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Phytoremediation

In-situ Applications

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Concepts and Strategies in Plant Sciences

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Preface

My experiences working on water quality issues in Africa, Asia, the Caribbean, Central America, and South America has shown me that traditional pollution remediation methods used in economically advantaged countries are not sustainable for economically emerging nations. While consulting on a petrochemical contaminated soil project in Western Africa I became displeased evaluating the feasibility and costs of traditional chemical and physical remediation technologies used in the Europe and the United States. The technologies were cost prohibitive and not sustainable for the stakeholders in the contaminated regions of Western Africa. At that time bioremediation was in its infancy and was not recommended for the project. Ultimately, I found out about the bioremediation that focused on petrochemicals. Plus, I learned it would have been cost-effective to use successfully in the African remediation site. After that, I was introduced to phytoremediation while doing technology transfer consulting and promotion for bioremediation researchers. My past research investigations on plants focused on application by using plants as research models for environmental stress and toxicology So, I promoted phytoremediation as a fascinating application of the basic plant sciences.

This book is intended to showcase successful in situ phytoremediation applications in a variety of remediation situations. These showcased investigations are particularly important to pollution problems in economically emerging countries that are limited in the resources to carry out high tech traditional pollution remediation. The research comes from junior and senior researches to provide a balance of viewpoints on the direction of phytoremediation research. The investigations are consistent with the United Nations Sustainable Development Goals and reflect future best practices in pollution remediation for economically emerging nations. Phytoremediation is not a fad. It is still an emerging science that has to be scrutinized, field tested, and subjected to cost-benefit analyses to find the best models for each remediation need. In addition, further studies are needed on blending phytoremediation with other remediation strategies improve the efficiency of remediation. The advancement of phytoremediation as a means of ensuring environmental resilience is also essential to take full advantage of its remediation features.

Kingwood, TX, US Brian R. Shmaefsky

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Chapter 1
Principles of Phytoremediation

Brian R. Shmaefsky

Abstract Phytoremediation, a form of bioremediation, is one viable option for removing pollution from contaminated soil and water. Bioremediation was developed as an inexpensive, environmentally friendly, and sustainable alternative to traditional chemical and physical pollution remediation methods. Bioremediation began with the use of bacteria and later other microorganisms, to extract or degrade inorganic and organic contaminants in soil and water in situ. It then evolved to other applications in combination with traditional chemical and physical remediation methods. Phytoremediation was came about from basic research studies on the physiology of halophytic and hyperaccumulating plants. At first, plants provided successful for extracting salts, metals, and radionuclides from soil and water. Further, studies discovered that plant roots and the rhizosphere were capable of extracting or degrading organic pollutants such as pesticides and petrochemicals. The in situ case studies showcased in this book demonstrate how phytoremediation is a sustainable means of pollution remediation in economically emerging countries and is consistent with the United Nations Sustainable Development Goals.

Keywords Bioremediation · Environmental pollution · Phytoremediation · Phytotechnology · Traditional remediation

1.1 Introduction

Phytoremediation is a means of applying the plant sciences to the better of human living conditions. It makes use of plant physiology and rhizosphere organisms as inexpensive and reliable approaches to removing some of the most hazardous or persist pollutants in regions with few financial resources available for pollution remediation in soils or waterways (Schwitzguébel et al. 2011). Some of these applications can be adapted to remediating airborne pollutants (Argawal et al. 2019). Phytoremediation is not a fad and it is most applicable when costly pollution remediation methods

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and technologies are not available (Bandari 2018). This view is supported by early efforts to accelerate the technology transfer of phytoremediation research (Boyajian and Carreira 1997; Salt et al. 1998). Aside from remediating customary pollution sites, phytoremediation has gained the interest of groups and governments evaluating community-based phytoremediation in grassroots efforts to remediate contaminants in community gardens, densely populated slums, farmlands, municipal parks, rural communities, and small towns (Smith 2015).

1.1.1 Origins of Phytoremediation

Humans and plants have coevolved since the hominid lineage branched from its Australopithecus ancestors (Martin and Li 2017). As societies progressed, people learned that a methodical understanding of plants was essential for their survival of people starting in Neolithic times, about 3000 BCE. This ancient knowledge, or protobotany, allowed people to use plants for food, medicines, and the construction of homes and tools (Day 2019). Archeological studies provide no doubts that ancient people made rational decisions about food plants that were applicable for cultivation and long-term subsistence. The use of plants for other purposes varied based on environment and culture. Plants used for building structures and burning were often selected based on the climate and the available of plants in a particular location (Garrison 1998). Medicinal uses of plants did not start out as a scientific pursuit and were primarily based on anecdotal evidence, non-controlled quasi-experimental, or cultural beliefs (Petrovska 2012).

The modern field of scientific botany, or plant sciences, was first published on papyrus documents around 400 BCE in Greece. During that period, Aristotle and Theophrastus developed a systematic characterize plants. Similar efforts on plant classification were recorded in China around 60 CE (Hardy and Totelin 2015). It is generally accepted in the European literature that Carolus Clusius heralded in modern botany around the 1500s CE. Clusius' work paved the way for a host of studies on plant anatomy, physiology, and reproduction carried out in Europe in the 1600s and 1700s CE based on microscopic studies and simple chemical analysis experiments (Egmond 2010). The 1800s CE was noted advances in plant diseases and inheritance. The advent of molecular biology brought forth more advances in botany including precise plant physiology investigations, genomics studies, and genetic modification (Iriti 2013). During this period, a rapid growth of biotechnology applications and innovations was developed leading to the first attempt at phytoremediation in 1983 by hyperaccumulating plants (Hakeem 2014).

Phytoremediation is a specific category bioremediation that makes use of metabolic processes in plants and in the rhizosphere to remove polluting substances from the environment (DeLorenzo 2018). Initially, bioremediation was developed as an alternative to traditional chemical and physical methods of remediating pollution contaminating soils and water, such as chemical neutralization or bulk soil removal (Conesa et al. 2012). Later, bioremediation efforts were adapted to removing air pollution (Devinny et al. 2017). Anthropogenic environmental contamination is an expected outcome of human activities in any type of societal survival strategy. Hunter-gatherer societies typically avoiding the buildup of pollution by migrating away from contaminated sites. The simplest forms of pollution, food waste, and human excrement became problematic for people during the first confirmed human urban settlements established by (Hershkovitz et al. 2018). This was determined by evidence of rodent infestation remains plaguing second millennium BCE archeological sites in the Near East (Weissbrod et al. 2014).

1.1.2 History of Pollution Remediation

Pollution mitigation in human population centers was first developed around 800 BCE by the Romans. This was evident in the aqueduct systems and excrement collection procedures that involving transporting the pollutants from the population centers for dilution in waterways or dispersal on agricultural lands (Markham 1994). Municipal waste pollution was less of a problem in ancient times and was typically buried or burned very much as it done today in many regions. Globally, other pollutants associated with early crafting, manufacturing, mining, smelting, and tooling were not considered hazardous and accumulated in the environment often with harmful effects on the environment and on human population (Zalasiewicz et al. 2010).

Environmental decay due to anthropogenic activity was likely recognized by ancient civilizations, but there was not much that could be done at the time to remediate any problems. Unfortunately, like in many regions of the world today, pollution was tolerated as a requisite consequence of commerce and settlement lifestyles. Pollution started becoming a grave problem around 1000 CE with the birth of the coal-burning era and expansion of mining operations. Societies in the medieval period saw worsening pollution which led to public concerns and calls for political action. It was not until the 1600s CE when Europe showed the first records of pollution control methods that typically involved pollution fines and the development of early technologies for pollution remediation such as sewage septic systems in the middle 1800s CE (Hughes 2016). The amount of pollution produced globally started increasing dramatically since the early 1900s CE; any efforts for pollution control focused on various strategies to contain or reduce pollution.

Almost all of the modern strategies for reducing pollution were expensive and involved either penalties, transport to specialized landfills, or manufacturing practices that reduced or recycled wastes. Prosperous industrialized nations benefited from these practices which were unfeasible to practice in emerging nations. It was not until the 1980s CE that pollution remediation became a concern primarily in the USA with the development of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), or Superfund (Beins and Lester 2015). The strategies needed to carry out environmental remediation as proposed in CERCLA were even more costly than pollution prevention and pollutant storage (Markham 1994). Again, countries with emerging did not have the economies to model remediation efforts in the USA and similar programs in Europe. By the 2000s CE, prosperous industrialized nations were seeing great improvements in environmental quality while pollution in countries with emerging economies was worsening remaining a persistent problem (Fig. 1.1).

A factor exacerbating pollution in countries with emerging economies is the pollution haven hypothesis. The pollution haven hypothesis is global economy observation in which differences in environmental regulations will cause the inter-country relocation of dirty industries to countries that are already heavily impacted by protracted pollution problems (Xiang et al. 2018). Potential pollution haven regions that have been identified are Central East European Countries (Martínez-Zarzcoso et al. 2016), Southern Africa (Nahman and Antrobus 2005), Asia (Shaprio 2013), and Latin America (Birdsall and Wheeler 1993; Sapkota and Bastola 2017). The susceptibility of a country or region becoming a pollution haven is calculated using the Kuznets curve which is a correlation between environmental quality and economic development (Fig. 1.2). In certain situations, indicators can predict that pollution gets worse as the modernization of a country's economy increases. This trend continues until the average income reaches a certain level as development progresses (Kaika and Zervas

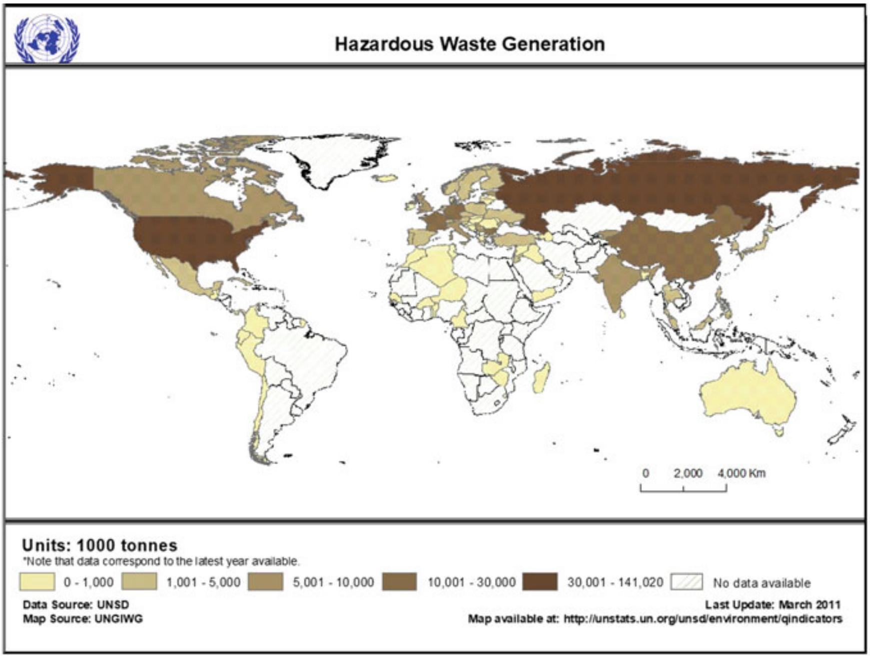

Fig. 1.1 Hazardous waste production is not equally distributed worldwide. Many of the nation that produce the wastes lack the resources to reduce, store, and remediate hazardous waste pollution. Image courtesy of the United Nations Statistics Division

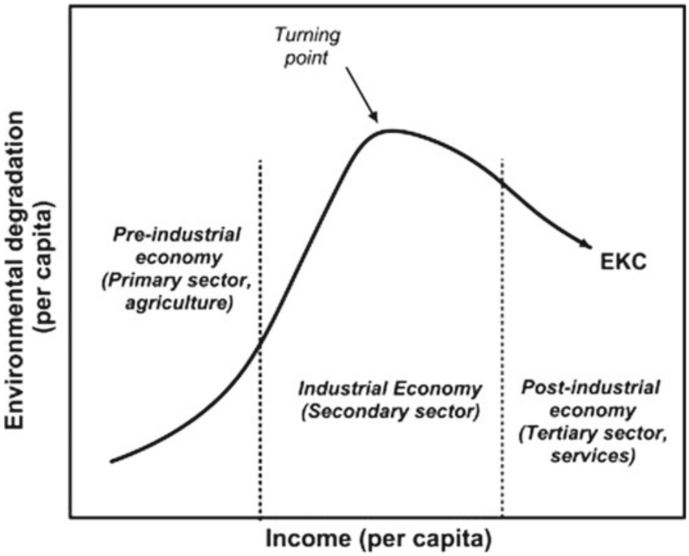

Fig. 1.2 The Kuznets curve helps predict the susceptibility of a region to being a pollution haven. Image from Kaika and Zervas (2012). The environmental Kuznets curve (EKC) theory—Part A: Concept, causes, and the CO_2 emissions case. The environmental Kuznets curve (EKC) theory—Part A: Concept, causes, and the CO_2 emissions case. Energy Policy. 62:1392–1402

2012). Pollution haven regions would benefit the most from inexpensive and sustain pollution prevention and remediation efforts.

The mounting pollution problem in emerging economies was formally recognized by the United Nations Environment Program at the United Nations Conference on the Human Environment (Stockholm Conference) in June 1972 (Brisman 2011). According to Brisman, "the main purpose of the conference was to serve as a practical means to encourage and provide guidelines for action by Governments and international organizations designed to protect and improve the human environment." In 2017, the fifteenth meeting of the Chemical Review Committee of the Rotterdam Convention concluded that "the Stockholm Convention provides an effective and dynamic framework to regulate POPs throughout their lifecycle, addressing the production, use, import, export, releases, and disposal of these chemicals worldwide. However, inadequate implementation is a key issue that has been identified in the evaluation. Mechanisms and processes required by the Convention to support Parties in meeting their obligations have all been put in place, with the exception of procedures and mechanisms on compliance." The key challenge for emerging economy countries was the financial infrastructure needed to support the pollution remediation initiatives outlined by the United Nations (UN 2018). It appears that the Stockholm Conference differentially benefited countries with the means to reduce environmental pollution.

Pollution problems have been officially recognized by the United Nations as one consequence of the country's non-sustainability. In June 1992, the United Nations Conference on Environment and Development (UNCED), also known as the Rio de Janeiro Earth Summit, generated a comprehensive action plan for building global partnerships for sustainable development to improve human living conductions and protect the environment from anthropogenic activities and natural disasters (Dodds et al. 2016). The action plan is divided into seventeen sustainable development goals, three of which are directly applicable to reducing environmental pollution using sustainable methods: Goal 6—Clean Water and Sanitation, Goal 14—Life Under Water, and Goal 15—Life on Land. Goal 10, Reduce Inequalities, sets best practices for reducing economic equities that hinder access to pollution remediation and increase the likelihood of becoming a pollution haven (Gaffney 2014). In the sustainable development goals, phytoremediation is one of the recommended sustainable pollution remediation best practices, particularly for counties with emerging economies (Haller et al. 2018).

1.2 Traditional Methods of Removing Contaminants

1.2.1 Traditional Soil Remediation

As discussed earlier, soil contamination, or land pollution, is an ancient problem that has become more complex with the advent of industrialization and urbanization. Typically, soil contamination is defined as the occurrence of hazardous materials at harmful concentration levels to humans or to the environment in soils. Some contaminants, such as arsenic or sulfates, are natural pollutants. However, most remediation efforts focus on anthropogenic contaminants from a variety of sources (Mirsal 2008). The most common soil contaminants are minerals and metals, organic compounds, and xenobiotics directly and indirectly from agricultural, industrial, and municipal sources (Duarte et al. 2018). Future technologies and increasing global urbanization will be exacerbating soil pollution problems with higher levels of contaminants and emerging pollutants (Noguera-Oviedo and Aga 2016).

There are many traditional on-site, or in situ, and off-site chemical and physical soil remediation methods used today (Nyer 1998). Traditional soil remediation begins with mapping the contamination site to determine the probable extent of the contamination plume. The next step is collecting homogenized soil samples in the potential plume area. Soil sampling is typically done with non-contaminated augers, shallow sampling tubes, or deep sub-soil probes. Sampling can also be done with scoops, shovels, or spades (Couch et al. 2000). Commonly, samples are preserved and transported to chemical testing laboratories. On-site testing can also be done using portable testing laboratories. Soil pollution screening tests usually involve standard assays that characterize the pollutant and determine pollutant levels; this task varies in complexity, particularly if the area has many sources of contamination (EPA 2018;

ASTM 2019). Containment in a contaminated site is a standard procedure before any remediation can proceed (Zhang 2009).

The simplest method of soil pollution remediation is removing the soil using the physical removal method of dredging or excavation (Wang and Leonard 1976). This process involves digging up the contaminated soil and transporting it off-site for disposal or treatment. Soils with hazardous contaminants are normally disposed in either a hazardous waste landfill or hazmat holding facility. The major limitations of this method are safe and affordable storage and transportation of the contaminated soil. Studies show that this model of soil pollution remediation is not optimal or preferred for economically emerging countries due to deficiencies in hazardous materials handling technologies and safe handling practices. However, it is more economical than other traditional remediation strategies (Manap and Voulvoulis 2015).

In many situations, it is not prudent to remove and transport contaminated soil. Soil removal can spread and worsen contamination in an area. Plus, the storage or future remediation of the soil transported off-site is often costly. Solidification and stabilization is a process that encloses the pollution on-site for storage or future remediation (Scullion 2006). This process involves using some type of chelating agent to stabilize the pollutant in the soil, to reduce leaching, followed by solidification of the soil with binding agents or soil amendments that made the soil impermeable and immobile. Soil stabilization varies with the chemical characteristics of the contaminant. Chemical methods can be used to react with the pollution, typically forming precipitants or compounds that bind to the soil. Metal oxides (Komárek et al. 2013), phosphates (Hettiarachchi et al. 2000), and clays such as palygorskite (Álvarez-Ayuso and Garcıa-Sánchez 2003) are common stabilizers for heavy metal pollutants in soil. Organic pollutants, such as PCBs and pesticides, are less likely candidates for soil stabilization (Uqab et al. 2016). They are best stabilized using physical methods that absorb and trap the contaminants. Studies have used activated carbon, plant polymers, liquefied humus, and iron nanoparticles to bind and stabilize organic pollutants (Singh and Misra 2016). Current solidification agents also vary based on the soil structure and nearby geological features. Cement was the first material used for soil stabilization (Glasser 1997). Cement-free methods using clay are being tested for solidification to reduce soil compaction and reduce solidification costs (Wang et al. 2019). The greatest limitations of this method are the depth of the soil and future use of the site. Structures constructed over the site might compromise the integrity of the solidification (Stojić et al. 2018).

During thermal desorption, the contaminated soil is heated in a chamber to vaporize the soil contaminants. This can be done off-site or on-site depending on cost-effectiveness. In addition, it is effective for removing heavy metal (Sierra et al. 2016) and organic (Kastanek et al. 2016) pollutants. It has been tested with some effectiveness at removing pollutants on-site from contaminated agriculture soils proposed for further food production (O'Brien 2016). Vaporization takes place in rotary dryer or thermal screw dryer. Rotary dryers indirectly heat the soil in a rotating cylinder, while thermal screws circulate hot oil or steam directly on the soil as it passes through an auger. Thermal desorption can be achieved using low temperatures (LTTD) or high temperatures (HTTD). Organic pollutants are usually removed from soil using

LTTD; the off-gassed contaminants are collected in vapor condensation systems and are not fully degraded into nonhazardous byproducts. Heavy metals are removed with HTTD; the off-gas is collected using air pollution scrubber units that require further treatment to reduce any toxicity. There are several limitations for thermal desorption in economically emerging countries. A primary limitation is the cost of the thermal desorption unit as well as the added cost of heating the unit. Another limitation is the off-gas usually has to be treated as a hazardous material and requires further remediation (Zhou et al. 2019).

The process of in situ oxidation is a flexible chemical method of removing contaminants from soils, particularly contamination that spreads to contiguous groundwater. An off-site strategy called ex situ soil oxidation is an alternative method requiring transportation to a treatment facility (Zhang 2009). It is best used with volatile and semivolatile organic contaminants and has been used extensively on US Superfund sites (EPA 2017; Tsitonaki and Bjerg 2008). This process involves pumping oxidizing compounds into an injection well inserted into the contaminated soil. Oxidants such as hydrogen peroxide, ozone, permanganate, and persulfate are commonly used. In certain soil, iron catalysts may be needed to facilitate oxidation (EPA 2017). The site is recurrently sampled until the contaminants are degraded in situ. This method can be done in an off-site facility; the soil can be reused once the contaminants are degraded. Limitations are primarily related to the effectiveness of oxidation in different types of soils and in complex heterogeneous contamination events. Its applicability in emerging economies is promising, but still under investigation (Pac et al. 2019).

The emerging strategy of electroremediation can be used along or in combination with other remediation efforts to remove soil contaminants (Page and Page 2002). This process is most feasible in situ and uses a low-voltage direct current charge to remediate heavy metals in soils. The electrodes are inserted into slotted PVC-lined wells dug around the contaminated site. The anodes and cathodes set up an electrokinetic migration potential that attracts the heavy metals which then become immobilized in wells. The electrodes also facilitate migration of the heavy metals by producing acidic pH conditions in the contaminated soil (the US Army Environmental Center 2000). Limitations in producing an adequate electrokinetic field and a uniform soil pH in many types of soils restrict the utility of this process. Plus, the procedure is not practicable in large remediation sites likely found in countries with emerging economies (Cameselle and Reddy 2019).

Nanoremediation is the newest of the traditional soil remediation methods that use chemical or physical separation of pollutants from soil. This technology uses a variety of nanoparticles to degrade or immobilize soil contaminants. In current applications of nanoremediation, the nanoparticles are composed of zero-valent iron particles. The zero-valent iron either acts like a catalyst to facilitate contaminant degradation or alters the soil matrix to immobilize the contaminants (Machado et al. 2017). Currently, nanoparticles are used for remediating heavy metal contamination (Gil-Díaz et al. 2017). Nanoremediation has been combined with electroremediation to remove organic pollutants (Gomes et al. 2016). Its application in emerging economies is restricted for various reasons, primarily due to the cost of purchasing or synthesizing the volume of zero-valent iron nanoparticles needed for large remediation sites (Gavaskar et al. 2005).

1.2.2 Traditional Methods of Removing Water Contaminants

Water pollution is often defined as the presence of anthropogenic or naturally occurring harmful substances, primarily biological or chemical, in groundwater or surface water. As with soil pollution, the anthropogenic contamination of ground and surface water is an ancient problem that was exacerbated by the growth of human settlements during Paleolithic times (Armelagos 2009). Unlike soil pollution, water pollution can disperse rapidly and globally through the water cycle. Global industrialization greatly intensified the severity of water pollution. Particularly, harmful anthropogenic water pollutants were synthetic pesticides and plastics (Bell et al. 2019; Markham 1994). Unfortunately, water pollution control up until the 1980s CE was not adequate and reducing or remediating water pollution and remains inadequate in many countries with emerging economies (Goel 2006).

Many entities involved in water quality management characterize water pollution into the following categories: chemical, effluent, industrial specific, microbiological, and radiochemical. Chemical pollution is typically divided into inorganic and organic pollutants. The environmental impacts of chemical pollutants can alter pH, increase chemical oxygen demand, and alter salinity and toxicity. Effluent pollution is usually associated with municipal activities and is often made up of an unpredictable combination of pollutants. Industrial specific pollution would include sediment and thermal pollution (Helmer and Hespanhol 2019).

Traditional water pollution remediation strategies are often divided into two groupings: groundwater remediation and surface water remediation (Bell et al. 2019). Several of the methods used in soil remediation also apply to the removal of contaminants from groundwater. Surface water strategies are facilitated by having easier access to the pollution; however, the pollutants are difficult to contain after a contamination event.

1.2.2.1 Traditional Groundwater Remediation

Strategies for traditional groundwater remediation can be done within ex situ or in situ processes. The simplest and most common ex situ remediation method is to physically pump contaminated water out of the soil through a well and then collect the water in containers for disposal or cleanup processing. Pumping systems are relatively simple and inexpensive to operate and ideal for countries with emerging economies (Dermatas 2017). Unfortunately, there is no generalized method for pumping the water out of the soil. Pumping systems and well designs vary greatly with the site characteristics including soil type and the local of the water in the soil profile (EPA

2017). Pumping permits flexibility in that the contaminated water can be treated on-site or off-site. Ex situ treatments of groundwater use standard on-site or off-site water treatment for the storage or neutralization of liquid hazardous wastes (LaGrega et al. 2010).

In situ air sparging is a remediation technique developed for saturated soils and shallow groundwater pollution conditions. In the literature, it is also called air stripping and volatilization. Its utility has been expanded to aquifers by enhancing the technique with surfactants (Kwon et al. 2019). Organic pollutants are currently the only target contaminant that works with air sparging. Air sparging is achieved by injecting air directly into the groundwater. The air bubbles volatize the contaminants so that the pollutants can be extracted by vapor phase technologies. The process could be enhanced with chemical decomposition methods such as oxidation (Brusseau and Maier 2004). The major limitation of the process is site-specificity based on soil makeup and the degree of water saturation. Air injection wells must be designed for the particular site. Its use is promising for countries with emerging economies (Naidu 2013).

In situ remediation of groundwater can be achieved with mixed success using the solidification and stabilization processes applied to soil remediation. Studies by the EPA demonstrated that solidification and stabilization is effective for groundwater contaminated with heavy metals, radioactive materials, semivolatile organics, and nonvolatile organics. It was ineffective for volatile organics (EPA 2009). As discussed earlier, the greatest limitations of this method are the depth of the soil and future use of the site. This process of groundwater remediation is feasible in countries with emerging economies as a stopgap effect. It is not environmentally or economically sustainable for large-scale groundwater pollution (Dermatas 2017; EPA 2009).

Also, discussed earlier was in situ oxidation as an adaptable chemical method of removing pollutants from soils that also have contaminated groundwater. Specific applications of in situ oxidation have been tested on various groundwater pollution cases (Siegrist et al. 2011). As with the treatment of soils, limitations are primarily related to the effectiveness of oxidation in different types of groundwater environments and in situation with complex heterogeneous contamination of the groundwater. Its applicability in emerging economies is promising and still under investigation.

Electroremediation has also be tested as a strategy for in situ groundwater remediation. Early tests on aquifers (Shiba et al. 2000) shallow groundwater situations (Fallgren et al. 2018) were promising for inorganic and organic pollutants. The process is more sophisticated than the electroremediation of soils; however, it appears to be cost-effective for countries with emerging economies.

The feasibility of using nanoremediation on groundwater pollution is still under consideration as far as its cost and environmental safety (Bardos et al. 2018). This method is best for remediating soils contaminated with heavy metals. As discussed earlier with soil remediation, the nanoparticles used to trap or degrade pollutants are composed of zero-valent iron particles (Machado et al. 2017). This technique is effective in sites contaminated with a mixture of heavy metals that may actually be cost-effective in the future for groundwater treatment in countries with emerging economies (Liu et al. 2015).

Prevention of nonpoint and point source pollution events in surface waters definitely outweighs costs and outcomes any remediation option, particularly in countries with emerging economies. Unlike groundwater, surface water is simple and rapid to collect using wide-ranging pumping systems and highly adaptable containment booms. Unfortunately, the containment of pollutant plumes in flowing water and large non-flowing bodies of water is minimal or nonexistent and the plumes disperse as micropollutants which are difficult to recover and are subject to biomagnification (Schwarzenbach et al. 2006). Traditional methods of surface water pollution treatment vary greatly based on the environmental fluid dynamics, or water hydraulics, of the body of water (Singh and Hager 1996). Important factors for effective and sustainable surface water remediation are containment, hydrodynamics, microbial load, sediment load, and water quality (Mekala and Davidson 2015). Hydrodynamic characteristics are the major factor because it is possible to enclose the pollution lentic systems, non-flowing bodies of water, whereas in lotic systems, flowing bodies of water, there are negligible pollution containment possibilities.

1.2.2.2 Traditional Surface Waters Remediation

The simplest traditional method of remediating lotic aquatic systems, such as rivers and tidal regions, is through purification. Purification involves injecting clean water into the aquatic system to flush the pollutants downstream or into the tidal outflow while diluting the pollution plume. This process does not remover the pollutants. Rather, it dilutes the pollutants to subthreshold levels of environmental and human toxicity and facilitates natural biological, chemical, and physical degradation processes. This process can be enhanced using optimal control theory to improve water quality efficiently (Alvarez-Vázquez et al. 2009). This is an underexploited technology in many economically emerging countries. Purification can be supplemented with in situ oxidation (Andreottola and Ferrarese 2008) and nanoremediation (Rasalingam et al. 2014) with significant success at improving degradation of the pollutants with a considerable cost to the process.

In another traditional remediation process, polluted lotic water can be diverted to retention ponds or pumped into containers for on-site or off-site treatment using a variety of wastewater purification processes (Ramalho 2013) and hazardous materials neutralization or disposal methods (Wang et al. 2004). A major problem with the dilution and diversion methods is that they only reduce the pollutants from the water and do not remove pollutants in the soils of the river banks and benthic regions (Domínguez et al. 2016). Initial methods for addressing the complete contamination issue of lotic water and adjacent soils were studied in small-scale and field-scale experiments (Sheng et al. 2012).

As mentioned earlier, pollutants in lentic systems are contained systems and it is somewhat of a simpler remediation process using many of the traditional methods for cleaning flowing waters. In addition, in situ flocculation, used alone and in conjunction with other traditional remediation methods, has been shown effective in large lakes (Chen et al. 2015). As with lotic systems, pollutants in lentic systems do not remove pollutants in the soils of the littoral zone soils and benthic regions (Domínguez et al. 2016). However, there are traditional in situ, such as capping and neutralization (Zoumis et al. 2001), and ex situ, such as dredging (Cooke et al. 2005), methods of sediment remediation for lentic systems. Overall, surface water traditional remediation methods vary in their success and cost. Most of these remediation methods are not sustainable in any country and do not impart resiliency to further contamination. However, early studies showed that it is possible to combine traditional remediation with emerging strategies in the bioremediation of soils and water to improve and possibly reduce the cost of pollution mitigation (Lynch and Moffat 2005).

1.3 A Survey of Bioremediation

In contrast to the chemical and physical methods used in traditional pollution remediation, bioremediation is based on the principle that all organisms remove inorganic and organic substances from the environment to carry out their growth, metabolism, and reproduction. Bioremediation using natural, selectively bred, genetically modified organisms can be used to clean unwanted substances from air, soil, raw materials, and water for pollution management and industrial processing (Shmaefsky 1999). It is typically divided into bacterial bioremediation, mycoremediation, and phytoremediation. Protists currently play a small role in bioremediation except in applications where they facilitate the bioremediation of other organisms (Rubenstein et al. 2015).

1.3.1 History of Bioremediation

Ancient Babylonians were actually the first to make use of rudimentary bioremediation around 4000 BCE. They deposited human feces and urine into large cesspools where the sewage biologically degraded until it was diluted with freshwater and passed through hydraulic systems that fed the wastewater into waterways (George 2015). Sewage treatment remained somewhat unchanged until the 1800s CE in France and the United Kingdom with the development of the first septic system designed to biodegrade sewage into a quality of water similar to modern secondary treatment (Cotteral and Norris 1969).

The first recorded trial study on bioremediation was performed in the 1960s CE by petroleum engineer George M. Robinson. He used various mixtures of bacteria to degrade petroleum produces vitro and in holding tanks (Sonawdekar 2012). Robinson's work was supported by actual field experiments on petroleum-contaminated groundwater in the 1970s CE (Raymond et al. 1975). In the 1970s CE, Robinson commercialized his discovery and made use of various strains of Pseudomonas to clean fuel from decommissioned Queen Mary passenger ship's fuel storage tanks, clean oil residues in restaurant grease traps, remove odors from zoo animal wastes, and supplement sewage treatment. However, Robinson's major contribution was the use of Pseudomonas to remediate petroleum pollution in soils and water (Adams et al. 2015); other naturally occurring bacteria were recruited into bioremediation based on particular metabolic pathways suitable for specific pollutants. Following Pseudomonas, other commonly used bioremediation bacteria were *Alcanivorax borkumensis*, *Dechloromonas aromatic*, *Deinococcus radiodurans*, *Methylibium petroleiphilum*, and *Phanerochaete chrysosporium* (Antizar-Ladislao 2010). The arrival of genetically modified bacteria brought about the desire to produce bacteria specifically engineered for bioremediation (Kumar et al. 2013). Bacteria have proved successful in the in situ and ex situ bioremediation of inorganic and organic pollutants in soil and water and are cost-effective for countries with emerging economies.

Experiments using fungi as bioremediation organisms got its start in the 1990s CE and led to the first trials on mycoremediation. Fungi were exploited because, compared to bacteria, they showed a greater diversity of enzymes capable of degrading pollutants and xenobiotic compounds (Kulshreshtha et al. 2014). Dozens of fungi, both mycelial and yeast forms, have been tested. The most studied fungi for mycoremediation are *Agaricus*, *Bjerkandera*, *Irpex*, *Lentinula*, *Pestalotiopsis*, *Phanerochaete*, *Pleurotus*, and *Trametes*. They are equally effective to bacteria at remediating inorganic and organic pollutants. The literature shows that they are superior at colonizing various substrates in a wide variety of natural and artificial environments. However, organic substrates, such as algal polymers or wood chips, are often needed for mycoremediation of water contaminants (Harms et al. 2011; Rhodes 2014). As with bacterial bioremediation, mycoremediation appears cost-effective for countries with emerging economies.

1.3.2 Mechanisms of Bioremediation

The metabolic mechanisms of bacterial and fungal bioremediation include intrinsic enzymatic activities that degrade food sources or deactivate environmental toxins. Microorganisms can also be genetically engineered to express enzymes that alter or break down xenobiotic chemicals. A primary limitation of bacterial bioremediation is the bioavailability of enzymes that biologically convert many substances into innocuous products and byproducts (Kang 2014). To degrade the pollutant, a majority of the bioremediation microbes carry out metabolic reactions involved in aerobic metabolic pathways that use oxygen as an electron acceptor. Anaerobic bioremediation microbes use carbon dioxide, certain metals (Fe^{3+} and Mn^{4+}), nitrate, and sulfate as electron acceptors (Hatzikioseyian 2010). The role of the contaminants in nascent bioremediation applications is either an organic source of carbon dioxide or a source of electrons for the microorganisms. In a cometabolism pathway, the contaminant undergoes a process similar to detoxification. Cometabolism requires a primary food source for the microorganisms to degrade the contaminant (Frascari et al. 2015). The established methods making use of microorganisms in bioremediation include bioaugmentation, biofiltration, ex situ bioreactors, biostimulation, bioventing, composing, and landfarming (Baker and Herson 1994; Adams et al. 2015).

Bioaugmentation is the in situ or ex situ addition of bioremediation enzymes or organisms on contaminated materials. Bacteria and bacterial enzymes are most often used in bioaugmentation. It is commonly used to facilitate the remediation of wastewater and has been applied extensively in petroleum cleanup and landfill maintenance. In agriculture, bioaugmentation is used to remove excess nutrients from farm runoff. Bioaugmentation is often used in countries with emerging economies (Hernandez-Soriano 2013).

Biofiltration can be used in two different applications. One form of biofiltration is a specialized application of bioremediation used to remove organic vapors from volatile emissions. Microorganisms are embedded in a biofilter matrix that captures and traps the vapors for microbial degradation. Another form of biofiltration uses biofilters placed in holding tanks to remove contaminants from materials through the filter or trapped in the filter. Inexpensive biofiltration units have been used successfully in countries with emerging economies (Mara 2013).

Bioreactor remediation typically uses large environmentally controlled mixing tanks as a container for ex situ bioremediation. Biodegradation in bioreactors can be achieved with a mixture of microorganisms or a cocktail of specific enzymes. Bioreactors are often associated with the remediation of excavated soils, solid wastes, and pumped contaminated water. It is very simple to monitor the rate and accomplishment level of the degradation or detoxification processes (Robles-González et al. 2008). Automated bioreactors tend to be very costly, but there are designs that are inexpensive and relay on manual techniques to operate and monitor the bioremediation process. They are usually too costly to use in countries with emerging economies except in situations where the extracted contaminant has a large economic value that compensates for the cost of the unit.

Biostimulation is an economically feasible bioremediation process that uses nutrients, such as fertilizer or nutrient molecules, or substrates, such as enzyme cofactors, to stimulate the naturally occurring organisms in the contaminated site. The process is mostly done in situ, but it has also been used ex situ off-site. It is most useful in sites with low levels of contaminants. In some situations, biostimulation is encouraged adding small amounts of a related pollutant to the remediation site. Biostimulation is economically feasible for emerging economy countries in situations of low levels of contaminants (Adams et al. 2015). Bioventing is related to biostimulation. It differs in that the naturally occurring organisms in the contaminated are stimulated by oxygen vented to the contaminated site. It is used primarily in situ for contaminated soils. It is a relatively inexpensive technique, but it is not suitable for remediating halogenated gases (Lui et al. 2017).

