of LCO (lipo-chitin-oligosaccharides) molecules, which in turn control infection and nodule growth in the root tissue (Rajaram and Apte 2008). Usually, it pierces the root hair and multiplies there in special root structures called root nodules. The quantity of nitrogen fixed depends on host, strain of *Rhizobium*, and existing environmental conditions. They are very proficient biofertilizers for legumes as far as the magnitude of nitrogen fixation is concerned. The nod, nif, and fix genes control the nodulation and nitrogen fixation by the bacterium (Liu and Golden 2002).

13.3.1.2 Blue Green Algae/Cyanobacteria

BGA (Blue green algae) are the most ancient organisms possibly the first among those that started evolving oxygen. These appear in numerous shapes (single celled, branched, or unbranched with filaments). The majority of them possess special structure called heterocyst whose role if to fix nitrogen. The algae that are frequently applied in fields belong to *Anabaena*, *Nostoc, Scytonema, Tolypothrix*, etc. (Buikema and Haselkon 2001). These are widely used in rice fields. BGA secrete numerous growth-promoting substances like amino acids, vitamins, polysaccharides, sugars, etc. which boost the yield of crops (Schiefer et al. 2002).

13.3.1.3 Mycorrhiza

Mycorrhiza is the best example of the symbiotic association between fungi and plant roots (higher plants). The fungi defend the plants against various stresses and enhance their growth. These fungi colonize the root cortex and mycelia of the plants and help them to obtain nutrients from soil. These fungi are cosmopolitan in soil and are seen in the roots of Thallophytes, Gymnosperms, Pteridophytes, and Angiosperms. Plants, on the other hand, protect fungi from root pathogens and also provide them with carbohydrates, hormones, nutrients, etc. The mycorrhizal plants have better forbearance to poisonous metals, salinity, elevated soil temperatures, and unfavorable pH. Such plants also resist transplantation shocks. They play a significant task by enhancing growth and nutrient uptake in plants (Vessey 2003).

13.3.2 Free-Living Biofertilizers

Since the description of PGPR by Kloepper and Schroth (1978), many different bacteria genera have been described as PGPR: *Pseudomonas, Azospirillum, Azotobacter, Gluconacetobacter, Herbaspirillum, Bacillus, Burkholderia, Erwinia,* *Caulobacter, Azotobacter, Chromobacterium, Serratia, Microccocus, Flavobacterium, Actinobacter, Enterobacter, Arthrobacter, Agrobacterium, Hyphomycrobium*, and fungus such as *Trichoderma*, among others (Gupta 2004).

Many PGPR have been described as endophytic bacteria. It is not clear if the plant growth promotion effects are a consequence of plant-microbe interaction in the external part of the rhizosphere or if an endophytic state is necessary (Hayat et al. 2010). Many different mechanisms have been claimed to be responsible for the plant growth promotion effect after in vitro experiments under controlled conditions. In some cases, the use of appropriate mutants helps in the definition of these mechanisms. But since different mechanisms are always present in a single strain, it is almost impossible to know which are the main mechanisms operating and driving the plant growth promotion. Irrespective of the real mechanisms operating in PGPR with a positive effect in the field, the use of these microorganisms has dramatically increased in recent years and will probably continue to grow because biofertilizers appear as a valuable opportunity for future sustainable agriculture. Many commercial products already exist which are based on *Pseudomonas* or *Azospirillum* strains in the market (Yang et al. 2009). The different mechanisms operating in PGPR can be classified as: N_2 (nitrogen) and P (phosphorus) nutrition effects, and plant root development and fitness mediated by phytohormones (Ahemad and Mohammad 2010).

13.4 Phytohormone-Mediated Mechanism of Plant Growth-Promoting Bacteria (PGPB)

One of the most visible effects on plants after inoculation with PGPB is the huge development – and sometimes changes in the architecture – of the root of the plant. This general improvement of root growth, including root-hair development, is one of the characteristic phenotypes of the interaction plant-PGPB.

It is likely that water and mineral uptake is consequently improved because of the increase in the root system, although the specific mechanism is not completely clear. Changes in hormone balance, enhancement of proton-efflux activity, and modification in a wide range of related enzymatic activities would be part of the mechanisms behind this phenotype (Backman and Sikora 2008).

13.4.1 Cytokinins

The role of cytokinins in the promotion of root development is not clear, but cytokinin-producing PGPB stimulate nodulation in legumes when co-inoculated with rhizobia. Besides, it has been demonstrated recently that there is a Nod factor-independent mechanism for infection and nodulation, possibly mediated by rhizobial cytokinin. This particular area deserves more attention in the future (Riefler et al. 2006; Sokolova et al. 2011).

13.4.2 Auxins

The general root improvement phenotype can be reproduced by replacing phytohormones with PGPB. Auxin-related substances, such as indole acetic acid (IAA), appear to be involved in one of the most important mechanisms regarding the general root development improvement. Nevertheless, bacterial production of IAA in plants has not yet been demonstrated. There are no IAA completely deficient mutants, but IAA attenuated mutants were ineffective as PGPB, compared to parental strains (Aloni et al. 2006; Ahmed and Hasnain 2010).

13.4.3 Ethylene

Ethylene is related to general plant responses when a stress condition appears, even if it is a very low stress situation. When this happens, the plant synthesizes ethylene and stops its growth temporarily. This is because of the regulatory effects of ethylene on different cell functions. 1-aminocyclopropane-1-carboxylate is a precursor of ethylene synthesis. The enzyme ACC deaminase is present in some bacteria which can even use ACC as C (carbon) and N sources (Butterbach et al. 2013). When ACC deaminase is expressed by rhizospheric bacteria, root growth and development is enhanced. It is probably because of the elimination of the inhibitory concentrations of ethylene produced by the plant. This enzyme is not present in every bacteria and its activity is codified by a single gene acdS. The introduction of this gene from *Pseudomona putida* into other bacteria species confers plant growth-promoting functions to the recipient bacteria that are absent in the parental strain. This represents a potential biotechnology-based tool to improve microorganisms to be used as biofertilizers (Reid 1981).

13.4.4 Helper Bacteria

In the studies of plant microbe interaction which induced some kind of plant growth promotion, there are other cases that do not fit into the previous definitions but which can be considered as another kind of biofertilizer. That is the case of bacteria which improve a plant-microbe interaction as a third partner in the interaction. An example can be found in rhizospheric actinomycetes isolated from legumes or actinorhizal nitrogen-fixing nodules which are able to stimulate nodulation, consequently nitrogen fixation in the plant, and finally plant growth. This tripartite plant-microbe interaction is not well known in terms of mechanism. However, it clearly shows that biofertilizers can be improved by the use of more than one microorganism at a time (Egamberdiyeva 2007).

13.5 Significance of Genetically Modified Microbes in Agriculture

Numerous genera of bacteria have great impact on growth and development of plants. Among these are the bacteria that are used as biocontrol as they are able to curb plant diseases. Some other bacteria increase plant growth by increasing the availability of nutrients. Such bacteria are known as plant growth-promoting rhizobacteria (PGPR). These are applied either directly to soil or as seed coating. Nevertheless, to put forth their growth-enhancing effect, huge quantities of the introduced PGPR should stay alive in the rhizosphere (root) and soil. Accordingly, the effectiveness of PGPR is not always enough for marketable usage, and there is a requirement to advance their performance. One of the probable ways is to genetically modify the microbe to ease up their survival (Brown et al. 2015).

Genetically modified organisms symbolize a genetic reserve. These microorganisms may find application as donor or recipient of genes of interest. Microbes play a vital role in various sectors of agriculture, pharmaceutical industries, and environmental management (Cohen et al. 1973). Genes of microbes can be optimized or improved by means of various genetic modifications using Recombinant DNA technology (Tabashnik et al. 2011). Usually, this is dependable on the recognition and selection of the mutants with favorable traits. In numerous cases, the usage of molecular biology tools or recombinant DNA technology allows the discovery of the genes and signals concerned in the advantageous interaction (endophytic, mycorrhizal, and diazotrophic) between the microbe and plant. These symbiotic interactions can assist plant growth and development through nitrogen uptake, siderophore production, phosphate solubilization, etc. (Ruiz et al. 2010; Ritika and Uptal 2014).

Recombinant biotechnology offers an advantage to decrease the employment of synthetic fertilizers. Biofertilizer technology has considerably developed in the market. The nature of multiple mechanisms discovered for PGPR actions intimidate the use of genetically modified organisms as biofertilizers (Tabashnik et al. 2011). Further, the knowledge of microbial ecology and its dynamics will surely enhance the biofertilizer technology (Kakumanu et al. 2012). Microbes are particularly targeted for genetic improvement since they are given huge importance in modern agriculture as they are used as biofertilizers. Biofertilizers represent an alternative to synthetic fertilizers which are facing lots of disparagement due to their negative impact on the ecology and human wellbeing. Thus, there is an important requirement to build up eco-friendly control using existing microbes. Such microbes would offer protection to plants against pathogens and would be economical, reliable, and effective (Pishchik et al. 2002). To obtain this target, better-quality strains are needed. Thus, genetically modified microbes could be used for this purpose. Efforts are in progress to formulate proficient biofertilizers compatible with a broad choice of plants and soil by means of genetically engineered techniques. For example, biofertilizers have been formulated based on nitrogen-fixing rhizobial bacteria occurring naturally in the nodules of leguminous plants. Nevertheless, these microbes are not competent enough to supply nitrogen to non-legumes. In such cases, genetic engineering is of special importance, as it assists in the development of efficient delivery systems. In this way, non-legumes could be grown together with symbiotic rhizobial root nodules devoid of externally applied nitrogen fertilizers (Aloni et al. 2006). The foreign genes used for transforming microbes could be integrated into host genome. For this, the regulatory area of the gene should be modified in promoter or terminators in sites so as to optimize the inserted gene's function within the host. Adding a particular gene which can bestow biocontrol ability could improve the biocontrol ability of microbes lacking such genes (Dash et al. 2016). For example, many rhizobacteria with biocontrol activity produce chitinases. However, few rhizobacteria like *Pseudomonas putidri and Rhizobium melliloti,* both of which are outstanding root colonizers, are deficient in synthesizing chitinase (Bagwan et al. 2010). Incorporation of the chitinase gene into their genome has made them proficient in defending the plant against fungi (Huang et al. 2001).