Composting and landfarming are two inexpensive bioremediation processes that stimulate naturally occurring or supplemented bioremediation microorganisms. Compositing is typically performed ex situ and involves mixing contaminated soil or water with compose that contains bioremediation microorganism. Once the process is done, the compost can be used for soil supplementation or disposed in a sanitary landfill. Landfarming in an in situ process that using soil amendment and tilling practices to stimulate the bioremediation organisms added to contaminated soils. Both of these processes are most effective against organic pollutants at low to moderation contamination levels (Bandyopadhyay et al. 2018).

1.4 A Survey of Phytoremediation

1.4.1 Phytoremediation Defined

The focus of this chapter is the use of plants, phytoremediation, as a bioremediation agent. Phytoremediation is considered a subset of phytotechnology according to the International Phytotechnology Society. The official definition of phytoremediation is defined as "the uses plants to absorb pollutants from soils or from water." Phytotechnology is defined as "the science of using plants to solve environmental problems such as pollution, reforestation, biofuels, and landfilling" according to the International Phytotechnology Society (International Phytotechnology Society 2019).

1.4.2 History of Phytoremediation

It is generally accepted that the idea of using plants for bioremediation was formalized by Robert Richard Brooks research studies on hyperaccumulating plants in the 1960s CE (Brooks 1998). Hyperaccumulating is naturally capable of growing in soils or water with high concentrations of metals that would normally harm other plants. They can tolerate large concentrations of the metals in their tissues while exhibiting no signs of cytotoxicity. Some of these plants have specialized metal transporter proteins that facilitate the uptake of metals that are typically not transported into cells (Rascio and Navari-Izzo 2011). Brooks directly and indirectly contributed to the discovery of hundreds of hyperaccumulating plants selectively capable of up-taking and accumulating various metals as aluminum, arsenic, cadmium, cobalt, copper, chromium, lead, manganese, mercury, molybdenum, nickel, selenium, thallium, and zinc (Brooks 1998). Later, it was discovered in a host of studies that certain hyperaccumulating plants could uptake radioactive materials (Fulekar and Singh 2010).

Studies conducted in the 1990s by academic researchers and the US Environmental Protection Agency paved the way for using plants for the bioremediation of organic contaminants in soil and water. These plants were not the bioaccumulation plants used for remediating metals; rather, these plants were capable of degrading or detoxifying a variety of organic chemical pollutants in soil and water. The organic chemicals these plants could remediate included crude oil, explosives, herbicides, landfill leachates, pesticides, petrochemicals, and wastewater components (Tsao 2003).

1.4.3 Mechanisms of Phytoremediation

The mechanisms of phytoremediation include phytoextraction, phytostabilization, phytotransformation, phytovolatilization, and rhizodegradation. These physiological processes are similar to traditional chemical remediation methods and microbial bioremediation mechanisms. Plus, phytoremediation is subject to some of the constraints of other remediation methods, such as optimal concentration of the contaminants, environmental pH, and soil or sediment composition. Many phytoremediation plants have unique needs in that they may require a cometabolism relationship with microorganisms in order to carry out remediation (Hooda 2007).

Phytoextraction, as described earlier, makes use of hyperaccumulating plants that naturally uptake, translocate, accumulate, and sometimes metabolically degrade contaminants using unique carrier proteins, transporters, and enzymes. It is one of the earliest of the phytoremediation methods and is primarily effective for the remediation of metals and radioisotopes. This number of plants suitable for phytoextraction keeps growing and includes alga, ferns, and mosses (Singh and Ma 2007). Phytodesalination is a variation phytoextraction that uses halophytic plants to uptake and sequester salts from soil or water (Jlassi et al. 2013).

Phytostabilization relies on plants that have the ability to stabilize or immobilize metals in soils. It is typically used to reduce leaching of contaminants from soils and decrease soil erosion and runoff. This is achieved with root exudates that bind to soil particles, metals, and certain organic molecules. The root exudates are usually a complex mixture of amino acids, carbohydrates, enzymes, lipids, organic acids, and phenolic compounds. Sometimes, a combination of plants is used to achieve a particular composition of exudates (Hillel 2005).

Phytotransformation, also known as phytodegradation, refers to the use of plants to break down organic contaminants. The plants used in phytotransformation take up the organic materials through the roots and perform the bioremediation intracellularly. Biodegradation is typically achieved using hydroylases that attach hydroxyl functional groups to the contaminant molecules or oxidases that modify the contaminant functional group. The contaminants are often modified with the second phase of metabolism using detoxification enzymes. Phytotransformation is relatively inexpensive and has been shown effective against atrazine, PCPs, pesticides, petrochemicals, and TNT.

Phytovolatilization exploits transpiration and sometime phytotransformation to remove contaminants from soil and water. In this process, plants uptake the contaminants in the roots. The contaminants are then transported to the leaves where the contaminant is removed by transpiration as a volatile substance. Many of the compounds are degraded or detoxified before being transpired. This process is most effective on organic pollutants. Phytovolatilization has also be used to remediate mercury which is converted to its elemental form. Other studies used phytovolatilization to remove arsenic and selenium from soil and water (Arya et al. 2017).

Rhizodegradation, often called phytostimulation, takes advantage of the plant–soil interactions in the rhizosphere that degrade contaminants. The rhizosphere is a thin region of soil modified by a complex mixture of root exudates and a unique microbiome made of up bacteria, fungi, and protists. Rhizosphere dynamics has been the subject of basic ecological research for many years. However, it is only recently that these findings are being applied to agriculture, land management, and phytoremediation. The plant-microbiome environment is proving effective at degrading metals, organic pollutants, radionuclides, and xenobiotic compounds (Dzantor 2007). Rhizofiltration is a variation of rhizodegradation for remediating groundwater and surface waters. In this application of bioremediation, the rhizosphere acts as a filter that uptakes and degrades water contaminants (Hanus-Fajerska and Koźmińska 2016).

1.5 Genetic Modification and Phytoremediation

Advances in producing genetically modified organisms (GMOs) have contributed greatly to the plant sciences, particularly early in the history of phytotechnology (Cherian and Oliveira 2005). Genetic engineering provides the opportunity to impart phytoremediation properties into any plant increasing. This increases the options for selecting native plants to carry out phytoremediation more effectively than introduced plants not fully acclimatized to the remediation site as evident in plant physiology studies (de Mello-Farias et al. 2011). Genetic engineering also permits the use of crop plants (Agnihotri and Seth 2019) or other commercially useful plants (Das et al. 2016) for phytoremediation in which the spent plants are repurposed.

Researchers have currently isolated several groups of “phytoremediation genes” that can be transfected into host plants to impart phytoremediation properties. These include genes for cytochromes, mono-oxidases, specific reductases, and specific synthetases for biodegradation. A wide array of genes are available for inducing hyperaccumulation or phytoextraction including alpha-glutamyl-cysteine (alpha-Glu-Cys) synthetase, ATP sulfurylase, cysteine synthase, glutathione reductase, metallothionein, phytochelatin synthase, serine acetyltransferase, and metal-specific transferases (Cherian and Oliveira 2005).

One drawback to integrating GMO plants or microorganisms into phytoremediation is resistance by governments or the public about releasing GMOs into the environment (Shmaefsky 2010). Another disadvantage to GMO phytoremediation is the commercialization (Qaim 2009) and economics (Barragán-Ocaña et al. 2019) of using in economically emerging countries.

1.6 The Reality of Phytoremediation

Phytoremediation as an exclusive or supplemental means of remediating soil and water pollution is very promising for countries with emerging economies, as well as economically advantaged countries. In economically emerging countries, phytoremediation as a sole remediation method is inexpensive compared to traditional chemical and physical remediation methods and requires a minimum of engineered technologies (Prabakaran et al. 2019). Supplementing phytoremediation with traditional remediation technology in any country can improve the expediency of severe pollution situations as is evident in trial applications on the US Superfund sites (Rock and Sayre 2007) and military remediation operations (Siebielec and Chaney 2012). Urban areas in economically emerging countries can chiefly benefit from hybrid phytoremediation efforts (Banjoko and Eslamian 2015). It appears from the literature that the diversity of plants used for phytoremediation may exceed the variety of bioremediation microorganisms and can be used in conjunction with traditional chemical and physical remediation as well as phytoremediation (Ijaz et al. 2016).

Consequently, there is abundant potential for using phytoremediation in a spectrum of climates and in extreme environmental conditions. Invasive plants, when grown in a contained site, are proving highly effective for countries that do not have native phytoremediation plants (Prabakaran et al. 2019). All countries have the option of encouraging technology transfer opportunities for phytoremediation green technologies. Even, early assessments of phytoremediation showed that each country can tailor the technology transfer agreements based on the specific needs and economic limitations (Flathman and Lanza 1998; Sridhar et al. 2002). Recent assessments of phytoremediation as a viable green technology are supporting this view (Gerhardt et al. 2017).

Phytoremediation has its technical limitations as is true for any other remediation strategy. One strategic consideration is the long growth periods needed for plant growth or acclimatization. Another tactical concern is that the contaminants must be in close proximity to the plant roots. Plus, the concentration of the contaminants impacts the success of roots absorbing or degrading the contaminants (Ansari et al. 2015). As mentioned earlier about microbial bioremediation, soil or water chemistry and composition can inhibit phytoremediation. Also, plants may be more susceptible than bacteria and fungi to the toxic effects of high levels of contaminants. In spite of these limitations, phytoremediation is equivalent to traditional in situ remediation and may be more environmentally sound than traditional ex situ remediation (Gatliff et al. 2016).

In support of phytoremediation, there are efforts to improve the utility of phytoremediation by recycling or repurposing the plants after they have served their bioremediation purpose. Typically, after a phytoremediation treatment is completed, the plants need to be disposed in some way. Depending on the nature of the contaminant, the plants are placed in a municipal landfill, incinerated, or disposed as hazardous materials. It would be worthy to somehow reuse or recycle the plants. Early studies recognized the feasibility of reclaiming metals that were accumulated in the biomass of harvested phytoextraction plants (Cunningham and Ow 1996). This is particularly valuable for retrieving the rare earth metals electronic waste sites undergoing phytoremediation effects. Studies on various phytodegradation and phytostabilization plants show that harvested plants have the potential of being used as animal feed (Ghaly et al. 2005). Similar attempts are being investigated using harvested phytodegradation and phytostabilization plants for human consumption (Mitton et al. 2016). The use of energy crops, for producing biofuels or combustible biomass, has also been investigated (Pandey et al. 2016). Spent phytoremediation plants have shown value as a feedstock for anaerobic digestion products (Cao et al. 2014).

One caution about the economics of phytoremediation is ensuring that phytoremediation is equally effective as and less costly than traditional chemical and physical remediation. Cost-benefit calculations on phytoremediation are available and show that researchers must be aware of bias favoring phytoremediation over other remediation methods. Overall, on study concluded that "Considering the loss caused by environmental pollution, the benefits of phytoremediation will offset the project costs in less than seven years" for economically emerging countries (Wan et al. 2016). Calculations are also available for measuring the sustainability and resiliency value of phytoremediation. Sustainability and resiliency values will be specific for each circumstance and will be dependent on a society's environmental ethics and political views (An et al. 2016).

It is important to consider the public perceptions of any new technology when assessing its feasibility. Biotechnology still faces negative public sentiments which inhibit the growth of certain facets of the industry. Phytoremediation as a remediation method is viewed positively by the public and seen as an environmentally friendly. However, people do not trust remediation processes in general because the public believes that site may still have harmful levels of some of the known contaminants or may harbor an unidentified contaminant (Weir and Doty 2014).

The in situ case studies in this book represent a small body of successful phytoremediation efforts that are particularly relevant to countries with emerging economies or economically advanced countries seeking viable options for sustainable and resilient remediation efforts (Balkema et al. 2002). Phytoremediation is not a fad or a panacea. It is another individual strategy or supplemental strategy for environmental remediation. Likely, the future of phytoremediation will involve a combination of strategies that improve the economic sustainability of environmental remediation and increase the resilience from potentially damaging pollution events (Farraji et al. 2016).

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Chapter 2
Phytoremediation of Agricultural Pollutants

Muhammad Imran Khan, Sardar Alam Cheema, Sara Anum, Nabeel Khan Niazi, Muhammad Azam, Safdar Bashir, Imran Ashraf and Rashad Qadri

Abstract Agricultural pollution is a global environmental concern. Agricultural pollution is mainly caused by the application of farming inputs (e.g., fertilizers and pesticides) and practices (e.g., excessive tillage of the land and runoff). Agricultural pollutants may include essential plant nutrients (e.g., excessive amounts of nitrate and phosphate), toxic inorganic (e.g., heavy metals), and organic compounds (e.g., pesticides). Due to their high toxicities, agricultural pollutants pose a grave threat to the biological system. Thus, the removal of such toxic substances is crucially important for the safety of the ecosystem and human health. Phytoremediation is believed to be a promising option for the removal of agricultural pollutants and holds a great promise as a mean to cleanup polluted water and soil environments. In this chapter, we compiled data regarding phytoremediation of organic and inorganic agricultural pollutants and discussed different strategies of plants for pollutant removal. Although plants alone have the ability to utilize different strategies to remove the toxic agricultural pollutants, integrated approaches such as microbes and plant associations (rhizoremediation) are seemed to be attractive options for improving removal of agricultural pollutants.

Keywords Agricultural pollution · Heavy metals · Pesticides · Phytoextraction · Rhizoremediation

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2.1 Introduction

Soil is a vital and nonrenewable resource for agriculture (Maliszewska-Kordybach et al. 2009), and agriculture is a natural process for food production which traditionally does not damage the land and its surrounding environment. However, modern agricultural practices are producing the unwanted materials as byproducts of agricultural activities. These modern farming practices and their unwanted byproducts are causing the deterioration of the land, ecosystem, and the environment and directly or indirectly impacting the life on the planet.

Agricultural pollution could be referred as the agricultural practices that result in the contamination or degradation of the environment and surrounding ecosystems and cause damage to human health and their economic interests (Mmolawa et al. 2011). Agricultural field is related to environmental pollution in two ways: (1) Nonagricultural resources are producing environmental pollutants that can affect agricultural crops directly, and (2) agricultural activities are creating other environmental pollutants impacting air, environment, and other surrounding areas (Abbasi et al. 2014). The relationship of agriculture with the abiotic and biotic factors of environment makes a loop referred as pressure-state-response (PSR) loop. Pressure is stress on environment from farming practices making alterations in the existing state of environment, state is a condition of the current environment and its resources, and response is reaction shown by the society to the persisting stresses on the changing environmental conditions (Abbasi et al. 2014).

Agricultural pollution may come from a variety of different sources, ranging from a point source (PS) pollution (from a single discharge point) to nonpoint source (NPS) pollution (from more diffuse and landscape-level sources) (Zazai et al. 2018). In general, management practices play an important role in the level and impact of agricultural pollution. Management practices could range from an animal management and housing to the spread of fertilizers and pesticides in global farming practices (Oh et al. 2014). Farmers have the ability to some extent to control PS of pollution as they can treat and manage runoff water coming from a field that is channeled through a pipe into a stream or river. However, it is difficult for them to effectively control NPS agricultural runoff pollution, particularly occurring during storms and/or rainy seasons. In NPS pollution, the water leaves fields from numerous points and not just through a single pipeline. This type of runoff and subsequent contamination is of serious concern to the general public, governments, and environmentalists.

According to the recent reports of US Environmental Protection Agency (USEPA), agricultural pollution is the third largest source of pollution of lentic environments (i.e., lakes, ponds, and reservoirs) and overall a sole reason for the disturbance of lotic environment (i.e., streams and rivers) (Abbasi et al. 2014; Paul et al. 2014). According to the data published by the National Summary of Assessed Waters Report in 2010, approximately 53% of global streams and rivers have been affirmed unfit for their designated uses (Rabotyagov et al. 2013). Pollution adversely affects the water chemistry and overall quality of water due to exuberant enrichment of food chain (Moss 2004) and percolation of biocide (Corsolini et al. 2002; Cold and Forbes 2004).

The sources and causes of agricultural pollution may include (but not limited to) application of fertilizers and pesticides, heavy metals (HMs), excessive tillage of the land, runoff, soil erosion and sedimentation, introduction of invasive species, genetic contamination or modification to increase resistance to pest and diseases, animal management, and ecological effects. These sources of agricultural pollution have several transmission pathways to the environment (Fig. 2.1).

Since agricultural pollution is not a single or static component, its negative impacts are carried over as soil, water, and air pollution (Newete and Byrne 2016). It can adversely influence each and every aspect of the surrounding environment and all living organism including plants, microorganisms (MOs), animals, and humans. Adverse effects of agricultural pollution may include (but not limited to) algal bloom (due to eutrophication), rashes and other skin problems, neurological disorders, and respiratory illnesses (due to inhaling polluted air), liver, kidney, and stomach problems and cancer (due to swimming and drinking of polluted water) (Abbasi et al. 2014; Paul et al. 2014; Edao 2017). Infants drinking water with high levels of nitrates get affected by the blue baby syndrome (BBS) which is often fatal. Another problem is the formation of hypoxic areas or dead zones where there is no existence of aquatic life. Examples of such zones include Chesapeake Bay and Gulf of Mexico. In addition, the toxins produced as result of algal blooms may enter into the food

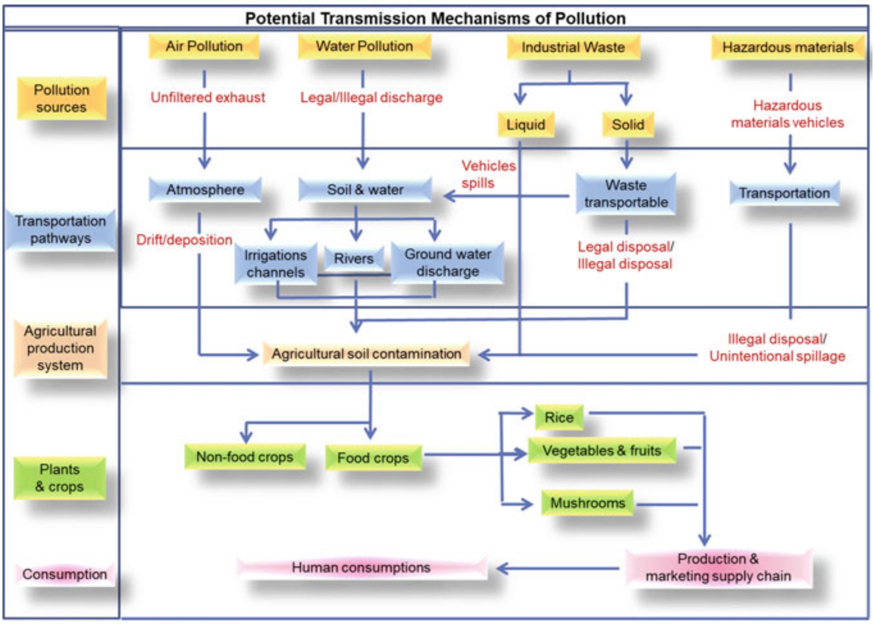

Fig. 2.1 Transmission mechanisms of pollution in agricultural environments (modified from Lin et al. 2017)

chain and cause deaths of larger marine animals such as turtles, seals, and dolphin (Li et al. 2014; Zango et al. 2013).

In short, agricultural pollutants are present in all compartments of environment (i.e., air, water, and soil) and pose a serious threat to ecosystem due to their higher toxicities (Moss 2008; Aelion 2004). Thus, the removal of agricultural pollutants from the polluted sites is crucially important for the safety of environmental and human health. Till now, several methods have been developed for the removal of agricultural pollutants including physical, chemical, and biological approaches. Each of the possible approaches has its own advantages and disadvantages. Among all these approaches, biological (plants or microbially mediated) option is considered the most economical and eco-friendly (Bilgin and Tulun 2016).

Phytoremediation approach utilizes different plants to extract, immobilize, accumulate, or degrade contaminants from soil and water environments (Placek et al. 2016). Some plants have ability to remove contaminants from soil by direct uptake, followed by subsequent transport, accumulation, and transformation to a less or non-toxic compounds (Moosavi and Seghatoleslami 2013; Waoo et al. 2014; Dhir 2017). Phytoremediation includes different approaches such as phytoextraction, phytoaccumulation, phytodegradation, phytostabilization, phytotransformation, rhizofiltration, phytovolatilization, and rhizoremediation (Edao 2017; Fasani et al. 2018; Ting et al. 2018).

Although phytoremediation is still actively being investigated, plant–microbial associations are seemed to be very effective and important for improving the remediation of organic and inorganic agricultural pollutants. A number of studies have investigated the phytoremediation of either organic or inorganic agricultural pollutants focusing on the interactions between pollutants, climatic conditions, characteristics of the substrate, and the selection of suitable plant species (Djordjević et al. 2016; Dželetović et al. 2009; Gajić et al. 2009; Gajić et al. 2013; Gajić et al. 2016; Kostić et al. 2012; Kumari et al. 2016; Maiti and Jaswal 2008; Mitrović et al. 2008; Nikolić and Nikolić 2012; Nikolić et al. 2014; Nikolić et al. 2016; Pandey 2012; Pandey 2015; Pavlović et al. 2016; Pilon-Smits 2005; Rakić et al. 2015; Randjelović et al. 2016). However, studies on the subject covering all types of agricultural pollutants are very limited. Thus, there is lack of comprehensive and up-to-date reports regarding phytoremediation of all types of agricultural pollutants. Here in this chapter, we summarize the current status of phytoremediation covering both organic and inorganic agricultural pollutants.

2.2 Agricultural Pollutants and Their Sources

2.2.1 Major Agricultural Pollutants

There are several agricultural pollutants but they are broadly classified into organic and inorganic pollutants. Organic pollutants include pesticides, herbicides, weedicides, and various organic compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and phenolic compounds. Depending on the target pests, pesticides could be a fungicide or insecticide. Some specific synthetic chemical pesticides used to control various insect pest and diseases include glyphosate, acephate, DEET, propoxur, metaldehyde, boric acid, diazinon, dursban, dichlorodiphenyltrichloroethane (DDT), and malathion. Inorganic agricultural pollutants mostly include HMs such as mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), selenium (Se), and lead (Pb). Depending on the type of crops, agricultural activities and practices either inorganic or organic or both could be the cause of pollution (Mao et al. 2013).

2.2.2 Mechanism and Sources of Organic and Inorganic Agricultural Pollutants

There are several sources for agricultural pollution (Fig. 2.1). However, mostly agricultural pollutants enter into the environment through various agricultural practices and farming operation. Major contributing activities causing agricultural pollution are pesticides use and fertilizer application (Zazai et al. 2018). Fertilizers application improves the fertility and nutrient levels in the soil, enhances crop growth and development, and eventually increases crop production. Fertilizer may be comprised of chemical or mineral ingredients. In general, nitrogen (N), phosphorous, and potassium are present as primary source nutrients in these fertilizers and have a very important role in improving the crop productivity. On the other hand, however, when a fertilizer, particularly N fertilizer is applied to the field, only a partial amount of applied fertilizer is taken up by the plants (less than 50%) and major part of it is wasted through leaching and volatilization processes (Lassaletta et al. 2014). Leaching causes groundwater contamination while volatilization (in the form of N oxides) results in air contamination (Savci 2012).

Although the use of fertilizers has been declined in the developed world due to their adverse effects on the environment, these are still being used extensively in the developing countries. Moreover, fertilizers result in the discharge of more than 1% of GHGs into the environment (Kongshaug 1998). Ammonium fertilizers result in the emission of ammonia gas which is itself a very toxic gas. Ammonia is transformed to nitric acid by oxidation process resulting in the acidic rain, which then not only badly affects the infrastructure and buildings but also crops and all other living organisms. Nitric acid produces nitrous oxide (Joly and Roy 1993), one of the GHGs having a high warming potential. These are considered to be 300 times more harmful than CO_2 and cause cancer in humans (Vogtmann and Biedermann 1985).

Nitrates play a key role in surface and groundwater contamination. Extensive use of fertilizers and pesticides, and intensive agriculture increase the presence of nitrates in soil, water, and food. Methemoglobinemia occurs in infants and is caused by the excess of nitrates in the drinking water. This is because of nitrate present in the digestive tract is converted into nitrite and form bond with hemoglobin instead of oxygen (L'hirondel et al. 2006). Eutrophication is also caused by nitrates and phosphates in surface waters (Smith and Schindler 2009; Pestana et al. 2018). During long-term exposures, nitrogenous fertilizer concentrations of 10 mg L^{-1} can negatively affect freshwater invertebrates (*Eulimnogammarus toletanus*, *Cheumatopsyche pettiti*, *Echinogammarus echinosetosus*, and *Hydropsyche occidentalis*), amphibians (*Pseudacris triseriata*, *Rana temporaria*, *Rana pipiens*, and *Bufo bufo*), and fishes (*Oncorhynchus tshawytscha*, *Oncorhynchus mykiss*, and *Salmo clarki*) with a recommended maximum concentration of NO_3–N (i.e., 2 mg L^{-1}) for protecting sensitive animals of freshwater bodies (Camargo et al. 2005).

Numerous agricultural operations and activities such as application of chemical fertilizers, poultry breeding and livestock, aquaculture and rural population are accountable for increased N, ammonia, and phosphorus levels, and chemical oxygen demand (COD) that are released into the water systems (Wu et al. 2013). Fertilizers containing high level of potassium and sodium have negative effects on soil properties such as reduction in soil pH, destroying the soil structure, and decrement in the efficiency of field crops (Savci 2012). In short, different pesticides and HMs enter through different sources and become part of environment following various mechanisms (Fig. 2.1).

2.3 Strategies for the Removal of Agricultural Pollutants

Several physical, chemical, and biological techniques have been developed to clean up the contaminated environment. These strategies include air sparging, excavation, bioremediation, the use of bioreactors, biofilters, bioventing, biosorption (Sud et al. 2008; Farooq et al. 2010), biosparging, capping, composting, bioaugmentation (Singh 2003; Singh 2008) flushing, in situ oxidation, the use of permeable reactive barriers, natural attenuation, soil washing, electrokinetic remediation (Gomes et al. 2012), solvent extraction, land farming, extraction, thermal desorption, and thermal enhancement (Liu et al. 2018; Parween et al. 2018; Ye et al. 2014; Doty 2008; Khalid et al. 2017) (Fig. 2.2). These strategies mainly depend on the nature and concentration of the contaminant. Numerous factors have to be considered prior to choosing and applying a method for the remediation. For example, what are the contaminants, what the concentration of observed contaminants is, and what is the medium (soil, sediment, groundwater, or surface water) in which the contaminants are found, and finally someone needs to consider the cost of the whole procedure and efficiency of

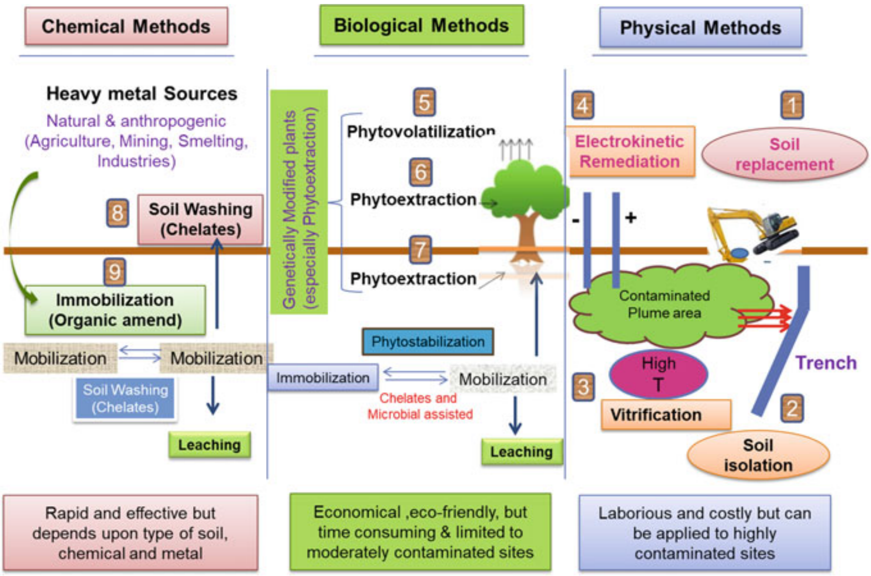

Fig. 2.2 Different soil clean-up methods (modified from Khalid et al. 2017)

the technique for removing the targeted pollutants taking into account the environmental factors of the polluted site (Sharma et al. 2017). For instance, land farming is used for in situ remediation. This technique is effective during the early stages of treatment in decreasing concentrations of a contaminant but degradation rates severely reduce at the later stage, particularly for recalcitrant compounds such as PAHs (Gavrilescu 2005). However, the presence of plants may boost the degradation of these more complex and larger toxic compounds. This technique is more effective for volatile and small compounds than the complex and larger compounds (Walton and Anderson 1992).

Other methods such as solvent extraction or soil washing are very costly and destructive to the environment. Mostly, these methods need secondary remediation processes for the extracted pollutants. In addition, physical methods have similar problems as that of chemical methods. They are not only expensive to perform (Cunningham and Ow 1996) but also end up with incomplete detoxification or partial remediation, leaving site or system less or more toxic and incomplete and need secondary remediation process for completion (Vidali 2001). Chemical methods of soil remediation often result in a deterioration of the soil ecosystem. Therefore, in the last years, the successful attempts have been made for the development of economical and environmentally friendly biological technologies such as phytoremediation (Hernández-Allica et al. 2006; Gómez-Sagasti et al. 2012; Yang 2018).

Phytoremediation is a technology that uses the natural biological processes of plants and rhizosphere MOs for removal or transformation of contaminants to the safe level in soil. The technology is applied "in situ" and is characterized by its positive impacts on the environment. Although the use of plants for the remediation of soil contaminated with radionuclide was determined in 1950s, the term "phytoremediation" was coined up in 1991 and improvement initiated during few past decades (Gerhardt et al. 2009). Phytoremediation has also been known as "agro-remediation," "botano-remediation," "green remediation," and "vegetative remediation." For the remediation of groundwater and soil contaminated by a variety of organic pollutants, phytoremediation is now considered as a promising option (Aken et al. 2010).

Ideally, plants suitable for phytoremediation must be fast-growing and have deep root system and large biomass (Schnoor 1997). They must have easily harvestable above-ground parts and accumulate good amount of contaminant in above-ground biomass. Plants use variety of mechanisms to deal with the HMs, hydrocarbons, and other organic compounds such as herbicides, fungicides, and pesticides removal from the contaminated environment (Fig. 2.2). Very often, plants chelate the pollutants in the soil in inactive forms or make their complex in tissues and stock the pollutants in vacuoles, away from the sensitive cell cytoplasm and sometimes seize them in their cell walls (Wani et al. 2017). Organics may be degraded by following the sequence: Degradation, volatilization, or sequestration in the root zone depending on the properties of pollutants. Plants can successfully remove various organic pollutants from the polluted environment such as TCE (the most common pollutant of groundwater) (Newman et al. 1997), explosives such as TNT (Hughes et al. 1997), petroleum hydrocarbons and fuel additive MTBE (Davis et al. 2003), herbicides such as atrazine (Burken and Schnoor 1997) and polychlorinated biphenyls (PCBs). In short, phytoremediation is an evolving technology and has the potential to remove a variety of contaminants from soil and water environments (Bhadra et al. 1999). Various phytoremediation techniques for the removal of environmental pollutants are listed in Table 2.1.

Phytoremediation has some advantages over other treatments. For example, it is in situ, passive, solar-driven, and thus, costs only 10–20% of mechanical treatments (Susarla et al. 2002). It is an environmentally friendly approach (Cunningham and Ow 1996; Sharma et al. 2015; LeDuc and Terry 2005), visually attractive and the structure of the soil is remained undisturbed (U.S. EPA 2000). It is beneficial due to its noninvasiveness, landscape restoration, increased activity and diversity of soil MOs and decreased human exposure to the polluted environment. The main disadvantage of this technique is the requirement of time, and longtime is required for the remediation process due to slow plant growth. Other disadvantages are poor efficiency in contaminant removal particularly when present at low bioavailable concentration and the inability of the roots to reach the contaminant at certain required depths (Chaudhry et al. 2002). Some of the aforementioned weaknesses of phytoremediation can be overcome through use plants in combination with free-living rhizosphere MOs and their processes.

Table 2.1 Various phytoremediation strategies for the removal of environmental pollutants

Strategies	Action/process	Merits	Demerits	Applicability	Contaminant type
Phytovolatilization	Contaminant uptake by plants from soil and release in vapor form to atmosphere	Economical and less disruptive	Restricted to volatile contaminants and no control after contaminant release to atmosphere	Small to medium scale and long-term	Inorganics/organics
Phytostabilization	Plant roots decrease contaminant bioavailability and mobility in soils via sequestration	Economical, less disruptive	Temporary solution, effectiveness varies with soil, plant and contaminant type	Small to medium scale and short-term	Inorganics
Rhizofiltration	Absorption and adsorption of contaminant on plant roots	Good for both terrestrial and aquatic plants for either in situ or ex situ applications Contaminant does not accumulate in upper parts of plants	Temporary solution	Small to medium scale and short-term	Inorganics/organics
Phytodegradation	Microbe-assisted degradation in the rhizosphere region	Economical and eco-friendly	May produce toxic metabolites	Large-scale and long-term	Organics
Phytoextraction	Uptake, translocation of contaminant from soil to the aboveground harvestable plant parts	Economical, eco-friendly, and less disruptive	Effectiveness depends on growth and tolerance of plants, and bioavailability of contaminant in soil	Large-scale and long-term	Inorganics

(continued)

Table 2.1 (continued)

Strategies	Action/process	Merits	Demerits	Applicability	Contaminant type
Chelate assisted phytoextraction	Use of organic and inorganic ligands to enhance phytoextraction capacity of plants	Fast and enhance contaminant uptake and translocation	Costly, can be disruptive, effective for low-moderately contaminated soils, groundwater contamination risk	Small to medium scale and long-term, low to moderate levels of contamination	Inorganics
Microbial assisted phytoextraction	Use of microbes to enhance phytoextraction capacity of plants	Economical, fast, enhance plant growth, contaminant uptake and translocation	Depends on microbes, soil, plant and contaminant type	Large-scale and long-term	Inorganics

2.4 Phytoremediation of Nitrates and Phosphorus

2.4.1 Phytoremediation of Nitrate

N is a vital structural component of plants and therefore is an essential nutrient required for plant growth and development. Although highly abundant in nature, it is a growth-limiting factor for plants. Main reason behind being a limiting factor is its presence in dinitrogen form, which cannot be assimilated by plants. Major forms of inorganic N available to be assimilated by plants are nitrate and ammonium but their relative abundance in natural soils is relatively low (Castro-Rodríguez et al. 2016). To overcome their deficiency in soil for plant growth, application of fertilizers is required. In the last decades, intensive N fertilization in agriculture has improved global food production. However, over application of N fertilizers has resulted in environmental problems with adverse effects including air pollution, surface, and groundwater pollution and N-induced eutrophication of aquatic and terrestrial systems (Galloway et al. 2008; Schlesinger 2009).

Phytoremediation is an appropriate option to remove N from contaminated environment using wetland or terrestrial plant species. Phytoremediation could be the most useful method of interception of contaminants on their path to the aquifers. Under certain circumstances, it is feasible to treat pollutants in shallow aquifers by in situ methods. Terrestrial plants species are used to remove nitrate from contaminated leach fields and shallow subsurface such as land application of pumped groundwater (pump and treat method). In addition, phytoremediation can be used to treat nitrate contaminated runoff water from furrow or flood irrigated fields. Phytoremediation can also be an option for pump and fertilize concept, where the N in pumped water is accounted for fertilizer input rate calculations.

In most of the cases, phytoremediation application using terrestrial plants remains limited to the vadose zone and the top surface of the saturated zone. Because roots of plants do not grow enough deep to reach to even the shallow saturated zone. Although it depends on the soil and other growth conditions, roots of the plant species cannot grow longer than 4 m. For example, under ideal conditions the root systems of sorghum or rye and clover or alfalfa can spread around 1.5 and 3 m, respectively. Since typically leach field depth is up to 2 m below ground surface, these depths of roots are adequate for the uptake of a contaminant in leachate of contaminated systems.

However, for treating the deeper contaminated environment the contaminants can be moved upward through evapotranspiration. For example, a dense plantation having high evapotranspiration rates can be used to produce a depression zone in a shallow water table, resulting in a flow of contaminated water toward the phytoremediation site, making feasible the remediation of the deeper saturated zone. Some more examples of terrestrial plant species used for phytoremediation of nitrates include (but not limited to) phreatophyte trees (i.e., poplar, willow, cottonwood, aspen), legumes (i.e., clover, alfalfa, cowpeas), and grasses (i.e., rye, bermuda, sorghum, fescue) (Schnoor 1997). Phreatophyte trees have ability to transpire much more water than typical agricultural crops. Poplar trees have the ability to remove nitrate from contaminated waters (O'Neill and Gordon 1994). In fact, studies confirmed that poplars are very efficient and well adapted to the acquisition and removal of nitrates, through low- and high-affinity nitrate transporters (encoded by a large gene family) (Min et al. 1998).

More than 96% of NO_2 can be removed from industrial wastewater by *Chlorella vulgaris*, *Synechocystis salina*, and *Gloeocapsa gelatinosa* (Dominic et al. 2009). Approximately 90% of NO_3 can be removed from artificial wastewater by *Phormidium uncinatum* (Olguín 2003), 100% from municipal wastewater by *Chlorella* and *Scenedesmus* (Hammouda et al. 1995), 81% from industrial wastewater by *Chlorella vulgaris*, *Synechocystis salina,* and *Gloeocapsa gelatinosa* (Dominic et al. 2009). More than 98% of NH_4 can be removed from piggery wastewater by *Chlamydomonas*, *Chlorella,* and *Nitzschia* (de Godos et al. 2009), 60–80% and 97–100% from municipal wastewater by *Chlorella vulgaris* and *Scenedesmus obliquus*, respectively.

Studies also showed that water hyacinth, a free-floating macrophyte, was able to achieve high nitrate removal efficiency of 83% in synthetic medium with initial nitrate concentration of 300 mgL^{-1} (Ayyasamy et al. 2009). Xu and Shen (2011) found that the duckweed (*Spirodela oligorrhiza*) system was able to remove 84% total nitrogen (TN) from swine lagoon water. Rhizomes of sweet flag (*Acorus calamus L.*), common reed (*Phragmites australis*), and broadleaf cattail (*Typha latifolia*) have ability to remove N and high tolerance to N-based compounds (Marecik et al. 2013). Phytoremediation studies on a constructed wetland affirmed that wetland species have the potential to be used for treatment of wastewater with a high level of N compounds (Podlipna et al. 2010). Water hyacinth (*Eichhornia crassipes)* is also used for the removal of ammoniacal nitrogen (Ting et al. 2018). Higher removal of ammonium nitrogen, nitrate nitrogen, sulfate, total organic carbon, dissolved oxygen, and total dissolved solid from wastewater by water hyacinth were observed (Parwin and Paul 2018). Further, *Sparganium americanum Nutt*. (found in USA and Canada) was reported with ability to remove phosphorus and nitrogen from runoff of the agricultural field (Ito and Cota-Sánchez 2014).

2.4.2 Phytoremediation of Phosphorus

Phosphorous (P) is the second major nutrient for the growth of plants. Excessive and inappropriate use of P fertilizer causes environmental pollution. The P is one of the major nutrients contributing in the eutrophication of lakes, ponds, and other natural water bodies. Its presence causes several problems in water and its quality including increased cost of purification, reduction in conservation and recreational value of impoundments, loss of biodiversity and the possible toxic and lethal effects of algal toxins on drinking water (Ojoawo et al. 2015).

Although suspended solids can be used to clean the P contaminated water as they provide charge surface to bind the P compounds from the wastewater, discarding the suspended solids often create secondary problems. Instead of suspended solids, biological means (e.g., MOs and plants), and chemical precipitates are used to incorporate the P. Several plants species have ability to remove P from the contaminated water. For example, Xu and Shen (2011) found that the duckweed *Spirodela oligorrhiza* system has potential to uptake approximately 90% of P from swine lagoon water. Likewise, *Salvinia molesta* is a macrophyte species and has the capability to remove up to 95% P and significantly reduced P concentration in water (less than 0.72 mg/L) (Ng and Chan 2017). Water lettuce (*Pistia stratiotes*), water spinach (*Ipomoea aquatica*), and water hyacinth (*Eichhornia crassipes*) have been successfully used in phytoremediation for the removal of N and P compounds (Ho and Wong 1994; Jianobo et al. 2008; Akinbile and Yusoff 2012) and were found helpful in improving wastewater quality (Hu et al. 2008). Approximately, 65–75% of PO_4 can be removed from industrial wastewater by *Chlorella vulgaris*, *Synechocystis salina,* and *Gloeocapsa gelatinosa* (Dominic et al. 2009), 92% of PO_4 from municipal wastewater by *Chlorella vulgaris* (de-Bashan and Bashan 2003), and 72–87% of PO_4 from piggery wastewater by *Spirulina* (Olguín 2003). Approximately, 80–100% of N and P removal was reported by microalgae *Nannochloropsis oceanica* and *Scenedesmus quadricauda* (Silkina et al. 2017). Halophytes (salt tolerant plants) have great potential to remove N and P from water, even at salt levels similar to seawater (Szota et al. 2015). *Canna x. generalis* is also an efficient plant for phytoremediation of N and P and has a good potential for removal of phenolic compounds. *Azolla filiculoides* is a water fern used for phytoremediation of phosphorus (P) due to its N-fixing ability and high growth rate.

2.5 Phytoremediation of Heavy Metals

HMs are the metallic elements and possess a relatively high density (i.e., at least five times greater than that of water). HMs pollution is a global concern because substantial amounts of these elements are released into the environment annually through different activities (i.e., natural and anthropogenic) (Meng et al. 2011). This can result in economic losses. Importantly, various animal and human health problems are resulted from HMs contamination in the food chain (Mahar et al. 2016). The main hazards to human health from HMs are derived from exposure to higher concentration of Cr, Pb, Cd, Hg, and As. Cr, Cd, Pb, As, Hg, and Ni are known to have carcinogenic effects on human beings (IARC 2014). HMs have ability to interact with the process of carcinogenesis and cause DNA damage through reducing the efficiency of cell defensive systems. Therefore, they can act as cancer promoters, in some cases also by modulating the processes of cell adhesion with consequences for the ability to produce metastases. HMs are able to interact with cell components, producing, directly or indirectly, DNA damage; thus, they act as cancer promoters (Beyersmann and Hartwig 2008).

HMs can be placed into five distinct groups depending on their anthropogenic sources of contamination: (1) Agriculture (Zn, As, Pb, Cd, Cu, Se, and uranium (U), (2) industry (Cd, Hg, As, Cr, Cu, Co, Ni, and Zn), (3) metalliferous mining and smelting (Cd, Pb, As, and Hg), (4) waste disposal (As, Pb, Cu, Cd, Cr, Zn, and Hg), and (5) atmospheric deposition (As, Pb, Cr, Hg, Cu, Cd, and U). Most of the HMs coming from agricultural source are very toxic; thus, their removal from the contaminated site is very crucial for the safety of ecosystem. Phytoremediation is a suitable option for the remediation of HMs. In addition, revegetation for remediation of contaminated sites improves the physicochemical and biological properties of sites by adding organic matter, improves microbial activities and nutrients levels (Arienzo et al. 2004). Nevertheless, the selection of plants for phytoremediation depends on many factors such as type of contaminant, the characteristics of the contaminated site, and the choice of phytoremediation approach.

Metallophyte plants have mechanisms to tolerate high concentrations of HMs and are considered as an appropriate choice for phytoremediation (Whiting et al. 2000; Boularbah et al. 2006). Depending on the mechanism to deal with metal contamination, metallophytes can be classified as: (i) *Accumulators*, they show an active metal uptake and translocation to aerial parts (Okem 2014; Boularbah et al. 2006), (ii) *Indicators*, they regulate metal uptake so that internal concentrations reflect external soil concentrations (Singh et al. 2015; Edao 2017; Mkumbo et al. 2012; Okem 2014), and (iii) *Excluders*, they restrict the entry of metals into the root and/or their transport to the shoots (Barrutia et al. 2011; Edao 2017). Some metallophytes are also called hyperaccumulators, because they have specialized mechanisms for the accumulation of HMs over 1% of their dry weight, in some cases reaching up to 10%. Ideally, a hyperaccumulator plant must tolerate high levels of a contaminant in root and shoot and has rapid uptake and translocation rates of a particular contaminant.

Mitch (2002) investigated hyperaccumulating plants for improving the removals of HMs as 10 mg kg $^{-1}$ for Hg, 100 mg kg $^{-1}$ for Cd, 1000 mg kg $^{-1}$ for Cr, Co, Pb, and Cu, and 10,000 mg kg $^{-1}$ for Ni and Zn. *Jatropha curcas* plant roots have greater phytoremediation ability and low translocation factor than all other plant tissues and showed the best removal of Hg from contaminated water and soil (Marrugo-Negrete et al. 2015). *Juncus subsecundus* was found to be very efficient for Cd removal from the contaminated soil (Zhang et al. 2012). *Elodea canadensis* and *Potamogeton natans* are submerged plant species having the ability to uptake Cu, Cd, Pb, and Zn (Fritioff et al. 2005). A liliaceous plant species, *Chlorophytum comosum*, is an ornamental plant having the ability to tolerate high levels of many HMs. This plant has a greater role in Cd removal from contaminated site (Wang et al. 2012). *Eleusine indica* and *Sonchus arvensis* act as agents of phytoremediation of Cd contaminated soil. Furthermore, *Sedum alfredii* has been shown to be highly efficient in phytoremediation of HMs. *Eucalyptus globulus* was also used for metal purification for its resilient and unpalatable nature (Luo et al. 2018). Some phytoremediation techniques used for removal of HMs are given below.

2.5.1 Pytoextraction of HMs

Phytoextraction is also called phytoabsorption or phytoaccumulation. In this method, HMs are removed by up taking through root form the water and soil environment and accumulated into the shoot part (Amin et al. 2018; Rafati et al. 2011; Seema et al. 2015; Amanullah et al. 2016). Two types of phytoextraction approaches are used to remove the toxic contaminant from the soil environment. The first approach is called hypernatural accumulation, while the second approach is called induced or assisted hyperaccumulation. Plants are potentially used to remove the contaminants from the soil and water body in the first technique while in the second technique addition of conditioning fluids carrying other soil or chelating agents is needed to improve the solubility of HMs so that plants can easily absorb the HMs. Very often, natural hyperaccumulators can tolerate high levels of toxic HMs (Zhuang et al. 2007).

So far, approximately 400 plant species have been investigated and identified as hyperaccumulators (Boularbah et al. 2006). *Noccaea caerulescens* is probably one of the most extensively studied hyperaccumulator (Baker et al. 1994; Brown et al. 1994, 1995; Robinson et al. 1998; Hammer and Keller 2003; Schwartz et al. 2003; Hernández-Allica et al. 2006; Epelde et al. 2010). *Noccaea caerulescens* has an incredible capacity to accumulate Zn and Cd in its aboveground tissues. *Arabidopsis halleri* is recognized for its Zn and Cd hyperaccumulating capabilities (Bert et al. 2000; Kupper et al. 2000). Fern (*Pteris vittata*) has been discovered as hyperaccumulator (Ma et al. 2001). A great number of plant species have been identified as nickel (Ni) hyperaccumulators, and *Alyssum* species have been extensively studied for their Ni phytoextraction potential (Bani et al. 2015). Mustard (*Brassica juncea*) and Sunflower (*Helianthus annuus*) are the plant species having promising potential for phytoextraction of Cd (Shakoor et al. 2017). Different examples of metals extracted by plants are given in Table 2.2.

Researchers have reported the phytoremediation ability of plant species belonging to various botanical families including Fabaceae, Poaceae, Brassicaceae, Asteraceae, and Chenopodiaceae. Even phytoremediation ability of Chlorophyceae are well documented (Gawronski and Gawronska 2007; Balaji et al. 2014a, b, 2016; Anjum et al. 2014). HMs take-up limit, accumulation, exclusion, compartmentation, and mechanisms of metal tolerance vary among different plant species and different parts of plants (Sharma et al. 2015; Amin et al. 2018). Some examples are *Noccaea caerulescens* (Mohtadi et al. 2012*), Silene vulgaris* (Pradas del Real et al. 2014), *Biscutella laevigata* (Poscic et al. 2015), *Silene armeria* (Llugany et al. 2003) *Agrostis capillaris* (Bech et al. 2012), *Thlaspi arvense* (Martin et al. 2012), and *Pteris vittata* (Ma et al. 2001).

Table 2.2 Various plant species used for the phytoextraction of heavy metals

Sr. no.	Plant species	Contaminant	References	Sr. no.	Plant species	Contaminant	References
1	*Noccaea caerulescens*	Zn	Baker et al. (1994)	22	*Noccaea caerulescens*	Zn, Cd	Epelde et al. (2010)
2	*Noccaea caerulescens*	Zn, Cd	Brown et al. (1994)	23	*Brassica juncea*	Hg	Meng et al. (2011)
3	*Noccaea caerulescens*	Zn, Cd	Brown et al. (1995)	24	*Populus* spp.	Cd, Zn	Marmiroli et al. (2011)
4	*Brassica juncea*	Zn, Cd, Pb, Ni, Cu, Cr	Kumar et al. (1995)	25	*Pteris vittata*	As	Kalve et al. (2011)
5	*Alyssum* spp.	Ni	Robinson et al. (1997)	26	*Isatis pinnatiloba*	Ni	Altinozlu et al. (2012)
6	*Brassica napus*	Zn, Cd	Ebbs et al. (1997)	27	*Arabidopsis thaliana*	Cd	Khoudi et al. (2013)
7	*Noccaea caerulescens*	Zn, Cd	Robinson et al. (1998)	28	*Populus* spp.	Cd, Zn	Hu et al. (2014)
8	*Arabidopsis halleri*	Zn, Cd	Bert et al. (2000), Kupper et al. (2000)	29	*Alyssum* spp.	Ni	Bani et al. (2015)
9	*Pteris vittata*	As	Ma et al. (2001)	30	*Salix* spp.	Cd, Zn	Greger and Landberg (2015)
10	*Noccaea caerulescens*	Zn, Cd	Schwartz et al. (2003), Hammer and Keller (2003)	31	*Sedum plumbizincicola*	Cd, Zn	Deng et al. (2016)
11	*Alyssum* spp.	Ni	Li et al. (2003)	32	*C. monensis, P. aquilinum (L) Kuhn, M. verna, Silene ciliata, A. cantabrica*	Zn	Fernández et al. (2017)

(continued)

Table 2.2 (continued)

Sr. no.	Plant species	Contaminant	References	Sr. no.	Plant species	Contaminant	References
12	*Salix* spp.	Cd, Zn	Hammer et al. (2003)	33	*F. rubra, Leontodon taraxacoides, E.telmateia*	Hg	Fernández et al. (2017)
13	*Arabidopsis thaliana*	Cd, P54	Song et al. (2003)	34	*Erica cinerea, L. periclymenum, D. glomerata, L. taraxacoides*	As	Fernández et al. (2017)
14	*Berkheya coddii*	Ni	Mesjasz-Przybylowicz et al. (2004)	35	*Noccaea caerulescens*	Zn, Cd	Rosenfeld et al. (2018)
15	*Populus* spp.	Cd, Zn	French et al. (2006)	36	*Typha latifolia, Chrysopogon zizanioides*	Hg, As, Pb, Cu, Zn	Anning and Akoto (2018)
16	*Salix* spp.	Cd, Zn	French et al. (2006)	37	*Brassica napus L*	Zn, Cu, Cd	Lacalle et al. (2018)
17	*Noccaea caerulescens*	Zn, Cd, Pb	Hernández-Allica et al. (2006)	38	*Sedum plumbizincicola*	Cd, Zn	Li et al. (2018)
18	*Brassica juncea*	Cd, As	Gasic and Korban (2007)	39	*Pteris vittata L*	As	Huang et al. (2018)
19	*Salix* spp.	Cd, Zn	Maxted et al. (2007)	40	*Sesamum indicum L., Cyamopsis tetragonoloba L*	Cu	Amin et al. (2018)
20	*Helianthus annuus*	Zn, Cd, Pb	Nehnevajova et al. (2007)	41	*Helichrysum italicum*	Cd, Co, Cr, Cu, Ni, Pb, Zn	Brunetti et al. (2018)
21	*Schima superba*	Mn	Yang et al. (2008)				

2.5.2 Phytovolatilization of HMs

During phytovolatilization, HMs are taken up from the polluted environment and are passed through and/or modified by the plants and finally released to the atmosphere through transpiration process of the plants (Ferroa et al. 2013). Some HMs such as Hg, Se, and As are present in the environment as gaseous species. They are taken up by the pants and converted to less toxic forms. Plant species such as *Arabidopsis thaliana*, *Chara canescens,* and *Brassica juncea* are able to uptake HMs and transform them into gaseous states inside the plant followed by their release into the atmosphere (Verbruggen et al. 2009). As was found to be efficiently volatilized by *Pteris vittata* (Sakakibara et al. 2011). *Arabidopsis thaliana* and *Brassica juncea* have ability to grow under high concentration of Se and volatilize Se (Bañuelos and Mayland 2000).

HMs conversion to gaseous forms occurs through a specific mechanism inside the plants governed by specific enzymes and genes. Very few plants are present in nature which have the ability to volatilize metals. In general, phytovolatilization uses genetically modified plants, with improved ability to remove HMs. *N. tabacum* and *Arabidopsis thaliana* have been genetically modified through the addition of mercuric reductase (a gene for Hg volatilization) (Rugh et al. 1998). Transgenic plants genetically engineered with Hg volatilizing bacterial genes (i.e., merA and merB) are capable to remove 1000 times more Hg than the respective wild-type plants (Rugh et al. 1996). Likewise, a gene encoded as *sterol methyl transferases* (SMT) enzyme from *Astragalus bisulcatus* was acquainted with *Brassica juncea* and *Arabidopsis* showed higher Se tolerance, accumulation, and volatilization. Toxicity of volatilized Se compounds (i.e., dimethyl selenide) is approximately 600 fold lower than the inorganic Se forms which are present in the soil (Deesouza et al. 2000).

Moreover, *cystathionine gamma-synthase* (CGS) enzyme is reported to play an important role Se volatilization. The modified brassica (expressing CGS) accumulated approximately 70% and 40% lower Se level roots and shoots, respectively, than in wild-type plants (Van Huysen et al. 2003). Similarly, encoding and expression of As (III)-*S-adenosylmethionine methyltransferase* (arsM) gene in an As-sensitive *E. coli* strain showed the biosynthesis of various volatilized forms of As (Qin et al. 2006). Although phytovolatilization technique is considered more effective technique for the removal of HMs from the soil environment, it has more limitations as compared to other remediation techniques (Padmavathiamma and Li 2007).

2.5.3 Phytostabilization of HMs

Phytostabilization is also called phytoimmobilization. In this method, different types of plants are used to stabilize a contaminant from soil environment (Ali et al. 2013; Rajkumara et al. 2013). The main objective of phytostabilization is to immobilize HMs in the vadose zone through precipitation or accumulation by roots within the rhizosphere. Phytostabilization prevents leaching of HMs by reducing water percolation through the soil matrix, restricts soil erosion and movement of HMs to other areas, and reduces direct contact between HMs and soil (Bolan et al. 2011). Following this process, Pb is precipitated as phosphate (Cotter-Howells and Caporn 1996) and Cd forms different complexes with sulfide (De Knecht et al. 1994) in the root zone of *Agrostis capillaris* and *Silene vulgaris*, respectively. Willows (Salix spp.) have ability to tolerate stress of HMs and are considered as one of the best plants for both phytoextraction and phytostabilization (Sylvain et al. 2016). Some plants such as *Agrostis* spp. and *Festuca* spp. are commonly used for phytostabilize Zn, Cu, and Pb in Europe (Galende et al. 2014). Jadia and Fulekar (2008) investigated sorghum crop for its ability to phytostabilize HMs using vermicompost as a natural fertilizer. Different studies on phytostabilization of HMs are summarized in Table 2.3.

As described above, although the movement of HMs can be stopped through phytostabilization, it cannot provide a permanent solution to remove the HMs from the soil. Basically, phytostabilization is the management approach for reducing the toxicity of metal in the environment (Vangronsveld et al. 2009). Plants for phytostabilization should be metal tolerant, have an extensive root system, produce a large amount of biomass, and keep root-to-shoot translocation as minimum as possible to restricts the entry of a toxic compound into the food chain (Gómez-Sagasti et al. 2012). Many excluder plants such as *Agrostis capillaris*, *A. stolonifera*, *Festuca rubra*, and *Lolium perenne*, *Trifolium repens* meet these characteristics and have been successfully applied for the revegetation of contaminated sites (Pérez-de-Mora et al. 2006; Bidar et al. 2007; Epelde et al. 2009). Plant species undergoing phytostabilization lower the bioavailability of toxic substances in the soil by emitting compounds (e.g., phenolic compounds, phytosiderophores, and organic acids) into the rhizosphere (Li et al. 2016). Various grass species, including red fescue (*Festuca rubra L.*), turned out to be the most useful in the phytostabilization of HMs in soils (Gajić et al. 2016). Some macrophytes used for phytostabilization include *Typha latifolia*, *Typha angustifólia*, *Typha domingensis*, *Phragmites australis*, and *Phragmites communis*.

2.5.3.1 Aided Phytostabilization of HMs

In aided phytostabilization (also called chemophytostabilization), different organic or inorganic amendments are used in combination with metal tolerant plants during phytostabilization to reduce metal bioavailability (*i.e.*, chemical stabilization) and to facilitate and enhance vegetative growth on contaminated soils by improving their biological and physicochemical properties (Alvarenga et al. 2009a). Additionally, the incorporation of organic amendments in HMs contaminated soil facilitates plant colonization by the addition of essential nutrients and improving the organic matter and pH values (Alvarenga et al. 2009a, b; Epelde et al. 2009). This technology is considered as the most promising option for the remediation of sites highly contaminated with HMs (Alkorta et al. 2010). Different studies on this approach are summarized in Table 2.3. Aided phytostabilization, on the other hand, relies on applying plants

Table 2.3 Various plant species used for the phytostabilization or aided phytostabilization of heavy metals (modified from Burges et al. 2017)

Sr. no.	Plant species	Contaminant	References
1	*Agrostis capillaris*	Zn, Cd, Pb, Cu	Vangronsveld et al. (1996)
2	*Alnus* spp.	As, Pb, Cu, Ni	French et al. (2006)
3	*Agrostis stolonifera*	Cd, Pb, Zn, As, Cu	Pérez-de-Mora et al. (2006)
4	*Populus* spp.	As, Pb, Cu, Ni	French et al. (2006)
5	*Salix* spp.	As, Pb, Cu, Ni	French et al. (2006)
6	*Trifolium repens*	Cd, Pb, Zn	Bidar et al. (2007)
7	*Lolium perenne*	Cd, Pb, Zn	Bidar et al. (2007)
8	*Lolium perenne*	Cu, Pb, Zn	Arienzo et al. (2009)
9	*Lolium perenne*	Cd, Pb, Zn	Alvarenga et al. (2009a), Epelde et al. (2009)
10	*Pteridium aquilinum*	Pb, Zn	Lee et al. (2014)
11	*Agrostis capillaris*	Cu	Touceda-González et al. (2017)
12	*Populus* spp.	Cu	Touceda-González et al. (2017)
13	*Salix viminalis*	Cu	Touceda-González et al. (2017)
14	*Lotus corniculatus L*	Hg, As	Dragomir et al. (2009), Boldt-Burisch et al. (2013)
15	*Anthyllis vulneraria*	Hg	Dragomir et al. (2009), Boldt-Burisch et al. (2013)
16	*Cytisus striatus*, *Genista legionensis*	Pb	Fernández et al. (2017)
17	*Helianthus tuberosus L*	Hg	Lv et al. (2018)
18	*Festuca rubra L*	Pb, Cd, Zn	Radziemska (2018)
19	*Phragmites australis, Arundo donax*	As, trace metals	Castaldi et al. (2018)
20	*Lupinus albus L*	Cu, As	Fresno et al. (2018)

and soil additives for the physical stabilization of soil as well as the chemical immobilization of contaminants. Mineral sorption materials can be successfully applied as effective soil additives aiding the above-mentioned technique (Radziemska et al. 2013; Li et al. 2015).

2.5.4 *Rhizofiltration of HMs*

Rhizofiltration is a type of phytoremediation technique in which HMs are absorbed or adsorbed on the roots of plants followed by their subsequent filtration or removal from water through root biomass. Root systems of different plants such as grasses, sunflower, and mustard are used to remove the toxic HMs including Cd, Ni, Cu, Zn, and Pb (Lee and Yang 2010). Several plant species are capable for rhizofiltration such as *Azolla pinnata* (for Cu), *Lemna minor* (for Cr), *Pistia stratiotes* (for Ag, Cu, Cr, Cd Hg, Zn, and Pb), *Lemna gibba*, *Potamogeton crispus*, and *Myriophyllum heterophyllum* (for Cd), and sunflower *(Asteracaea* spp.) (for U).

Dushenkov et al. (1995) found that many terrestrial plants (grown hydroponically) including Indian mustard *(B. juncea (L.*) *Czem*) and sunflower (*H. annuus L.*) have the potential to effectively remove Cu, Cr, Cd, Ni, Zn, and Pb from aqueous solutions. Moreover, among different plant species (i.e., Indian mustard, sunflower, tobacco, corn, rye, and spinach) sunflower was found to have the greatest ability for Pb removal. Bioaccumulation coefficient of Indian mustard was found to be 563 for Pb and was proven efficient for removing a wide range of Pb levels (4–500 mg/L). Some studies on phytoremediation (rhizofilteration) in aqueous medium are summarized in Table 2.4.

2.5.5 Dendroremediation of HMs

Dendroremediation is the use of tree plants to evaporate water and to extract pollutants from the soil. Tree plants have been investigated for their phytostabilization potential due to a number of supportive characteristics such as deep and massive root systems and litter addition to the surface resulting in an organic cover that improves nutrient cycling, water holding capacity, and soil aggregation (Pulford and Watson 2003; French et al. 2006; Kidd et al. 2015; Touceda-González et al. 2017). Interestingly, the high transpiration rate and water demand of some tree species such as *Salix* spp. help in reducing the downward flow of water through soil, thus lowering the risk of metal leaching (Pulford and Watson 2003).

2.6 Phytoremediation of Pesticides

According to the USEPA, a pesticide could be a substance or a mixture of substances used to prevent, mitigate, repel, or destroy pests [MOs, insects, animals (mice), or unwanted plants (weeds)]. Although pesticide is considered as an important part of modern agriculture, their extensive uses cause severe and irreversible damage to farmland, soil quality, and environment. A greater part of applied pesticides never reach their intended target organisms (Niti et al. 2013) and thus cause the pollution of the environment (Fig. 2.3). Through air, water, and soil dispersion, they become part of human foods. Soil application of pesticides results in higher and unacceptable accumulation of their residues and metabolites.

Table 2.4 Various plant species used for phytoremediation (rhizofiltration) potential on water (hydroponics) and/or soil environments

Sr. no.	Plant species	Pollutants	Outcomes	Scale	References
1	*Eichhornia crassipes*	Cd, Zn	Cd (ug/g): Shoots 148 and Roots 2006; Zn (ug/g): Shoots 1899 and Roots 9646	Aqueous metal solution	Mohamad and Latif (2010)
2	Water hyacinth	Cu, Zn	99.4 mg Cu and 83 mg Zn per 1 g biomass	Aqueous solutions	Buasri et al. (2012)
3	*Lemna minor*, *Elodea Canadensis*, *Leptodictyum riparium*	Cd, Pb, Zn, and Cu	Good accumulation	Water under lab conditions	Basile et al. (2012)
4	*Scirpus mucronatus*, *Rotala rotundifolia*, *Myriophyllum Intermedium*	Ni	*M. intermedium* was best Ni accumulator	Water and soil at different Ni levels	Marbaniang and Chaturvedi (2013)
5	*Ceratophyllum demersum*, *Myriophyllum spicatum*, *Eicchornia crassipes*, *Lemna gibba*, *Phragmites australis Typha domingensis*	Cd, Co, Cu, Ni, Pb and Zn	High levels of heavy metal accumulation	Water of El-Temsah Lake	Kamel (2013)
6	*Ceratophyllum demersum*, *Myriophyllum spicatum*	Pb	Plants accumulated high amount of Pb	Water at different Pb levels	El-Khatib et al. (2014)
7	*Ceratophyllum demersum L.*, *Potamogeton alpinus Balb*	Cu, Fe, Ni, Zn, and Mn	*C. demersum* was a better accumulator	Water of Iset' river, Ural region, Russia	Borisova et al. (2014)
8	*Ceratophyllum demersum*	Cd	*C. demersum* had strong ability to remove Cd	Water at different Cd b levels	Al-Ubaidy and Rasheed (2015)
9	*Utricularia gibba*	Cr	*U. gibba* efficiently removed Cr	Water at 50 µM Cr(VI) solution in lab conditions	Augustynowicz et al. (2015)
10	*Baccharis latifolia*	As, Pb		Soil	Menezes et al. (2015)
11	*Brassica juncea*, *Lupinus albus*	As, Hg	Total accumulation of As and Hg were 42% for *L. albus* and 85% for *B. juncea*	Microbe-assisted phytoremediation of soil	Franchi et al. (2017)

(continued)

Table 2.4 (continued)

Sr. no.	Plant species	Pollutants	Outcomes	Scale	References
12	*C. salviifolius, S. atrocinerea, D. glomerata, B. pinnatum, A. braun-blanquetii*	Hg		Higher soil to plant transfer	Fernández et al. (2017)
13	*S. perennis*	Pb, Zn, Cu, Fe	Higher immobilization and translocation by *S. perennis*	Coastal environment	Idaszkin et al. (2017)
14	*S. subterminalis*	Cu, Zn	Roots of *S. subterminalis* were good accumulator of Cu and Zn	Water	Sánches-Martínez et al. (2017)
15	*Myriophyllum aquaticum*	Cd, Cr, Ni, Zn	Higher concentration of Zn and Cd in plant shoots than shoots	Water	Colzi et al. (2018)
16	*Echinodorus cordifolius*, *Cyperus alternifolius*, *Acrostichum aureum*, *Colocasia esculenta*	As	*E. cordifolius* was the best for arsenic removal among tested species	Soil	Prum et al. (2018)

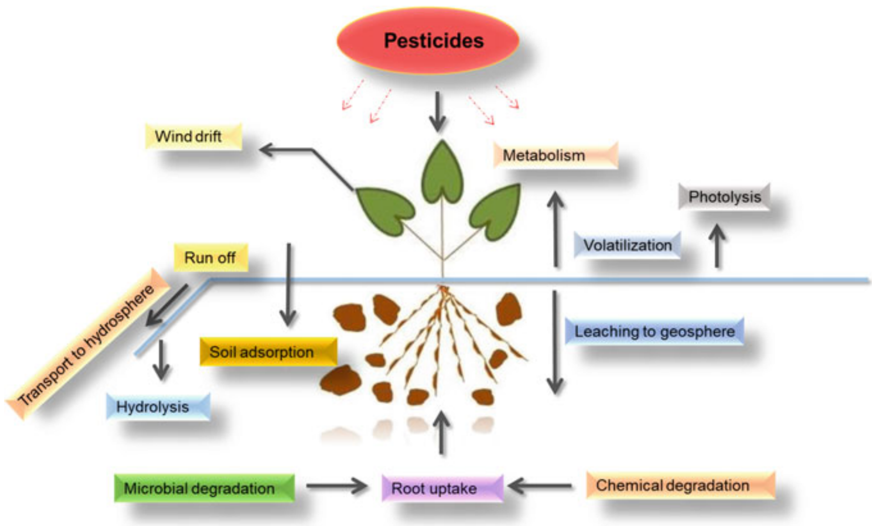

Fig. 2.3 Fate of pesticides in environment (modified from Ahemad and Khan 2013)

Potential impacts of pesticides on human health and environment have been now recognized by governments and the public. Pesticides accumulation in soil adversely impacts soil health and agriculture productivity. They may result in long-term changes in soil microflora by inhibiting nitrogen fixation by soil MOs (i.e., *Rhizobium, Azospirillum,* and *Azotobacter,*) and cellulolytic and phosphate solubilizing MOs. Pesticides residues in animal and other food products eventually accumulate in human body especially in blood, adipose tissue, and lymphoid organs and result in immunopathological effects which acquire autoimmunity, immunodeficiency, and hypersensitivity reactions such as dermatitis, eczema, allergic, or respiratory diseases. Some pesticides are known to cause mutations in chromosomes of animals and men, leading to carcinoma of lungs and liver (Lake et al. 2012; Gilden et al. 2010). Toxicity of herbicides, such as fluroxypyr, isoproturon, and prometryn on *Chlamydomonas reinhardtii*, and their degradation and accumulation by the microalgae have been reported (Zhang et al. 2011; Bi et al. 2012; Jin et al. 2012). The presence of pesticide residues have been observed in many countries in water (Kumari et al. 2008), air (Lammel et al. 2007), soil (Fuentes et al. 2010), milk (Zhao et al. 2007), fishes (Malik et al. 2007), food commodities (Bajpai et al. 2007), and even in human blood and adipose tissue (Ridolfi et al. 2014). Thus, remediating contaminated environment to protect human health and to achieve sustainable development has become a desirable goal (Cheng et al. 2016).

One potential solution to this problem involves the removal of these toxic chemicals from the soil and water environments using plants. Recently, several studies reported the phytoremediation of petroleum hydrocarbons such as toluene, benzene, xylene, ethylbenzene, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pentachlorophenol, chlorinated aliphatics (*trichlorethylene, tetrachloroethylene, and 1,1,2,2-tetrachloroethane*), ammunition wastes (*2,4,6-trinitrotoluene* or TNT, and RDX), metals (Pb, Cd, Zn, As, Cr, Se), pesticide runoff and wastes (atrazine, alachlor, and cyanazine), radionuclides (strontium-90, cesium-137, and U), and nutrient wastes (ammonia, nitrate, and phosphate) (Jee 2016). Some recent studies have shown the potential of various aquatic plants for pesticide removal from the water column (Anderson et al. 2011; Elsaesser et al. 2011; Locke et al. 2011; Gao et al. 2000; Dosnon-Olette et al. 2009). Different plant strategies for the removal of pesticides are detailed below.

2.6.1 Phytoaccumulation/Phytoextraction of Pesticides

Phytoaccumulation studies largely emphasize on two pathways by which organic contaminants can enter into plants: (i) the soil-to-plant route and (ii) the air-to-plant route. In soil-to-plant pathway, the organic compounds within the soil near the root surface have one of the two fates: (a) absorption by the roots and translocation to the aerial parts through the xylem vessels and (b) adsorption on the roots (especially in the cases of lipophilic compounds like hexachlorocyclohexane (HCH) isomers, where absorption and translocation are not permitted for the reason of high lipophilicity).

In the air-to-plant route, the organic contaminant is partitioned between plant and air by the process of volatilization and further adsorbed on leaves. The lipophilic contaminants enter the aboveground parts of the plant by air-to-plant pathway. Results of field assay performed with two plants, *Cynara scolymus* and *Erica sp.,* show that both plants accumulated HCH, with comparatively high accumulation in the aboveground tissues than roots. HCH adsorption from contaminated soil by the roots (soil → root route), either followed by the volatilization of contaminant and subsequent adsorption by the aerial plant parts (soil → air → shoot route) or contact with HCH-contaminated particles suspended in air (soil particles → shoot route), was major means of accumulation. Several plants including vegetables and cereal crops have ability to remove different pesticides from contaminated soil (Table 2.5).

Uptake of organochlorine pesticides (OCPs) by plant roots occurs through simple diffusion by the cell wall and further translocation through the xylem vessels. Endosulfan sulfate, DDE, g-chlordane, and g-HCH were detected in all *Schoenoplectus californicus* (bulrush) tissues (Miglioranza et al. 2004). Mitton et al. (2016) reported that sunflower showed the highest phytoextraction capacity for endosulfan among different plant species (i.e., soybean, tomato, sunflower, or alfalfa. *Cucurbita pepo* plants were shown to accumulate several organic contaminants under field conditions, including chlordane (Mattina et al. 2003), Dieldrin, Endrin (Matsumoto et al. 2009; Otani et al. 2007), and HCH (Moklyachuk et al. 2010). Sojinu et al. (2012) reported that *P. purpureum* could be used for cleanup of OCP polluted sites. Some studies on phytoaccumulation of pesticides are listed in Table 2.6.

2.6.2 Phytodegradation of Pesticides

Phytodegradation, which is also known as phytotransformation, involves taking up and subsequent degradation or metabolic transformation of the contaminant by the plants (Mitton et al. 2018; James et al. 2008). Results of Xia and Ma (2006) showed the successful degradation and removal of ethion, an organophosphorus insecticide, by water hyacinth (*Eichhonia crassipes*) from water. Likewise, poplar was found to be able to take up, hydrolyze, and dealkylated atrazine to less toxic metabolites in different parts of plants (i.e., stems, roots, and leaves) (Chang and Lee 2005). In another study, an aquatic plant elodea (*Elodea canadensis*) was able to successfully dehalogenate DDT (Garrison et al. 2000). Some examples of phytodegradation of pesticides are given in Table 2.7.