Nitrogen-fixing property of *Rhizobium* inoculants could be augmented by means of genetic engineering tools. An additional way is by planting the crops that use nitrogen more proficiently. An example of such crops is genetically modified Canola which exhibits a noteworthy decline in the amount of nitrogen fertilizer that is leached into the soil or lost into the atmosphere, and hence it improves the economies of farmers through the enhanced profitability. Moreover, biofertilizers when formulated by means of molecular technologies can improve the cellular pathways of phytohormone production like auxin, cytokinin, etc. which assist in plant growth and development (Nautiyal et al. 2008). Similarly, numerous pseudomonads in the soil manufacture siderophores that can chelate Fe ions, and thus escalate Fe uptake by the plants. The genetically altered strain of *S. melliloti* (RMBPC-2) has added genes that manage the enzyme nitrogenase from plants to bacteria (Boccia and Sarnacchiaro 2015). Likewise, *Trichoderma* species are extensively found in the soil. *Trichoderma harzianum* is an efficient rhizopsphere colonizer and can parasitize disease-causing fungi. Many extracellular enzymes like glucanases, chitinases, and proteases synthesized by *Trichoderma* have been improved by the addition of chitinase genes, especially *S. marcessens* (Awais et al. 2010). Thus, such genetically modified strains could act as efficient biofertilizers and will aid in crop improvement.

13.6 Genetically Modified Organisms in Soil and Their Survival

Microbes introduced in soil face various biotic and abiotic factors that affect their survival rates. High moisture content, hydrogen ion concentration, and clay content have a constructive effect on microbial survival. On the other hand, presence of competing microbes or dry periods and predation by protozoa affect the microbial growth negatively (Castiglioni et al. 2008). Among the microbes that are well adapted to rhizosphere are members of genera *Rhizobium*, *Pseudomonas*, *Bacillus*, *Azotobacter*, *Azospirillium, Agrobacterium,* and *Xanthomonas.* Microbial survival is governed by the interaction between the environment and bacterial physiology. As a result of these interactions, bacteria can switch metabolism to various physiological states. They can either form dwarf cells or become resistant to stress. Besides, they can form exopolysaccharides for defense or can form spores or associations with plants (Oh et al. 2009). The survival rates of these bacteria can be studied by following the wild-type strain. In reality, this extrapolation needs to be applied with few security measures. To begin with, the expression of the inserted gene needs a surplus energy that could lessen their environmental fitness. Besides, the addition can disrupt some unfamiliar functions declining the competiveness of the strains. Lastly, the genetically modified microbes can acclimatize to the prevailing ecological conditions through natural selection. This statement is supported by the fact of evolutionary adjustment or adaptation of bacteria to degrade 2,4-dichlorophenoxyacetic, a herbicide, to acid. This resulted in augmented competitive fitness to usage of succinate as a substrate. Genetically modified microbes have been observed to survive better than the normal wild strains. Nevertheless, improved endurance of genetically modified microbes has been in frequently been observed under field circumstances. Moreover, some modified microbes have been found to outcompete by their parental strains. Besides, it is believed that the occurrence of a number of constitutively expressed marker genes in genetically modified microbes has negative consequence on its survival in competition to wild-type strain (Nelson et al. 2007).

13.7 Environmental Impact of Genetically Modified Microbes

Genetically modified microbes have diverse effect on the environment. It encompasses events like organic substrate, changes in population structure, displacement of species, production of toxic metabolites, changes in population structure, which may lead to disorder in ecological processes (Snow et al. 2005). Minute changes in community symphony are hard or even impracticable to resolve, and their connection to microbial diversity and ecosystem functioning is not quite obvious (Lemaux 2008). Different bacteria perform different functions. Therefore, vanishing of a small number of bacteria would be hard to sense (Wang et al. 2003). Thus, it may be concluded that only severe disturbances might influence the soil microbial communities to the extent that only few functions will be badly affected.

Cultural bacteria are one of the main troubles in microbial ecology. However, various DNA/RNA-based techniques have been used to detect the impact of genetically modified microbes on the microbial community. These techniques do not demand the culture of bacteria. Besides, techniques like gel electrophoresis, restriction fragment length polymorphism, single strain conformation polymorphism, etc. are used to examine shifts in community structures (Okeno et al. 2012; Sandeep et al. 2016).

13.8 Role of Biofertilizer Strains

Genetically modified microbes offer an improved nutrient accessibility to crops, and thus augment development in plants. The most significant biofertilizer are bacteria, like *Rhizobium* and *Azospirillum* that mainly assist in nitrogen fixation. Symbiotic bacteria like *Rhizobium, Sinorhizobium*, and *Bradyrhizobium* form root nodules in leguminous plants and fix nitrogen. These bacteria have been reported to survive in soil for years, in some cases even devoid of definite host (Ngwako 2008). Such microbes have been utilized extensively as plant inoculants to increase crop productivity. Nevertheless, yield enhancement is changeable, and the success of inoculants seems to be reliant on competition with indigenous strains that are generally least effective (Qaim 2009).

13.9 Genetically Modified *Rhizobium* and *Azospirillum* Strains

Plants get all their nutrients from the soil except carbon dioxide which plants obtain from the air. Nature has developed diverse mechanisms to provide nutrients to plants through renewable resources. One of the best examples is nitrogen fixation by leguminous plants (Horvath et al. 2012). Unluckily, not all plants are gifted with such mechanisms. Thus, plant yield greatly depends on the use of chemical fertilizers. Some fertilizers are very mobile and are, therefore, supplied in huge amounts to plants. Many fertilizers are very mobile in the soil and are supplied in greater concentration than required by the plant. The loss of valuable compounds is not only of economic significance, but also leads to grave ecological problems. Besides, it may also accumulate in the soil. Numerous strategies have been designed to enhance nutrient uptake by crops (Newell-McGloughlin 2008). These comprise formulation of plant growth-promoting bacteria and slow release fertilizers (Lavakush et al. 2014).

PGPR can put forth their consequence in both direct and indirect way. For direct way, phytostimulation is the best example (Ma et al. 2003). Many bacteria able to produce plant growth stimulating factors like cytokinins and auxins. This promotes plant growth and aids in enhanced nutrient uptake by plants. Indirect path includes exercise of biocontrol of pathogens and deleterious microbes (Brooks and Barfoot 2009).

13.10 Genetically Modified *Azospirillum* Strains Enhance Nitrogen Uptake

Azospirillum is known for its property of enhancing plant growth through enhancing nitrogen uptake. This is done via production of phytohormones by *Azospirillum* strains (Gonzalez et al. 2015). Nonetheless, the mechanisms by which these bacteria create phytohormones are still not definite and need an improved understanding. To clarify these mechanisms, numerous significant queries should be addressed:

- The formation of GM *Azospirillum* strains with known production levels of Indole-3-acetic acid
- The biochemical and genetic basis of the production of Indole-3- acetic acid
- Testing the result of these genetically modified bacteria on plants and on the environment under the field milieu

Currently, GM strains of *Azospirillum* with such fundamental characteristics are obtainable. Experiments with these strains are mainly focused on nitrogen fixation and impact on residential microbial population and plant growth. These experiments are carried out under lab conditions (green house and growth cabinet). In spite of the improvement of these experiments, broad and vigilant testing under control is needed prior to field release of such strains.

13.11 Genetically Modified Rhizobium Strains with Improved Competitiveness

Legume inoculation with proficient nitrogen fixing bacteria is broadly utilized to augment production in leguminous crops. Such inoculation is not at all times booming because native soil microbes with less nitrogen-fixing ability can outcompete the introduced strains in terms of nodulation initiation. For better use of rhizobial inoculants, their ability to dominate nodulation is must (McAllister et al. 2012). Thus, inoculants strains are modified in such a way that maximum quantities of root nodules are formed. In this backdrop, *Sinorhizobium melliloti* has been genetically modified to enhance nodulation in alfalfa roots. This genetic alteration involves alteration of the expression of *nifA* gene which is accountable for the management of all other nitrogen fixation *(nif*) genes (Bakshi 2003). Thus, wild-type strains were mixed with GM strains, and it was found that the latter occupied most of the nodules of alfalfa roots. The exact means of this augmentation is not implicit, but it is hypothesized that *nifA* regulates the expression of genes other than *nif* cluster that aids in nodule development (Beyer et al. 2002).

The capability of strains of *Rhizobium* to proficiently distinguish the plant root is an important characteristic that adds to their nodule competiveness (Kanchiswamy et al. 2015). It is very significant since the proficient inoculation means lesser dosage of bacterial strains (Overton 2014). In addition, the progress of the inoculation strain toward the root is another important factor governing the competiveness. It has been found that in genetically engineered flagellated *R. leguminosarum* strains, the nodulation is much more compared to flagella deficient non-motile strain. Thus, root attraction is also important for better plant development and growth (Liddycoat et al. 2009; Barrows et al. 2014).

13.12 Effect of Genetically Modified *Rhizobium* on Arbuscular Mycorrhizal Fungi

Mycorrhizal fungi represent the group of fungi that form symbiotic association with the plants. Research has been done to see whether the GM *Rhizobium* strains enhance the nodulation or interfere with the symbiotic association in plants. It has been observed that GM *S. meliloti* strain do not hamper mycorrhiza formation but enhances nodulation. Genetically modified *meliloti* increased arbuscular myccorhizal colonization units and augmented nutrient acquirement capacity of mycorrhizal plants (Papagianni 2004; Van 2007).

13.13 Field Release of Genetically Modified Rhizobium Strains

Numerous *Rhizobium* species have been genetically modified to perk up the nitrogen fixation or to study their survival by utilizing marker genes through field trials. Tn5-marked legumino serum strain persisted for 5 years when introduced into the field. The perseverance of the strain was credited to the type of soil, climate, and the host plant (Huang et al. 2004). The usage of GM *R. meliloti* strain, with supplementary copies of dctABC and nifA genes, had been found to upregulate alfalfa yield under field trials. Nonetheless, at sites with native rhizobial populations, alfalfa productivity did not increase. The outcome of a Tn903-marked *R. meliloti* strain introduced into alfalfa field plots was calculated and it was observed that cell number declined drastically after inoculation (Podile and Kishore 2007; Hussain et al. 2002).

Effect of wild-type strains and genetically modified *S. meliloti* strains was studied on indigenous microbial communities by means of restriction fragment length polymorphism and temperature gradient electrophoresis. Wild-type strains had only limited effects compared to GM strains. Likewise, Luc-marked *S. meliloti* in a field research with *Medicago sativa* was analyzed. The study was observed for 12 weeks. Single-strand cell protein banding patterns revealed shifts confirming the effect of inoculum on native microbial population (Gouse 2012; Scalenghe et al. 2012).