External metabolic function implies the secretion of enzymes, in the rhizosphere zone, where they hydrolyze and/or degrade complex organic pollutants into simpler molecules that are further incorporated into plant tissue. Importantly, external degradation by enzymes is essential, particularly for contaminants that cannot be taken up by the plants due to their large size and complex nature (Uqab et al. 2016). Various types of plant enzymes have been discovered, that breakdown pesticides, explosives, hydrocarbons, ammunition waste, and other xenobiotic compounds. Lists of

Table 2.5 Selected reports on phytoremediation of pesticide contaminated soils (modified from Morillo and Villaverde 2017)

Sr. no.	Pesticide	Pesticide class	Scale	Plant used/operation conditions	Outcomes/pesticide removal	References
1	DDE	Organochlorine insecticide (metabolites)	Field experiment	Zucchini, pumpkin, spinach	40, 70 and 20% removal of DDE by zucchini, pumpkin, and spinach, respectively	White (2001)
2	Aldicarb	Carbamate pesticide	Growth chamber	Corn, mungbean and cowpea	Corn, mungbean and cowpea efficiently removed Aldicarb	Sun et al. (2004)
3	DDT	Organochlorine insecticide	–	*Cichorium intybus, Brassica juncea*	Promising results obtained on DDT degradation	Suresh et al. (2005)
4	PCP	Organochlorine pesticide	Greenhouse experiment	Rhizoremediation (P) (wheat) + Bioaugmentation (I) (*S. chlorophenolicum*)	40% removal from soil only with P and 80% removal with I + P	Dams et al. (2007)
5	DDT	Organochlorine insecticide	Greenhouse experiment	Alfalfa + arbuscular mycorrhizal fungus + Triton X-8100	66.8–95.4% of DDT removed in the rhizosphere soil	Wu et al. (2008)
6	DDT	Organochlorine insecticide	Greenhouse experiment	*Cucurbita pepo* ssp. Six amendments to increase soil OM (2.4–27.3%)	Root DDT concentrations lower in soils with high OM	Lunney et al. (2010)
7	DDTs	Organochlorine insecticide and metabolites	Greenhouse experiment	Pumpkin/surfactants (Biosolve, Aqueduct) or mycorrhizal fungi	Soil amendments did not increase DDTs extraction from soil	Åslund et al. (2010)

(continued)

Table 2.5 (continued)

Sr. no.	Pesticide	Pesticide class	Scale	Plant used/operation conditions	Outcomes/pesticide removal	References
8	4,4 DDE, 2,4 DDD, 4,4 DDT, α-HCH, β-HCH and γ-HCH	Organochlorine insecticide and metabolites	Greenhouse experiment	*A. annua*, *K. sieversiana*, *K. scoparia, X. strumarium, A. annua, A. artemisiifolia, E. canadensis*	All showed good capabilities to translocate pesticides from roots to aboveground tissues	Nurzhanova et al. (2010)
9	Endosulfan	Organochlorine insecticide	Greenhouse experiment	*Ocimum basilicum L.*, *Ocimum minimum L*	37% of Endosulfan was removed from soil with *O. basilicum*	Ramírez-Sandoval et al. (2011)
10	DDTs	Organochlorine insecticide and metabolites	Greenhouse experiment	Willow trees + organic amendments: root exudates, Tween 80, sodium citrate and Oxalate	Increased p,p′-DDE/p,p′-DDT ratio when compared with initial soil	Mitton et al. (2012)
11	Cypermethrin	Pyrethroid insecticide	Greenhouse experiment	*Pennisetum pedicellatum* Rhizoremediation	100–65% removed from soil for 10–100 mg/kg in 60d	Dubey and Fulekar (2013)
12	Lindane	Organochlorine insecticide	Greenhouse experiment	*Jatropha curcas* Rhizoremediation	89–72% removed from soil for 5–20 mg/kg in 300d	Abhilash et al. (2013)

(continued)

Table 2.5 (continued)

Sr. no.	Pesticide	Pesticide class	Scale	Plant used/operation conditions	Outcomes/pesticide removal	References
13	DDTs and HCHs	Organochlorine pesticides and metabolites	Greenhouse and field experiments	17 naturally growing plants	*A. annua* accumulated 8 mg/kg of pesticides in plant tissue. *X. strumarium* and *S. dulcamara* extracted 70–80% pesticides from soil	Nurzhanova et al. 2013)
14	DDTs	Organochlorine insecticide and metabolites	Greenhouse experiment	Tomato, sunflower, soybean, alfalfa	Tomato the best phytoremediator plant	Mitton et al. (2014)
15	Endosulfan	Organochlorine insecticide and metabolites	Field experiment	Seven naturally growing plants	*V. zizanioides* and *D. longiflora* accumulated 343 and 163 ng g^{-1} of Endosulfan	Singh and Singh (2014)
16	Endosulfan	Organochlorine insecticide	Greenhouse experiment	tomato, sunflower, soybean, alfalfa	72% removal from bulk soil by alfalfa	Mitton et al. (2016)
17	Pyrethroid	Organochlorine and pyrethroid	Lab experiment	*Eichornia crassipes, Pistia Strateotes*	Up to 76% removal of pyrethroid	Riaz et al. (2017)

Table 2.6 Phytoaccumulation or phytoextraction of organochlorine pesticide by various plant species (modified from Singh and Singh 2017)

Sr. no.	Plant species	Target plant organ	OCPs	References
1	Carrots, beets, potatoes spinach, lettuce, dandelion, zucchini, tomatoes, peppers, corn bush beans, and eggplant	Root, aerial tissue	Chlordane	Mattina et al. (2000)
2	*Brassica juncea*, *Cichorium intybus*	Root	DDT	Suresh et al. (2005)
3	*Phragmites australis*, *Oryza sativa*		DDT	Chu et al. (2006)
4	*Chenopodium* sp., *Avena sativa*, *Solanum nigrum*, *Cytisus striatus*, *Vicia sativa*	Root, stem, leaves	HCH	Calvelo-Pereira et al. (2006)
5	*Zea mays*, alfalfa, ryegrass, and teosinte	Root, shoot	DDT	Mo et al. (2008)
6	*Acorus gramineus*	Root, rhizome, leaves	Dieldrin	Chuluun et al. (2009)
7	*Sesamum indicum*	Root, stem, leaves	HCH	Abhilash and Singh (2010a)
8	*Withania somnifera*	Root, stem, leaves	HCH	Abhilash and Singh (2010b)
9	*Ricinus communis*	Leaf, stem, root,	DDT	Huang et al. (2011)
10	*Zea mays*, *Brassica campestris*		Endosulfan	Mukherjee and Kumar (2012)
11	Tea garden	All plant tissues	HCH	Yi et al. (2013)
12	*Phragmites australis*	Root, rhizome, shoot	HCH	Miguel et al. (2013)
13	*Vetiver zizanioide*, *Digitaria longiflora*	Root, stem, leaves	HCH	Singh and Singh (2014)
14	*Spinacia oleracea*	Root, leaves	HCH	Dubey et al. (2014)
15	*Eichornia crassipes, Pistia strateotes*	Roots, shoots	Organochlorine	Riaz et al. (2017)

OCPs: Organochlorine pesticides
DDT: 1,1,1-Trichloro-2,2, bis(p-chlorophenyl) ethane
HCH: Hexachlorocyclohexane

Table 2.7 Uptake and phytodegradation of pesticides by different plant species

Sr. no.	Plant species	Pesticide	Results	References
1	*Hordeum vulgare*, *Triticum aestivum*	Carbofuran, terbuthylazin	Barley and wheat removed substantial amount of pesticides	Matthies and Behrendt (1995)
2	*Ceratophyllum demersum*, *Elodea canadensis*	Metolachlor, atrazine	Plants removed and metabolized >90% of metolachlor and a significant amount of atrazine	Rice et al. (1997)
3	Hybrid poplars (*Populus deltoides x nigra*)	Atrazine	Atrazine was taken up and degraded in plant tissues	Burken and Schnoor (1997)
4	*Hordeum vulgare*	Dodemorph, tridemorph	Tridemorph accumulated in roots and dodemorph translocated to shoots	Chamberlain et al. (1999)
5	*Juncus effusus*	Chlorpyrifos, atrazine	Both pesticides were taken up by plants but chlorpyrifos was metabolized faster than atrazine	Lytle and Lytle (2000)
6	*Myriophyllum aquaticum, S. oligorrhiza*, *E. canadensis*	Malathion, demeton-S-methyl, crufomate	*M. aquaticum* removed 58–83% of the added pesticides	Gao et al. (2000)
7	*Nicotiana tobacum*, *Gossypium hirsutum*	Sulfentrazone	Herbicide uptake rate increased with decrease in soil pH	Ferrell et al. (2003)
8	*Cucurbita pepo*, *Cucurbita*, *Medicago sativa*, *Festuca arundinacea*, *Lolium perenne*	DDT, DDD, DDE	*C. pepo* species (pumpkin and zucchini) extracted highest amounts of pesticides	Lunney et al. (2004)
9	Hybrid poplars (Populus deltoides x nigra)	Atrazine	Atrazine was taken up and degraded by poplars	Chang and Lee (2005)
10	*Myriophyllum aquaticum*	Atrazine, cycloxidim, terbutryn, trifluralin	Atrazine and cycloxidim were taken up more than terbutryn and trifluralin by the plant	Turgut (2005)

(continued)

Table 2.7 (continued)

Sr. no.	Plant species	Pesticide	Results	References
11	*Cucurbita pepo*, *Cucumis sativus*	Chlordane	Highest bioaccumulation of chlordane was in the root tissue	Mattina et al. (2005)
12	*Brassica oleracea var. botrytis*, *Spinacia oleracea*	HCH, DDT	Both the plants extracted these pesticides from soil	Tao et al. (2005)
13	*Solanum tuberosum*, *Daucus carota*	Chlorinated pesticides (OCPs)	Carrots and potatoes were found to remove 52–100% of OCPs	Zohair et al. (2006)
14	*Hybrid aspen*	Bisphenol A (BPA)	Degradation	Limura et al. (2007)
15	Tobacco (*Nicotiana tabacum* 'Xanthi')	1,2-Dichloroethane	Degradation	Mena-Benitez et al. (2008)
16	*E. canadensis*, *Myriophyllum spicatum*, *Potamogeton lucens*	Atrazine, Isoproturon, Diuron	*M. spicatum* was found to be the more sensitive macrophyte	Knauert et al. (2010)
17	*Lemna Minor*	Isoproturon, Glyphosate	Removal of isoproturon and glyphosate were 25% and 8%, respectively	Dosnon-Olette et al. (2011)
18	*Arabidopsis*	Trichlorophenol (TCP)	Degradation	Su et al. (2012)
19	*C. mexicana*, *C. vulgaris*, *M. reisseri*, *S. obliquus*	Atrazine	*C. Mexicana* showed better accumulation of atrazine than others	Kabra et al. (2014)
20	*Phragmites australis*	Tebuconazole, Imazalil	*P. australis* promoted tebuconazole and imazalil removal from hydroponic solution	Lv et al. (2017)

important enzymes associated with phytodegradation of pesticides and other organic contaminants are given in Table 2.8.

Various plant species have been reported for phytodegradation of different organic pollutants. For example, poplar, brassica spp., *Leucaena leucocephala* (a tropical tree), and other herbaceous plants are known for dehalogenation and detoxification of gasoline additives; Rye, cucurbita, and leucaena for degradation of pesticides;

Table 2.8 List of important enzymes associated with phytodegradation of pesticides and other organic contaminants (modified from Jee 2016)

Sr. no.	Enzyme	Target organic contaminant
1	Arly aclyamidase	Herbicide and fungicide, acylanilide herbicides
2	Dehalogenase	Chlorinated solvents (perchloroethylene, trichloroethylene and dichloroethylene)
3	Cytochrome P450 monoxygenase	Herbicides (atrazine, norflurazon, and chlortoluron), chlorinated solvents (perchloroethylene, trichloroethylene and dichloroethylene), xenobiotics (PCBs)
4	Glutathione s-transferase	Organophosphorus insecticides
5	Peroxygenases	Xenobiotics
6	Peroxidases	Polycyclic aromatic hydrocarbons, organochlorines, trinitrotoluene, chlorinated solvents, phenolic compounds and dye
7	Laccases	Chlorinated solvents and phenolic compounds
8	Tyrosinase	Chlorinated solvents and phenolic compounds
9	N-glucosyltransferases	Xenobiotics
10	Nitrilase	Nitrile group containing herbicides *e.g.* bromoxynil
11	Nitroreductase	Explosives (trinitrotoluene and hexahydro-1,3,5-trinitro-1,3,5-triazine)
12	N-malonyltransferases	Xenobiotics
13	Organophosphorus hydrolase (OPH)	Xenobiotics compounds
14	Organophosphorus acid anhydrolase (OPAA)	Xenobiotics compounds
15	O-demethylase	Alachlor, metalachor
16	O-glucosyltransferases	Xenobiotics
17	O-malonyltransferases	Xenobiotics
18	Phosphatase	Pesticides (Organophosphates)
19	Esterases	Ester containing xenobiotics (triactin and p-nitrophenylaceta), herbicide *e.g.* 2,4-D (2,4-di-chlorophenoxy) acetic acid

Arabidopsis, poplar, parrot feather, tobacco, canola, bean, and alfalfa, for the degradation of explosives; and rye, poplar, *Sesbania cannabina*, willow, fescue, pothos, bruguiera, kandelia, and californian grasses for detoxification of petroleum hydrocarbons (Jadia and Fulekar et al. 2009; Farhana et al. 2012). Several reports have shown the resistant behavior of leguminous plant species against HMs. These plants significantly improve the dissipation of organic pollutants including PAHs and polychlorinated biphenyls (PCBs) (Hamdi et al. 2012; Li et al. 2013). The tropical tree *Leucaena leucocephala* has been found to be highly effective in taking up the ethylene dibromide (EDB, an insecticide) (Doty et al. 2003; Newman and Reynolds 2004). Similarly, *Ricinus communis* (a tropical plant species) has been found to be effective in the degradation of 15 persistent organic pollutants (POPs) including hexachlorocyclohexane (HCH), DDT, heptachlor, aldrin, and others (Rissato et al. 2015).

2.6.3 Phytovolatilization of Pesticides

Phytovolatilization refers to the transpiration of contaminants following their uptake from the water or soil. Phytovolatilization is mostly applicable to the contaminants having high volatility such as trichloroethylene (TCE), ethylenedibromide (EDB), methyl tert-butyl ether (MTBE), and carbon tetrachloride (CTC).

2.6.4 Rhizoremediation of Pesticides

Rhizoremediation is the removal of contaminants through combined efforts of plants and rhizospheric microbes. The rhizosphere is an area of the soil volume around roots and is a complex environment supporting a good number of metabolically active microbes, which are several orders of magnitude greater than the non-rhizospheric soil (Capdevila et al. 2004; Gerhardt et al. 2009). Rhizoremediation is one of the options used in combined remediation (Fig. 2.4) where plants are assisted with microbes for improving the remediation process and plant growth. The *Brassica nigra* was found to be effective in removing PCBs from Aroclor 1242-contaminated soil (Singer et al. 2003). The *Spartina pectinata* and *Carex aquatilis* have been reported to be among the most efficient and effective plants for rhizoremediation of PCBs (Smith et al. 2007). Eevers et al. (2018) studied that inoculation of *C. pepo* plants with a consortium of *S. taxi* UH1, *M. radiotolerans* UH1, and *E. aerogenes* UH1 can significantly (46%) increase the phytoremediation potential of the plants in DDE-contaminated soils. Also, *Zehgrnah* plants have good abilities for the rhizodegradation of atrazine. Some examples of pesticides rhizoremediation by various plants are listed in Table 2.9.

There are three major biochemical processes by which xenobiotic (pesticides) metabolism occurs in higher plants, animals, and human: (a) Phase-I transformation or conversion, (b) phase-II conjugation, and (c) phase-III compartmentalization (Fig. 2.5). In phase-I, hydrophobic contaminants get transformed into less hydrophobic metabolites through epoxidation, N-, O-, S-dealkylation, peroxidation, aromatic and aliphatic hydroxylation, sulfoxidation, oxidative desulfuration, or reduction by cytochrome P450s. Thus, preliminary and essential steps toward detoxification and

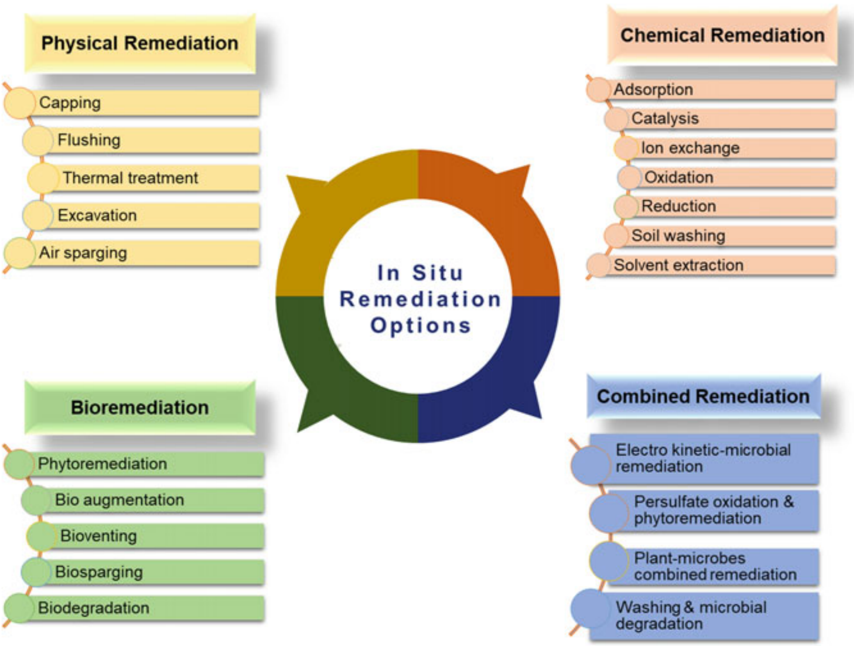

Fig. 2.4 In situ remediation options for soil and sediment contaminated with organic and inorganic pollutants (adapted from Song et al. 2017)

Table 2.9 Rhizoremediation of pesticides (modified from Singh and Singh 2017)

Sr. no.	Pesticides	Plant	References
1	HCH	*Kochia* sp.	Singh (2003)
2	HCH	*Cytisus striatus, Avena sativa*	Calvelo-Pereira et al. (2006)
3	HCH	*Zea mays*	Boltner et al. (2008)
4	HCH	*Cytisus striatus and Holcus lanatus*	Kidd et al. (2008)
5	PCB mixture Delor 103	*Silybum marianum, Solanum nigrum*	Mackova et al. (2010)
6	HCH	*Jatropha curcas*	Abhilash et al. (2013)
7	HCH	*Phragmites australis*	Miguel et al. (2014)
8	Endosulfan	*Vetiveria zizanioides*	Abaga et al. (2014)
9	Endosulfan sulfate	*Zea mays*	Somtrakoon et al. (2014)

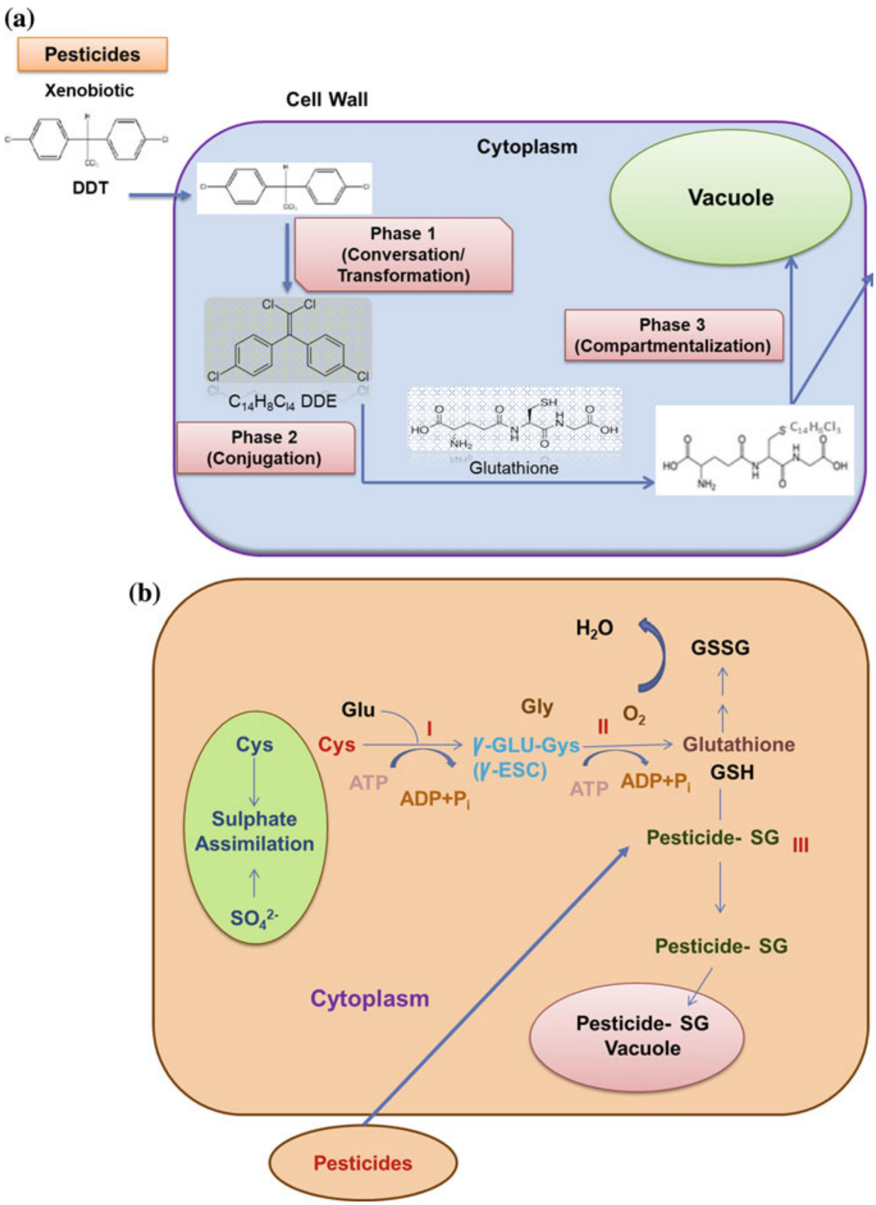

Fig. 2.5 Pesticide detoxification mechanisms in plant cell. **a** Modified from Singh and Singh 2017; **b** modified from Hussain et al. 2009. *Abbreviations* Cys, cysteine, γ-Glu-Cys, γ-L-glutamyl-L-cysteine, γ-ECS, γ-glutamylcysteine synthetase, GSH, glutathione, GSSG, oxidized glutathione

excretion are the reactions catalyzed by cytochrome P450s (Schmidt et al. 2006a, b; Abhilash et al. 2009; Singh and Singh 2017).

Phase-I process generally results in the formation of metabolites that are less toxic. Phase-II conversion involves direct conjugation of organic contaminants or their metabolites from phase-I reactions with glutathione, amino acids, or sugars, thus producing hydrophilic compounds. Lastly, during phase-III, there occurs deposition of conjugated metabolites in cell walls or vacuoles (Singh and Singh 2017). Lately, phase-III has further been classified into two autonomous phases, one of which is restricted for transfer and storage in the vacuole, and the other involved in cell wall bindings or excretion (Fig. 2.5a) (Singh and Singh 2017). Figure 2.5b shows the energy utilization steps along with other enzymatic reaction steps similar to Fig. 2.5a. Here, in the first two steps, glutathione (GSH) is synthesized in two ATP-dependent steps catalyzed by γ-glutamylcysteine synthetase (γ-ECS) and glutathione synthetase (GSHS) and produces conjugate with the molecules of pesticides. Eventually, glutathione S-transferase (GST) shifts this conjugated molecule from cytoplasm to molecules where mineralization of pesticides molecule occurs (Fig. 2.5b).

2.7 Phytoremediation of Other Pollutants

In addition to toxic nutrients, pesticides, and HMs, there are several other contaminants present in the water and soil (probably in trace amounts). These may include textile dyes, surfactants, and detergents (Rane et al. 2015). *Alternanthera philoxeroides* plant has been reported to be effective in removing highly sulfonated textile dye (i.e., Remazol Red). In addition, some wild plants such as *Blumea malcolmii, Phragmites australis, Ipomea hederifolia,* and *Typhonium flagelliforme* have been identified for the removal of textile dye (Rane et al. 2014). Common ornamental plants such as *Aster amellus, Glandularia pulchella, Petunia grandiflora, Portulaca grandiflora, Tagetes patula,* and *Zinnia angustifolia* have an ability to remediate textile dye from polluted soil. Also, aquatic macrophytes due to their stress tolerance characteristics and strong phytoremediation potential have been found to be able to dissipate dyes and other pollutants (Rane et al. 2015). Grassed waterways, vegetated ditches, vegetated filter strips, and constructed wetlands have been successfully reported for removing pesticide and reducing movement of nutrients in runoff from container nurseries and agricultural land (Briggs et al. 1998; Stehle et al. 2011; Maillard et al. 2011; Tanner and Sukias 2011).

2.8 Major Challenges to Phytoremediation

- *Slowness*: Phytoremediation is a very slow process which makes it very challenging work to adopt.
- *Stresses*: Different abiotic (e.g., temperature, precipitation, and nutrients) and biotic (e.g., plant pathogens, insect pests and/or animals, and competition by weed species) stresses to plants are the challenge to phytoremediation.
- *Physical constraints*: For instance, low moisture availability to plants due to hydrophobic pollutants in soil, minimum access to pollutants due to the smaller root lengths, and disposal of contaminated roots or woods.
- *Phytoremediation complexity in the field*: Several variables can contribute to ambiguous and misleading results from the field. For example, an uneven distribution of contaminants in the field results in heterogeneity in outcomes, and variability in soil structure, root structure, soil pH, soil organic composition, microbial activity and moisture content and microbial activity, time and resource constraints in extensive field sampling, aeration of field, removal of contaminant in control due to the occurrence of photooxidation, complexity in rhizosphere, solubility, and bioavailability of contaminants.
- *Regulatory acceptability*: Introduction of non-native microbial and/or plant species into field sites can cause potential ecological risks. Non-native species can propagate and spread from the site and may displace the native species. Hydrocarbon contaminants, contributed from microbial processes, cause difficulty in distinguishing between petrogenic and phytogenic compounds leading to overestimation of target contaminant level in the soil.
- *Application of genetically modified organisms (GMOs) in the field*: GMOs have low public acceptance due to several reasons. For example, genetic material inserted in the organism can be transferred to indigenous populations. GMOs often fail to compete with native strains. In addition, silencing of transgenes in plants makes the use of GMOs technology unpredictable and inappropriate.

2.9 Overcoming the Challenges

- *Strategies and approaches for reducing ecological risk*: Use of native species for phytoremediation would be the best way to reduce the ecological risk. Use of biological containment system is another option to circumvent the weakness.
- *Strategies and approaches for decreasing stresses that restrict plant growth in the field*: Use of plant growth-promoting rhizobacteria (PGPR) would be an option. PGPR are known to enhance nutrient uptake and plant growth and improve phytoremediation ability of contaminant-tolerant plants.
- *Improved protocols and methodologies for sampling, monitoring, and analyzing research results obtained from the field*: Most of the methods for phytoremediation

are developed by the Remediation Technologies Development Forum (a group of academic, government, and industry partners). These methods are mainly intended to improve the standards for number of replications, plot size, plant and soil sampling procedures, choice of plant species, hydrocarbon and microbial analyses, time-points and/or endpoint, and statistical treatment of data. For example, use of conservative biomarkers for normalization of data, application of stable isotope probing and gas chromatography–mass spectrometry (GC-MS) for the fate of contaminants and use of advanced molecular biological tools such as next-generation sequencing for identification and characterization of useful microbes.

2.10 Conclusions

Agricultural pollutants in the environment pose a severe threat to all living organisms including plants, animals, and human beings. Phytoremediation could be a feasible option for the economical and eco-friendly removal of these pollutants. Phytoextraction seems to be the most effective phytoremediation option for inorganic agricultural pollutants (heavy metals) through the use of hyperaccumulators. Among different plant strategies, integrated approaches such as microbes-assisted rhizoremediation seem to be a promising option and have good potential for the removal of organic agricultural pollutants. For further development of phytoremediation, integrated multidisciplinary research approaches and efforts are required through combining plant biology, soil microbiology, and soil biochemistry along with agricultural and environmental engineering.

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Chapter 3
Phytoremediation of Soils Contaminated by Hydrocarbon

José G. Chan-Quijano, Manuel J. Cach-Pérez and Ulises Rodríguez-Robles

Abstract It is estimated that more than one-third of the world soils are seriously contaminated due to anthropological activities. Much of this contamination is due to oil industry activities which cause significant changes in the ecosystems due to the processes of exploration, refining, transportation and commercialization of products derived from oil. Plants have become biotechnologies for the recovery of hydrocarbon-contaminated soils given that they can absorb and degrade significant amounts of the pollutants. Most plants live in symbiosis with ectomycorrhizal fungi and/or arbuscular mycorrhizas that can facilitate the remediation of contaminated soils. In addition, rhizosphere microorganisms such as bacteria, fungi and nematodes have the ability to consume hydrocarbons as sources of energy and carbon, thereby playing a very important role in the remediation of contaminated soils. The remediation of areas contaminated with oil hydrocarbons is making it necessary to conduct studies on each contaminant regarding the damages and/or benefits they may be causing in the rhizosphere and in plant physiology.

Keywords Hydrocarbons · Hydrocarbonoclastic bacteria · Mycorrhizae · Phytoremediation · Rhizosphere · Soil microorganisms

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3.1 Introduction

On a global level, more than one-third of the world soils are seriously contaminated due to anthropological activities (FAO 2011; Abhilash et al. 2013; Weber et al. 2013; Prasad et al. 2016). One of these activities is the oil industry, which has been the direct cause of significant changes in the ecosystems due to the processes of exploration, refining, transportation and commercialization of products derived from oil (Rivera-Cruz et al. 2005). Oil is a very complex mixture which contains mainly hydrocarbons (molecules with carbon and hydrogen atoms) and compounds with heteroatoms such as sulfur (S), nitrogen (N), oxygen (O) and low concentrations of metallic constituents, mainly nickel (Ni), vanadium (V), sodium (Na), calcium (Ca) and copper (Cu) (Namihira-Guerrera 2004; PEMEX 2011; Feijoo-Ruiz 2012).

Contamination by petroleum hydrocarbons (PH) has become a critical environmental problem, affecting the homeostasis of the soil system through the PH contamination generated and causing a negative impact on the safety of ecosystems and human health (Tripathi et al. 2015). However, as the soils become more and more limited by the contamination, the need to recover these affected areas is increasingly evident (Wagner et al. 2016).

In the search to find a solution for the problem of soil pollution from oil spills, approximately three decades ago, a research project was initiated, which has allowed the use of diverse flora as raw material for environmental decontamination (Sangabriel et al. 2006; Ochoa-Gaona et al. 2011; Prasad et al. 2016). One of the first studies dealing with the effect of oil-contaminated soils on plants was Bossert and Bartha (1985), and specifically Radwan et al. (1995) who used the roots of the *Senecio glaucus* L. for remediation processes in soils contaminated by hydrocarbons. On the other hand, Cunningham and Berti (1993) addressed the remediation of contaminated soils from a theoretical revision with plants, while Cunningham and Ow (1996) initiated the study of phytoremediation with an analysis of the promises and perspectives of this biotechnology.

In this way, plants have become biotechnologies for the recovery of contaminated soils given that they can absorb between 10–50% of some contaminants within their organs and tissues on interaction with water. The remediation can be *in situ* (in the contaminated site) or *ex situ* (in a laboratory or nursery); it generates little waste, creates socioeconomic benefits such as wood (in the case of timber species) or as firewood and thus as a source of bioenergy. In addition, remediation helps to improve the physico-chemical parameters (pH, texture, MO, CIC, N, P) and to reduce salinity in soils contaminated by hydrocarbons, thereby increasing nutrient availability, mitigating soil erosion, capturing carbon and increasing biodiversity (Abhilash et al. 2012; Hu et al. 2012; Chan-Quijano 2015; Thijs and Vangronsveld 2015; Tripathi et al. 2016).

The upper terrestrial plants consist of an aerial system and a root system which can represent between 10 and 20% of the total plant material in forest trees, 10–50% in cultivated plants and 50–80% in grassland vegetation. The root system is responsible for anchoring the plants and for proportioning water and nutrients. In doing this, the roots also absorb oxygen in order to produce the necessary energy for the metabolic processes during photosynthesis. In this way, root respiration, along with the microorganisms and fauna of the soil, all contribute significantly to soil respiration and the liberation of CO_2 in the pore spaces; this is important as it decomposes the organic material and at the same time degrades the contaminating agents (Strawn et al. 2015; Blume et al. 2016).

The root system of plants is divided into thick roots (>2 mm in diameter) and fine roots (<2 mm in diameter); the extremities of the fine roots present a large number of root hairs with a thickness of 5–20 μ and a length of up to 1 km; these only remain functional for a few days and then die. Their function is to increase the surface area of absorption of the root which is why they invest the energy to carry out this activity (Blume et al. 2016). These roots are affected in the event of an oil spill; initially, the plants which cannot support the contaminant die, while those that are able to become acclimatized to the affected area begin to suffer a state of stress, resulting in the appearance of chlorosis on the leaves, slow growth and a reduction in root growth and leaf production (Rivera-Cruz 2011; Ochoa-Gaona et al. 2011).

In the soil–root interface, the narrow volume surrounding the roots (a few mm) is known as the rhizosphere; this is defined as the direct interaction between the microorganisms and the root of the plants, or as the compartment of the soil influenced by the plant roots (Atlas and Bartha 1998; Gregory 2006a; Lugtenberg 2015). It is characterized by various processes such as the exudation of organic compounds, root respiration (absorption of O_2 and liberation of CO_2), liberation of protons and other mineral ions and the absorption of water and solutes which modify significantly the properties and the function of the soil and also favor microbial activity, with the aid of the exudation from the root. The main process associated with the rhizosphere is formed mainly by organic acids of low molecular weight which assist in the degradation of the hydrocarbons with metabolic processes (Morel et al. 1999; González-Mendoza 2013).

Given that oil hydrocarbons initially damage the soil and the plants (death of foliage, damage to the root and wood tissues), the aim of this chapter is to explain the degradation of the hydrocarbons with the rhizosphere of plant species which have potential in the remediation of soils contaminated by oil.

3.2 Contaminated Soil and the Rhizosphere

The plants used for the remediation processes of soils contaminated with hydrocarbons must be fast-growing, resistant and competitive with a capacity of tolerance to the contaminants, as well as good liberation of exudates for the proliferation of microorganisms and a greater development of biomass and roots. Once germinated, the plants need soils in optimal conditions in order to continue their development; in other words, the physical, chemical and biological properties must be in excellent health and have good nutritional quality (Morel et al. 1999; Fenner and Thompson 2005; Gregory 2006a). However, many of the aspects of plant root growth reflect an acclimatization and adaptation to demanding environments, showing complex growth patterns and tropism which allow them to explore and exploit a heterogeneous environment full of obstacles such as the contaminants (Pepper et al. 2004; Taiz and Zeiger 2010).

At best, plant roots, in particular those of the trees, can penetrate down to deeper levels of the soil (in comparison with grasses), and in doing so, they achieve a propagation of the microorganisms at different depths, with which they are able to incorporate nutrients, deliver oxygen and improve redox conditions which help in the degradation of oil hydrocarbons (Pérez-Hernández et al. 2016). Moreover, most plants, in particular trees, live in symbiosis with ectomycorrhizal fungi and/or arbuscular mycorrhizas (Bonfante and Desirò 2015).

Blume et al. (2016) mention that both thick and thin roots penetrate the thick pores of the soil (diameter >10 μm) and that the numerous root hairs penetrate a large part of the mesopores (2–10 μm), allowing the absorption of water and nutrients. In the range of fine pores (<0.2 μm), these substances can only reach the plant roots by means of slow diffusion processes along the gradients of concentration in the soil solution. In contrast, oxygen is administered to the roots mainly through the large, thick pores in the soil (between 6.5 and 9.3 μm). The density of root length frequently reaches various meters by dm^{-3}. However, normally, less than 1% of the total soil volume available is rooted by the plants, up to a maximum of 10–20% even in the A horizons. In this way, the dynamics of the biogeochemical properties of the rhizosphere and their relationship with soil aggregation have morpho-functional mechanisms such as root depth, root-aggregate contact, density and distribution of the roots, size, distribution and form of the pores created by the roots and the soil structure (Gregory 2006a, b; Gregory et al. 2009; Torres-Guerrero et al. 2013). However, almost all the plant processes are directly or indirectly affected by the water supply. More than 90% of the living structures in plant cells (protoplasm) consist of water; this utilization of water varies among plants from 15 to 100% humidity of the soil (moisture content); in addition, water enters the plants through the leaves, stems and mainly through the roots (Aguilera-Contreras and Martínez-Elizondo 1996).

When the oil falls on the ground or in the water, it adheres to the bark of the roots, forming a layer which does not allow water absorption, causing the slow death of the tree (Radwan et al. 1995; Tansel et al. 2015; Feng et al. 2017). In the same way, the hydrocarbons provoke deformations in the calyptra and, as a consequence, induce damage to the apical meristem of the root; they also obstruct the absorbent, root hairs, which do not allow the passage of water and nutrients to the rest of the plant (Gregory 2006a; Taiz and Zeiger 2010; Feng et al. 2017). When an oil spill occurs in the soil, the oil undergoes a process of intemperization; the volatile hydrocarbons begin to evaporate and the aromatic hydrocarbons (nonvolatile) such as benzene, toluene, xylene, napthalene, biphenyls, dimethylphenanthrene, methylcrisine, methylpirene, benzanthracene and benzopyrene remain in the soil and are deposited in the form of asphalt, provoking toxicological damage to the ecosystem (Toledo 1982; Ferrera-Cerrato and Alarcón 2013).

When the oil falls on the soil, it infiltrates vertically. The heavier hydrocarbons, such as fuel oil, penetrate more slowly, while the lighter ones, such as benzene, show a rapid movement in the soil profile; however, this varies depending on the soil group (Toledo 1982). Moreover, the oil also modifies the structure of the soil (ruptures of the aggregates), reducing the exchange of gases with the atmosphere, increasing the content of organic carbon (through oxidation processes) and thereby reducing the cation exchange capacity (by loss of bases), resulting in an acidification of the soil (Elías-Murguía and Martínez 1991; Zavala-Cruz et al. 2002; Weil and Brady 2008; Ferrera-Cerrato and Alarcón 2013).

This acidification is involved in the capture or liberation of ions and in the catalysis of the redox reactions which are seen to be saturated or limited by the concentrations of hydrocarbons, since it essentially transforms carbon (C), nitrogen (N) and sulfur (S) in ions or molecules which are easily absorbed by plants and microorganisms. Similarly, when the value of pH is not optimal in the soil, this gives rise to serious problems for the development of microorganisms and plants, given the elevation of toxicity in the aluminum (Al), iron (Fe) and manganese (Mn) and a deficiency of calcium (Ca), magnesium (Mg) and molybdenum (Mo) (Sposito 2008).

In addition, when the concentrations of hydrocarbons in the soil are greater than 3000 mg kg^{-1} (milligrams over kilograms), the apparent density tends to decrease to 0.6 Mg m^{-3} (megagrams per cubic meter); this can vary the quantity of organic materials found in the area; the organic material will be influenced by biogenic material (decomposition of plant and animal species) and the petrogenic material (hydrocarbons; Martínez and López 2001; Beltrán-Paz and Vela-Correa 2006).

The organic contaminants such as hydrocarbons integrate with the organic material of the soil due to their greater hydrophobicity, allowing the microorganisms to carry out the mineralization of the contaminant (Cang et al. 2013; Tripathi et al. 2015). These contaminants are submitted to different biotic and abiotic interactions, such as adsorption, volatilization, chemical oxidation, photolysis and microbial degradation (making the contaminant less toxic or innocuous, while also helping in the detoxification through biostimulation among the roots and microorganisms; Zhao et al. 2008; Lors et al. 2012; Masakorala et al. 2013).

The degradation of the hydrocarbons that reach at deeper levels of the soil will depend on root development and soil transpiration (Komives and Gullner 2006; Pérez-Hernández et al. 2013, 2016). When the roots reach these depths, metabolic transformation processes occur, mediated by a large variety of enzymes, allowing the contaminants to be assimilated by the plant tissues (Kuiper et al. 2004; Mezzari et al. 2004, 2005). The process of metabolic transformation of the contaminants will depend on the physico-chemical and structural properties of the soil, as well as its relationship with the rhizosphere, given that the hydrocarbons are organic compounds and moderately hydrophobic (characterized with the partition coefficient of octanol–water, log K_{ow}, with values between 1 and 3; Mezzari et al. 2011).

According to Kuiper et al. (2004), the exudates deriving from the plants, such as amino acids and sugars, among others, can help to stimulate the survival and biostimulation of the microorganisms, resulting in a more efficient degradation of the contaminants. In the same way, the root system of the plants helps in the propagation of the microorganisms, which filter down to impermeable layers of soil affected by the oil spill.

In order for the plants to become acclimatized, they must adjust to the conditions of the affected area. Their capacity to achieve this depends on nutrient availability, the physico-chemical properties of the soil, their biomass production and their response to the stress caused by the oil hydrocarbons (Kuppens et al. 2015; Tripathi et al. 2016). In addition, the conditions of temperature, humidity, sunlight, rainfall, wind and water in the soil all help to accommodate the plants so that they can adjust to the area (Mclntosh et al. 2017). Water, for example, plays a vital role in the extraction of nutrients and hydrocarbons, as these elements can be dissolved in water and thus assimilated by the plants during the process of absorption (Licht and Isebrands 2005).

The plant absorbs nutrients and water through the roots in order to develop; therefore, the intimate contact between the surface of the root and the soil is essential. However, this contact is easily broken when the soil is altered, degraded and/or contaminated (Taiz and Zeiger, 2010). In particular, one of these mechanisms of acclimatization of the plants to contaminated soils is that the new roots, which develop after a contamination event, try to reestablish the optimal contact with the soil, which contributes to a greater resistance of the plant to stress (Luo et al. 2016).

The work of the rhizosphere is based on the catabolic potential of the microorganisms which have the capacity to tolerate the hydrocarbons with the support of the exudates from the roots which creates a favorable microenvironment (Ortega-Calvo et al. 2003). The effect of the rhizosphere is carried out between 1–5 mm of the root surface and the soil. Given that the roots exudate organic compounds, the microbial populations increase their activity 5 to 100 times more, in comparison with soils without plants (Atlas and Bartha 1998; Gregory 2006a; Lugtenberg 2015).

Among the exudates released by the plants can be found sugars, fatty acids, amino acids, water, inorganic ions, oxygen, riboflavin, carbon dioxide, bicarbonate ions, protons, electrons, ethylene, mucilage, enzymes, siderophores, allelopathy inducing compounds, as well as root residues which include calyptra cells and cellular contents, to mention a few (Uren 2007; Ferrera-Cerrato and Alarcón 2013). These are liberated through physical and environmental effects such as luminosity, temperature, pH, damage to the root and the water content in the soil (Ferrera-Cerrato 1995). The exudates are generated inside the mitochondria, in the cytosol and in the vacuole of the plant cells, from the tricarboxylic acid cycle (Young et al. 1998; González-Mendoza, 2013).

Similarly, the exudates have an influence on the solubility of essential and nonessential elements through the acidification, chelation, precipitation and oxide reduction processes in the rhizosphere and also through microbial activity, which contributes to root growth and the elimination of oil hydrocarbons thanks to the mutualistic interactions among arbuscular mycorrhizal fungi, microorganisms and plant roots (Strong and Phillips 2001; Zavala-Cruz et al. 2002; Oldroyd 2013; Philippot et al. 2013).

The rhizosphere, therefore, is an interface between the roots of the plants and the soil where the interactions between the microorganisms and invertebrates intervene in the biogeochemical cycle and in many other aspects such as plant growth, tolerance to biotic and abiotic stress, degradation of oil hydrocarbons and in the complex and dynamic ecology for the improvement and functionality of the ecosystem (both natural and contaminated).

3.2.1 The Role of the Microorganisms and the Rhizosphere in the Degradation of Hydrocarbons

The degradation of oil hydrocarbons by microorganisms is widely used, given that it is an efficient and economical method for the detoxification of contaminants while respecting the natural environment. Plant roots are fundamental for stimulating the proliferation of degrading microorganisms within the dynamic region of their rhizosphere; therefore, they are of significant importance in phytoremediation (Radwan et al. 1995; Masakorala et al. 2013). Microorganisms such as bacteria, fungi and nematodes have the ability to consume hydrocarbons as sources of energy and carbon, thereby playing a very important role in the remediation of contaminated soils.

Bacteria are the most active degrading agents of oil hydrocarbons (Hassaine and Bordjiba 2015; Mayz and Manzi 2017). These bacterial groups use naphthalene and phenanthrene or other hydrocarbons catabolically as the only source of carbon and energy, while the compounds which are less soluble in water, such as anthracene, pyrene and fluoranthene are used as growth sources. These bacteria, capable of eliminating the hydrocarbons, are known as hydrocarbonoclasts (Table 3.1; Kube et al. 2013).

There are also native microorganisms of the Gammaproteobacteria class which can metabolize hydrocarbons at extremely low temperatures, for example, the genera which degrade the alkene hydrocarbons such as *Alcanivorax* spp. and *Cycloclasticus* spp.; also the *Pseudoalteromonas* spp., which can decompose the aromatic hydrocarbons (Pham and Anonye 2014).

Then, we have the *Bacillus* sp., *Rhodococcus* sp., *Mycobacterias* sp., *Pseudomonas* sp. and several yeasts such as *Micromycetes* sp. which use simple and complex organic compounds as a source of energy, since their metabolic versatility allows them to convert substrates which are generally nondegradable into easily absorbed metabolites or susceptible to enzyme catalysis (Mackey and Hodgkinson 1996; Rolling et al. 2003; Echeverri-Jaramillo et al. 2010). Besides inhabiting approximately 0.1% of the contaminated sites (Matsumiya et al. 2007), the *Pseudomonas* sp. can attain an efficiency of up to 92.46% in the degradation of 0.1% polycyclic aromatic hydrocarbons *in situ* in the laboratory, which would suggest that this bacteria and its lipopeptides have great potential in the remediation of contaminated soils (Xia et al. 2014). It is also capable of producing surfactant compounds which provide an efficient degradation of hydrocarbons such as phenanthrene (86.65%); this degradation is by the metabolic pathway of the protocatequito (Masakorala et al. 2013).

Table 3.1 Genus of hydrocarbonoclastic bacteria which eliminate hydrocarbons

Genus	Reference
Alcaligenes sp.	Kim et al. (2000)
Alkanibacter sp.	Zhao et al. (2008)
Altererythrobacter sp.	Kim et al. (2000)
Arthobacter sp.	Radwan et al. (1995), Rivera-Cruz (2011), Zhang et al. (2011)
Azospirillum sp.	Rivera-Cruz (2011), Masakorala et al. (2013)
Bacillus sp.	Radwan et al. (1995), Rolling et al. (2003)
Microcella sp.	Zhao et al. (2008), Philippot et al. (2013)
Mycobacterium sp.	Parés and Juárez (2002), Xia et al. (2014)
Nicardioides sp.	Iwabuchu et al. (1998), Ortega-Calvo et al. (2003)
Promicromonospora sp.	Wu et al. (2017)
Pseudomonas sp.	Parés and Juárez (2002), Philippot et al. (2013), Xia et al. (2014)
Rhodococcus sp.	Radwan et al. (1995)
Sphingomonas sp.	Wu et al. (2017)
Tistrella sp.	Xia et al. (2014)
Xanthomonas sp.	Iwabuchu et al. (1998), Xia et al. (2005)

Surfactin, fengycin and liquenisina are recognized as common metabolites produced by *Bacillus* sp. and these form the group of lipopeptides (Radwan et al. 1995; Das and Mukherjee 2007; Mayz and Manzi 2017). This group of bio-surfactants comprises a hydrophobic fatty acid and one molecule of hydrophilic peptide; it contains a low critical concentration of micelles, stable emulsion property, strong surface activity and an excellent foaming property, as well as the presentation of stable physico-chemical properties at different temperatures and pH levels (Das and Mukherjee 2007), which produce degradation of the hydrocarbons, due to the fact that the microorganisms use the *n*-alkanes and the polycyclic aromatic hydrocarbons, such as fluorine, naphthalene, phenanthrene and pyrene, as carbon sources (Van Beilen et al. 2001; Zhang et al. 2011; Xia et al. 2014).

Temperature and pH have an influence on the bio-stimulation of microorganisms which in turn is associated with the capacity of the bacteria for degradation of the polycyclic aromatic hydrocarbons (Masakorala et al. 2013). This involves a complex process of monooxygenase and dioxygenase; in other words, they transfer oxygen atoms to the contaminated substrate (Hayaishi 2005; Sligar et al. 2005; Waterman

2005), thereby achieving a degradation through the pathways of salicylate or protocatechuate decarboxylase; these compounds provoke the oxidative rupture of the aromatic ring by the lactonizing enzyme (Parés and Juárez 2002; Lalucat et al. 2006).

Degradation of the alkane and alkene hydrocarbons involves the assimilation of O_2 molecular alkanes. This assimilation is carried out by bacteria such as the *Pseudomonas* sp. and members of the coryneform group and actinomycetes, in particular those of the genera *Mycobacterium* sp. and *Nocardia* sp. (Parés and Juárez 2002). Rivera-Cruz (2011) reported low population densities of *Azospirillum* sp., *Azotobacter* sp., phosphate solubilizing bacteria and heterotrophic fungi in the rhizosphere of two soils contaminated with total oil hydrocarbons with concentrations of 25,000 $\pm$ 345 mg kg^{-1} (Eutric Fluvisol soil) and de 65,890 $\pm$ 156 mg kg^{-1} (Mollic Gleysol soil).

The ectomycorrhizal fungi act with the root system to improve the absorbent surface of the plants; they also participate in nutrient recycling and are often more resistant to abiotic stress such as contamination from oil spills (Thijs and Vangronsveld 2015). In addition, with the help of these arbuscular mycorrhizal fungi, billions of bacteria help to absorb minerals and to produce vitamins and plant hormones which are able to degrade organic compounds such as the hydrocarbons (Bonfante and Desirò 2015; Lugtenberg 2015; Thijs and Vangronsveld 2015).

The roots of the plants must be able to tolerate the contaminants and, in conjunction, to develop the architecture of their roots in order to produce a biochemical environment very different from that which can be expressed in uncontaminated soil. Moreover, the roots must have an interrelationship with the different physical, chemical and biological factors of the affected soil in order to generate the acclimatization, growth and development of the plant (Ferrera-Cerrato and Alarcón, 2013). Once the plant is acclimatized, the degradation process of the organic contaminants among the microorganisms and the rhizosphere begins; this is usually beneficial for plant growth because the hydrocarbons become less toxic or innocuous (Chan-Quijano 2015; Thijs and Vangronsveld 2015).

3.3 Degradation of Hydrocarbons Through the Combination of Tree Species and Organic Fertilizers

Research on the key factors and biogeochemical processes that form the microbiota in the rhizosphere is still scarce in tropical areas and even more so in the areas impacted by hydrocarbon contamination. The plant must resist hydric stress, chemical toxicity, mechanical impedance and nutrient deficiency, to mention just a few; evaluations of root development in plant species which must withstand oil hydrocarbons are also scarce, and the same can be said regarding the studies of plant physiology in contaminated environments.

According to Albrecht and Kandji (2003), Alberto-Pardos (2010) and Philippot et al. (2013), the development of the rhizosphere contributes to the conservation of soil and to the mitigation of the effects arising from global environmental change; this is due to the fact that the roots store a significant amount of carbon at a greater depth, making its release more difficult. Moreover, the application of organic fertilizers favors biostimulation of the microorganisms present in the soil, as well as an increment in their diversity; thus, they could represent an alternative in the degradation of hydrocarbons and, at the same time, capture CO_2 in the roots (Adekunle, 2011; Wang et al. 2011).

Velasco-Trejo and Volke-Sepúlveda (2003) mention that the use of organic fertilizers presents important perspectives in the resolution and remediation of soils contaminated with hydrocarbons. Chan-Quijano (2015) reports that, with the combination of organic fertilizer (sheep manure in a dosage of 3.85 g kg^{-1}) and *Tabebuia rosea* (Bertol.) DC. in a soil contaminated with 158,674 mg kg^{-1} of oil hydrocarbons, a degradation of 85% was achieved over a period of one year; in other words, 135,113 mg kg^{-1} of oil hydrocarbons was eliminated.

In this way, the use of fertilizers associated with plant species increases the α diversity, and the activities of the microorganisms in the contaminated soil increase the degradation of oil hydrocarbons (Chan-Quijano 2015; Wu et al. 2017). Moreover, with the addition of nutrients to the soil through organic fertilizers, there is a corresponding increase in the number of microorganisms which degrade oil hydrocarbons, and thus, the rate of contaminant elimination increases (Litchfield 2005). For this reason, biodegradation by bacteria has been taken into consideration as a potentially useful tool in the remediation of soils contaminated by oil hydrocarbons (Yuste et al. 2000).

When the organic fertilizers and the plants are combined (with the aid of the roots), these two elements, in conjunction, can participate significantly in the degradation of contaminants or in the active absorption, in the case of heavy metals. These biotechnologies are less expensive and more environmentally friendly and are also more efficient in the cleansing of contaminated sites (Litchfield 2005; Rivera-Cruz 2011; Ferrera-Cerrato and Alarcón 2013; Chan-Quijano 2015). However, the plant roots occasionally suffer from a negative geotropism; that is to say, a knot is formed due to the concentration of hydrocarbons found in the contaminated soil as a result of a deficiency in oxygen, nutrients and water in the soil; moreover, when knot formation does not occur, development of the root occasionally presents shorter lengths in comparison with plants growing in non-contaminated soil. The formation of a greater number of secondary roots has also been observed in the species growing in contaminated soils (Fig. 3.1).

3.4 Perspectives and Necessary Research

According to Thijs and Vangronsveld (2015), the rhizosphere is a specific subset with the soil and the microorganisms; these organisms are involved in the biodegradation

Fig. 3.1 Negative geotropism (knot formation) in the main root of two tree species **a** *Swietenia macrophylla* and **b** *Tabebuia rosea* developed in soil contaminated with hydrocarbons, **c** and **d** are the same species but growing in uncontaminated soils

processes of the organic contaminants. It is important, therefore, to carry out studies on the rhizosphere in tropical areas and on native species, given the lack of sufficient information. It is also necessary to evaluate the behavior of the physico-chemical parameters and the biogeochemical characteristics between the contaminated soil and the rhizosphere of the plants at different depths, since the electric properties of the contaminated area change with time (Luo et al. 2016).

The use of native tree species in association with their rhizosphere helps the areas affected by oil hydrocarbons and, at the same time, provides certain benefits to the local inhabitants, for example, as timber species, living fences, raw material for craft trades, firewood, among others. At the same time, the people living in the area can foment a biologically based economy for the sustainable development of the impacted areas while also providing bioproducts such as biofuels, biopaints, biolubricants, among others, and also ecosystem services (Ceccon and Miranda 2012; Hu et al. 2012; Ceccon et al. 2015; Prasad 2016; Tripathi et al. 2016; Wagner et al. 2016).

However, in order to work with the rhizosphere in the evaluation, behavior and response of the plant species to be used in the remediation of soils contaminated with hydrocarbons or other contaminants, it is necessary to elaborate a profile of the contaminated soil to determine (1) the current ecological state and the degree of contamination, (2) the level and type of contaminants and (3) the toxicity of the contaminants. In addition, with the support of laboratory work and specialized equipment, we can determine (1) the morphology and physiology of the plants in order to understand the level of stress inflicted by the contaminant (tolerance and resistance to the contamination) and (2) the level of accumulation/acclimatization/adaptation of the plants (Tripathi et al. 2015, 2016).

The procedure described above can provide support in the ecological restoration and remediation of the affected areas through frameworks of ecological and sociocultural value, as well as economic aspects for a sustainable remediation (Fig. 3.2).

In addition, certain guidelines must be established for the remediation of soils contaminated by hydrocarbons (IMP 2010; Chan-Quijano et al. 2015), in order to put into effect strategies of remediation and restoration in the areas contaminated by oil spills with the aid of the rhizosphere provided by certain plant species (Ochoa-Gaona et al. 2011; Qixing et al. 2011) and to implement rehabilitation processes (the oil tends to concentrate in only one part of the altered habitat), the recovery

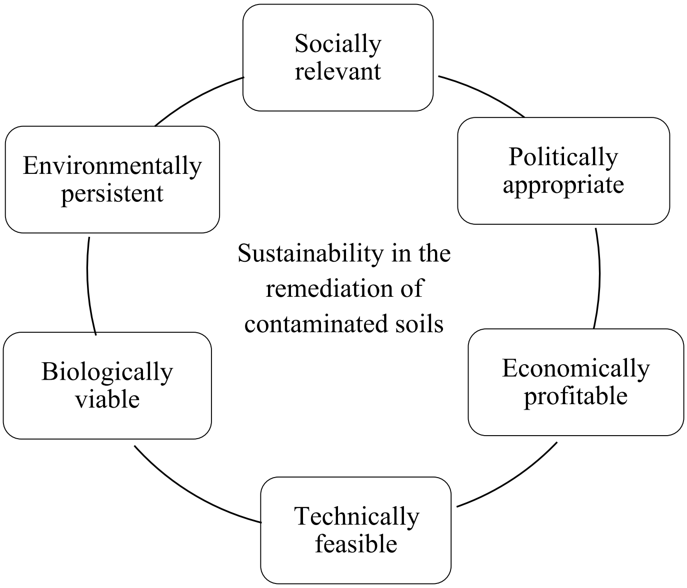

Fig. 3.2 Frameworks of ecological, sociocultural and economic values for a sustainable remediation

(rehabilitation of the gravely perturbed habitat), the recreation (construction) of an alternative, but desirable state in a gravely perturbed site where very little remained to be restored, improvement (ecological improvements) and mitigation or compensation (very often focused on a different system) in order to restore the structure and function of the contaminated ecosystems (Bradshaw 1987; SER 2004; Cooke and Suski 2008; Qixing et al. 2011).

The degradation of oil hydrocarbons requires a metabolic activation exercised by biological activities including mutagenicity or carcinogenicity, mediated through the formation of metabolites such as flavanone, flavone, iso-flavanone, 7-hydroxyflavone and 6-hydroxyflavone, to mention a few (White and Burken 1998; Yan et al 2004; Thijs et al. 2017).

When studying the rhizosphere of plants for the remediation, it is necessary to implement plant physiology as part of the conservation and management of populations and ecosystems. Physiology has been used very little in the field of restoration ecology. It is possible to use physiological metrics, such as gas exchange, transfer of energy, changes in metabolism, stress response, nutritional state and gene expression, among others, in order to understand the biogeochemical, metabolic and enzymatic processes of root function and of the plants in general, growing in contaminated soils, as well as to have a better understanding of the factors influencing their structure (Cooke and Suski 2008).

In relation to the application of genomic tools, including genomic sequencing, expressed sequence tags, transcription profiles and molecular markers, this would be very useful in monitoring activity to determine if the hydrocarbons penetrate the plant and with this information to evaluate the quality of the wood from tree species which are used in the remediation of soils contaminated with oil hydrocarbons; metaproteomics can also be used to evaluate the functional and phylogenetic relationships of the microorganisms in the degradation of oil hydrocarbons in contaminated soils (Merkle and Nairn 2005; Batista et al. 2016).

Plants are autotrophic organisms which are capable of using sunlight and carbon dioxide as sources of energy and carbon. The roots of the plants absorb a wide range of natural and anthropogenic, toxic compounds for which they have developed a number of extraordinary mechanisms of detoxification. Further basic and applied research is required in order to generate sufficient knowledge of the natural mechanisms of detoxification of many contaminants, deriving from the hydrocarbons (Alagic et al. 2015). It is important to mention that each hydrocarbon differs in its chemical composition, and for this reason, the Environmental Protection Agency (EPA) of the USA published a list of 126 priority contaminants which cause the most damage to ecosystems and human health (Yan et al. 2004; EPA 2014). Thus, further studies must be carried out on cytotoxicity in the microorganisms and phytotoxicity in the plant species and the rhizosphere which will be used in the remediation of soils contaminated by hydrocarbons in tropical areas.

3.5 Conclusions

The study of the remediation of areas contaminated with oil hydrocarbons is faced with a challenge to develop innovative and cost-effective solutions for the decontamination of contaminated environments. To achieve this, it is necessary to conduct studies on each contaminant regarding the damages and/or benefits they may be causing in the rhizosphere and in plant physiology.

The public in general should be encouraged to participate in the recovery of contaminated areas with the use of native plant species which provide more viable benefits for the sustainability of the ecosystem and for society. Studies on the rhizosphere must be integral, with the evaluation of soil quality, during and after the site remediation process.

Phylogenetic and physiological responses of the microbial community in the contaminated soils and their relationship with the rhizosphere must be evaluated in order to understand all the possible processes in the behavior of oil hydrocarbons in the soil resource.

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Chapter 4
In Situ Phytoremediation of Metals

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Abstract Metals are ubiquitous for life sustenance on earth, but their tremendous accumulation in ecosystems has caused contamination of soil and water resources. "Ex situ" and "in situ" are two possible remediating options. Ex situ remediation involves excavation of polluted soil followed by treatment, rendering it an expensive cleanup method. In situ phytoremediation is the onsite contaminant removal through plant uptake in a cost-effective and eco-friendly way. Phytoextraction and phytostabilization are two commonly practiced in situ phytoremediation strategies.

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This chapter focuses on basic concepts of in situ phytoremediation and removal of toxic heavy metals from soil–water environment.

Keywords Asteraceae · Brassicaceae · Crassulaceae · Heavy metals · Hyperaccumulation · Lamiaceae phytoremediation · Phytostabilization · Phytoextraction · Soil–water environment

4.1 Introduction

Metals are vital for the sustenance of all life forms on this planet. Plants, animals, microbes and humans all require balanced amount of metals for their metabolic activities and various physiological functions. These are required in very trace amounts, but some metals such as lead (Pb), cadmium (Cd), chromium (Cr) and mercury (Hg) have no known biological function. By definition, metals are the elements that have the ability to form positive ions (cations) and metallic bonds. These are solids at room temperature (except mercury), malleable, shiny and have high molecular weights. Based on their intrinsic properties, metals are grouped into alkali metals such as lithium (Li), sodium (Na) and cesium (Cs), alkaline earth metals such as beryllium (Be), magnesium (Mg) and strontium (Sr), transition metals such as iron (Fe), nickel (Ni) and zinc (Zn) and metalloids such as boron (B), arsenic (As) and tellurium (Te). Some metals have atomic mass >20 and specific gravity >5 and are referred to as heavy metals (HMs), for example Cd, Pb and Cr. Metals are found naturally as they were integrated into earth crust during earth formation and by asteroid bombardment some billion years ago. However, recently some synthetic metallic polymers and organic metals, used in some sophisticated devices, have been developed artificially (MacDiarmid 2001; Rasmussen 2016).

Metals are widely used by human beings for industrial, construction, manufacturing, packaging and other commercial purposes. Due to their high demand, metal mining and environmental accumulation is on rise worldwide. Especially, the industrial revolution has caused 1000-fold increase in the heavy metals concentration of the environment over the past three centuries. Several factors contribute to metal pollution such as mining, industrial activities, improper disposal of wastes, inefficient reclamation activities, less public awareness and lack of proper policies. Resultantly, terrestrial and aquatic environments have been contaminated, posing threat to humans, plants, terrestrial animals and aquatic life. Especially, the situation is more alarming in developing countries where the accumulation of metals has climbed to non-acceptable limits, and the inhabitants have limited resources to remove the contaminants from the environment.

Remediation of metal-contaminated sites is a challenging work, especially those affected by heavy metals, as they are toxic and non-degradable. To extract and get rid of heavy metals in a safe way, an appropriate remediation technology has to be adopted. Several remediation technologies have been developed to decontaminate affected sites and to restore terrestrial and aquatic environments in their natural state. In general, these can be grouped into (1) physical, (2) chemical and (3) biological remediation techniques. Physical procedures may involve soil washing, soil flushing, incineration, excavation, landfilling, etc., while chemical processes may include filtration, flocculation, reverse osmosis, vitrification, precipitation, etc. Biological remediation technique deals with specialized plants and microbes that have the ability to accumulate and degrade contaminants. The adoptability of any remediation procedure may depend on several factors such as contaminant type and its extent, environmental conditions at the site, remediating time, cost of remediation, etc. Moreover, each remediation technique has its own merits and demerits. For example, excavation of a contaminated soil and its off-site disposal is a rapid way to get rid of pollutants; however, it is mere translocation of pollutants from one place to another and not a permanent solution. Similarly, high costs and spreading of pollutant are some other issues associated with it.

To describe each metal or metalloid in great detail here will be out of the scope of this chapter, therefore metals or metalloids, only of environmental significance, are discussed in phytoremediation perspective. The main focus of this chapter is to discuss in situ phytoremediation technologies aimed at soils and water.

4.2 What is In Situ Phytoremediation?

Phytoremediation is a cost-effective remediation technology which implies plants to remediate contaminated environments including soils, water and atmosphere. It is an alternative to conventional remediating techniques. The word "phytoremediation" is a combination of two Greek words; "phyto" meaning plant, and "remedium" meaning to restore or clean. Generally, the task of phytoremediation is accomplished by an already known plant species which has the ability to accumulate significant amounts of contaminant in its harvestable biomass without suffering from toxic effects of the contaminants. Use of native plants for phytoremediation is highly desirable as they have maximum adoptability to the local environmental conditions and have good growth and more survival chances (Chandra and Kumar 2017). In recent years, several new plant species with high metal accumulating capabilities have been identified or developed through genetic engineering techniques (Rascio and Navari-Izzo 2011).

Phytoremediation technologies can be broadly categorized into "in situ" and "ex situ" based on the location where the technology is being employed. "In situ" is basically a Latin word, meaning "in the original place or in the appropriate position". This phytoremediation technology involves the removal of contaminants from the affected site using specialized plants. In simple words, in situ is the onsite remediation technology while ex situ is the dislocation of the contaminated soil followed by remediation procedure. It can also be called as an off-site remediation technology.

Role of soil microbes like rhizosphere bacteria and mycorrhizal fungi is very promising in phytoremediation (Rajkumar et al. 2012). The primary objective of using soil microbes is to mobilize metals for plant uptake or immobilize metals in the rhizosphere to restrict downward leaching. Plant-associated microbes help in phytoremediation through acidification, chelation and reduction of metals in the soil. Besides this, soil microbes, by releasing 1-aminocyclopropane-1-carboxylic acid (CCA) deaminase, may help plants withstand against heavy metal stress in soils (Dimkpa et al. 2009).

As phytoremediation can be applied both in situ and in ex situ conditions, it has attracted the attention of landowners, industrialists, environmental conservationist and legislators in recent years. Besides environment cleanup, phytoremediation has now become a profitable business in many countries and many commercial phytoremediation companies are now working in various parts of the world.

4.3 Mechanisms of In Situ Phytoremediation

Phytoremediation consists of several remediation technologies like phytoextraction, phytostabilization, phytovolatilization and phytodegradation, each having its own characteristics and applications. At the moment, phytoextraction and phytostabilization are more practiced in situ phytoremediation techniques.

4.3.1 Phytoextraction

Extraction of metals from contaminated soil by hyperaccumulating plants is called phytoextraction. The process involves metal uptake by plants and its translocation from roots to above ground tissues followed by repeated biomass harvesting. Several plant species have the ability to store significant amounts of metals in their harvestable biomass such as Indian mustard, poplar tree, alfalfa, cabbage, sunflower, fern (Alkorta et al. 2004; Rascio and Navari-Izzo 2011; Krämer 2010). Phytoextraction is accomplished by either continuous accumulation of metals in the plant tissues by natural process or by stimulating the availability of metals in the soil by some stimulants, thereby increasing metal plant uptake, as natural phytoextraction is a slow process. Hyperaccumulating plants usually accumulate more than 1% of metals in their above ground harvestable biomass. Till to date, more than 400 plant species have been identified with the ability to accumulate several times greater metal concentrations in their tissues without showing visible signs of toxicity. While some hyperaccumulating plants can uptake more than one metal, mostly they are metal-specific. Phytoextraction is also used nowadays to extract valuable metals from the metal-loaded soils, a process called phytomining (Sheoran et al. 2013, 2009).

Several environmental factors may affect metal uptake in plants such as initial concentration of metals in the soil, soil pH, soil texture, temperature, soil microbial community and chemical nature of the co-pollutants (Magdziak et al. 2015). As phytoextraction is a slow process, the mobility of heavy metals in the soil environment needs to be accelerated using chemical agents such as ethylenediamine tetraacetic acid

(EDTA), *N*-(2-hydroxyethyl)-ethylenediaminetetraacetic acid (HEDTA), diethylenetriamine pentaacetic (acid DTPA) (Chen and Cutright 2001) or some other synthetic agents which have acidic properties like ammonium sulfate (NH_4SO_4) or ammonium nitrate (NH_4NO_3) (Nehnevajova et al. 2005), which promote metal attachment to the plant roots and their onward translocation to aerial parts. Although these chemicals increase the bioavailability of metals in the soil for plant uptake, yet they may create some added problems like spreading of metals to the uncontaminated soils or downward leaching to the groundwater. These hazards can be eliminated by ex situ phytoextraction approach and via periodic application of these chemical agents.

4.3.2 Phytostabilization

Phytostabilization involves retaining HMs in the soils at non- or less-toxic forms to prevent further spread and exposure. This is an integrated approach achieved by controlling soil erosion through appropriate plant cover, applying organic amendments to reduce metal solubility and by immobilizing metals in the root zone to reduce plant uptake and leaching. Root exudates contain organic acids, siderophores and phenols that play important roles in complexion of metals and converting it into less soluble forms such as metal sulfide and metal carbonate. Moreover, metals get attached to the root surface and accumulated in the root. Rhizosphere microbes and their secretions also play significant roles in phytostabilization. Arbuscular mycorrhizal fungi (AMF) are colonized in some plant roots and sequester HMs in their hyphae (Miransari 2011). Moreover, AMF secrete a glycoprotein called glumulin which makes complexes with metals in the soil environment (Javaid 2011).

Phytostabilization is a more feasible technology for remediating large areas affected by metal pollution where engineering procedures are not cost-effective. However, it is applied to the soils contaminated by low metal levels at shallow depths. Moreover, it is less effective if the targeted metal is too toxic for plant or highly mobile in the soil. It is very important that plants used in phytostabilization should be drought and salt resistant, in addition to having metal resistance, as areas to be remediated posses adverse environmental conditions. Phytostabilization is a favorable remediation technology for mine tailings as the area for remediation is diverse and uneconomical by engineering procedures (Mendez and Maier 2008b; Santibáñez et al. 2008). Major tailing sites are found in the USA, South Africa, Mexico, Chile, India and Spain. Generally, the environmental conditions in the mine areas remain very harsh and unfavorable for plant growth due to less microbial dwelling, low soil organic matter content, less soil moisture and low nutrient availability, so it is very important that plants used for phytostabilization should be native and environmentally compatible. Several plant species including *Atriplex* spp., *Larrea tridentate*, *Baccharis sarothroides*, *Acacia* spp., *Prosopis* spp., *Eucalyptus* spp. have shown promising results for stabilizing Cu, As, Fe, Pb and Zn in mine tailings (Santibáñez et al. 2008; Li et al. 2015).

4.3.3 Phytovolatilization

Phytovolatilization is another promising phytoremediation technology which involves uptake of metals or contaminant by plant roots and their translocation into atmosphere in a gaseous state via evapotranspiration process. Plants with high transpiration rates are more suitable for phytovolatilization. This technology is more promising in volatilizing volatile organic compounds (VOCs) such as trichloroethylene (TCE). However, some metals can also be volatilized by this process. For instance, selenium (Se) is converted by dimethylselenide [$Se(CH_3)_2$] and transferred to the atmosphere (Wu et al. 2015). Similarly, methyl Hg from soil is transpired as Hg^0 (Heaton et al. 1998).

4.3.4 Phytodegradation

Phytodegradation is the detoxification of contaminants through plants. This technology is more promising to degrading organic xenobiotics such as chlorinated hydrocarbons and herbicides which affect shallow groundwaters, soils and sediments. The process involves contaminant uptake by plant and then conversion into less-toxic metabolites. For example, trichloroethylene, a chlorinated hydrocarbon, was converted by poplar trees into trichloroethanol, trichloroacetic acid and dichloroacetic acid (Kassel et al. 2002). Similarly, atrazine, a popular herbicide, was dealkylated by hybrid poplar tree (Burken and Schnoor 1997). Moreover, organophosphorus pesticides like malathion and crufomate were phytotransformed by aquatic plants like parrot feather, duckweed, elodea (Gao et al. 2000). This technology has potential applications in areas like landfills, petrochemical sites, fuel storage sites and areas affected by agrochemicals. However, the levels of contaminant should be less toxic for plant and be accessible to plant roots.