Genetically modified *Rhizobium leguminosarum* strains, marked with HgCb resistance genes (mer genes) and lacZ genes, were inoculated in the rhizosphere of *Pisum sativum*. Three modified strains were utilized. In these strains, nitrogen-transforming ability was monitored. The field experiments revealed that all tested strains colonized the rhizosphere to the same extent. These results specify that even though the presence of the plant had a substantial impact on carbon mineralization in soil, the impact of genetically modified *Rhizobium* strains is almost identical to that of wild-type strain (Ritika and Uptal 2014). *Alcaligenes faecalis,* a non-nodule forming bacterium, has been genetically modified and introduced into rice fields in China, to observe its effect on crop productivity. *A. faecalis* was genetically modified by the insertion of a constitutively expressed nifA regulatory gene (Gray and Smith 2004). Nitrogen fixation got enhanced compared to non-treated fields. Besides, there was a considerable increase in the yield. The effect of this introduction was studied by DGGE of amplified 16S rDNA in a microcosm experiment. These strains survived well in the rhizosphere. The survival of the strain and the augmentation in crop yield denote GM *A. faecalis* is a good candidate for commercial use. Besides, it is ecologically safe strain (Metsheka et al. 2002).

13.14 Conclusion

Biofertilizers represent the central part of green agriculture. These contain proficient strains of microbes, organic products, and departed or rotten parts of plants which provide nutrients to soil. These gradually promote crop yield by increasing soil fertility. It is necessary to identify the positive aspects of biofertilizers so as to apply it to modern agriculture. Usage of biofertilizers containing advantageous microbes improves the crop productivity to a larger extent. Biofertilizers play an important role in maintenance of soil quality. This would in turn guard the environment and would require less expenditure. Besides, biofertilizers when formulated using genetically modified strains can improve the biological pathways of production of plant growth-promoting substances and hence enhance the yield. Genetically modified microbes offer plentiful advantages in this area, as particular metabolic processes could be tackled with extra accuracy and totally novel functions could be introduced in microbes. In spite of the fact that field trials with GM biofertilizers are limited, the preliminary results regarding their use are promising with respect to enhanced performance in modern agriculture. Genetically modified biofertilizers have been introduced with enormous success regarding their activity and survival rates. Till date, non-target effects of genetically modified biofertilizers that have been reported are insignificant and diminutive in comparison to natural variants. Thus, overall genetically modified microbes contribute to an improved nutrient accessibility in plants and aid in plant growth or development.

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Chapter 14
Nanotechnology: A Modern Technique for Pollution Abatement

Bhat Mohd Skinder and Saima Hamid

14.1 Introduction

In 1974 “Professor Norio Taniguchi” coined the term “nanotechnology” at the University of Tokyo. Translated version of nanotechnology into English: “Nanotechnology is the production technology to get the extra high accuracy and ultra-fine dimensions, i.e., the preciseness and fineness on the order of 1 nm (10^{-9} meter in length).” Nanomaterials are defined as those materials which have structured components with at least one dimension less than 100 nm (Oberdorster et al. 2005). Nanoscience is the study of phenomena and material manipulation on atomic, molecular, and macromolecular scales in order to realize and exploit properties that vary considerably from those on a larger scale. Nanotechnology not only encompasses science, engineering, and technology on a nanoscale, but it includes imaging, measuring, modeling, and manipulating matter (Singh et al. 2020). Conventional techniques such as landfill disposal and isolation are somewhat efficient but costly and take enough time to reach targets, but nanotechnology could be a useful substitute for current site remediation practices (Salipira et al. 2007). Conventional techniques also produce undesirable byproducts like dichloroethylene, and vinyl chloride are byproducts during in situ remediation of trichloroethylene. It is extremely difficult to operate remediation of aquifers with existing standard procedures, because the “contaminants” such as “chlorinated hydrocarbons” rove to the water-table and core areas. Nanotechnology can effectively target all these limitations (Masciangioli and Zhang 2003). Nanoparticles offer numerous benefits and

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can be transported easily due to their small size and large surface area (large surface results in high enzymatic activity) (Karn et al. 2009). Thus the particle size is extremely small in size and can be injected into the very small spaces of the underground contaminated sites without any excavation for the longer period of time as it remains active for a long time for the better treatment process (Zhang 2003). However, studies revealed that these NPs have limited movement from their injection point in remediation processes (Tratnyek and Johnson 2006). Nanoparticles can be attached to a concrete matrix to be used as free particles to treat "polluted water" or "gaseous stream," and movement of these NPs can be controlled by sedimentation process (Zhang 2003; Bora and Dutta 2014). Nanotechnology offers a wide variety of material types, including nanoscale zeolites, carbon-nanotubes, enzymes, dendrimers, metal-oxides, and bimetallic-particles, used for remediation purposes. Iron being a powerful reducing agent thus has an essential role in the remediation of pollutants like poly-halogenated organic compounds and heavy metals in the environment (Karn et al. 2009). Iron nanoparticles are most frequently used in remediation of surface pollutants such as petrochemicals and even subsurface pollutants like pesticides, chlorinated solvents such as tricholoroethylene (TCE), fertilizers, and heavy metals (Fig. 14.1) (Ponder et al. 2000; Shipley et al. 2010; Kanel et al. 2005; Watlington 2005; Rickerby and Morrison 2007). Pesticides such as 2,4-dichlorophenoxyacetic acid (2, 4-D) are also successfully degraded by magnetic NPs (Fang et al. 2011).

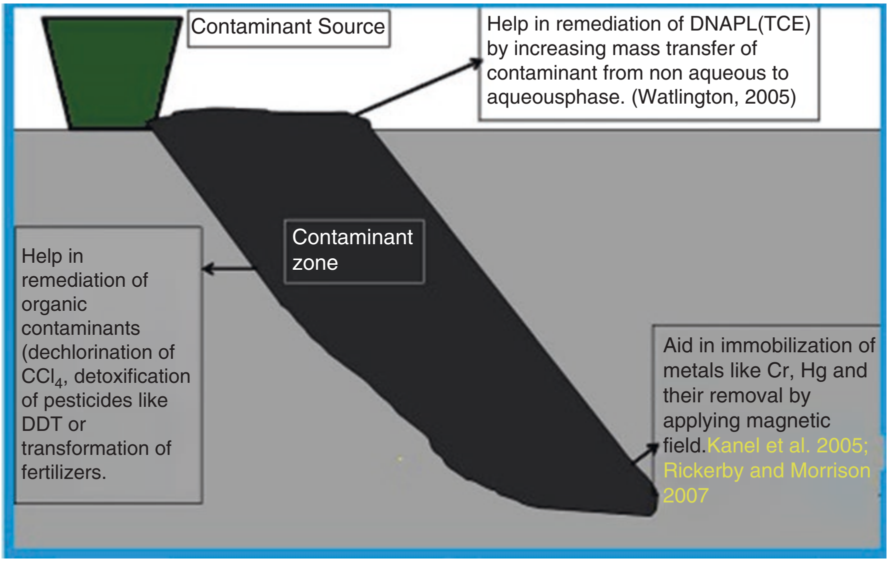

Fig. 14.1 Diagrammatic representation of the use of FeNPs for the degradation of various environmental pollutants (such as organic, inorganic, and petrochemical compounds)

14.2 Nanoremediation

Nanotechnology played a great role in microbial remediation as the greatest challenge in bioremediation has been to increase bioavailability/solubility and consequently the degradation rate. In the present situation, to increase the solubility of the "contaminant," surfactant micelles are used, but they tend to breakdown when contacted with the soil and interact with the liposome of microorganisms, thus regulating the competency of bioremediation. However, nanotechnologies have revealed an encouraging step in this direction. The solubilization rate of phenanthrene (PHEN) by using amphiphilic polyurethane (APU) NPs has increased significantly (Tungittiplakorn et al. 2005). These particles are made from antecedent chains of polyurethane acrylate anionmer (UAA) or poly(ethylene) glycol (PMUA), which have hydrophobic centers that show high PHEN attraction. By developing a nanoparticle-suspension competing with non-aqueous phase liquids (NAPLs), they improve polycyclic aromatic hydrocarbons (PAHs) desorption and movement. In contrast to surfactant, by altering the hydrophobic segment of the antecedent chain, the attraction of NPs to contaminant (hydrophobic) may be improved and mobility/movement may be better by regulating the load density of the altered NPs. Alternative benefit in bioremediation offered by NPs is in the form of NPs from magnetite. "Magnetite-NPs are formed under inert conditions by co-precipitation of ferrous and ferric salts." This technology instructs great industrial application in terms of cost-effectiveness, easier reusability, and separation. The magnetite NPs are used on *Rhodococcus erthyropolis* and *Pseudomonas delafieldii* as bacterial strains of bio-desulfurization activity. The use of magnetite NPs demonstrated better activity of desulfurization. The cells covered with altered magnetite NPs from ammonium oleate showed repeated bio-desulfurization activity, and by using an external magnet, it can be collected on the surface of the flask (Li et al. 2009)

The methods involved in nanoremediation are use of reactive nanomaterials for the conversion and decontamination of pollutants. They (nanomaterials) are pollutant specific in both the "chemical reduction" and "catalysis" in the process of mitigation. For in situ remediation of groundwater or soil contamination, no water is pumped out or no soil is transported to other site/disposal sites for surface treatments (Otto et al. 2008). Different nanoscale materials such as: carbon nanotubes, metal oxides, fullerenes, zeolites, titanium dioxide (TiO_2), fibers, and various noble metals (bimetallic nanoparticles (BNPs), e.g., Ag-Au BNPs) are being used. Nanoscale zero-valent iron (NZVI) is currently most widely used in the nanotechnology.

14.3 NZVI

NZVI particle ranges from 10 to 100 nm in diameter. Typically, a noble metal can be added as a catalyst (e.g., palladium, silver, copper). There is a catalytic interaction between the "second metal" and iron (Fe) and also supports the dissemination and mobility of the NPs once inoculated into the ground (Tratnyek and Johnson 2006). There may be more than two metals in BNPs, the "second metal" is generally less reactive and promotes oxidation of Fe or transfer of electrons (EPA 2007). There are some noble metals, particularly palladium, catalyze de-chlorination, and hydrogenation, thus making remediation more efficient (Li et al. 2006). The fundamental chemistry of Fe′s reaction to pollutants in the environment (particularly chlorinated solvents) was broadly studied and applied in ZVI permeable reactive barriers (ZVI-PRBs) of micrometer scale. "Beta elimination" and "reduction chlorination" are the two main degradation pathways for chlorinated solvents. The most common occurrence of beta elimination is when there is direct contact between "contaminant" and "Fe particle."

For example: the pathway of tricholoroethylene (TCE) (EPA 2007).

$$\text{TCE} + \text{Fe}^0 \rightarrow \text{Hydrocarbon} \quad \text{products} + \text{Cl}^- + \text{Fe}^{2+} / \text{Fe}^{3+}$$

Under reducing circumstances endorsed by nZVI in ground water, the following reaction takes place:

$$\text{PCE} \rightarrow \text{TCE} \rightarrow \text{DCE} \rightarrow \text{VC} \rightarrow \text{Ethene}$$

where PCE: perchloroethylene
DCE: dichloroethylene
VC: vinyl chloride

Nanoscale Fe particles are very active in transforming and detoxifying different environmental pollutants, including organic chlorinated solvents, polychlorinated biphenyls (PCBs), and organo-chlorine pesticides. Amending FeNPs can improve the speed and efficiency of remediation processes.

14.4 Nanotechnology and Wastewater Treatment

Nanotechnology is very efficient and flexible, and multifunctional processes are designed to deliver inexpensive water, quality wastewater treatment, and high-performance resolutions that rely less on large infrastructures (Qu et al. 2013a, b). Nanotechnology promises not only to overwhelm main tests faced by current treatment technologies, but also to provide novel treatment abilities that might permit the fiscal use of unconventional water sources to multiply the water supply.

14.4.1 Bioactive NPs for Water Disinfection

As a result of population "explosion," water contamination due to germs and additional pollutants get worsened, but nanotechnology provides alternatives for cleaning the water bodies and fulfilled the need of clean water. The alternative provided by nanotechnology is antimicrobial nanotechnology (Li et al. 2008; Mamadou et al. 2009). Several experiments have been made by using different nanomaterials for antimicrobial activities and have revealed significant results (Li et al. 2008). Some antimicrobial experiments are briefly highlighted below:

- Bacterial cell components and viruses are damaged by ROS (reactive oxygen species) formed by photocatalytic process (e.g., ZnO, TiO_2, and fullerol).
- The bacterial cell wall gets dwindling (e.g., AgNPs, ZnO, chitosan, peptides, carboxyfullerene, and CNTs).
- Disruption of mitochondrial energy transduction (e.g., Ag and aqueous fullerene NPs).
- Synthesis of DNA and activities of enzymes gets inhibited (TiO_2).
- The combination of magnesium oxide (MgO), AgNPs, and cellulose acetate (CA) fibers acts as potential biocide against bacterial spores, Gram +ve and Gram –ve bacteria (Savage and Diallo 2005).

14.4.2 Nano-adsorbents Based on Metal

Metal oxides like iron oxide, titanium dioxide, and alumina are low cost and effective adsorbents for heavy metals. The absorption and adsorption are regulated by complexation between dissolved metals and oxygen in metal oxides (Koeppenkastrop and Decarlo 1993). It is a two-step process: In the first step, metal ions get rapidly adsorbed on the outside surface, and in the second step, there is a speed limiting intra-particle diffusion along microporous walls (Trivedi and axe 2000). Due to high specific surface area, the shorter intra-particle diffusion space and the larger number of sites for surface reactions (i.e., corners, edges, vacancies). Their nanoscale counterparts have faster kinetics and greater adsorption capacity. For example, adsorption of arsenic (As) increased more than 100 times as nano-magnetite particle size fell from 300 to 11 nm (Yean et al. 2005). This increase in adsorption was attributed to the increase in specific surface area as magnetite particles of 300 and 20 nm have alike surface area and stabilized As adsorption capacity (Auffan et al. 2008, 2009). However, when particle size was reduced to <20 nm, the standardized adsorption capacity of the specific surface area increased, with 11 nm magnetite NPs absorbing three times more As, proposing a “nanoscale effect.” This “nanoscale effect” has been accredited to the change in the structure of the “magnetite surface” creating new adsorption sites (vacancies) (Auffan et al. 2009). Some Fe oxide NPs, e.g., nano-maghemite and nano-magnetite, may be super-paramagnetic besides high adsorption capacity. Magnetism is extremely volume-dependent as it stems from the atomic magnetic dipole’s collective interaction. When size of a ferro or ferrimagnetic substances decrease to the critical value (40 nm), the magnet changes from multiple domains to a single domain with greater magnetic sensitivity (Yavuz et al. 2006). If the size decreases further, magnetic particles are converted into super-paramagnetic, losing permanent magnetic moments when reacting to an external magnetic flux that permits easy magnetic field separation and recovery. In a core

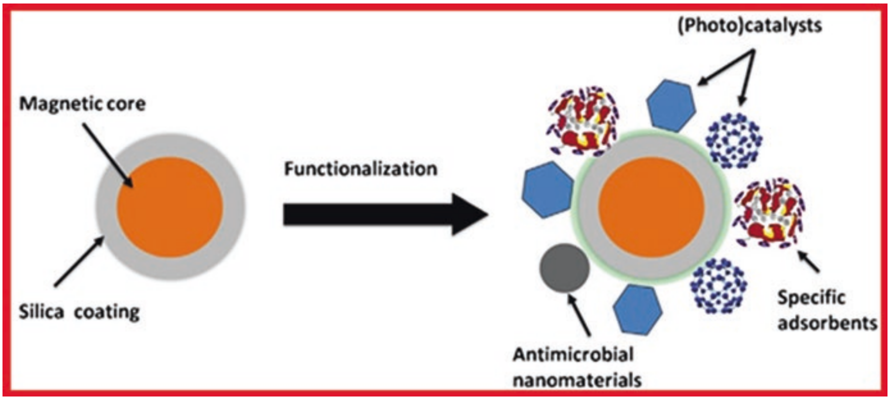

Fig. 14.2 Nanoparticles with multifunctional magnetic parts

shell nanoparticle structure, magnetic NPs are used as the core material, shell delivers the desired function, and the magnetic core performs magnetic separation. Silica is used as silica coating and helps in functionalization (Fig. 14.2).

By applying moderate pressure, nanocrystals of metal oxide are compacted into porous pellets without significantly affecting their surface area (Lucas et al. 2001). Nanomaterials based on metals were experimented to eliminate a range of heavy metals such as Hg, Cr, As, Pb, Cd, Cu, and Ni. They also demonstrated great potential for activated carbon outcomes (Sharma et al. 2009). The As removal application has attracted a great deal of attention among them. Despite being a good adsorbent for various organic and inorganic pollutants, activated carbon has restricted As capacity, especially As(V) (Daus et al. 2004). Several nanomaterials of "metal oxide" with nano-sized magnetite and TiO_2 have revealed superior performance of "As adsorption" to "activated carbon" (Deliyanni et al. 2003; Mayo et al. 2007). Metal(hydr)oxide NPs can also be infused on the activated carbon skeleton or other materials (porous) to immediately remove As and organic co-contaminants that favor point-of-use (POU) applications (Hristovski et al. 2009a, b)

14.5 Regeneration and Reuse

Metal oxide nano-adsorbents can be easily regenerated by altering the pH value of a solution, and its adsorption capacity is well maintained even after several reuse cycles and renewal (Sharma et al. 2009; Hu et al. 2006). However, there are reports of reduced adsorption capacity after regeneration (Deliyanni et al. 2003). Nano-adsorbents based on metals can be formed at comparatively low cost. The great capacities of adsorption, easy to separate, low cost, and easy renewal make it technologically and economically advantageous.

14.6 Carbon-Based Nano-adsorbents

14.6.1 Removal of Organic Contaminants

Nano-adsorbents based on carbon, for instance, "carbon nanotubes (CNTs)," are cylindrical and are discovered as replacements for activated carbon. CNTs are categorized as single-walled carbon-nanotubes(SWCNTs) and multi-walled carbon-nanotubes (MWCNTs). CNTs have great specific surface area with adsorption sites that can be highly evaluated. They can also modify their surface chemistry accordingly (Yang and Xing 2010). CNTs' hydrophobic surface in aqueous medium forms loose bundles/aggregates that reduce the "active surface area" but are great-energy sites for organic contaminant adsorption in water (Pan and Xing 2008). The availability of bigger pores and extra-reachable sorption sites in bundles are reasons for CNT's adsorption of huge organic contaminants (Ji et al. 2009). CNTs may also adsorb polar organic molecules due to various CNT-pollutant interactions like hydrophobic effects, covalent bonding, H-bonding with acids, connections with polycyclic aromatic hydrocarbons, OH-groups, amines, and electrostatic interactions with +vly charged organic pollutant molecules such as antibiotics (Ji et al. 2009; Lin and Xing 2008; Yang and Xing 2010).

14.6.2 Removal of Heavy Metal Ions

Heavy metal pollution is very dangerous to an aquatic system. To remove cadmium (Cd^{2+}) from aqueous solutions, surface-oxidized CNTs with H_2O_2, $KMnO_4$, and HNO_3 are used (Li et al. 2003). CNT oxidation may have higher adsorption capacity with faster kinetics for metal ions. The oxidized CNT surface includes functional groups which have good heavy metal ion adsorption capacity such as carboxylic acid (COOH), hydroxyl (OH), and carbonyl (Fig. 14.3). The initial metal ion concentration, temperature, contact time, and solution pH play important roles in sorption of cadmium (Cd^{2+}) ions onto raw-MWCNTs, o-MWCNTs(oxidized-MWCNTs), and e-MWCNTs (ethylenediamine-functionalized MWCNTs). The experiments have shown that adsorption of Cd^{2+} ions by o-MWCNTs and

Fig. 14.3 Oxidation of functional groups on CNT surfaces

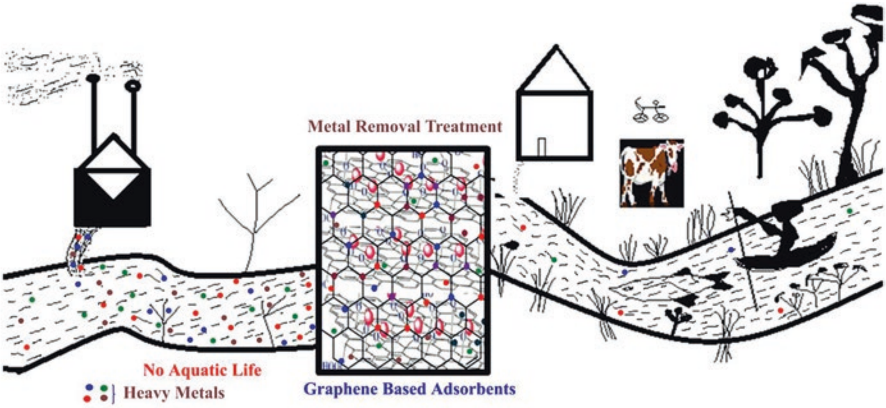

Fig. 14.4 Role of nano-adsorbents based on graphene in abatement of heavy metal pollution (Kumar et al. 2019)

e-MWCNTs was strongly pH dependent (Vukovic et al. 2010). Similarly nano-adsorbents based on "graphene" and its derivatives play an important and key role in the effective abatement of heavy metal pollution (e.g., lead (Pb-II)) (Fig. 14.4) (Kumar et al. 2019)

14.7 Nanotechnologies in Air Pollution Abatement

14.7.1 Nanotechnology for the Adsorption of Toxic Gases

Nanotechnology not only cleans the "waste water" but also plays an important role in the cleanup of toxic gasses in an ambient air. There is a hexagonal arrangement in the graphene sheet of carbon atoms of CNTs along the axis of the tube. The strong interaction occurs between two dioxin rings and CNT surfaces. In addition, dioxin molecules interact through a porous wall, i.e., 2.9 nm, on the entire surface of nanotubes, and may raise the potential for adsorption within pores if there is a possibility of overlapping events. Strong oxidation resistance of CNTs also benefited from high temperature regeneration of the adsorbent. As SWCNTs as well as MWCNTs, CNTs are unique macromolecules with a single-dimensional structure, thermal stability, and extraordinary chemical properties. As superior adsorbents, these nanomaterials have revealed good potential to remove different types of organic and inorganic contaminants, together in an aqueous environment and air streams. The pore structure and functional group plays an important role in CNTs adsorption capacity of pollutants. SWCNT and MWCNT's have potential applications because of their unique electronic properties and structures. SWCNTs, for instance, have been conveyed to be a chemical sensor of NO_2 and NH_3. The electrical resistance of SWCNTs changed significantly, either up or down, on exposure to NH_3or NO_2 gas. You can also use SWCNTs and MWCNTs as hydrogen storage. CNTs were also used as quantum nanowires, emitters of electron fields, supports for catalysts, etc.