4.4 Advantages of In Situ Phytoremediation

In situ phytoremediation has several advantages over conventional methods of remediation. Some major benefits are discussed here for general reader interest:

- In situ phytoremediation is a cost-effective remediation technology as it is solar-driven. It is an alternative to engineering operations which have high energy costs. Generally, the cost of in situ phytoremediation is far less than engineering solutions or chemical treatments such as "digging and pumping," soil washing, heat treatment of soil. The engineering solutions have high actual costs due to several overheads in addition to "paid" amount for remediating a contaminated site (Linacre et al. 2005). According to earlier estimates, 300 billion $ would be required to clean contaminated sites in the USA (Raskin et al. 1997). Cost of phytoremediation can be best judged by a recent study which demonstrated that cost of in situ phytoremediation was 122 € per m^3, while for off-site landfilling, it was 231 € per m^3. In situ phytoremediation is more promising in resource-poor developing countries where the area to be remediated is large, and the availability of proper funding for cleanup technologies is either insufficient or scarce.

- In situ phytoremediation is an "easy to apply" technology which can be used for soils affected by variety of organic or inorganic contaminants. Hyperaccumulating plants can accumulate single contaminant or multiple contaminants in the harvestable parts without showing toxicity symptoms.
- In situ phytoremediation is effective in broad climatic conditions. It has been tested in both temperate and arid environments for the remediation of mine tailings where soils are less weathered with low water holding capacity and unfavorable pH and have less or no organic matter and plant nutrients (Mendez and Maier 2008a). Plants used in phytoremediation withstand such unfavorable environmental conditions, as they are either native to the environment or genetically engineered to grow in such harsh conditions.
- Ex situ remediation involves heavy machinery use for excavation, distant translocation, and use of reactants like hydrogen peroxide (H_2O_2), which make it an unpleasant technology. In situ phytoremediation is an eco-friendly and aesthetically pleasing remediating technology that ensures sustainability of valuable resources by least affecting topsoil and ecosystem.
- In situ phytoremediation promotes microbial growth and biological activities in the root zone making grounds for natural degradation of xenobiotics. It also helps to scavenge greenhouse gases and promotes carbon sequestration.
- Plant canopy, developed for in situ phytoremediation, provides sanctuary to many birds and other small beneficial animals, making it aesthetically pleasing.
- The environmental waste produced as a result of in situ phytoremediation is far less than engineering cleanup solutions. It is estimated that an area of 2 acre, when excavated up to 1.6 ft, can produce 5000 tons of disposable waste. But in case of phytoremediation, only 25–30 tons of waste generation is expected. Moreover, chances of contaminant further spread are reduced due to plant cover which reduces soil erosion and pollutants suspended in the air.
- In situ phytoremediation can also be used to extract valuable metals such as gold, zinc, copper, nickel and iron from soils and sediments.

4.5 Limitations of In Situ Phytoremediation

Despite several advantages, in situ phytoremediation has some limitations also.

- A major limitation of in situ phytoremediation is the growing of candidate plants on hyper-polluted sites which are phytotoxic. Toxicants beyond plant's threshold level affect normal growth of the plants as they lack enzymes that catabolize contaminants as soil microbes do.

- Although faster than natural attenuation, unassisted contaminant removal through in situ phytoremediation is a slow process, and also seasonal in case field crops are grown. Cleanup process may require repeated cultivation of plants, which is a time-consuming process.
- In situ phytoremediation is depth-limited. Contaminants found below root zone cannot be pulled out by plants roots. Similarly, contaminants strongly adsorbed to soil particles may be difficult for plant roots to extract.
- As fertilization and irrigation are required for vegetation growth, chances are there for groundwater pollution due to contaminant leaching and biomagnification.

4.6 In Situ Phytoremediation of Some Important Metals

Plants, used in phytoremediation, should be hyperaccumulating, metal-tolerant, environmentally compatible, fast-growing, able to produce high biomass, with large root system, and unable to transfer genes horizontally. Generally, plants that accumulate >10,000 $\mu g\ g^{-1}$ Zn and Mn, >1000 $\mu g\ g^{-1}$ As, Cu, Co, Ni, Se and Pb, and >100 $\mu g\ g^{-1}$ Cd are considered hyperaccumulators. Moreover, they have bioconcentration factor (BCF) and translocation factor (TF) greater than 1. BCF and TF are determined by the following formulae:

$$\mathrm{BCF} = \text{Metal concentration in plant roots} \div \text{Metal concentration at site}$$

$$\mathrm{TF} = \text{Metal concentration in roots}/\text{Metal concentration in shoots}$$

In situ phytoremediation of some important metals is discussed below:

4.6.1 Nickel (Ni)

Nickel is a silvery-white hard, ductile transition metal found as Fe–Ni ore naturally. It is resistant to corrosion (oxidation) and is used for plating of iron and other metals. Nickel is essential for microorganisms and plants as it is the functional moiety of some important enzymes. Earlier reports suggest that Ni, in Ni-hyperaccumulating plants, provides protection against pathogen attack (Boyd et al. 1994; Davis and Boyd 2000). It tends to accumulate in leaves, stems and roots, but its concentration remains higher in the leaf epidermal vacuoles, mesophyll and vascular bundles (Mesjasz-Przybylowicz et al. 2016). Key mechanism of Ni hyperaccumulation in plants is coordinated by carboxylic acids such as citrate and malate. However, the translocation within plants is mediated by histidine (Kozhevnikova et al. 2014). Till to date, approximately 450 Ni-hyperaccumulating plants have been identified that mainly belong to Asteraceae and Brassicaceae families, largely consisting of small shrubs such as *Alyssum murale*, *Alyssum corsicum* and woody trees such as *Phyllanthus balgooyi*, *Phyllanthus securinegioides* and *Rinorea bengalensis* (Mesjasz-Przybylowicz et al. 2016; van der Ent et al. 2017). *Streptanthus polygaloides* is one of the highest Ni-hyperaccumulators which can accumulate up to 16,400 μg g^{-1} Ni on dry weight basis (Boyd et al. 1994). Similarly, *Alyssum bertolonii* demonstrated an extraordinary ability to accumulate Ni (10,000 μg g^{-1} on dry weight basis) (Robinson et al. 1997). Previously, *Alyssoides utriculata* Medik, a Mediterranean evergreen shrub, demonstrated BF and TF higher than 1 on serpentine soils with an average accumulation of Ni higher than 1000 μg g^{-1} in leaves (Roccotiello et al. 2015). Use of rhizobacteria has been reported in *Alyssum murale* to enhance Ni hyperaccumulation (Abou-Shanab et al. 2003). In another study, the same plant, grown on an ultramafic area in Albania, extracted 25 kg Ni ha^{-1} in plant biomass under fertilized conditions (Bani et al. 2007). Although grasses have low Ni phytoextraction ability than aforementioned plant species, their use as in situ Ni-extractants is promising due to rapid and easy growth, and low cost. Previously, mixture of three grasses triggered 49% decline in Ni contents of an industrially multi-metal-polluted soil (Salinas et al. 2012).

4.6.2 Arsenic (As)

Arsenic is a common metalloid used in batteries, ammunitions, pesticides and insecticides. It plays roles in normal body functions; however, increased As concentration may impact human health. Arsenic pollution is widespread due to use of As-laden agrochemicals and As-contaminated groundwaters for irrigation (King et al. 2008). Several As hyperaccumulating plants have been identified till to date. Chinese brake fern, *Pteris vittata*, is a well-known As-hyperaccumulator perennial plant, which can accumulate up to 2.3% As in its plant biomass on dry weight basis. Previously, *Pteris vittata* extracted 3.5–11.4% As (of total As in paddy soils) and significantly reduced As uptake in the rice grain (Ye et al. 2011). Similarly, *Pteris vittata* effectively remediated groundwaters polluted with As (Natarajan et al. 2011). Some other aquatic plant species such as *Eichhornia crassipes*, *Lemna minor*, *Ipomoea aquatica* have also shown potential to clean up As-contaminated water (Alvarado et al. 2008; Rahman and Hasegawa 2011). Hyperaccumulation of As has been reported in several mushroom species also (Vetter 2004). In a very recent study, an edible mushroom, *Cyanoboletus pulverulentus*, has been reported to have As accumulation of 1300 mg kg^{-1}, questioning its suitability as food, and suitability as a potential As phytoremediation plant (Braeuer et al. 2018). *Melastoma malabathricum*, a flowering weed with medicinal properties, has also shown translocation factor greater than 2 for As accumulation in stems and leaves (Selamat et al. 2014). However, in situ phytoremediation of As was not that much successful with field crops, especially under multi-metal soil-contaminated conditions (Vamerali et al. 2011).

4.6.3 Iron (Fe)

Iron is the fourth most abundant element in the earth crust found in different oxidation states, mostly as Fe^{+2} and Fe^{+3} oxides. It is the main oxygen-carrying molecule in the human body and a part of functional groups of various enzymes. Due to its large industrial usages, the widespread Fe pollution is common in urban areas, affecting drinking water quality. Especially, under acidic conditions like sulpfide deposits, it becomes an environmental risk because of its conversion from Fe^{+3} to Fe^{+2}, which is a more soluble form of iron under anaerobic conditions. Some naturally grown grass species such as *Setaria parviflora* and *Paspalum urvillei* have been assessed to phytoremediate iron from soil (Santana et al. 2014). Similarly, *Centaurea iberica* and *Carthamus oxyacantha*, grown in mining areas of Iran, demonstrated extraordinary ability to accumulate 35,722.80 mg kg^{-1} Fe in their harvestable parts (Nematian and Kazemeini 2013). Another grass species, *Setaria sphacelata*, also has the ability to accumulate high amounts of iron (Itanna and Coulman 2003). Similarly, *Centella asiatica*, an aquatic plant, phytoremediated Fe from a red soil of tropical area (Irshad et al. 2016).

4.6.4 Cobalt (Co)

Cobalt is generally considered a non-essential element for plants growth; however, it is beneficial. It is added to the environment mainly through industrial wastes and agriculture fertilizers. Normal plant concentrations of Co are found in the trace amounts. Plants that can accumulate 300 $\mu g\ g^{-1}$ are considered suitable for in situ phytoremediation (van der Ent et al. 2013). Plants such as *Crotalaria cobalticola*, *Haumaniastrum robertii*, *Crassula vaginata* and *Alyssum bracteatum* can accumulate 100 times more Co than non-accumulating plants. Alyssum species have accumulated more than 1000 $\mu g\ g^{-1}$ of Co (Malik et al. 2000) while *Berkheya coddii* up to 5000 $\mu g\ g^{-1}$ (Lange et al. 2017). However, these plants have some shortfalls such as less biomass producer, slow growth and difficult cultivation. Many Co-accumulating plant species including *Lamiaceae*, *Asteraceae*, *Crassulaceae* from D. R. Congo and other countries have been reported (Lange et al. 2017). Among several plant species tested, *Gossypium hirsutum* and *Pennisetum purpureum* removed Co at the rate of 38.9% and 33.4%, respectively, from soils subjected to sewage irrigation waters for more than half a decade (Lotfy and Mostafa 2014).

4.6.5 Copper (Cu)

Copper is an essential plant nutrient which naturally exists as copper oxide and copper sulfide. In plants, it is mainly regulated internally; however, higher external concentrations may cause disturbance in Cu homeostasis and may affect plant physiological functions. Both industrial and agricultural activities have contributions to elevated Cu levels in the environment in addition to natural processes like mineralization and weathering of Cu rocks. Besides, environmental degradation, Cu-rich ores are becoming short with the passage of time. Bioleaching and phytoextraction are two possible solutions to get this valuable metal back. In bioleaching, specific bacteria breaks bond between sulfur and copper, enabling later separation from the ore while phytoextraction involves use of Cu-hyperaccumulating plants. Several plants from different taxa including *Asteraceae*, *Leguminosae*, *Labiaceae*, *Brassicaceae* have been reported to extract Cu from contaminated environments. Among different *Brassicaceae* spp., *Brassica juncea* accumulated highest amount of Cu in a soil irrigated with sewage effluents (Purakayastha et al. 2008). In another experiment, *Helianthus annuus*, *Amaranthus paniculatus* and *Brassica juncea* removed 34–38.3%, 28.6–30.6%, 27.9–32.2% Cu, respectively, from industrial soil under nitrogen-fertilized conditions (Rahman et al. 2013). However, Cu-removal efficiency of *Brassica juncea* and *Brassica napus* was declined when Cu contamination was coupled with Zn (Ebbs and Kochian 1997). Attempts have also been made to remediate Cu-contaminated soils with vegetables, for example *Cicer arietinum* (Kambhampati and Vu 2013).

4.6.6 Selenium (Se)

Selenium is an essential element for biota but required in trace amounts. The difference between essentiality and toxicity of Se is very minute. Marine and terrestrial systems are major sources of Se while anthropogenic activities are the main causes of Se contamination. It is very mobile in both selenate and selenite forms. Selenosis, a diseased condition caused by excessive biological load of Se, may affect fish, waterfowl and mice. Seleniferous soils contain high load of selenium. Brassicaceae family of plants has shown promising results in de-selenation of Se-laden soils, especially *Brassica napus* and *Brassica juncea*. To remediate Se in Kesterson Reservoir in USA, *Brassica napus* was employed which removed 24% of the total Se from the affected site (Bañuelos et al. 1998). In another study, *Brassica juncea* removed 40% of the total Se, provided in effluents, in comparison with *Hordeum vulgare* which removed only 12% of Se under same conditions (Bañuelos et al. 2000). In a multi-cropping system-based comparison, *Brassica napus*-based cropping system removed 716–1374 g ha^{-1} y^{-1} and 736–949 g ha^{-1} y^{-1} Se at flowering and maturity stages, respectively, from a seleniferous soil in a long-term experiment (Dhillon and Dhillon 2009). The Se-phytoextractability of *Brassica juncea* has been further improved by overexpressing genes involved in glutathione synthesis and reduction of selenate in plants (Bañuelos et al. 2005).

4.6.7 Lead (Pb)

Lead, a ubiquitous environmental toxicant, is a soft, malleable metal found in ionic, oxide and hydroxide and some other forms. However, only exchangeable and water-soluble Pb is bioavailable. It causes toxicity in plants and builds up in humans causing severe medical complications. Especially, children are at high risk of contamination, for which no levels of Pb are safe. It is mainly derived by Pb mining and is extensively used in various industrial products. In recent years, Pb has build up exponentially in the terrestrial and aquatic environments. Very high levels of Pb have been observed in cultivated and uncultivated lands, posing serious environmental threats. In situ phytoremediation of Pb is possible using Pb-hyperaccumulating plants such as *Brassica juncea*, *Thlaspi rotundifolium* and some fodder crops. Initial studies for Pb phytoextraction were done on sunflower. Use of chelating agents has increased Pb solubility in soil solution and phytoextractability of *Zea mays* and *Pisum sativum* was increased 120-fold in terms of Pb translocation from root to shoots and build up to 10,000 mg kg^{-1} (Huang et al. 1997). In a similar study, *Bidens maximowicziana*, a Pb-hyperaccumulating plant, triggered Pb accumulation up to 1905.57 mg kg^{-1} in the above ground parts (Wang et al. 2007). *Viola principis* is a multi-metal accumulating plant. It *accumulated* 2350 mg kg^{-1}, 1032 mg kg^{-1} and 1201 mg kg^{-1} of Pb, As and Cd, respectively, on dry weight basis, and both BCF and TF were greater than 1 (Wan et al. 2017). In a Thailand Pb mine area, 12 native species of plants were investigated for phytoextraction of Pb, in which *Bidens pilosa* demonstrated highest Pb phytoextraction ability [1000 mg kg^{-1} with a TF greater than 1 (Yongpisanphop et al. 2017)]. However, a very recent article by Richard Blaustein suggests that phytostabilization, coupled with compost, may be a best future strategy to get rid of Pb (Blaustein 2017).

4.6.8 Cadmium (Cd)

Cadmium is one of the most toxic trace metals in the environment having no known physiological role in plants. It adds to environment through mining, industrial wastes and using phosphatic fertilizers. Due to highly bioavailability and readily uptake by plants, a mounting concern prevails about its entry into the food chain and serious effects on human health. Plants that can accumulate up to 0.01% of Cd on dry shoot basis are considered Cd-hyperaccumulators. In situ phytoremediation of Cd has been tested in many herbaceous plants. Till to date, maximum Cd removal has been achieved with *Thlaspi caerulescens* (Koopmans et al. 2008). Chelating agents such as citric acid have markedly increased the hyperaccumulation ability of plants, for example *Sedum alfredii* (Sun et al. 2009). *Thlaspi praecox* phytoremediated Cd-laden soils by accumulating 7428 mg kg^{-1} Cd in shoots (Vogel-Mikuš et al. 2006). Brassicaceae family has several plant species which can phytoremediate Cd. Eighteen landraces of *Brassica rapa* were tested for phytoremediating Cd, and three were found suitable on the basis of Cd removal efficiency (Li et al. 2016). *Arabidopsis halleri*, basically a Zn hyperaccumulator, has the ability to store 1000 mg kg^{-1} in shoots on dry weight basis, although the plant was less tolerant to Cd as compared to Zn (Zhao et al. 2006). In another experiment, *Arabidopsis halleri*, when cultivated five times on a Cd-contaminated soil, removed 60–80% of soil Cd (Kubota et al. 2010).

4.6.9 Chromium (Cr)

Chromium, in trace amounts, is a part of biomolecules and has some roles in human metabolism. Its use in stainless steel formation was a major breakthrough which led to its widespread use. The major contribution of Cr in the environment occurs due to metallurgical, petrochemical and agricultural applications. As a result, industrial wastes contaminated with Cr, has polluted water and soil resources, threatening human health. Chromium, in its hexavalent form (Cr^6), is highly toxic for humans. Chromium toxicity has been reported in many plant species (Ahmad et al. 2016). Several plant species are available for in situ phytoremediation of Cr-contaminated soils. Previously, *Brassica campestris*, significantly accumulated Cr from sandy and silty clay loam soils (Dheri et al. 2007). In another comparative experiment, *Helianthus annuus*, performed very well to extract Cr from a Cr–Co–contaminated soil (Lotfy and Mostafa 2014). The Cr extraction efficiency has been further improved by citric acid application (Farid et al. 2017). Some field crops have also been tested to remediate Cr-polluted soils for example *Zea mays* (Chigbo and Batty 2014), *Triticum aestivum* (Nayak et al. 2015), *Sorghum bicolor* (Revathi et al. 2011). Moreover, some tree species have also phytoremediated Cr-contaminated soils. A study on *Barringtonia acutangula*, an evergreen semi-aquatic tree, revealed that over 1000 mg kg^{-1} Cr was accumulated in its shoots (Kumar et al. 2014).

4.6.10 Mercury (Hg)

Mercury is found in nature in several forms; however, methylmercury is one of the most toxic forms of Hg whose formation is mediated by bacteria. Its biomagnification, especially through consumption of seafood contaminated with methylated Hg, may cause serious health complications. *Jatropha curcas* plants accumulated Hg with TF and BCF greater than 1 during a four months exposure to Hg-contaminated soil (Marrugo-Negrete et al. 2015). In another experiment, among 25 native plant species, *Jatropha curcas*, in addition to *Piper marginatum* and *Stecherus bifidus*, phytoremediated low Hg-contaminated soil (Marrugo-Negrete et al. 2016). Similarly, *Brassica juncea* and *Lupinus albus* efficiently extracted Hg from a multi-metal-contaminated soil in the presence of mobilizing agents (Franchi et al. 2017). Some cultivated crops have also been used for the remediation of Hg-contaminated soils such as *Hordeum vulgare*, *Triticum aestivum* and *Lupinus luteus*, among which barley showed maximum phytoextraction of 719 mg ha^{-1} Hg (Rodriguez et al. 2005). Naturally, Hg-hyperaccumulating plants are very limited; however, transgenic plants have got improved capacity to detoxify and volatize ionic and methyl Hg such as *Arabidopsis thaliana* and *Nicotiana tobacum* (Heaton et al. 1998). However, the major drawback associated with it is the atmospheric pollution of Hg due to involvement of volatilization process.

4.7 Conclusions and Future Recommendations

Removal of toxic heavy metals from soil and water is mandatory for food chain safety. In situ phytoremediation is the most viable option to clean environment and contaminated sites. Several plant species belonging to Asteraceae, Brassicaceae, Lamiaceae, Crassulaceae families have the ability of hyperaccumulating HMs. The success of phytoremediation is dependent on toxicant removal efficacy of plant, environmental conditions, acceptable limits of HMs at the affected site and remediating time. However, 100% contaminant removal by in situ phytoremediation is not possible under aforementioned conditions. The in situ phytoremediation system, however, can be made more efficient by exploiting soil microbes and applying synthetic chelating agents and natural organic amendments. Moreover, there is a need to further improve phytoextraction ability of hyperaccumulating plants by probing genetic pathways, so that it may become more acceptable cleanup technology.

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Chapter 5
In Situ Phytoremediation of Uranium Contaminated Soils

Abdul G. Khan

Abstract Human demand for energy, like traditional sources such as oil, coal and petrol, is gradually diminishing due to gradual consumption, world faces energy crisis. Development and use of nuclear energy from uranium (^{235}U) is one of a few options available to meet this shortage, but mining and processing of uranium mineral resources is causing uranium pollution of our air, waters and soils. Depleted uranium (DU), the by-product of ^{235}U extraction, is the major source of DU contamination. Uranium has long shelf-life, and it remains for a long period of time in the environment and causes long-term potential hazard to human health and environment. Therefore, there is an urgent need to address this problem. Various remediation technologies like physical (coagulation, precipitation, evaporation, extraction and membrane separation technologies) and chemical (chemical extraction and leaching, hydrolysis, etc.) methods to remediate U-contaminated soils and waters are being developed and tested, but they are all very costly and only applicable to small contaminated sites. In this review, various in situ biological remediation technologies such as bioremediation and phytoremediation are discussed with reference to their benefits and limitation. Application of synergistic relationships of uranium-contaminated soils and bioenergy production by using biocrops like vetiver grass (*Vetiveria zizanioides* (L.) Nash) and industrial hemp plants (*Cannabis sativa* L.) are discussed in relation to in situ phytoremediation. Potential of various chemical (NPK fertilizers, chelating agents, etc.) and biological (inoculating plants with PGPR, symbiotic bacteria and AM fungi) applications for greater uptake of nutrients including uranium to increase plant growth and produce greater bioenergy biomass are suggested to take into consideration when implementing in situ phytoremediation strategy. The potential of mycorrhizo-remediation of U-contaminated mine sites by the mycorrhizal roots of bioenergy crop plants like vetiver grass and industrial hemp crops was highlighted. It is anticipated that in situ mycorrhizoremediation strategy applied to uranium-contaminated mine sites (rhizoengineering) will prove to be the most promising uranium contaminant stabilization and bioenergy biomass production on marginal lands.

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5.1 Introduction

The phenomena of increasing environmental contamination of our water and soils by a combination of potentially toxic organic, inorganic and radioactive elements are a serious environmental issue globally. Human demand for energy, to cope with the increasing world population, has caused an unprecedented energy crisis. As the traditional coal, oil, gas, etc., are being gradually consumed to meet this demand, and the green energy sources, such as solar, wind and hydropower, are too expensive and not capable of providing enough energy to meet the power demand of the planet, attention has been diverted to nuclear energy. Nuclear power is cheaper than alternative energy resources, although not cheaper than the natural gas but far more efficient than the alternatives, and it emits no carbon (Karakosta et al. 2013). Nuclear reactors are being designed by a US-led association of 13 countries around the globe which continue to rely on nuclear power (Adamantiades and Kessides 2009). China is the biggest player so far in this field, and it has already 36 reactors in operation, another 20 under construction, and more than 100 reactors planned. Countries like India, Japan, Russia, etc., are also boosting their share of energy they get from nuclear power, and this trend is forecast to grow even further over the next decade (Outsider Club 2018). Hence, it appears that nuclear energy is here to stay, and the future energy requirements will be increasingly met by nuclear energy derived from uranium.

5.1.1 Uranium—History, Discovery, Occurrence and Uses

Uranium was discovered by Klaproth in 1789 (Emsley 2001). Initially, the U oxide was used as pigment in glasses, glazes and enamels until 1940 (Emsley 2001). Although its radioactivity was discovered in 1896 by Henri Bacquerel, commercial interests in U were not realized until after World War II when the most abundant isotope of U, ^{226}Ra', resulting from the decay of ^{238}U, was used in cancer therapy by Cerveira in 1951 (Cited by Abreu and Magalhaes 2018). The Chernobyl nuclear accident in 1986 in Ukraine's nuclear power station drew the public attention to the environmental impact of radioactive waste produced by mining, extraction and processing of its ore. This has raised public health concerns and demands urgent action for removal of U from polluted environments.

Occurrence of U in our soils is primarily due to the Earth's crust containing U and its decay products. All minerals containing rocks have U as natural constituent. Another source of uranium in our environment is due to the interactions of the cosmic rays in the atmosphere which also contribute to the natural occurrence of radionucleotide contamination of our air (Abreu and Magalhaes 2018). Anthropogenic activities like uranium mining, extraction and processing by man during the eighteenth century also generated radioactive nuclides in our soil, air and water environments (Cuney 2009).

5.1.2 Uranium and Human Health

The mass concentrations of U and its decay products in the earth's crust and soil vary between 0.3 and 1.0 mg U/kg, but due to anthropogenic activities by man, U concentration can reach to 100 mg/kg (Kabata-Pendias 2011). Such high levels of uranium concentrations can cause toxicity to the biota. More soluble forms of uranium and its compounds when man is exposed to can cause cancer of blood, lung, lymph nodes, bones, kidney and other internal organs (Chevari and Likhner 1968; Harley et al. 1999; Mkandawire 2013).

Migration of contaminants like uranium and its associated radionuclides from the waste and tailing dumps in abandoned uranium mining and processing sites into non-contaminated sites as dust or leachate through the soil and the spreading of sewage sludge are examples of events that contribute towards contamination of our ecosystems. With the boost of industrialization and urbanization in the past few decades or so in the world, the environmental safety of our soils becomes crucial due to using sewage irrigation and sludge farm applications, stockpiled radionuclides wastes, different kinds of industrial wastewaters, exhaust gases, livestock manures, etc. This, coupled with the movement of contaminants up the food chain, has become human health hazard issue and is increasingly becoming a global environmental, economic and planning issue as well. Although uranium has no biological function, a wide range of both aquatic and terrestrial flora and fauna take up uranium from their environments, and this endangers human health (Fisenne et al. 1988). As uranium can be found in P-fertilizers, if the rock phosphate is of sedimentary origin, it can be carcinogenic and mutagenic, and its contaminants in soil, air and water environments endanger both human and animal health causing damage to kidneys, increasing the risk of getting cancer, and can also affect reproduction and foetal development (Bednar et al. 2007; Schnug and Haneklaus 2015). Effects of chemical toxicity of uranium isotope, ^{238}U, pose a serious problem of environmental contamination and human health risks (Abreu and Magalhaes 2018; Bini and Bech 2014). Yue et al. (2018) reviewed the known information on depleted uranium entry routes into our air, soil and water environments, its toxicological mechanisms and its radiological and chemical toxicity effect on human health.

5.1.3 Uranium as Source of Energy

Causes of increasing environmental contamination of our soils and water by uranium and its decay products include various human activities such as mining, nuclear fuel enrichment processing and waste disposal, industrial production and use of phosphate fertilizers, nuclear weapon production, which all contribute to increasing uranium contamination of our environment during the last few decades all over the world. Uranium mining has increased many folds to meet the energy demand and resulted in degradation and pollution of terrestrial ecosystems causing an irreparable damage to the almost non-renewable soil resources. Besides mining for nuclear power, other examples of the increased use of uranium in recent times include producing and testing of nuclear and conventional military weapons produced with depleted U, along with development of nuclear fuel enrichment processing, industrial production and use of phosphate fertilizers, etc., have all contributed to increasing production of nuclear waste containing uranium.

5.1.4 Uranium Mining and Environment Contamination

Various activities during uranium mining and processing also release uranium and uranium compounds in the environment (Gavrilescu et al. 2009). Uranium rocks and uranium mill tailing are the major contributors responsible for soil contamination with uranium and its compounds.

Uranium can disperse on soil surfaces by runoff, into the groundwater by leaching, and into air by wind, subsequently endangering flora and fauna, including human health and urgently requires proper management of uranium-contaminated environments and its radiation impact (Zhu and Chen 2009a, b). These authors stressed the proper management of uranium-contaminated environments as a matter of urgency specifically in times of Nuclear Renaissance which calls upon a holistic strategic approach from U exploitation to its processing in the nuclear fuel cycle with appropriate considerations of environmental and radiation impacts.

As a result of the trend of mining and processing nuclear radioactive uranium mineral resources to meet the increasing energy demand, environmental contamination is also increasing and the former uranium mining sites, uranium treatment plants, heaps and tailings, contribute to pollution of large areas of soil and water all over the world (Markel and Arab 2015). International Atomic Energy Agency (IAEA) and EPA have published various safety reports and extensive range of documents dealing with the uranium mining activities producing uranium ore concentrates and associated risks involved in disposal of tailings leading to radiation protection as regular part of operations (EPA 1994, 2004; IAEA 1982, 1995, 1996, 1997, 1998, 2006, 2011; IAEA-OECD 2015).

As pointed out above, at the end of uranium ore exploitation, mining areas posed not only an extensive environmental contamination and health risks, but also caused toxicity to the soil biota due to high quantities of radioactive wastes in soils, even many years after the closure of mining operations. These uranium mining wastes contain radionuclides such as ^{230}Th, ^{226}Ra, ^{210}Pb, ^{210}Po and extracted fractions of uranium. Plus chemical additives used for uranium recovery from the ore are also present in the tailings (Jha et al. 2016). These chemically toxic radionuclides and acid and alkaline additives in the uranium mill tailings are known to cause various radiological hazards in the biotic and abiotic components of the ecosystem. These leachates from the contaminated uranium waste dumps spread to soils, surface waters and ground waters around the uranium mining and processing sites, and air (Abreu and Magalhaes 2018). These radionuclides in soils and their geochemical properties are affected by various soil factors including soil biota, i.e. bacteria, actinomycetes, fungi, flora and fauna (Kabata-Pendias 2011). These radionuclides in the contaminated soils can be immobilized by complexation processes with organic matter or fixed by precipitation (Adriano 2001).

Concerns from ex-mining sites by the inhabitants are being voiced as use of such sites is required for agriculture or residential purposes. Radioactive uranium contaminants from the soils and plants growing in it may become part of the food chain by animals including human. This soil–plant–man pathway for radionuclides' transfer to human beings is considered to be responsible for uranium toxicity and human health (IAEA 1982).

The damage to the human health as outlined above and to our environment caused by uranium contaminants is becoming an acute problem all over the world and represents a technical challenge, as utilization of these contaminated lands for urban and/or agricultural purposes requires a safe and efficient decontamination process.

5.1.5 Recent Publications Re U and Environmental Contamination

Some important reviews have been published recently as books (Ahmad and Rasool 2014; Anjam et al. 2012; Bech et al. 2014, 2018; Bini and Bech 2014, Bini et al. 2018; Merkel and Arab 2015; Prasad et al. 2018; Raskin and Ensley 2000), book chapters (Abreu and Magalhaes 2018; Aleksandra 2011; Alves et al. 2018; Bini et al. 2018; Ozyigit and Dogan 2015; Woods et al. 2015; Waggitt 2015); review articles (Adams et al. 2015; Harley et al. 1999; Malaviya and Singh 2012; Marques et al. 2009, 2011; Mitchell et al. 2013; Newsome et al. 2014; Purakayastha and Chhonkar 2010; Austruy et al. 2014; Sheoran et al. 2009; Zhu and Chen 2009a, b; Ye et al. 2017); International Atomic Energy Agency reports/documents (IAEA 1995, 1996, 1997, 1998, 2006, 2011, OECD-IAEA Joint Report 2015); Outsider Club Special Report (2018), regarding the issue of uranium contamination of our ecosystems, factors for formulating a strategy for environmental restoration or uranium mining and milling sites and reviewing practices for the close-out of uranium mines and mills, and the use of plants as low-cost and environmentally friendly in situ technology to remediate such soils has been published during the last decade or so. Details covered in these literatures have been excluded in this review, and readers are requested to refer to them and the references therein for more details.

5.2 Aim and Objectives of This Review

This review focuses on the challenges and complexities associated with the remediation of uranium-contaminated waste sites. Various physical, chemical and biological strategies have been proposed and studied at both laboratory and field levels. Because the soil parameters such as soil type and its physicochemical properties, uranium speciation, presence of coexisting ions and organics, etc., in the soil environment influence U concentration in it, no universal approach can be developed for its remediation. Speciation and mobility of U, which in turn is controlled by the oxidation state of the U, plays a vital role in determining the suitable strategy to be adopted for decontamination (Sylvakumar et al. 2018).

The review is also aimed at exploring the potential of universal plant symbiotic mycorrhizal fungi and multipurpose perennial bioenergy plants such as *Cannabis sativa* L. and *Vetiveria zizanioides* (L.) Nash for simultaneous execution of phyto-mycorrhizo-remediation and bioenergy (biogas, bioethanol, biodiesel, oil, fibres, food and feed, medicines, etc.) production during the process to address the two major issues of energy crisis and environmental contamination.

5.3 Remediation Strategies for U-Contaminated Soils

Remediation of soils contaminated with heavy metals and radioactive wastes as by-products of mining processes are generally persistent in the soils, and it is a very expensive and difficult venture (Bech et al. 2014). Any disposal plan to remove/store the tailings from the uranium mining and processing sites requires the waste volume to be significantly reduced to minimize the cost and safety issues associated with the long-term site management (Jha et al. 2016).

Various on-site or off-site physical methods such as coagulation, precipitation, extraction management and decontamination strategies, or chemical approaches such as chemical leaching or co-precipitation, have been proposed for soils contaminated with potentially toxic and radioactive elements, depending upon their nature, concentration, distribution and the physiochemical characteristics of the site, in order to reclaim the degraded land (Khan et al. 2000; Li and Zhang 2012).

Uranium has been mined using in situ recovery (ISR) methods from U deposits (Cuney 2009). ISR method allows for the recovery of uranium without the need for removing the ore body from the ground and therefore has many advantages over traditional open pit or underground mining methods by reducing surface environmental impacts, safety hazards and production costs.

Marques et al. (2011) grouped the classical in situ remediation techniques into two groups, (1) containment and confinement of the contaminated soil by sealing, modifying, encapsulating in order to reduce their mobility and bioavailability; and/or removing/destroying the contaminant by physical, chemical or a combination of the both technologies; and (2) biological in situ remediation techniques.

5.3.1 Containment and Confinement Remediation Technique

Behaviour of uranium in soils is a complex phenomenon, and it is hard to predict uranium bioavailability based on soil parameters as many soil and environmental factors and processes may act simultaneously (Vandenhove et al. 2001). As uranium has long shelf-life and its destruction or degradation is not possible, both health and environmental risks to the environment and health caused by uranium radioactivity require specific remediation strategies to reclaim the old uranium mining areas after ceasing uranium ore exploitation processes (EPA 1994).

Various physicochemical techniques are as follows: (1) excavation of solid contaminated waste, dumping it in land filling, allowing it to decompose and eventually recovering waste land for recreation and eventually for construction; (2) physical separation of contaminants into concentrate of the desired substance from the mineral ore and tailings; (3) high-temperature thermal treatments of the contaminated solid to reduce the mobility of the contaminant; (4) polymer microencapsulation of the contaminant to solidify and stabilize by using thermoplastic or thermosetting resins; (5) pyrometallurgical separation of contaminant by processing at elevated temperatures for recovery of the contaminant from the waste material; (6) using chemical and electrochemical processes such as hydrolysis, chemical extraction and leaching, electrolytic removal of contaminants from solutions, etc. (Dushenkov 2003; Khan et al. 2000).

All the above-listed physicochemical remediation techniques to clean up U-contaminated soils are very costly, e.g. in USA, the cost of conventional technology to remediate radionuclide is to be more than \$200–\$300 billion (Entry et al. 1996), only applicable to small contaminated sites (hot spots), and cannot be generally applied for in situ remediation of large mine spoil waste areas (Khan et al. 1997). There is an urgent need not only to take curative, but also preventative measures to remediate land contaminated by mining, smelting and manufacturing activities during the past few decades or so all over the world for urban or agricultural developments.