Dioxin adsorption and associated compounds (e.g., polychlorinated dibenzofuran and polychlorinated biphenyls) are stable and extremely toxic contaminants. Dibenzo-p-dioxins belong to a family of compounds containing two rings of benzene, linked by two atoms of O_2. It contains in-between 0 and 8 atoms of chlorine attached to the ring. Dibenzofuran is a similar yet distinct compound in which oxygen bridges only one of the connections among two benzene rings. Dioxin toxicity varies as per the number of chloro-atoms. Dioxins that have only one or no chloro-atom are non-toxic, whereas dioxins that have more than one chloro-atom are toxic. Tetraklorodibenzo-p-dioxin (TCDD) is a compound known to be carcinogenic and affects the immune and endocrine systems to humans. These compounds are mainly generated from the incineration processes of wastes of organic compounds (10–500 ng/m^3). Dioxin emission regulations are complex and vary from country to country. Nevertheless, dioxin concentrations should generally be reduced to <1 ng/m^3. Since 1991, in Europe and Japan adsorption using activated carbon has been widely used to eliminate dioxins from incinerators. There is higher efficiency of dioxin removal by activated carbon adsorbent as compared to normal adsorbents, since the bonding energy between activated carbon and dioxin is much higher than the other adsorbent such as clay, α-Al_2O_3, and zeolites (Cudahy and Helsel 2000). However, keeping in view the toxicity of dioxin, it needs a more proficient adsorbent than activated carbon to lessen the emissions of dioxin to a minor level. CNTs have been revealed efficient in dioxin removal as dioxins have strong interaction with CNTs almost three times stronger than interaction with activated carbon (Long and Yang 2001a, b). This could be due to the curved surface of the nanotube compared to the flat sheet surface which provides stronger interaction forces among CNTs and dioxin (Bhushan 2010). Developing technologies to eradicate emissions of NO_x from the fossil fuel combustion have made significant efforts. Common adsorbent for removing NO_x at low temperatures includes activated carbon, zeolite, an ion exchange, and FeOOH distributed on active carbon fiber. Due to the reactivity of "surface functional groups," NO can be adsorbed effectively to activated carbon, but not significant. Long and Yang (2001a, b) found that CNTs can be used to remove NO as an adsorbent. NO_x adsorption may be associated with unique CNT structures, electronic properties, and functional surface groups. When NO and O_2 pass through CNTs, NO is oxidized to NO_2 and then gets adsorbed on the surface of nitrate(NO_3) species. The absorption of NO_x amounted to about 78 mg/g CNTs. Mochida et al. (1997) supported this idea by reporting NO to NO_2 oxidation at room temperature on activated carbon fiber. Similarly, oxides of sulfur (SO_x) also get adsorbed on CNTs compared to NO_x, although the adsorption rate is not promising when CO_2 is present.

Global warming is one of the main apprehensions at present times across the globe. Lots of efforts were made to control greenhouse gases like CO_2, methane, nitrous oxide, etc. One of such efforts was the introduction of Kyoto Protocol which came into the power from February 16, 2005, for the capture like carbon sequestration and storage of CO_2 released from different fossil-fueled factories/power plants. Different CO_2 capture technologies have been investigated, including adsorption, absorption, cryogenic, membrane, and others (White et al. 2003; Aaron and Tsouris 2005). The most advanced process recognized between these technologies was adsorption–regeneration technology. However, there is still too high energy needed for the absorption process. The Intergovernmental Panel on Climate Change (IPCC) decided that designing a large-scale adsorption process could be practicable and developing a new generation of material capable of efficiently adsorbing CO_2 would undoubtedly increase the effectiveness of adsorptive separation in a flue gas application (Metz et al. 2005). These adsorbents include molecular baskets based on activated carbon, SWNTs, silica adsorbents, zeolite, and nano-porous silica. The chemical modification of CNTs will be able to capture CO_2. In general, CO_2 adsorption performance on modified CNTs increases as relative humidity increases, but it decreases as temperature increases. In addition to NO_x and SO_x, atmospheric reactions such as soot, nitrous acid, poly-aromatic compounds form many chemical substances and volatile organic compounds (VOCs) are also removed from the air (Santiago and Indarto 2008; Natalia and Indarto 2008; Indarto et al. 2009; Indarto 2012). There has been advancement in novel materials that removes VOCs, NO_x and SO_x from air at room temperature. This novel material is highly porous manganese oxide produced by AuNPs (Sinha and Suzuki 2007). Tests were conducted using three main components of organic indoor air pollutants to demonstrate the effectiveness of this catalyst: acetaldehyde, toluene, and hexane. It has been revealed that such catalysts removed and degraded all the three pollutants effectively as compared to the conventional catalyst systems. One of the reasons for successful removal of pollutants is porous manganese oxide having much greater surface area than all the previously compounds known. This greater surface area makes volatile molecules more adsorbent, and adsorbed pollutants are effectively decomposed. Due to the presence of free radicals, surface degradation is very effective. The presence of Au NPs helps to reduce the typically very high barrier of radical formation. This process has opened up the possibility of applying additional nano-metal components (Sinha and Suzuki 2007).

14.7.2 Nanotechnology for Pollution Sensors and Detectors

Long-term introduction to particulate matter and heavy metal pollution has long been agreed to be an important factor in initiating health problems. Particulate sizes in urban areas typically range from 100 to 300 nm in diameter, whereas heavy metals can be found in different concentration ranges (Johnston 2002). Furthermore, microorganisms cannot break down heavy metals. There is a high degree of difficulty in recovering contaminated soil with heavy metal that increases pressure in the development of sensors on-site that can be detected (Choi 2003). Rapid and accurate sensors capable of sensing contaminants at the molecular level can increase human capacity to protect human health and environmental sustainability, where the available contaminant sensing technology is extra-sensitive and less expensive. One of the desired technologies is a continuous monitoring tool capable of providing information, particularly in very short analytical time about pollutants (Masciangioli and Zhang 2011). A “nanocontact sensor” has been developed, and “this sensor” can detect certain metal ions without the need for preconcentration. This sensor is particularly suitable for detecting heavy metal ions on-site, including radioactive elements. Nanocontact sensors can be made in miniature size and automatic mode so they can be easily used on site or brought to the ground. The uses of these sensors are also cheap (cost-effective) because they ate using simple electrochemical techniques made from conventional microelectronics manufacturing equipment (Tao 2002). Biosensors based on nanotechnology were developed using biomaterials (Staiano et al. 2010). Liu et al. (2007) have found a way to increase the test strips nanoprobe sensitivity to enable a portable biosensor to be created. Portable biosensors are capable of detecting people exposed to chemicals quickly. Wang et al. (2007) produced a label nanoparticle in the Pacific Northwest National Laboratory (PNNL), which enables sensors to sense and infer biomarker signals. The approach is based on the immunoassay method of electrochemistry. This method involves using specific antibodies to attract disease biomarkers. The supply of ‘label’ on the second nanoparticle antibody amplifies the signals of the biomarker. This increases the sensitivity level that will improve the detector’s accuracy in identifying biomarker concentrations in biological samples (Lin and Gavaskar 2004; Smart et al. 2006). Nanowires and nanotube-based sensors offer remarkable capacity as chemical and biological sensor materials (Smart et al. 2006). SWCNTs exhibited a quicker response and advanced sensitivity than conventional samples currently used to detect gas molecules like NO_2 and NH_3. In this case, gas particles are bonded directly to the SWCNT surface and affect the sensor’s electrical resistance. The ability to attain greater sensitivity at room temperature is additional benefit of SWCNTs as sensors. Conventional solid sensors are usually operated at 200–600 °C temperatures.

14.7.3 Cantilever Sensors

A cantilever sensor is a device made from a nano-coated silicon and is sensitive to specific pollutants (Filipponi and Sutherland 2010). Typically, a cantilever is 10–500 μm in length, but it is less than several micrometers thick. Nano-coated cantilever array interactions between pollutants because the array to bend as a result of surface pressure changes. A laser beam can detect pollutant mass quantitatively and will measure the small bending. To sense VOCs, pesticides, heavy metals, and harmful bacteria such as salmonella, cantilever sensors were developed. Figure 14.5 illustrates a schematic diagram of biosensors based on cantilever. The molecular probe (sample) is only suitable for the target molecule. The cantilever arm will bend and react when the target molecule is attached. The reaction will thus detect and signal the presence of target molecules.

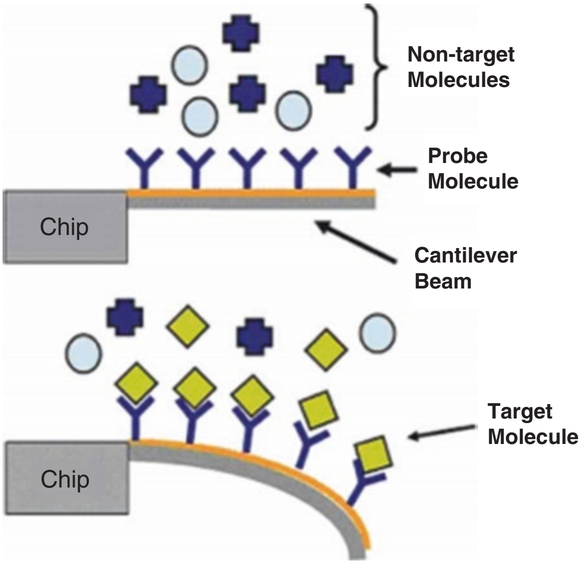

Fig. 14.5 Principle of working of cantilever-based biosensors: (**a**) before and (**b**) after interaction between the "target molecule" and the "probe"

14.7.4 *Other Advances in Nanotechnology Sensors*

Some of the sensor based technologies are listed below (Berger 2008)

1. Functionalized-tetraphenylsilole NPs are used to detect cancer substances in minute concentrations. Examples are Cr(VI) and Ar(V) for detectable substances.
2. The use of peptide nanoelectrodes was based on the thermocouple concept. A peptide molecule is placed in a separation gap of "nano-distance" to form a molecular junction. Once a specific metal ion is connected to the gap, a unique value will result in the electrical current being conducted. The metal ion is easily identified.
3. Composite electrodes (nanotubes and copper) to detect organo-phosphorus pesticides, carbohydrates, etc.
4. Nanospheres of polymers were made to measure organic pollutants at very small concentrations in ppb.

14.8 Green Manufacturing

Green manufacturing involves developing industrial processes, e.g., water-based processes, take preference over organic solvent-based processes, reducing or minimizing the use of harmful substances and using energy-efficient processes. The development of aqueous micro emulsions as a substitute to VOCs in the cleaning industry is an example of green nanotechnology. Though nanotechnology risk offers a wide variety of potential uses and speedy advances, this technology may have unintentional effects on the environment and human health as well. Materials that are offensive in majority form, but can be converted highly toxic on the nanoscale if they arrive and build up in the supply of "drinking water" and the "food chain" and are not biodegradable. A specific concern is the intake of airborne NPs and their impact on lungs, with recent studies showing a similar response by the human body to certain forms of CNT as asbestos particles when inhaled in adequate quantities cause lung diseases (Buzea et al. 2007). There is a lack of understanding about fate and behavior of NPs in the environment and humans, thus exacerbating these concerns in current situation. The development of this technology, however, is very early and the amount of testing for toxicity and potential health risks is extremely limited (Wickson et al. 2011). Research on nanotechnology risk assessment to determine the potential impacts of NPs on the environment and human health is crucial in helping to balance the benefits of the technology and the potential unintentional consequences (Hyder 2003; Metz et al. 2005). Scientific authorities recognize this as a major challenge as they monitor the enormous volume of various NPs produced.

14.9 Conclusion

Nanotechnology has been proved among one of the best emerging environmental nanotechnology that revolutionized the pollution abatement processes through sophisticated techniques producing the less toxic toxicants as byproducts and also used to prevent pollution from occurring. It has replaced conventional technologies which are high cost, low efficiency, and not environmental friendly. Nanotechnology has been proved best in the cleanup process of every type of pollution like waste water (including heavy metal pollution), air, and soil pollution. It is also possible to use NPs and nanotubes as sensors for toxic substances, especially substances that are hard to sense with conventional technology because of very small in size and concentrations. Although nanotechnology has many applications, it needs to be further studied to evaluate its risk.

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Chapter 15

Restoration of Heavy Metal-Contaminated Environs Through Ectomycorrhizal Symbiosis

Rezwana Assad, Zafar Ahmad Reshi, Irfan Rashid, and Showkat Hamid Mir

15.1 Introduction

Metals with comparatively higher density, atomic number, or atomic weight are characterized as heavy metals. Examples encompass aluminum (Al), antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), caesium (Cs), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), palladium (Pd), platinum (Pt), potassium (K), rubidium (Rb), selenium (Se), silver (Ag), strontium (Sr), tin (Sn), titanium (Ti), tungsten (W), uranium (U), vanadium (V), and zinc (Zn). In biological science, metals that exert toxic effects on biological systems upon crossing a certain threshold concentration are labeled as heavy metals (Mishra et al. 2019).

Generally, metals can be classified as essential metals and non-essential metals. Calcium, chromium, cobalt, copper, iron, magnesium, manganese, nickel, potassium, selenium, sodium, vanadium, and zinc are some essential metals that serve as micronutrients and play important roles in vital life processes (Kumar et al. 2019). On the other hand, non-essential metals like aluminum, arsenic, cadmium, chromium, gold, lead, mercury, selenium, and silver have no biological role and are toxic to living organisms (Hrynkiewicz and Baum 2014). However, metals that are essential for plant growth at low concentrations exert toxic effects at higher concentrations due to their high chemical reactivity (Leyval and Joner 2001; Amir et al. 2014).

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Agrochemicals, atmospheric deposition, automobile exhausts, forest fires, fossil fuel combustion, industrial wastes, leaching from household pipelines and utensils, lead-acid batteries, microplastics, mining, paints, particle accelerators, refinery textiles, solar panels, tailings, treated timber, volcanic eruptions, wood preservatives, and weathering of rocks are some of the potential sources of heavy metals (Joshi and Luthra 2000; Gupta et al. 2018; Kumar et al. 2019). In disturbed ecosystems, heavy metals pose a serious environmental threat owing to their toxicity and persistence (Boudh and Singh 2019).

15.1.1 Influence of Heavy Metals on Living Systems

Heavy metal pollution poses serious environmental and health risks (Bücking 2011), which is a huge apprehension for ecologists and environmentalists (Pandey et al. 2016; Chatterjee et al. 2019). Heavy metals enter food chain and perturb the whole food web (Mishra et al. 2019). Some illustrious catastrophes of heavy metal contamination and subsequent toxicity include Minamata disease (Hg toxicity) in Japan, Itai-Itai disease (Cd toxicity) in Japan, Mariana dam disaster in Brazil, lead toxicity in Michigan (United States), and arsenic toxicity in West Bengal, India (Mishra et al. 2019).

Heavy metal pollution deteriorates soil, air, and water quality which consequently instigates health problems in humans, animals, and plants and adversely affects soil microbiota (Ahemad 2014). In humans, heavy metal toxicity causes chronic disorders, symptoms of which include: cancer, dementia in adults, depression, emotional instability, gastric disorders, insomnia, intellectual disability, joint pain, liver diseases, neurological disorders, numbness, renal disorders, vision disorders, or can even prove lethal (Gupta et al. 2018; Kumar et al. 2019). In plants, heavy metal toxicity leads to yield reduction, degradation of nutritional quality, chlorosis, seed germination inhibition, and physiological dysfunctioning (Ghani 2011; Kumar et al. 2019). At the cellular level, heavy metals alter enzyme specificity, damage cell membranes, disrupt DNA structure, enforce oxidative stress, and interrupt cellular functions (Bruins et al. 2000; Hrynkiewicz and Baum 2014).

Recently, ecosystem restoration has surfaced as one of the fundamental premises of global environmental policies (Jacobs et al. 2015). UN Convention on Biodiversity (CBD) targeted restoration of around 15% of the globally degraded ecosystems from 2011 to 2020 (CBD 2010; Chatterjee et al. 2019). In this direction, sustainable remediation of heavy metal is crucial for environmental protection and biodiversity conservation (Glick 2010; Tiwari and Lata 2018). This chapter presents an overview of heavy metals, their influence on living systems, heavy metal remediation through ectomycorrhizal symbiosis, mechanism involved in remediation of heavy metals through ectomycorrhizal symbiosis, and future research directions.

15.2 Heavy Metal Remediation Through Ectomycorrhizal Symbiosis

Restoration of heavy metal-contaminated environs can be achieved through reinstallation of efficient microbial community via soil health improvement and successful revegetation (Moynahan et al. 2002; Quoreshi 2008; Mishra et al. 2019). Globally, successful recuperation of sternly disturbed areas has been accomplished by the application of biological tools (Marx 1991; Malajczuk et al. 1994). For instance, phytobial remediation approach, which includes planting seedlings that are pre-inoculated with actinomycetes, growth-promoting bacteria, mycorrhizal fungi, and nitrogen fixers, is a promising approach of ecosystem restoration (Quoreshi 2008). Hitherto, inoculation of plants with apposite ectomycorrhizal fungi, either alone or in consortia, is the most eco-friendly approach for reclamation of disturbed areas (Quoreshi 2008).

ECM fungi, which share a strong relationship with their host plants, augment the growth of host plant by facilitating uptake of essential immobile mineral nutrients (like phosphorus, nitrogen, magnesium, zinc, etc.) and by escalating host plant tolerance to toxic metals (Meharg 2003; Sell et al. 2005; Chatterjee et al. 2019).

Application and potential success of ECM plants in the remediation of contaminated environs depends on several inter-related factors including pollutant properties (such as distribution, concentration, toxicity, bioavailability, etc.), soil characteristics (water availability, nutrient status), effect of ECM fungi on the mycorrhizospheric microbiota, and ECM-host plant communal activity in the symbiotic phase (Bücking 2011).

ECM fungi possess adaptive tolerance to heavy metals and have been found to grow in heavy metal-contaminated soils (Hrynkieiuicz et al. 2008). It has been recognized that under field conditions, selective ECM fungi besides augmenting the survival rate also enhance early growth performance of associated host plants (Danielson and Visser 1989; Quoreshi 2008), which consecutively facilitate restoration of contaminated sites through acceleration of phyto/mycoremediation processes (Gil-Martínez et al. 2018).

Ectomycorrhizal fungi serve a prominent role in heavy metal remediation (Yadav 2019). Gildon and Tinker (1981) did pioneer work in this field and reported the role of mycorrhizal fungi in heavy metal remediation. Since then, lot of work has been carried out in this field during past decades (Amir et al. 2014). Various ECM fungi have been reported to be useful for bioremediation of heavy metals (Table 15.1). ECM fungi belonging to genera *Albatrellus*, *Amanita*, *Boletus*, *Cantharellus*, *Clavariadelphus*, *Cenococcum*, *Hebeloma*, *Hygrophoropsis*, *Hysterangium*, *Inocybe*, *Laccaria*, *Lactarius*, *Leccinum*, *Paxillus*, *Piloderma*, *Pisolithus*, *Rhizopogon*, *Russula*, *Scleroderma*, *Suillus*, *Thelephora*, *Tomentella*, *Tuber*, and *Xerocomus* have been reported to remediate heavy metals such as Al, As, Cd, Cs, Ca, Cr, Cu, Fe, Pb, Mn, Hg, Ni, K, Rb, Se, Ag, Ti, and Zn (Ahonen-Jonnarth and Finlay 2001; Meharg 2003; Wallander et al. 2003; Sell et al. 2005; Bellion et al. 2007; Krznaric et al. 2009; Bücking 2011; Machuca 2011; Urban 2011; Amir et al. 2014; Khullar and Reddy 2016; Mao and Guan 2016; Yadav 2019).