5.3.2 *Biobased In Situ Radioactive Isotopes (Uranium) Remediation Techniques*

Uranium is the most abundant of the naturally occurring actinides, and it occurs primarily as 3 of its 17 known isotopes, i.e. ^{238}U 99.27%; ^{235}U 0.72%; and ^{234}U 0.1%, all radioactive, carcinogenic and mutagenic. De Filippis (2015) provided a list of U isotopes and radionuclides of importance in environmental and health concerns and present in uranium waste areas used for phytoremediation. Pollution of aquatic and terrestrial soils by radioactive elements (uranium, radium and thorium) due to mining and mineral processing of polymetallic ores is well documented worldwide.

Mining procedures also cause compacting and stripping of the soil at the mining site, destroying soil structure, resulting in its density and reducing its water holding capacity and aeration. All these factors reduce the soil organic matter or even destroy its indigenous micro-and macro-flora, including the rhizosphere and mycorrhizae, resulting in reduced soil pH, which in turn changes many metabolic processes and increases the bioavailability of toxic heavy metals, organic and non-organic chemical compounds and radioactive substances such as uranium. This degraded and contaminated soil spread by wind and/or water to, eventually, food chain causing harm to crops, animals and humans. Compounding this problem is the fact that traditional physicochemical methods of clean-up are expensive, difficult and inefficient. Those methods that are applied to soils and sediments may also be of high impact, hence detrimental to soil structure and fertility (Chaudhry et al. 1998).

During the last two decades, among the various biological decontamination strategies for U-radioactive-contaminated mine sites, bioremediation technique to vegetate and return such soils to stable ecosystems it supported prior to disturbance gained some popularity (Allen 1991). However, a number of environmental factors such as soil aeration, soil moisture, soil pH, soil temperature were found to affect the uptake of U by plants. Ebbs et al. (1998), for instance, used weak organic acids to uranium-contaminated soil to reduce pH to 6 and convert most of the uranium to uranyl cations and increase U-bioavailability for plant uptake, depending upon soil type, soil OM contents and of U contamination. As pointed out by Abreu and Magalhaes (2018), no universal approach can be developed for uranium-contaminated soil remediation. More recently used method of dealing with the uranium-contaminated soils is biobased in situ technique, i.e. *bioremediation*. Within bioremediation, the treatment of contaminant using plants is termed as *phytoremediation*, and technique using both plants and microbes is termed as *rhizoremediation* (Kuiper et al. 2004; Thijs and Vangronsveld 2015), which offer alternatives to the classical approach. Recently, Jamal et al. (2002) introduced the term *mycorrhizo-remediation* for enhanced zinc and nickel uptake from phosphorus-deficient and heavy metal-contaminated soil by mycorrhizal legumes such as soybean, alfalfa and lentil. These authors indicated that AM mycorrhizal fungi can be used as effective tools to supply sufficient Zn in generally Zn-deficient Pakistani soils. The implications of these results in mycorrhizo-remediation of agricultural soils were discussed by these authors. Khan (2006a, b) highlighted the ecological complexity and diversity of plant–microbe–soil combinations, particularly AM, and discussed the role AMF plays in phytorestoration of contaminated soils, i.e. mycorrhizoremediation. The author emphasized the need to improve our understanding of rhizosphere microbiota, including AM fungi, and to conduct research on selection of AMF isolates from rhizospheres of weed plants growing on contaminated soils for specific restoration purposes using mycorrhizoremediation strategy. Giasson et al. (2006) used this term, i.e. mycorrhizoremediation, as enhanced phytoremediation of heavy metal-contaminated soils. Kumar et al. (2018) regarded bioremediation consisting of phytoremediation and rhizoremediation which includes mycoremediation, rhizodegradation, organism-assisted phytoremediation and rhizosphere bioremediation, all of which involve remarkable interactions between plant roots, root exudates, rhizosphere soil and microorganisms to degrade contaminants into harmless compounds. Interactions between plant roots and their associated microorganisms increase the bioavailability and uptake of contaminants by its biodegradation processes. Abioye and associates (Abioye et al. 2012, 2017) regarded these interactions enhancing phytoremediation and detoxification of the contaminants. Symbiotic AM mycorrhizal fungal endophytes are ubiquitous and are associated with the roots of most halophytic, xerophytic and hydrophytic plants (Khan 1972, 1974, 1993a, b, 2004b; Khan and Belik 1995), which not only enhance host plant growth under stressed conditions but also control soil pathogens (Khan 1972). The presence of endophytic AMF with link with rhizosphere prompts more effective phytoremediation. Mycorrhizal onions were found to grow better in unsterilized coal wastes than non-mycorrhizal ones (Khan 1981, 1988).

Managing the microbial population in the rhizospheres by using an inoculum consisting of a consortium of PGPR, mycorrhiza-helping bacteria (MHB), nitrogen-fixing rhizobacteria, and AMF as allied colonizers and biofertilizers, could provide plants with benefits crucial for ecosystem restoration of soil contaminated by heavy metals, radionuclides, etc. (Khan 2002a, b, 2004a, b). It is important to use indigenous AMF strains which are best adapted to actual soil and climatic conditions for mycorrhizoremediation. If indigenous AMF in the contaminated soil to be phytoremediated exit, management of these indigenous AMF and their associate rhizobial microflora would be an important strategy to improve the chances of successful mycorrhizoremediation. Further research is needed on AMF ecotypes isolated and selected from U-contaminated soils and being used for specific restoration programs (Khan 2005a, b). Molecular tools such as taxon-specific primers could be successfully used to assess the success of AMF in colonizing plants used for phytorestoration of uranium-contaminated sites.

5.3.2.1 Bioremediation

With the boost of industrialization and urbanization in the past few decades or so in the world, the environmental safety of soil becomes sever due to using sewage irrigation and sludge farm applications, stockpiles radioactive and heavy metals mining wastes, different kinds of industrial wastewater, exhaust gas, livestock manures, etc., which all become the source of soil and water contamination. Although uranium has no biological function, a wide range of both aquatic and terrestrial flora and fauna take up uranium from their environments causing threat to the ecological environments, agriculture sustainable development, food safety and livestock/human health; and endangers human health (Fisenne et al. 1988).

The uranium-contaminated soils harbour viable and metabolically active microbiota which interacts with it, and other heavy metals present and have the potential to alter the solubility of a broad range of radionuclides including uranium. These indigenous microbes are known to impact the form and distribution of uranium in the environment and can affect the migration and transformation of contaminants through changing their physical and chemical characterizations (Prakash et al. 2013). The mechanisms, used by the microbes to interact with such soil and water contaminants, include precipitation, oxidation–reduction reaction, complexation and accumulation. Microbial leaching is commonly used for extracting valuable metals from low-grade ores, and it has some potential for remediation of mining sites, industrial waste products, detoxification of sewage sludge, etc. Sylvakumar et al. (2018) have illustrated the mechanism of microbial uranium extraction using biosorption and bioreduction processes. Suzuki and Banfield (2004) isolated heterotrophic bacteria from an acidic uranium-contaminated site in USA and postulated that they play an important role in natural attenuation and stimulated bioremediation of uranium and other toxic organic compounds. These microbes were found by the authors to be resistant to U toxicity and accumulated uranium in natural low pH soils. The indigenous microbes in the uranium-contaminated soils can dramatically impact uranium forms and distribution in the soil environment (Suzuki and Banfield 1999). Sakaguchi (1996) reported that the bacterial species (*Bacillus subtilis* and *Arthrobacter* sp.), isolated from U-contaminated sites, can accumulate high amounts of uranium from pH 4 in laboratory experiment. These indigenous microbes can be potentially exploited by identifying uranium-resistant strains to bioremediate such soils (Chung et al. 2014; Choudhary and Sar 2010; Merten et al. 2004). They play an important role at all stages of U in situ recovery (ISR). Indigenous microbes in the U-contaminated wastes carry endogenous genetic, biochemical and physiological properties that make them ideal agents for pollutant remediation of environmental contaminants including radionuclides (Prakash et al. 2013). Zammit et al. (2014) have reviewed the interactions between microbes and U and the possible effects this could have on ISR operations. These authors concluded that these microbes may affect ISR in either a positive or a negative way, e.g. assisting U mobilization via U oxidation or immobilizing it by reducing U into insoluble form, and that the indigenous microbes have a potential in increasing U recovery rates during mining stages or speed-up post-mining remediation strategy. Bioremediation techniques were classified by Azubuike et al. (2016) based on application principles, advantages, limitations and prospects. Mkandawire (2013) reviewed the issue of bioremediation of U from a biogeochemical point of view and discussed the potential and limitations of uranium bioremediation as an alternative to classical approaches applied to rehabilitation of uranium mining and processing sites. These authors also discussed human health concerns due to exposure and chemical, radiological, and ecotoxicological risks associated with uranium mining. Newsome et al. (2014) reviewed the mechanisms of uranium bioreduction and phosphate biomineralization and their role in in situ bioremediation of uranium. These authors demonstrated that the metabolism of anaerobic microbes has the potential to alter the solubility of redox-sensitive radionucleotides such as uranium (IV) at nuclear sites, and it plays important role in extracting uranium from low-grade U-waste sites, i.e. bioremediation. Although microbial cells of *Pseudomonas* spp. are reported to accumulate U into their cells due to increased membrane permeability caused by uranium toxicity (Suzuki and Banfield 1999), there is little evidence supporting bioaccumulation of uranium as a viable technique for bioremediation of uranium-contaminated soils.

Benefits of in situ bioremediation processes include uranium immobilization in place without above-ground exposure by using inexpensive biostimulants such as ethanol and lactate acid as electron-donors, and with no need to use non-native soil microflora. Groudev et al. (2001) found that the native indigenous microbes are effective in efficient bioremediation of the uranium-contaminated soils. The ability of contaminant biodegrading microbes to reclaim such soils and waters polluted by uranium and other substances hazardous to human health and/or environment can be exploited for bioremedial purposes. These authors conducted laboratory experiments with soil samples from soils contaminated with radioactive elements (uranium, radium and thorium) as a result of mining and mineral processing of polymetallic ores and found that an efficient remediation of the soil was achieved by an in situ treatment based on activity of the indigenous heterotrophic and chemotrophic anaerobic soil microflora, and anaerobic sulphate-reducing heterotrophs. Based on these results, the authors applied this method under real field condition in a heavily uranium-contaminated experimental plot and recorded the contents of radioactive elements decreased below the relevant permissible levels within 8 months of treatment. This biobased remediation of uranium contamination soils has a potential in the in situ uranium recovery or bioremediation of uranium-contaminated sites, due to the ability of the indigenous free-living microbes, such as fungi, bacteria, yeasts, actinomycetes and algae in the contaminated spoil heaps, to adsorb and precipitate uranium by using their enzymatic processes or through cell surface enzymatic processes or through cell surface components. Although this strategy has been reported as potentially promising at the laboratory scale, very few field studies have been reported due to various challenges and complexities listed above (Sylvakumar et al. 2018). Adams et al. (2015) reviewed technologies for carrying out bioremediation and highlighted the role biotechnological approaches such as biostimulation and bioaugmentation play in manipulation of processes of remediation. Azubuike et al. (2016) provided a detailed account of application, principles, advantages, limitations and prospects of bioremediation.

5.3.2.2 Phytoremediation

More recently, a relatively newer concept of using biological approach to reduce or eliminate soil contaminants like heavy metals, radionuclides, etc., is gaining popularity (Adriano et al. 1995; Adriano 2001; Purakayastha and Chhonkkar 2010; Chaney et al. 2010, 2014; Entry et al. 1996), which applies plants (phytoremediation or 'green remediation') to degrade, transform, accumulate or mobilize the contaminant in situ. Phytoremediation is not actually a new concept: constructed wetlands, reedbeds and floating-plant systems have been common for treatment of contaminated waste waters for many years. Phytoremediation term has been called green remediation, botano-remediation, agro-remediation and vegetative remediation (De Filippis 2015). The author also provided a comparative account of advantages and disadvantages of phytoremediation methods used based on combined reviews (for details see De Filippis 2015).

Current research efforts now focus on expanding phytoremediation strategy to address soil and air pollutants. Phytodecontamination strategies involve (1) phytoextraction, where plants accumulate the contaminants and are harvested for processing. Postharvest processing of contaminants includes thermal, microbial and chemical treatments; (2) phytodegradation, where plants, or plant-associated microflora, converts pollutants into non-toxic materials; and (3) phytostabilization, where pollutants precipitate to form solutions or are absorbed or entrapped in either plant tissues or the soil matrix. Sequestration can be enhanced either by amendments to the soil or through the action of the plants and their associated microflora (Cunningham et al. 1995). These authors have redefined plants as 'solar-driven pumping and filtering systems', and roots as 'exploratory, liquid-phase extractors'. This has given birth to a new technology terms like phytoextraction, phytoaccumulation or phytoremediation of contaminated soils. This plant-based remediation technology, i.e. phytoremediation, is applicable for removing contaminants from areas of low U concentrations with shallow soils and waters, although longer times may be required (Khan 2005a, b).

This alternative bioapproach has risen because plants have a remarkable ability to extract, concentrate and metabolize materials from air, soil and water. Baker (1981) proposed that plants respond to the presence of soil contaminants in three ways: (1) act as *contaminants accumulators* and survive despite concentrating contaminants in their aerial tissues; (2) act as *contaminant indicators* possess a mechanism that control the translocation of contaminants from the roots to the shoots; or (3) *contaminant excluders* control the translocation of contaminants from the roots to the shoots by various mechanisms such as rhizofilteration in which plant roots absorb and precipitate the contaminants. *Excluders* restrict contaminant uptake into the biomass, i.e. in situ phytoremediation.

In situ phytodecontamination strategies can be categorized under five major subgroups (Khan 2005a, b, 2009; Khan et al. 2000; Chaudhry et al. 1998):

(1) Phytoextraction (phytoaccumulation)—removal and concentrations of contaminants into harvestable plant parts.
(2) Phytodegradation (phytotransformation)—enzyme-catalysed degradation of contaminants within plant tissues by their associated microbes.
(3) Rhizofilteration—based on a combination of phytoextraction and phytostabilization through absorption of contaminant by plant roots from contaminated soil and water.
(4) Phytostabilization—immobilization and reduction in the bioavailability of contaminants by plant roots and their associated microbes and
(5) Phytovolatilization—volatilization of contaminants by plants from the soil into the atmosphere.

Among the above types of phytoremediation techniques, phytostabilization and phytoextraction are the most suitable for U-contaminated soils, and utilizing these can effectively remediate soil contaminated by PHC, heavy metals, radionuclides, salt and other soil and water contaminants. High-biomass-producing and uranium-hyperaccumulating plants (phytoextractors) needed to be used to transport and concentrate uranium into the above-ground plant parts. Other plants (non-accumulators) which can uptake uranium from soils but, instead of translocating it to the above-ground parts, stabilize it in the roots and rhizospheres by restricting its translocation and mobility, thus making it harmless (Ogar et al. 2014).

This in situ technology can be used to remediate uranium-contaminated environments and is a promising technology for long-term rehabilitation of uranium-contaminated sites, as it is economical, does not deteriorate soil microbiota and keeps soil properties intact by covering it by plants during treatment to reduce wind and water erosion (Baker et al. 1994; Truong 1999; Vandenhove and Van Hees 2005). Laurette et al. (2012) found that the uranium mobilization and its uptake by plants is dependent on its speciation and is an important factor in developing an efficient phytoremediation approach. These authors used X-ray absorption spectroscopy (XAS) and transmission electron microscopy (TEM) and showed that uranium complexation with endogenous phosphate residues leads to its precipitation and fixation in plant organs, avoiding translocation from roots to leaves. This complexation with a strong ligand, such as citrate, circumvents this precipitation and enhances root-to-shoot translocation in a uranium–carboxylate complex form (Huang et al. 1998). This relationship between uranium speciation in the environment and its mobility pattern in plants has implications in uranium phytoremediation strategies (Laurette et al. 2012).

Revegetation of contaminated sites not only controls soil erosion and aggregation, but also provides long-term ecological and environmental balance (Khan et al. 2000). However, as noted above, this technology has certain drawbacks such as low extraction efficiency, low ability of plants to generate large amounts of uranium-contaminated biomass and long period required for decontamination process. It is essential, therefor, to select plants as tools in this plant-assisted in situ remediation of uranium-contaminated soils, which are efficient in accumulating radionuclides in their aerial parts (hyperaccumulators), produce great biomass and tolerate uranium toxicity or those which restrict uranium mobilization and translocation to shoots, i.e. immobilize or inactivate uranium (phytostabilizers) and reduce its dispersion (Khan et al. 2000). Phytostabilization does not remove soil contaminants like U and heavy metals from soil but limits their migration. Therefore, for the phytostabilization technology to be an effective strategy for uranium-contaminated soil remediation to minimize the environmental impact after mining, ideal plants should have high growth rates, dense root systems and high rates of propagation.

As phytoremediation technology is a relatively slow process, it may take years to reduce uranium levels in soil to a safe and acceptable level due to small size and slow growth of most identified hyperaccumulator plants (Chaudhry et al. 1998). Phytoremediation, therefore, is not a quick fix strategy, as in addition to advantages of phytoremediation, there are a few limitations of phytoremediation which restrict its application. However, the costs involved in phytoremediation are lower than those of conventional strategies and can have large-scale applications. To make phytoremediation a viable and successful strategy for uranium-contaminated soils, choice of dominant indigenous plant species, capable of hyperaccumulating uranium or stabilizing uranium contents in their roots and reducing uranium mobility, should be the first option as they are uranium-tolerant and adapted to the local soil and climatic conditions. Bech et al. (2018) provided a historical overview of relationship between plants and ore minerals and use of metallophytes as 'indicator plants' in mineral exploration since 1930. First relationship between radioactive elements and plants was provided by Kovalesky in 1966 (Cited by Bech et al. 2018). The term hyperaccumulator was introduced by Brooks (1998) who published the book titled 'Plants that hyperaccumulate heavy metals'. Readers are advised to refer to Bech et al. (2018) for an excellent description of historical overview of phytoremediation technology, which is based on the properties of metallophytes. As noted above, Cunningham et al. (1995) was the first author to use the term phytoremediation which involves plants capable of degrading or accumulating pollutants in their vegetative parts and remove contaminants from their immediate environment. These plants remove, transfer, stabilize and/or degrade contaminants in soil, water, sediments, mine tailings and air.

5.3.2.3 Plants for In Situ Uranium Phytoremediation

More than 400 plant species have been recognized, worldwide, that have potential to remediate contaminated soils (Surriya et al. 2015). Many plant species, which are capable of translocating U and other organic and inorganic contaminants from soil to their above-ground parts (phytoextractors), have been reported for uranium phytoremediation in literature (see Malaviya and Singh 2012; Chaudhry et al. 1998; Baker and Brooks 1989; Brook 1998). De Filippis (2015) provided a comprehensive list of plant species where radionuclides' phytoremediation research has been reported in the literature and researchers are directed for references listed in this article. According to De Filippis (2015), it is expected that phytoremediation of radionuclide waste will become an integral part of the environmental management and risk reduction strategy all over the world for governments, industry and society.

Field experiments in East Germany by Willscher et al. (2013), using combined phytostabilization and phytoextraction strategies for phytoremediation of a former uranium mining site, provided evidence that plants like *Triticale*, *Helianthus annuus* and *Brassica juncea*, grown in uranium-contaminated soils amended with NPK fertilizer and microbes, can uptake uranium contaminants into their roots and shoots. These authors found that the transfer of uranium from soil to plant was influenced by many factors as discussed above.

In addition to all the complex soil and environmental variables involved in phytoremediation of uranium-contaminated soils, air and water, there are some major challenges faced by researches before adopting this strategy, such as: (1) the selection of plant and its ability to uptake a large quantity of uranium in its various parts; (2) uranium bioaccumulation in the food chain of animals, including man, (3) re-entry of uranium into the ecosystem and (4) subsequent disposal of uranium-loaded harvested biomass (Sylvakumar et al. 2018; Khan 2005a, b). Sylvakumar et al. (2018) illustrated the process involved in a typical phytoaccumulation and phytostabilization of uranium in the contaminated soil into different parts of the plants and listed various plants like banana, papaya, green chillies, bitter gourd and grasses like *Lolium, Festuca, Dactylis* and *Alopecurus* spp. capable of accumulating U from U-radionuclide-contaminated soils.

Due to limitation of fossil fuels like coal, petrol, gas and non-renewable energy demand, toxic effects of radioactive energy sources like uranium, bioenergy appears as an alternative sustainable solution for ever increasing global energy demand and is gaining popularity. Agricultural land is being used for starch crops like maize, alfalfa or oil seed crops such as sunflower and rapeseeds, or perennial crops such as Salix, to produce biomass for heat and power generation, and biofuel production such as biodiesel and bioethanol.

Recently, several of these edible and non-edible bioenergy crops have been tested by a few researchers for phytoremediation potential with encouraging results (for references see Bauddh et al. 2018; Gomes 2012; Rowe et al. 2009; Silveira et al. 2018), but more research is required to adopt this strategy commercially for implementation. Additional merits of using bioenergy plants include food, oil and biomass production and several other ecosystem improvements. However, agricultural crops like maize require annual planting and require management including fertilization and insecticide sprays compared with grasses. Farming of agricultural food crops as bioenergy crop is thus a relatively costly option. In contrast, bioenergy non-food grasses with their deep roots improve soil nutrient quality with minimal ploughing, thus reducing soil erosion. Furthermore, bioenergy crops can provide a greater wildlife habitat than food farms.

Application of bioenergy grasses for phytoremediation of contaminated soils with toxic substances including radionuclide element like uranium could be economically beneficial in the form of bioenergy, e.g. biogas, biofuels, but it requires a holistic approach. Amalgamation/coupling of sustainable phytoremediation with bioenergy is an integrated approach to address the issue of U-contaminated land towards the cleaner environment and a greener future (Guldhe et al. 2017). However, as pointed out by Guldhe et al. (2017), use of limited land resources for producing biocrops to meet the need of biomass for bioenergy production is coming up as a major challenge and needs to be addressed for a sustainable future and long-term problems of bioenergy crop plantation on existing land resources and ecosystem.

Phytoremediation of contaminated and pollutants lands, which are not suitable for agricultural purposes, by using mycorrhizal biocrops, can address this issue of food versus fuel debate. This integrated approach, however, has its own challenges like low yield, contaminated biomass, ecosystem imbalance, etc. This is where choice of bioenergy plants for phytoremediation of contaminated land becomes important, i.e. bioenergy plants producing high biomass with increased uptake of pollutants into their roots or shoots, minimal cost for required land, and with least environmental impact, will be ideal to generate higher biomass for bioenergy production and phytoremediation of contaminated land.

5.3.2.4 Bioenergy Plants for Simultaneous In Situ Uranium Phytoremediation and Bioenergy Production

Recently, fibre crops are being considered as alternative land use for radioactively contaminated arable land. An excellent collection of articles on this biofriendly approach linking phytoremediation with energy generation has been compiled by Bauddh et al. (2018) containing case studies on efficiency of phytoremediation plants in energy production. This approach, by amalgamating phytoremediation with energy production, fulfils the expanding energy demand required for expanding urbanization and industrialization and worldwide accelerated environmental pollution mitigation (Bauddh et al. 2018). It is a cost-effective technology which uses energy plants to provide renewable energy through biofuel, thus having the potential to resolve the issue of pollution and energy by addressing both the environmental sustainability and the economic viability. This approach will also tackle some other important global issues like global climate change, ocean acidification and land degradation through carbon sequestration, reduced emission of other greenhouse gases, restoration of degraded lands and waters (Bauddh et al. 2018; McLaughlin and Kszos 2005). A holistic approach is required to address all the aspects of using energy plants for phytoremediation of radionuclide-contaminated land and energy production.

During the current decade, many research articles have appeared in the scientific literature addressing the potential of non-food bioenergy plants that can fulfil the dual purposes of phytoremediation of radionuclide-contaminated sites and generation of energy. Vandenhove and Van Hees (2005), for example, investigated the transfer of radiocaesium to the fibre crops such as *Cannabis sativa* L. and flax (*Linum usitatissimum* L.), as well as the distribution of radiocaesium during crop conversion and found that the amount translocated to the usable parts both of hemp and flax were low enough to allow the production of clean end-products like fibre, seed oil, biofuel, etc., even on heavily contaminated land. Van Ginneken et al. (2007) also reported the idea of the combination of energy plant and phytoremediation of contaminated lands.

This review will select two U-accumulating fast-growing, large biomass-producing bioenergy plants which are suitable for phytostabilizing and/or phytoaccumulating U contents into their tissues, i.e. *Vetiveria (Chrysopogon) zizanioides* and *Cannabis sativa* L.

Vetiver Grass (*Vetiveria Zizanioides* (L.) Nash)

Vetiver grass, *Vetiveria zizanioides* (L.) Nash (now classified as *Chrysopogon zizanioides* (L.)) Roberty, belonging to family Poaceae, is a tall fast-growing perennial grass with a massive deep-penetrating root system (VIN 1993; Truong 1999, 2002; Truong et al. 2010; Maffei 2002). This grass has been used in many different countries for the management of mine tailings and unfavourable soil conditions (Benerjee et al. 2018). It is a remarkable plant due to its characteristic features which enable it to be tolerating extreme climatic conditions and a wide range of soil conditions like acidity, alkalinity, heavy metals and radionuclides. It has been shown to stabilize (phytostabilization) the uranium contaminants in soils by its massive root system penetrating up to 5 m of mine tailings and reduce uranium movement to food chain (Grimshaw and Helfer 1995). Banerjee et al. (2018) have illustrated the schematic representation of phytoremediation strategies using vetiver. These authors stated that the phytostabilization strategy using vetiver system plays an important role in immobilizing uranium in soil through absorption and adsorption of uranium or through root accumulation and precipitation within its root zone to prevent uranium-contaminated soil runoff, erosion and air dispersal. Proper mining site management is necessary for its reclamation to minimize the environmental impact. These authors provide diagrammatic representation of spoil dump slope stabilization and ecological restoration by Vetiver System Technology (VST). Successful application of the VST can reduce or even eliminate many types of natural hazards such as landslides, mudslides, road bund instability and erosion (Joseph et al. 2017; Khan 2006a, b).

Hung et al. (2012) assessed uranium uptake of vetiver grass from northern Vietnam and concluded that it can tolerate up to 70% of uranium in soils and could survive and grow well without fertilization. The authors noted that the translocation of uranium in roots for all the soil types studied was higher than its shoots and concluded that this grass could potentially be used for decontamination of uranium-contaminated soils. The authors recorded that during the experiment, no signs of uranium addition to the soil affecting the plant growth. At a level of 250 mg kg^{-1} of uranium concentration added to the soil, the grass survived and grew moderately. Their results further showed that the grass biomass was increased up to 100 times higher than the control. An increased translocation of uranium contents in vetiver grass shoot and root was found in their experiment irrespective of uranium contents in the experiment soil and soil types. Under acidic conditions, 80–90% of uranium was in the $^{+}$VI oxidation state as the uranyl (UO_2^{2+}) cation. Free UO_2^{2+} species of uranium in soil is the easiest for plants to uptake and translocate to its different parts (Ebbs et al. 1998; Vandenhove et al. 2001). Soil pH was also found to affect the bioavailability of U in soils for plants to uptake. Soil organic matter (OM) contents in soil also affect U availability by reducing uranium availability to the plant due to adsorbing uranyl cations by clay, i.e. adsorption mechanism seems to be good to fix uranium and not allow plant to uptake (Shahandeh and Hossner 2002). The role of arbuscular mycorrhizal fungi associated with *Vetiveria zizanioides* grown in heavy metal-contaminated soils in the phytoremediation greenhouse studies by Wong (Wong 2003; Wong et al. 2007) supported the conclusion drawn by others.

Recently, Raman and Gnansounou (2018) reviewed various studies regarding the phytoremediation potential of vetiver grass and highlighted its benefits and limitations in waste remediation that demands a sustainable approach. These authors regarded vetiver grass to play a pivotal role as phytoremedial agent for numerous categories and reviewed the literature using vetiver grass for mine site stabilization, landfill rehabilitation, leachate treatment and other land rehabilitation purposes. VT is regarded as a low-cost phytoremediation method for decontamination of uranium-contaminated soils.

Cannabis Sativa L.

Among several plants reported by various researchers that have potential for simultaneous phytoremediation and production of useful by-products like biogas, bioethanol, biodiesel, fibre, etc., *Cannabis sativa* L. (commercial hemp) is a multipurpose crop with a wide range of applications such as production of industrial fibre, oil, food, livestock feed, medicine, etc. (Kumar et al. 2018), as well as for remediation of contaminated soils (Campbell et al. 2006). It is also used for religious, spiritual and recreation purposes. This bioenergy crop produces a high biomass and is suitable for phytoremediation of contaminated soils and bioenergy production. Its cultivation is low cost with low environmental impact. It is adaptive to various climatic conditions and wide range of soils, and its biomass is used for non-food industries, which makes it an attractive plant for phytoremediation (Linger et al. 2002). Its seeds have high oil contents and used as food supplement due to its high percentage of poly-unsaturated fatty acid (Oomah et al. 2002). It is also a high-biomass-producing crop which can be fermented for the production of bioenergy, i.e. bioethanol or biobutanol. In fact, industrial hemp is one of the few bioenergy plants that produce high yields of both oil and biomass (Li et al. 2010). Under greenhouse conditions, the transfer of radiocaesium into the aerial parts of industrial hemp plants, i.e. phytostabilization, makes the end-product clean for biofuel, food, fibre and seed oils production (Campbell et al. 2006). It has also been used for remediation of radionuclide-contaminated soils (Vandenhove and Van Hees 2005). The potential of hemp as a decontaminator of heavy metals was explored by Ahmad et al. (2015) by identifying and characterizing two HM stress-tolerant genes, GSR and PLDa, in breeding programmes to produce transgenic HM-tolerant varieties. This shows the ability of hemp plants to tolerate HM like Cu, Cd and Ni in hemp plant leaves collected from the contaminated site.

5.4 Mycorrhizal Fungi and Bioenergy Plants

In the past, there has been considerable interest in the potential use of AM fungi in agricultural and forestry practices, but neglect of their importance in disturbed and contaminated derelict lands (Khan 2007). Mycorrhiza-associated plants have been reported growing on contaminated soils (Chaudhry et al. 1998, 1999; Chaudhry and Khan 2002, 2003; Khan 1978, 1999; Hayes et al. 2003). To improve plant health and increase biomass for enhanced phytoremediation potential and efficiency of bioenergy crops, and to overcome several phytoremediation limitations such as low biomass, low bioavailability of contaminant, we need to consider the potential of AMF and associate microbes (PGPR and MHB) in our efforts to phytoremediate contaminated and derelict lands (Khan 2002a, 2005a; Chaudhry et al. 1998; Khan et al. 2000). All ecosystems, including agricultural as well as contaminated derelict ones, have in situ soil microbial communities, integral component of which are VA mycorrhizal fungi and their propagules, which regulate nutrient transfer between plants and their rhizospheres via external mycelial hyphae (Khan 1971, 1972). Several greenhouse and field studies have shown that AM symbiosis can mitigate the negative effects of biotic and abiotic stresses on plant growth. These fungi are universal obligate symbionts with over 95% of land plants, including energy plants, and can be exploited to stimulate plant growth to produce greater biomass for using as source of renewable energy in the world. Potential of bioenergy biomass-producing plants, in conjunction with mycorrhizal fungi, can offer an alternative phytoremediation strategy, i.e. mycorrhizo-remediation. Unfortunately, relatively few studies have focused on the effects of rhizosphere microorganisms, particularly AM fungi, on the remediation of the radionuclide-contaminated soils, despite the important role that these microorganisms play in plant interactions with soil environment and in revegetation efforts following the removal of the contaminants (Ozyigit and Dogan 2015; Asmelash et al. 2016). Added to this, the effects of phytoremediation practices on the microbial communities of the remediated site have also been largely ignored, as these native microorganisms are adaptive to the site and may be essential for establishing vegetation on the degraded and contaminated land (Khan 2003). The role that AM fungi play in plant interaction with soil U contents is not fully explored and exploited for revegetation of U-contaminated wastelands. AM fungi should be considered as an essential component of soil microbiota and as a potential tool for re-establishment of plant cover and population diversity during ecosystem restoration following the mining activities, including U mining and processing (Turnau and Haselwandter 2002; Khan 2003; Thijs et al. 2017) The rate of reclaiming derelict land may be increased by AMF inoculation of plants used for revegetation as these fungi are well known to improve plant growth on nutrient-poor soils and enhance the uptake of P, Cu, Ni, Pb and Zn (Khan et al. 2000). Enhanced phytoaccumulation potential and prospects of Zn and Cd by mycorrhizal plant species growing in industrially polluted soils were reported by Rashid et al. (2009).

Early phytoremediation efforts have focused on the predominantly non-mycorrhizal plant families, e.g. Brassicaceae or Caryophyllaceae, so AM has not been considered as important component of phytoremediation practices. The AM fungi help to partially alleviate soil contaminant's toxicity and enhance plant growth by increasing mineral nutrition on such soils (Khan 2003; Jamal et al. 2002).

Manipulation of microbes in the mycorrhizosphere for the benefit of plant growth requires research at the field level (Khan 1975a, b, 2002b). Because of the ecological implications in restoring a functional ecosystem on derelict land, AM associations should be considered as an integral part of the studies assessing derelict land ecosystem dynamics. The phytoremediation of uranium-contaminated wastelands by using bioenergy plants and the course of plant succession in such environments may be strongly influenced by inoculation with AM fungi and their associated rhizobacteria.

The AM fungi are ubiquitous soil inhabitants, and most naturally growing terrestrial and aquatic plants are colonized by AMF in nature, i.e. mycorrhizosphere is the rule, not the exception (Smith and Read 2008; Allen 1991). Thus, if we are to understand the rhizosphere reactions and interactions, we must understand the mycorrhizosphere. Mycorrhiza-helping bacteria might be exploited to improve mycorrhization, and AMF to improve nodulation and stimulate PGPR (Khan 2006a). But the AMF cannot be grown in pure culture; all VAM inoculum must be grown on roots of an appropriate host plant. Their potential to enhance plant growth is well documented and recognized but not fully exploited. They are rarely found in nurseries due to the use of composted soil-less mixes, high level of fertilizer and regular application of fungicidal drenches. The potential advantages of the inoculation of nursery plants with AMF in agriculture, horticulture and forestry are not perceived by these industries as significant (Phillips 2017). This is partially due to inadequate methods for large-scale inoculum production. Pot culture in pasteurized soils has been the most widely used method for producing AMF inocula, but it is time consuming, bulky and often not pathogen free. To overcome these problems, soil-less methods such as aeroponic using atomising disc technology, improved aeroponic using latest ultrasonic nebulizer technology, hydroponic and axenic culture of AM fungi with transformed or non-transformed living roots of various hosts have been used successfully to produce AMF-colonized root inoculum (Sylvia and Jarstfer 1994; Mohammad et al. 2000; Khan 2007; Willey 2006) (for further references see Mohammad et al. 2002).

Our studies (Mohammad et al. 2004; Asif et al. 1997) reported improved growth of plants in a field containing low levels of P and a low population of indigenous AM fungi, when inoculated with commercially produced sheared-root inoculum of *Glomus intraradices*, indicating that the introduced AMF can compete with the indigenous AMF and benefit plant growth. Khan (1975a, b) may have been the first to demonstrate the potential of pre-inoculating plants with AMF and transplanting them into nutrient deficient field with its indigenous AMF population, but it is not known how long such introduced strains persist. The composition of soil microbiota, including indigenous and the introduced AMF community, and their interactions clearly have a relevance to mycorrhizoremediation of U-contaminated soils, but yet to be elucidated (Khan 2005a, b). Further research is also needed to investigate various chemical aspects of contaminant accumulation in the roots of the energy plants to be used for mycorrhizoremediation, the dynamics and persistence or decomposition of chelates and U-chelate complexes in the mycorrhizosphere, and other constrains of the processes of phytoaccumulation and phytostabilization (Fuentes et al. 2000). This knowledge may enable us to understand the soil and environmental remediation processes involved in U-contaminated site. We need to understand the mechanisms involved in U mobilization and its transfer in mycorrhizal non-food energy plants in order to develop future strategies to be used to optimize phytoremediation process involving AMF, i.e. mycorrhizoremediation.

5.5 Conclusion

In situ phytoremediation is an emerging technology to decontaminate U-contaminated soils and is becoming a fast field of research and development for application to radioactive waste. Many phytoremediation technologies and strategies can be employed to further implement this strategy of using plants to extract, immobilize, contain/or degrade contaminants from soil, water, or air, including PAHs, PCBs, TCE, TNT, TNT, metals, salt and radioisotopes. Commercial utilization of this green technology needs to be emphasized by industry and government to a broader and long-term management strategy (phytomanagement) to reclaim contaminated soils and water (Gerhardt et al. 2017). In practical application, integrated utilization of various remediation strategies discussed above should be based on many environmental, soil, contaminant factors in removing uranium contaminants from the contaminated environments efficiently and economically.