Ectomycorrhizal fungi in different forms like ECM sporocarps, ECM pure mycelium, ECM-rich soil, and ECM roots have been employed for remediation of heavy metal-contaminated sites (Fig. 15.1).

15.2.1 Mechanism Involved in Remediation of Heavy Metals Through Ectomycorrhizal Symbiosis

Detailed pathways, through which heavy metals are remediated by ectomycorrhizal symbiosis, have been postulated by several workers (See Hartley et al. 1997; Machuca 2011; Urban 2011; Amir et al. 2014; Khullar and Reddy 2016; Kumar et al. 2019; Mishra et al. 2019), which engross both direct and indirect mechanisms.

(a) *Direct/Specific Mechanisms of Heavy Metal Remediation*

Table 15.1 Summation of role of ectomycorrhizal symbiosis in restoration of heavy metal-contaminated environs

S. no.	Heavy metal	Fungi	References
1.	**Aluminum (Al)**	*Lactarius thiogalus* *Lactarius rufus* *Paxillus involutus*	Hentschel et al. (1993) and Kumar and Atri (2017)
		Rhizopogon roseolus *Suillus variegatus*	Ahonen-Jonnarth et al. (2000) and Machuca (2011)
		Hysterangium sp.	Ray et al. (2005) and Amir et al. (2014)
		Pisolithus tinctorius *Scleroderma verrucosum*	Ray and Adholeya (2009) and Machuca (2011)
		Rhizopogon roseolus	Agerer (2012)
		Amanita sp. *Cenococcum* sp. *Laccaria* sp. *Lactarius* sp. *Paxillus* sp. *Pisolithus* sp. *Scleroderma* sp. *Suillus* sp. *Thelephora* sp.	Amir et al. (2014)
		Astraeus hygrometricus *Scleroderma citrinum*	Kayama and Yamanaka (2014) and Kumar and Atri (2017)
2.	**Antimony (Sb)**	–	–
3.	**Arsenic (As)**	*Sarcosphaera coronaria*	Stijve et al. (1990) and Urban (2011)
		Pisolithus tinctorius *Scleroderma verrucosum*	Ray and Adholeya (2009) and Machuca (2011)
4.	**Beryllium (Be)**	–	–

(continued)

Table 15.1 (continued)

S. no.	Heavy metal	Fungi	References
5.	**Cadmium (Cd)**	*Laccaria laccata* *Pisolithus tinctorius*	Morselt et al. (1986), Howe et al. (1997) and Machuca (2011)
		Laccaria laccata	Galli et al. (1993), Machuca (2011) and Amir et al. (2014)
		Paxillus involutus	Godbold et al. (1998), Courbot et al. (2004), Bellion et al. (2007), Luo et al. (2011), Machuca (2011), Urban (2011), Ma et al. (2014) and Khullar and Reddy (2016)
		Laccaria bicolor	Ahonen-Jonnarth and Finlay (2001), Urban (2011) and Kumar and Atri (2017)
		Hysterangium sp.	Ray et al. (2005) and Amir et al. (2014)
		Hebeloma crustuliniforme *Paxillus involutus* *Pisolithus tinctorius*	Sell et al. (2005) and Bücking (2011)
		Boletus edulis	Collin-Hansen et al. (2007) and Machuca (2011)
		Amanita rubescens	Kozdroj et al. (2007) and Urban (2011)
		Pleurotus ostreatus	Serafin Muñoz et al. (2006) and Urban (2011)
		Cenococcum geophilum Tomentelloid fungi	Krpata et al. (2008) and Urban (2011)
		Pisolithus tinctorius *Scleroderma verrucosum*	Ray and Adholeya (2009) and Machuca (2011)
		Suillus luteus	Krznaric et al. (2009) and Khullar and Reddy (2016)
		Hebeloma cylindrosporum	Ramesh et al. (2009) and Machuca (2011)
		Hebeloma crustuliniforme	Zimmer et al. (2009) and Bücking (2011)
		Amanita vaginata *Laccaria laccata*	Urban (2011)
		Rhizopogaon roseolus	Agerer (2012)
		Rhizopogon roseolus *Suillus bovines*	Sousa et al. (2012) and Khullar and Reddy (2016)
		Amanita sp. *Cenococcum* sp. *Laccaria* sp. *Lactarius* sp. *Paxillus* sp. *Pisolithus* sp. *Scleroderma* sp. *Suillus* sp. *Thelephora* sp.	Amir et al. (2014)
		Lactarius piperatus	Nagy et al. (2014) and Kumar et al. (2019)
		Pisolithus albus	Khullar and Reddy (2016) and Reddy et al. (2016)
		Rhizopogon roseolus *Suillus bovinus*	Mao and Guan (2016)

(continued)

Table 15.1 (continued)

S. no.	Heavy metal	Fungi	References
6.	**Caesium (Cs)**	*Clavariadelphus truncatus*	Gaso et al. (2007) and Machuca (2011)
7.	**Calcium (Ca)**	*Piloderma croceum*	Blum et al. (2002), Hagerberg et al. (2005) and Urban (2011)
		Paxillus involutus	Wallander et al. (2003) and Urban (2011)
8.	**Chromium (Cr)**	*Hysterangium* sp.	Ray et al. (2005) and Amir et al. (2014)
		Pisolithus tinctorius *Scleroderma verrucosum*	Ray and Adholeya (2009) and Machuca (2011)
9.	**Cobalt (Co)**	–	–
10.	**Copper (Cu)**	*Paxillus involutus* *Suillus variegatus*	Ahonen-Jonnarth et al. (2000) and Machuca (2011)
		Pisolithus tinctorius	Meharg (2003)
		Paxillus involutus	Bellion et al. (2007) and Machuca (2011)
		Hebeloma cylindrosporum	Ramesh et al. (2009) and Machuca (2011)
		Amanita sp. *Cenococcum* sp. *Laccaria* sp. *Lactarius* sp. *Paxillus* sp. *Pisolithus* sp. *Scleroderma* sp. *Suillus* sp. *Thelephora* sp.	Amir et al. (2014)
		Pisolithus albus	Khullar and Reddy (2016) and Reddy et al. (2016)
11.	**Gold (Au)**	–	–
12.	**Iron (Fe)**	*Hebeloma crustuliniforme*	van Hees et al. (2006) and Machuca (2011)
		Hygrophoropsis aurantiaca	Borovička and Řanda (2007) and Urban (2011)
		Rhizopogon luteolus *Scleroderma verrucosum* *Suillus luteus*	Machuca et al. (2007) and Machuca (2011)
		Lactarius subdulcis *Xerocomus* sp.	Rineau et al. (2008) and Machuca (2011)
		Amanita sp. *Lactarius deliciosus* *Paxillus filamentosus* *Suillus bellinii* *Suillus granulatus*	Machuca (2011)

(continued)

Table 15.1 (continued)

S. no.	Heavy metal	Fungi	References
13.	**Lead (Pb)**	*Paxillus involutus*	Wallander et al. (2003) and Urban (2011)
		Clavariadelphus truncatus	Gaso et al. (2007) and Machuca (2011)
		Cenococcum geophilum Tomentelloid fungi	Krpata et al. (2008) and Urban (2011)
		Pisolithus tinctorius *Scleroderma verrucosum*	Ray and Adholeya (2009) and Machuca (2011)
		Inocybe curvipes *Rhizopogon buenoi* *Suillus granulatus* *Tomentella ellisii*	Huang et al. (2012) and Khullar and Reddy (2016)
		Amanita sp. *Cenococcum* sp. *Laccaria* sp. *Lactarius* sp. *Paxillus* sp. *Pisolithus* sp. *Scleroderma* sp. *Suillus* sp. *Thelephora* sp.	Amir et al. (2014)
14.	**Manganese (Mn)**	*Paxillus involutus*	Wallander et al. (2003) and Urban (2011)
		Pisolithus tinctorius	Amir et al. (2014)
15.	**Mercury (Hg)**	*Boletus aereus* *Boletus pinophilus*	Melgar et al. (2009) and Urban (2011)
16.	**Molybdenum (Mo)**	–	–
17.	**Nickel (Ni)**	*Laccaria bicolor*	Ahonen-Jonnarth and Finlay (2001), Urban (2011) and Kumar and Atri (2017)
		Hysterangium sp.	Ray et al. (2005) and Amir et al. (2014)
		Pisolithus tinctorius *Scleroderma verrucosum*	Ray and Adholeya (2009) and Machuca (2011)
		Cenococcum geophilum	Gonçalves et al. (2009) and Urban (2011)
		Pisolithus albus	Jourand et al. (2010) and Amir et al. (2014)
		Pisolithus albus	Majorel et al. (2012) and Amir et al. (2014)
		Amanita sp. *Cenococcum* sp. *Laccaria* sp. *Lactarius* sp. *Paxillus* sp. *Pisolithus* sp. *Scleroderma* sp. *Suillus* sp. *Thelephora* sp.	Amir et al. (2014)

(continued)

Table 15.1 (continued)

S. no.	Heavy metal	Fungi	References
18.	**Palladium (Pd)**	–	–
19.	**Platinum (Pt)**	–	–
20.	**Potassium (K)**	*Suillus granulatus*	Wallander et al. (2003) and Urban (2011)
21.	**Rubidium (Rb)**	*Clavariadelphus truncatus*	Gaso et al. (2007) and Machuca (2011)
		Suillus grevillei	Chudzynski and Falandysz (2008) and Urban (2011)
22.	**Selenium (Se)**	*Pleurotus ostreatus*	Serafin Muñoz et al. (2006) and Urban (2011)
		Albatrellus pes-caprae *Amanita strobiliformis* *Boletus edulis* *Boletus pinophilus*	Urban (2011)
23.	**Silver (Ag)**	*Amanita strobiliformis* *Amanita solitaria*	Borovička et al. (2007), Machuca (2011) and Urban (2011)
		Pleurotus ostreatus	Serafin Muñoz et al. (2006) and Urban (2011)
		Thelephoraceae Cortinariaceae Tricholomataceae Tuberaceae	Hrynkieiuicz et al. (2008) and Amir et al. (2014)
24.	**Strontium (Sr)**	–	–
25.	**Tin (Sn)**	–	–
26.	**Titanium (Ti)**	*Paxillus involutus*	Wallander et al. (2003) and Urban (2011)
27.	**Tungsten (W)**	–	–
28.	**Uranium (U)**	–	–
29.	**Vanadium (V)**	–	–

(continued)

Table 15.1 (continued)

S. no.	Heavy metal	Fungi	References
30.	**Zinc (Zn)**	*Suillus* spp.	Colpaert and Van assche (1992), Colpaert et al. (2005) and Urban (2011)
		Suillus luteus	Turnau et al. (2001), Muller et al. (2004, 2007) and Urban (2011)
		Pisolithus tinctorius	Meharg (2003)
		Paxillus involutus *Suillus bovinus*	Adriaensen et al. (2004), Fomina et al. (2006) and Kumar and Atri (2017)
		Suillus bovinus	Adriaensen et al. (2006) and Amir et al. (2014)
		Russula atropurpurea	Borovička and Řanda (2007) and Urban (2011)
		Paxillus involutus	Colpaert (2008) and Urban (2011)
		Cenococcum geophilum Tomentelloid fungi	Krpata et al. (2008) and Urban (2011)
		Hebeloma crustuliniforme	Zimmer et al. (2009) and Bücking (2011)
		Amanita vaginata *Scleroderma verrucosum* *Tricholoma scalpturatum*	Urban (2011)
		Inocybe curvipes *Rhizopogon buenoi* *Suillus granulatus* *Tomentella ellisii*	Huang et al. (2012) and Khullar and Reddy (2016)
		Amanita sp. *Cenococcum* sp. *Laccaria* sp. *Lactarius* sp. *Paxillus* sp. *Pisolithus* sp. *Scleroderma* sp. *Suillus* sp. *Thelephora* sp.	Amir et al. (2014)

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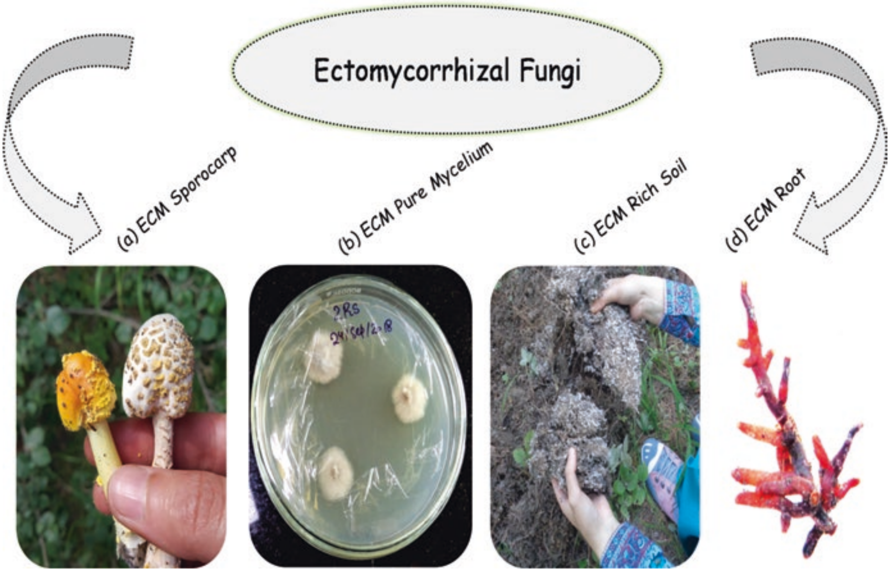

Fig. 15.1 Different existential forms of ectomycorrhizal fungi

Ectomycorrhizal fungi directly sequester heavy metals and other toxic pollutants through their dense hyphal network and allied dense hyphal slime (Denny and Ridge 1995). ECM fungi have role in metal immobilization through their protective metal-binding ability (Gadd 2016), which protect environs by locking metals and other hazardous pollutants (Yadav 2019).

This heavy metal accumulation ability depends on sensitivity level of ECM fungi to metal, in chorus with environmental factors (Khanday et al. 2016; Domínguez-Núñez et al. 2019). In ECM fungi, interspecific as well as intraspecific variations in sensitivity to metals have been reported (Hartley et al. 1997). The heavy metal tolerant ECM isolates effectively colonize heavy metal-polluted areas and serve as better filter than non-tolerant isolates (Colpaert et al. 2005, 2011).

Heavy metal-tolerant ECM fungi reduce heavy metal uptake and bring about their detoxification through several cellular exclusion mechanisms viz., extracellular heavy metal precipitation/inactivation, reduced metal uptake through filter function of the fungal sheath that obstruct the apoplastic movement of heavy metals, heavy metal mycosorption by fungal cell walls and fungal slimes (to constituents like chitin, melanin, and other cellulosic derivatives), enhanced heavy metal efflux through fungal cell membranes, alteration in specificity of metal transport channels, cytosolic metal ion chelation (by compounds like organic acids, glutathione, metallothioneins, and other compound-specific chaperones), compartmentation of heavy metals in chemically inactive forms inside the fungal vacuoles, adaptive reaction to oxidative stress [including enzymatic antioxidant systems (such as catalases, glutaredoxins, superoxide dismutases (SOD), and thioredoxins) and non-enzymatic antioxidant systems (such as glutathione, vitamins C, E and B_6)], and by enhancing expression of genes (like heavy metal transporter genes and metallothioneins) coding for heavy metal detoxifying proteins (Hartley et al. 1997; Jentschke and Godbold 2000; Jacob et al. 2001; Meharg 2003; Bellion et al. 2006; Hegedűs et al. 2007; Krpata et al. 2009; Bücking 2011; Colpaert et al. 2011; Machuca 2011; Urban 2011; Amir et al. 2014; Hrynkiewicz and Baum 2014; Khullar and Reddy 2016; Bhat et al. 2017; Tiwari and Lata 2018; Mishra et al. 2019; Singh et al. 2020).

(b) *Indirect/Non-specific Mechanisms of Heavy Metal Remediation*

Indirect mechanisms involve improvement of host plant growth and tolerance to environmental stress (Soares and Siqueira 2008). ECM fungi confer heavy metal tolerance to their host plants for surviving in contaminated environs, by forming a physical barrier and preventing translocation of heavy metals into the host (Bellion et al. 2006; Colpaert 2008; Futai et al. 2008; Itoo and Reshi 2013; Amir et al. 2014). However, ectomycorrhizal community composition has a prominent effect on the phytoremediation potential of host plants (Gil-Martínez et al. 2018). The heavy metal sequestration capability varies among ECM species (Melgar et al. 2016).

Bacteria associated with ECM fungi can further improve host plant adaptation to heavy metal pollution (Krupa and Kozdroj 2007; Amir et al. 2014). Furthermore, some bacteria known as mycorrhiza helper bacteria (MHB), which facilitate ECM formation, can also enhance bioavailability of heavy metals to host plant-ECM symbiotic association (Zimmer et al. 2009; Bücking 2011).

In metal-polluted environs, low-molecular-weight fungal organic acids (like oxalic acid, succinic acid, malic acid, citric acid), phenolic compounds, and metal-chelating agents (such as siderophores) of ECM fungi accumulate and sequester heavy metals in high concentrations (Ernst 1985; Ahonen-Jonnarth et al. 2000; Meharg 2003; Fomina et al. 2006; Machuca 2011; Itoo and Reshi 2013; Domínguez-Núñez et al. 2019). Several studies have confirmed that upon exposure to heavy metal stress, ectomycorrhizal-plants accumulate smaller quantity of metals within their tissues as compared to non-mycorrhizal plants (Adriaensen et al. 2004, 2005, 2006; Jourand et al. 2010; Kayama and Yamanaka 2014; Kumar and Atri 2017). Both host plant and associated ECM fungi possess different strategies of heavy metal remediation, which either act independently or operate together in symbiosis.

15.3 Future Research Directions

The role of ectomycorrhizal symbiosis in restoration of heavy metal-contaminated environs is a promising field of research owing to its eco-friendly, efficient, and economical nature. Future research directions in this field must include:

(a) *Study of additional ECM-plant symbiotic associations:* Worldwide, an estimated 25,000 species of fungi form ectomycorrhizal associations with woody plant families (Kumar and Atri 2017). However, till date, only a diminutive fraction of ECM-plant symbiotic associations have been studied with reference to their role in heavy metal remediation. Further studies in this direction will categorically lead to unearthing of fascinating novel ECM symbionts with exceptionally high remediation potential.

(b) *Study of other heavy metals:* Most of the research has been carried out only on few heavy metals such as Al, Cd, Cu, Fe, Pb, Ni, Ag, and Zn. Future research must be directed to other heavy metals like Sb, Be, Cs, Co, Au, Hg, Mo, Pd, Pt, Sr, Sn, W, U, and V.

(c) *Comprehension of basic molecular mechanisms:* Understanding basic molecular mechanisms of ECM-assisted heavy metal remediation is still a big challenge for scientists and needs intensive future research.

(d) *Transcriptomic approach:* Sequencing studies of transcript genomes of symbiotic ECM fungi by modern transcriptomic approach can lead to recognition of fungal symbiotic genes entailed in heavy metal tolerance. Further study of expression level of these genes and their products will be a major breakthrough in this field.

(e) *Bioengineering of ECM fungi:* Use of genetically engineered ECM fungal strains for detoxification and degradation of heavy metals is intriguing. However, strict regulatory guidelines of the Environmental Protection Agency, public non-acceptance, and bioethical issues hinder their application.

15.4 Conclusion

In disturbed ecosystems, heavy metals pose a serious environmental threat owing to their toxicity and persistence. Metals that are essential for plant growth at low concentrations exert toxic effects at higher concentrations due to their high chemical reactivity. Heavy metals enter food web and poses serious environmental and health risks. Restoration of heavy metal-contaminated environs can be accomplished through reinstallation of suitable ectomycorrhizal fungi. These ECM fungi serve a prominent role in heavy metal remediation. These fungi possess adaptive tolerance to heavy metals and confer heavy metal tolerance to their host plants for surviving in contaminated environs, by forming a physical barrier and preventing translocation of heavy metals into the host.

ECM fungi belonging to genera *Albatrellus*, *Amanita*, *Boletus*, *Cantharellus*, *Clavariadelphus*, *Cenococcum*, *Hebeloma*, *Hygrophoropsis*, *Hysterangium*, *Inocybe*, *Laccaria*, *Lactarius*, *Leccinum*, *Paxillus*, *Piloderma*, *Pisolithus*, *Rhizopogon*, *Russula*, *Scleroderma*, *Suillus*, *Thelephora*, *Tomentella*, *Tuber*, and *Xerocomus* have been reported to remediate heavy metals such as Al, As, Cd, Cs, Ca, Cr, Cu, Fe, Pb, Mn, Hg, Ni, K, Rb, Se, Ag, Ti, and Zn. These ECM fungi remediate heavy metals through direct and indirect mechanisms. Understanding basic molecular mechanisms of ECM-assisted heavy metal remediation is still a big challenge for scientists, and future research in this direction will categorically lead to discovery of fascinating remediation mechanisms of novel ECM symbionts possessing exceptionally high remediation potential.

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