But before applying the phytoremediation strategy, using energy plants, to radionuclide active waste sites, we need answers to many fundamental questions which require further research on uranium-contaminated soil, its biogeochemical properties and the role of AM fungi play in enhancing growth and biomass production. There is also a need to identify more plants with increased resistance to radionuclides and better adapted to radiation toxicity. Transgenic fast-growing tailored to remediate trees like willow and poplar, will play an important role in phytoremediation technology. Phytoremediation strategy to decontaminate U-mining wastes is underused despite its proven success and potential (Gerhardt et al. 2017).

Using mycorrhizal bioenergy plants like vetiver grass and commercial hemp, as phytoremediation agents for uranium-contaminated soil remediation, will not only reclaim the polluted land for agricultural and commercial use at a fraction of a cost but also provide a sustainable solution to the global energy demand and reduce pressure on food crops by producing a large biomass as value added source of renewable energy and generate economic returns and employment as potential source for rural development. These plants are among the ideal dedicated plants for bioenergy production and mycorrhizoremediation of uranium-contaminated and degraded mine sites. AMF technology is a potential mechanism to significantly improve soil structure and its biodiversity, improve survival, growth and establishment of seedlings on nutrient-poor degraded lands, i.e. improve the restoration success of degraded mine sites (For literature, see Asmelash et al. 2016).

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Chapter 6
Phytoremediation of Metals by Aquatic Macrophytes

K. C. Manorama Thampatti, V. I. Beena, A. V. Meera and Amrutha S. Ajayan

Abstract Phytoremediation is a plant-based and cost-effective technology that could be the possible potential method for providing an alternative to current treatment technologies for wastewater and contaminated ecosystems. It also enjoys popularity with the general public as a green technology. Aquatic macrophytes showed great potential in the field of phytoremediation. They are important tools for heavy metal removal since it basically involves the extraction and translocation of contaminants to aerial parts or inactivation of these toxic metals in a system. In order to exploit its full potential, a comprehensive understanding is needed as to how metal uptake, transport, and trafficking across plant membranes and distribution, tolerance, sensitivity, etc., take place under different environments. Aquatic plants in freshwater, marine and estuarine systems act as receptacle for several metals and have tremendous scope for application in remediation of heavy metals in the environment. Uptake and removal of contaminant varies for each category of aquatic macrophyte, viz. free-floating, submerged and emergent. The mechanisms of metal uptake, role of phytoremediators in metal pollution abatement and progress made in the practical application of phytoremediation of metals by aquatic macrophytes are reviewed in this paper. The paper discusses the phytoremediation potential of most promising aquatic macrophytes for different metals, their practical applications for environmental clean-up and method for safe disposal of phytoextracted biomass.

Keywords Phytoremediation · Aquatic macrophytes · Contaminated ecosystems · Green technology · Heavy metals · Remediation · Disposal methods · Phytoextracted biomass

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6.1 Introduction

Metal contamination of aquatic systems is ubiquitous around the globe. Rapid growth in population and massive industrialization and urbanization in recent years has enhanced the metal pollution of the biosphere paving way for severe environmental menace, since these metals may find their way to the human and animal system through plants. The peculiar geographic position of wetlands makes them more prone to metal contamination. The conventional remediation approaches like alkaline precipitation, ion exchange columns, electrochemical treatment, coagulation, filtration and membrane technologies are not economical and may produce adverse impacts on aquatic ecosystems though they have some merits (Volesky 2001; Rai 2008b). Phytoremediation is a plant-based and cost-effective technology that could be the possible potential method for providing an alternative to current treatment technologies for wastewater and contaminated ecosystems (Erakhrumen 2007; Liu et al. 2007; Heckenroth et al. 2016). It is the use of plants and associated soil microbes to reduce the concentrations or toxic effects of contaminants in the environments and is a relatively recent technology which is perceived as cost-effective, efficient, novel, eco-friendly and solar-driven technology with good public acceptance (Rai 2009; Greipsson 2011; Ali et al. 2013; Ansari et al. 2016). It also enjoys popularity with the general public as a "green clean" alternative to chemical plants and bulldozers (Pilon-Smits 2005; Malik et al. 2015) since it reduces the demand placed on the environment during clean-up actions, otherwise known as the footprint of remediation, and avoid the potential for collateral environmental damage.

Aquatic macrophytes showed great potential in the field of phytoremediation (Rai 2009; Abbasi and Abbasi 2010; Etim 2012; Priya and Selvan 2014; Misra and Shukla 2016; Akhtar et al. 2017). They are important tools for heavy metal removal since it basically involves the extraction and translocation of contaminants to aerial parts or inactivation of these toxic metals in a system (Garbisu and Alkorta 2001; Lombi et al. 2001; Prasad and Freitas 2003; Rai 2008a; Etim 2012; Stephenson and Black 2014; Hearth and Vithanage 2015; Akinbile et al. 2016; Akhtar et al. 2017).

Phytoremediation technology was developed on the basis of certain plant species called hyperaccumulators, which had very high genetic potential to accumulate a larger amount of certain metals in plant parts which can be used for their removal from soil and water. The absorbed metals travel from root through cell sap and finally get precipitated in vacuoles or cell membrane, where it will not affect the plant growth (Cunningham and Ow 1996), and because of this ability, they are widely used for environmental clean-up.

The development of phytoremediation technologies for environmental clean-up especially wetland ecosystems has now advanced to a stage where site-specific solutions are being developed based on contaminant chemistry, geologic particle-size distribution and stratigraphy, and costs. Studies conducted in this field in the last three decades have identified several plants with good phytoremediation ability, and many are being explored for applications in phytoremediation and phytomining.

Molecular tools are being used for better understanding of the mechanisms of phytoremediation. In order to exploit its full potential, a comprehensive understanding is needed as to how metal uptake, transport, and trafficking across plant membranes and distribution, tolerance, sensitivity etc. take place under different environments (Arunakumara 2011). The mechanisms of metal uptake, suitable phytoremediators and progress made in practical application of phytoremediation of metals by aquatic macrophytes are discussed in this paper.

6.2 Phytoremediation—A Site-Specific Green Technology for Environmental Clean-Up

A. Baumann, a German botanist reported the phytoremediation ability of *Viola calaminaria* for Zn in 1885 (Baumann 1885). This was the first scientific report on phytoremediation. The term phytoremediation (*phyto* a Greek word meaning plant and *remedium* a Latin word meaning correct evil) is relatively new, though the technique was an age-old one, and its industrial and environmental applications are quite recent. It is defined as the efficient use of plants to remove, detoxify or immobilize environmental contaminants in a growth matrix (soil, water or sediments) through the natural biological, chemical or physical activities and processes of the plants (Chaney et al. 1997). Rhizosphere microorganisms also assist these processes. Here, a diverse collection of plant-based technologies that use either naturally occurring or genetically engineered plants is employed for cleaning contaminated environments (Chaney et al. 1997; Cunningham et al. 1997; Flathman and Lanza 1998; Mudgal et al. 2010; Mishra and Shukla 2016).

Phytoremediation is amenable to a variety of organic and inorganic compounds and may be applied either in situ or ex situ. In situ applications decrease soil disturbance and the possibility of contaminant from spreading via air and water, reduce the amount of waste to be land filled (up to 95%) and are low-cost compared with other treatment methods (Etim 2012). Success of these plants in phytoremediation is assessed by estimating the quantity of contaminants removed from the site. Many of such plants also serve as bioindicators and biomonitors, have proven to be excellent tools in phytoremediation studies and could provide information which cannot be derived from technical measurements alone (Markert et al. 2003; Prasad 2008, 2011).

The greatest progress in phytoremediation research has been made with metals (Salt et al. 1995; Blaylock and Huang 2000; Prasad 2008; Thampatti et al. 2016; Akhtar et al. 2017). At least 45 families have been identified to hyperaccumulate heavy metals. The dominating families that include hyperaccumulators are Asteraceae, Brassicaceae, Caryophyllaceae, Cyperaceae, Cunoniaceae, Fabaceae, Flacourtiaceae, Lamiaceae, Poaceae, Violaceae and Euphorbiaceae. Brassicaceae had the largest number of taxa, viz. 11 genera and 87 species. The most studied plant on phytoremediation is *Thlaspi* species. The different species are known to hyperaccumulate more than one metal, *T. caerulescens*—Cd, Ni, Pb and Zn; *T. goesingense*—Ni and Zn; *T. ochroleucum*—Ni and Zn; and *T. rotundifolium*—Ni, Pb and Zn (Jadia and Fulekar 2009).

Aquatic plants in freshwater, marine and estuarine systems act as receptacle for several metals and have tremendous potential for application in remediation of metals in the environment (Prasad and Freitas 2003). Aquatic macrophytes, viz. *Eichhornia crassipes*, *Hydrilla verticillata*, *Typha angustata*, *Ipomea aquatica*, etc., can remove heavy metals like Zn, Cu, Pb, Ni and Cd from lakes and maintain water quality (KAU 2008; Rai 2008a, b, Kamal 2011; Thampatti et al. 2016; Akhtar et al. 2017; Meera 2017). Uptake and removal of contaminant varies for each category of aquatic macrophyte, viz. free-floating, submerged and emergent. Uptake of inorganic compounds, ionic or complexed is mediated by active or passive uptake mechanisms within the plant and is facilitated by membrane transporters. Assimilated and absorbed contaminant is then transformed and detoxified by a variety of biochemical reactions in the plant system using versatile enzymatic machineries (Dhir 2013).

6.3 Phytoremediation Techniques/Processes

Several types of processes/techniques are involved in phytoremediation which will facilitate their degradation/removal from the environment leading to an environmental clean-up. These processes are very much interrelated and depended on the plant physiological process driven by solar energy. Basic information for what is now called phytoremediation comes from a variety of research areas including constructed wetlands, oil spills, degradation of organic compounds and heavy metal accumulation by plants and microorganisms. It has been studied extensively in research and small-scale demonstrations, but full-scale applications are currently limited in number.

Depending upon the process by which plants/microbes are removing or reducing the toxic effect of contaminants from the soil and water, phytoremediation technology is broadly classified into phytoextraction, phytosequestration, phytodegradation, phytostabilization, phytovolatilization, rhizoremediation, rhizofiltration and rhizodegradation.

6.3.1 Phytoextraction

Phytoextraction, also called phytoaccumulation, refers to the uptake and translocation of metal contaminants in the soil by plant roots with subsequent transport to the aerial plant organs (Chaney 1983; Salt et al. 1998; Lasat 2002; Sheoran et al. 2011; Rafati et al. 2011; Bhargava et al. 2012). Metal translocation to shoots is a crucial biochemical process and is desirable in an effective phytoextraction because the harvest of root biomass is generally not feasible (Zacchini et al. 2009; Tangahu et al. 2011). Hyperaccumulators which absorb unusually large amount of metals in comparison with other plants form the basis for phytoremediation (Hadi et al. 2014).

Phytoextraction is divided into two categories: natural and induced. Natural phytoextraction requires the use of plants that efficiently absorb metals from soil/growth matrices to roots and translocate them to shoot and store in non-phytotoxic forms in aerial portion (Pollard et al. 2002; Wuana and Okieimen 2011). Most of such plants are metal tolerant and possess very high root surface area (Lombi et al. 2001). They accumulate particularly high levels of the toxic contaminants throughout their lifetime, while induced phytoextraction approaches to enhance toxin accumulation by the addition of accelerants or chelators to the soil/growth matrices. Chemicals that used to induce hyperaccumulation are various acidifying agents (Kamnev and Lelie 2000; Chen and Cutright 2001), fertilizers and chelating agents (Huang et al. 1997; Lasat 2002). Among the chelating agents, ethylenediaminetetraacetic acid (EDTA) is most widely used to assist in mobilization and subsequent accumulation of soil contaminants such as lead, cadmium, chromium, copper, nickel and zinc (Chen et al. 2004) and lead and cadmium (Hadi et al. 2014), but the use of chelating agents is highly expensive (Chaney et al. 2002). However, despite the success of this technology, concerns are there regarding the enhanced mobility of metals and the potential risk of leaching to waterbodies (Cooper et al. 1999).

Inoculation with microbial cultures enhanced the phytoextraction ability of several hyperaccumulators. Application of *Pseudomonas fluorescens* or *Trichoderma virens* to acid sulphate soils enhanced the phytoextraction of Zn, Cu, Cd and Pb by *Eichhornia crassipes* (KAU 2009) grown under graded levels of respective heavy metals (Zn and Cu @ 0, 10, 20, 40 mg kg^{-1} of soil, and Cd and Pb @ 0, 5, 10, 20 mg kg^{-1} of soil).

Phytoextraction cannot be used as a primary treatment method for highly contaminated areas with heavy metals like Cd, Zn, Cr and Pb, because of the prolonged time required for the complete clean-up (Thampatti and Sudharmaidevi 2014).

6.3.2 Phytosequestration

Phytosequestration is the ability of plants to sequester certain contaminants in the rhizosphere through exudation of phytochemicals and on the root through transport proteins and cellular processes. It reduces the mobility of the contaminant and prevents migration to soil, water and air either by phytochemical complexation and precipitation in the root zone or by inhibiting the transport proteins and stabilizes contaminants on the root surface, or by vacuolar storage of contaminants and preventing their further translocation to the xylem (Prasad 2011).

Plant species growing on metal-contaminated sites have the potential for phytosequestration of metals. Phytosequestration ability of *Hydrilla verticillata*, *Marsilea quadrifolia* and *Ipomea aquatic* for Fe, Zn, Cu, Cr, Pb, Cd, Hg and As was reported by

Ahmad et al. (2011). *Eleocharis acicularis* is well adapted to contaminated aquatic systems and possess the ability to sequester Sb, As, Cu and Zn from contaminated water and accumulate in plant parts (Ha et al. 2009).

6.3.3 Phytodegradation

Phytodegradation, also called phytotransformation, is the breakdown of contaminants taken up by plants through metabolic processes within the plant, or the breakdown of contaminants external to the plant through the effect of enzymes like dehalogenase and oxygenase produced by the plants. It is not dependent on rhizospheric microorganisms (Vishnoi and Srivastava 2008). Complex organic molecules are broken down to simple molecules. Pollutants are degraded, incorporated into the plant tissues and used as nutrients (Suresh and Ravishankar 2004; Trap et al. 2005; Prasad 2011). Phytodegradation is limited to the removal of organic pollutants only since heavy metals are non-biodegradable (EPA 2000). Research is going on the phytodegradation of various organic pollutants including synthetic herbicides and insecticides, even genetically modified plants are being used for this purpose (Doty et al. 2007).

6.3.4 Phytostabilization

Phytostabilization or phytoimmobilization is the use of certain plant species to immobilize contaminants in the soil (Singh 2012) and groundwater through absorption and accumulation by roots, adsorption onto roots or precipitation within the root zone by root exudates which immobilizes and reduces the availability of soil contaminants (Wong 2003; Ghosh and Singh 2005; Yoon et al. 2006). Plants reduce the mobility and bioavailability of pollutants in the environment either by immobilization or by prevention of migration and reduce bioavailability for entry into the food chain (Vangronsveld et al. 1995).

By excreting special redox enzymes, plants skilfully convert hazardous metals to a relatively less toxic state and decrease possible metal stress and damage. This technique can be used to re-establish a vegetative cover at sites where natural vegetation is lacking due to high metal concentrations in surface soils or physical disturbances to surficial materials, thereby decreasing the potential migration of contaminants through erosion and there to groundwater (Berti and Cunningham 2000; EPA 2000; Suresh and Ravishankar 2004; Robinson et al. 2006; Erakhrumen 2007; Prasad 2011; Singh et al. 2012b). Combining shallow-rooted plants with hardy, perennial, dense-rooted or deep-rooting trees can be an effective combination for phytostabilization (Berti and Cunningham 2000). Plants like vetiver, reed and bamboo are highly useful in stabilizing the contaminants accumulated in the shorelines of rivers and lakes. They also protect the waterbodies form contamination by the running water and eroded materials (Prasad 2004, 2011).

Commelina benghalensis and *Cynodon dactylon* were found to extract large quantities of Fe and Al from acid sulphate soils. When the above plants were grown under graded doses of Fe (upto 900 mg kg^{-1}) and Al (up to 500 mg kg^{-1}) in pots, they showed healthy growth without showing enhanced extraction with graded doses. They excluded the absorption of Fe and Al under high concentration, confirming their phytostabilization potential (KAU 2006, 2008). Leung et al. (2007) stated that *Cynodon dactylon* is a promising candidate for phytostabilization.

The mechanisms associated with phytostabilization are (1) accumulation of the absorbed metals in the roots (Wong 2003) or their immobilization in the rhizosphere itself (Meharg 2003), (2) mycorrhizal complexation by polyphosphates (Yang et al. 2005), (3) detoxification of metals in the rhizosphere by the secretion of organic acids (Quan et al. 2007; Brunner et al. 2008) or binding with pectins in the cell walls and to the negatively charged cytoplasmic membrane surfaces due to their strong electrochemical potential (Rengal and Zhing 2003; Kochian et al. 2005), (4) increasing the pH by root secretions (Vazquez et al. 2006) and (5) by the release of redox enzymes that convert toxic metals to less toxic forms (Ali et al. 2013). Plants that accumulate metals in high concentration in roots and restrict their translocation to shoots are good candidates for phytostabilization (Pignattelli et al. 2012). Metal excluders with minimum concentration in aerial plant parts are the ideal plants for phytostabilization (Kramer 2010) but their concentration should not exceed standards for agricultural products (Wei et al. 2005).

One of the advantages associated with this technology is that the disposal of hazardous material/biomass is not required and it is very effective when rapid immobilization is needed to preserve ground and surface waters. This method is particularly important in the remediation of As, Cd, Cr, Cu and Zn (Kunito et al. 2001). This clean-up technology has the disadvantage of contaminant remaining in the soil, and only their movement is limited. Hence, mandatory monitoring is required (Vangronsveld et al. 2009).

6.3.5 Phytovolatilization

It is the uptake and transpiration of a contaminant by a plant, with release of the contaminant or a modified form of the contaminant to the atmosphere from the plant (USEPA 2000; EPA 2000; ITRC 2009; Malik and Biswas 2012; Marques et al. 2009). In this process, the soluble contaminants are taken up with water by the roots, transported to the leaves and volatized into the atmosphere through the stomata (Newman et al. 1997; Davis et al. 1998) as biomolecules (Marques et al. 2009). Phytovolatilization may also entail the diffusion of contaminants from the stems or other plant parts that the contaminant travels through before reaching the leaves (Raskin and Ensley 2000).

Phytovolatilization can occur with contaminants present in soil, sediment or water. Mercury, selenium and arsenic are the primary metal contaminants that undergo phytovolatilization. Mercuric ion is transformed into a less toxic substance “elemental

Hg” through enzyme mercuric reductase and ultimately volatilizes to atmosphere (Rugh et al. 1998a, b). Se gets volatilized following its conversion to dimethylselenide by microbes and algae (Neumann et al. 2003). Se has been assimilated into organic seleno amino acids, seleno-cysteine and seleno-methionine which later can be biomethylated to form volatile compound dimethylselenide (Terry et al. 2000) which is released to atmosphere. Arsenic was successfully volatilized from the fronds of *Pteris vittata* in the form of arsenite and arsenate (Sakakibara et al. 2011).

But the practical application of phytovolatilization is questioned due to the release of toxic volatile compounds to the atmosphere which is likely to be recycled by precipitation and then redeposited back into lakes and oceans, repeating the production of methylmercury by anaerobic bacteria (Lin et al. 2002; USEPA 2000). Phytovolatilization is the most controversial of phytoremediation technologies (Padmavathiamma and Li 2007).

6.3.6 Rhizofiltration

This is mainly used to remediate extracted groundwater, surface water and wastewater with low contaminant concentrations. Rhizofiltration is the adsorption or precipitation of contaminants onto plant roots or absorption into the roots that are in solution surrounding the root zone (Dushenkov et al. 1995; Dushenkov and Kapulnik 2000; EPA 2000; Abdullahi 2015). The plants to be used for clean-up are raised in greenhouses with their roots in water rather than in soil and have to be acclimated before taking them to the contaminated fields. The plants are then planted in the contaminated area, and the roots extract the contaminants along with water. As the roots become saturated with contaminants, they are harvested and incinerated. Rhizofiltration can be used for Pb, Cd, Cu, Ni, Zn and Cr which are primarily retained within the roots (USEPA 2000; Surriya 2015; Galal 2017).

Rhizofiltration removes contaminants from water and aqueous waste streams, such as agricultural runoff, industrial discharges and nuclear material processing wastes (Salt et al. 1998; Henry 2000; Suresh and Ravishankar 2004). Absorption and adsorption by plant roots play a key role in this technique, and consequently, large root surface areas are usually required. *Eichhornia crassipes* an invasive weed of Vembanad wetlands, India, was very successful in removing Zn, Fe, Cd and Pb from the contaminated backwater system. *E. crassipes* and *Pistia stratiotes* removed Fe, Al, Cd, Pb and S from contaminated water through rhizofiltration (KAU 2009). *E. crassipes* (Nateewattana et al. 2010), and *Lemna minor* (Favas et al. 2012) are commonly suitable for rhizofiltration.

Ali et al. (2013) had classified rhizofiltration under phytofiltration which is the removal of pollutants from contaminated surface waters or wastewaters by plants (Mukhopadhyay and Maiti 2010). According to Mesjasz-Przybylowicz et al. (2004), phytofiltration may be rhizofiltration (use of plant roots) or blastofiltration (use of seedlings) or caulofiltration (use of excised plant shoots; Latin caulis = shoot).

The advantages of rhizofiltration are the ability to use both terrestrial and aquatic plants for either in situ or ex situ applications. Here, the contaminants do not have to be translocated to the shoots, and hence, apart from hyperaccumulators, other species can also be used (Raskin and Ensley 2000). The disadvantages are as follows: plants may first need to be grown in a greenhouse or nursery; there is periodic harvesting and plant disposal; tank design must be well engineered; and a good understanding of the chemical speciation/interactions is needed (USEPA 2000).

6.3.7 Rhizodegradation

Rhizodegradation also called enhanced rhizosphere biodegradation or phytostimulation is the breakdown of contaminants in the soil/plant root zone through microbial activity that is enhanced by the presence of plant exudates in the rhizosphere and is a much slower process than phytodegradation (USEPA 2000; Kuiper et al. 2004; Mukhopadhyay and Maiti 2010; Yadav et al. 2010). It is more useful for the degradation of organic chemicals (Zhuang et al. 2005).

Rhizosphere extends about 1 mm around the root and is under the influence of the plant (Pilon-Smits 2005). The increase in the number of microbes and their increased metabolic activities in the rhizosphere results in enhanced degradation of pollutants. A 10- to 100-fold increase in microbial activity was observed in the rhizosphere by the secretion of exudates containing carbohydrates, amino acids, flavonoids and nutrients. In addition to secreting organic substrates for facilitating the growth and activities of rhizospheric microorganisms, plants also release certain enzymes capable of degrading organic contaminants in soils (Kuiper et al. 2004; Yadav et al. 2010).

6.3.8 Rhizoremediation

Plants rather than doing the degradation create a niche for rhizosphere microorganisms to do the degradation of soil contaminants. Such plants harbour unique metal tolerant and resistant microbial communities in their rhizosphere who secrete plant growth-promoting substances/siderophores or phytochelators to alleviate metal toxicity. They help to take up minerals and pollutants, produce hormones and vitamins and degrade organic compounds and sequester metals (Thijs and Vangronsveld 2015). Soil pollutants that are remediated by this method are generally organic compounds. It has emerged as the most suitable method for petroleum-impacted soils. It can be promoted by the proper selection of suitable plant–microbe combinations, and its overall efficiency can be enhanced by adding suitable soil amendments (Hussain et al. 2018). Root exudates and root turnover can serve as substrates for microorganisms that perform pollutant degradation. Selection for organisms that may be useful in rhizoremediation has been attempted with good success and is proven to be economical, efficient and easy to implement under field conditions (Kuiper et al. 2004; Kamaludeen and Ramasamy 2008). Among the rhizosphere microorganisms involved in plant interactions with the soil milieu, the PGPR and arbuscular mycorrhizal fungi (AMF) have gained prominence all over the world to treat soil (Ma et al. 2011). Hansda et al. (2014) confirmed the favourable effect of PGPR on metal toxicity alleviation.

Ali et al. (2013) had added another technology, i.e. phytodesalination under phytoremediation. Phytodesalination is a recently reported and emerging technique (Zorrig et al. 2012). It refers to the use of halophytic plants for removal of salts from salt-affected system to support normal plant growth (Manousaki and Kalogerakis 2011; Sakai et al. 2012). Halophytic plants have been suggested to be naturally better adapted to cope with heavy metals compared to glycophytic plants (Manousaki and Kalogerakis 2011). Halophytes like *Suaeda maritima*, *Sesuvium portulacastrum* (Ravindran et al. 2007) and *Hordeum vulgare* were able to decrease salinity and sodicity of the phytodesalinized soil significantly (Rabhi et al. 2010).

Among the different phytoremediation techniques, phytoextraction is the main and most useful one for the removal of heavy metals and metalloids from polluted soils, sediments or water (Cluis 2004; Cherian and Oliveira 2005; Milic et al. 2012). It is the most promising for commercial application (Sun et al. 2011). The efficiency of phytoextraction depends on many factors like bioavailability of the heavy metals in soil, soil properties, speciation of the heavy metals and plant species concerned (Table 6.1).

Table 6.1 Summary of the different techniques of phytoremediation

Technique	Description
Phytoextraction	Uptake and translocation of metal contaminants in the soil by plant roots with subsequent transport to harvestable biomass mainly shoots
Phytosequestration	Sequestration of contaminants in the rhizosphere through exudation of phytochemicals and on the root through transport proteins and cellular processes
Phytodegradation	Degradation of organic xenobiotics by metabolic processes within the plant or contaminants external to the plant by enzymes
Phytostabilization	Immobilization of pollutants in soil by plant roots and reduce their bioavailability
Phytovolatilization	Conversion of pollutants to volatile form and their subsequent release to the atmosphere
Rhizofiltration	Sequestration of pollutants from contaminated waters by plants
Rhizodegradation	Degradation of organic contaminants in the rhizosphere by rhizospheric microorganisms
Rhizoremediation	Degradation of soil contaminants by unique metal tolerant and resistant microbial communities in the rhizosphere
Phytodesalination	Removal of excess salts from saline soils by halophyte

6.4 Selection of Plants

De Stefani et al. (2011) and Iulia (2015) suggested that the selection of plants for phytoremediation is highly important. The selected plants should be fast-growing and have high ability for the uptake of organic/inorganic pollutants (Roongtanakiat et al. 2007). The ability of pollutant removal varies from plant to plant and species to species within a genus. It is mainly determined by two key factors, i.e. shoot metal concentration and shoot biomass (Li et al. 2010). The rate of photosynthetic activity and plant growth are the major factors to be considered apart from the hyperaccumulation capacity while implementing a phytoremediation programme (Cunningham et al. 1995; Singh et al. 2003; Jamuna and Noorjahan 2009; Badar et al. 2012; Srivastava et al. 2016). Ideal characters for phytoremediators can be summarized as given below (Tong et al. 2004; Adesodun et al. 2010; Sakakibara et al. 2011; Shabani and Sayadi 2012; Ali et al. 2013).

(i) High growth rate,
(ii) Production of more above-ground biomass,
(iii) Widely distributed and highly branched root system,
(iv) More accumulation of the target heavy metals from soil (bioconcentration factor > 1),
(v) Translocation of the accumulated heavy metals from roots to shoots (translocation factor > 1),
(vi) Tolerance to the toxic effects of the target heavy metals,
(vii) Good adaptation to prevailing environmental and climatic conditions,
(viii) Resistance to pathogens and pests,
(ix) Easy cultivation and harvest,
(x) Repulsion to herbivores to avoid food chain contamination.

Phytoremediator plants can be tolerant, indicator, excluder or hyperaccumulator. Though all have some tolerance mechanisms to contaminated situations, studies have shown the genetic distinction of the mechanisms involved in (Assuncao et al. 2001; Warrier and Saroja 2002; Bert et al. 2003).

Hyperaccumulators take up particularly high amounts of a toxic substance, usually a metal or metalloid, in their shoots during normal growth and reproduction (Baker and Whiting 2002). The metal/metalloid concentration that must be accumulated by the plant before it is designated as "hyperaccumulator" depends upon the particular metal or metalloid in question. Baker and Brooks (1989) defined threshold concentrations for metals hyperaccumulated in plants as 100 $\mu g\ g^{-1}$ dry weight for As and Cd, 1000 $\mu g\ g^{-1}$ dry weight for Ni, Cu, Co, Pb, and 10,000 $\mu g\ g^{-1}$ dry weight for Zn and Mn. The defined levels of these elements are typically at a concentration of one order of magnitude greater than those found in non-accumulator species. Such plants have evolved biological mechanisms to restrict, tolerate or thrive on toxic metalliferous conditions (Whiting et al. 2002). However, excessive accumulation of these metals can be toxic to most plants (Salt et al. 1998; Etim 2012).

Distribution and accumulation pattern of heavy metal ions varies with plant parts and plant species. Heavy metals, Zn and Cd, were accumulated in higher concentration in the roots for *E. crassipes* and *Pistia stratiotes*, while Cu was concentrated more in leaves for *P. stratiotes* (Iulia 2015). The nature of the plant, different metal accumulation and defence mechanism is responsible for this varied behaviour. Literature reports showed that various species have unique ecophysiological behaviour and capacity to accumulate heavy metals which can compartmentalize efficiently in the cell wall, vacuoles or in other specific subcompartments of the cytosol in order to keep them away from active metabolic sites in plant cells (Memon and Schroder 2009).

Though hyperaccumulators are found in about 45 different families, with the highest occurrence among the Brassicaceae, the performance of many plant species are not satisfactory for the clean-up of heavily contaminated systems (Reeves and Baker 2000; Ali et al. 2013). But biotechnological methods can be used to develop plants with even better characteristics for phytoremediation such as the ability to accumulate multiple metals (McIntyre 2001; Eapen and D'Souza 2005; Ali et al. 2013). These advances are promising for improving the effective use of phytoremediation technology for cleaning up the soil of even highly contaminated sites.

6.5 Mechanism of Metal Uptake and Accumulation

Metal accumulating plants showed a range of mechanisms at cellular and molecular level that might be involved in the general homeostasis, detoxification and tolerance to metal stress (Hall 2002). The four processes that are crucial for metal accumulation are metal uptake by roots, transportation from roots to shoot, complexation with chelating molecules and compartmentalization into the vacuole (Hall 2002; McGrath and Zhao 2003).

Hyperaccumulators protect themselves from metal poisoning by a mechanism through which the heavy metal entering the cytosol of the cell is either immediately excluded or complexed and inactivated, thus protecting the catalytically active or structural proteins (Shah and Nongkynrih 2007). Heavy metal stress induced a decrease in photosynthetic pigments (Chlorophyll a and b), synthesis of new proteins or degradation of existing proteins but activated the defence mechanisms involving the ascorbate–glutathione cycle (Iulia 2015).

Plants take up heavy metals through their roots and in cases of submerged plants via their leaves also. Controversial interactions take place when the plants are exposed to more than one metal: synergistic or antagonistic effect, which can be explained by the competition or association of the heavy metals for the binding sites at membrane transporters, at metalloenzymes, at metallothioneins or at other target molecules with metal sensitivity (Sharma et al. 1999). Iulia (2015) reported enhanced phytoaccumulation capacity for the aquatic plants, *E. Crassipes* and *P. stratiotes* during the phytoremediation of multimetallic solutions than monometallic solutions, showing a synergistic effect on the uptake capacity. Quantity of bioavailable form of the metal is also very important that decides the metal extraction by plants (Vamerali et al. 2010). Metal availability and mobility are also influenced by rhizosphere microbes and root exudates.

6.5.1 Bioactivation of Trace Metals in the Rhizosphere

The bioavailability and plant uptake of heavy metals from substrate are predominantly controlled by metal content, pH, oxidation state of the mineral components, redox potential of the system, cation exchange capacity, organic substances and other elements in the rhizosphere. The rhizosphere provides a complex and dynamic microenvironment where microorganisms, in association with roots, form unique communities that have considerable potential for the detoxification of hazardous waste compounds, and their interaction can improve metal bioavailability in the rhizosphere through the secretion of protons (Ghosh and Singh 2005), organic acids (Ma et al. 2001), metal chelates (Ryan et al. 2001), phytosiderophores (Huang et al. 1998; Nair et al. 2007; Devez et al. 2009), phytochelatins, amino acids and enzymes (Abou-Shanab et al. 2006) and by microbial assistance (Khan et al. 2000).

But no plant species have been identified to handle high concentrations of toxic metals if they are present in solution. Hence, phytoremediator plants should be modified to handle the extreme situations.

6.5.2 Uptake into the Root

The metal uptake occurs in two pathways: extracellular (apoplastically), which is a fast process followed by intracellular (symplastically), which is a slow one. The apoplastic uptake takes place by physical and chemical sorption (adsorption) as well as by ion exchange processes. The intracellular uptake and the transport of the metals into the cells take place symplastically (Sune et al. 2007). Soluble metals can enter into the root symplast by crossing the plasma membrane of the root endodermal cells or they can enter the root apoplast through the space between cells. Some of the metals are transported into cells while some others are retained in the apoplast itself or bound to cell wall substances (Gregor 1999). Apoplast is an ion exchanger of comparatively low affinity and low selectivity. Transport systems and intracellular high-affinity binding sites such as channel proteins and or H^+ coupled carrier proteins then mediate and drive uptake of metal ions across the plasma membrane through secondary transporters such as channel proteins or H^+S^- coupled carrier proteins (Chaney et al. 2007). The membrane potential, negative on the inside of plasma membrane, may exceed −200 mV in root epidermal cells and provides a strong driving force for the uptake of cations through secondary transporters (Hirsch 1998). Inside the plant, most metals usually form carbonate, sulphate or phosphate precipitates, immobilizing them in apoplastic (extracellular) and symplastic (intracellular) compartments. Unless the metal ion is transported as a noncationic metal chelate, apoplastic transport is limited by the high cation exchange capacity of the cell walls (Raskin et al. 1997).

6.5.3 Translocation of Metals

Translocation into shoots is governed by the process of xylem loading, which could operate through cation–proton antiport, cation–ATPases or ion channel (Roberts and Tester 1995). Several chelators are involved in xylem translocation, including malate, citrate and histidine (Salt et al. 1995; Stephan et al. 1996; Von Wiren et al. 1999).

Once taken up by the plant, the movement of metal containing cell sap from roots to aerial parts is controlled by root pressure and transpiration pull (Robinson et al. 2003). The movement for efficient metal translocation to shoots requires radial symplastic passage and active loading into the xylem (Clemens 2006; Xing et al. 2008). Once loaded into the xylem, the flow of the xylem sap will transport the metal to the leaves, where it must be loaded into the cells of the leaf, again crossing a membrane. The cell types where the metals are deposited vary between hyperaccumulator species (Kupper et al. 1999).

For movement through xylem, which is more efficient, the metals must cross a membrane, probably through the action of a membrane pump or channel. Most toxic metals are thought to cross these membranes through pumps and channels intended to transport essential elements. Excluder plants survive by enhancing specificity for the essential element or pumping the toxic metal back out of the plant (Hall 2002).

Several cation transporters have been identified in recent years, most of which are in the ZIP (ZRT, IRT-like protein), *nramp* (natural resistance-associated macrophage protein), *ysl* (yellow stripe-like transporter), *nas* (nicotinamine synthase), *sams* (S-adenosyl-methionine synthetase), *fer* (Ferritin Fe (III) binding), *cdf* (cation diffusion facilitator), *hma* (heavy metal ATPase) and *ireg* (iron-regulated transporter) family (Guerinot 2000; Williams et al. 2000; Talke et al. 2006; van de Mortel et al. 2006; Kramer 2007; Memon and Schroder 2009).

6.5.4 Distribution, Detoxification and Sequestration of Metal Ion

The final step for the accumulation of most metals is the sequestration of the metal away from any cellular processes. Once the metals are translocated to shoot cells, they are stored in cellular sites, such as apoplast/epidermis/mesophyll/cell wall or vacuole, where the metal cannot damage the vital cellular processes. Cell walls play an important role in detoxifying metals in Ni/Zn/Cd hyperaccumulators. Vacuole is generally considered to be the main storage site for metals in plant cells. Compartmentalization of metals in the vacuole is an important part of the tolerance mechanism of some metal hyperaccumulator plants (Kramer et al. 2000).

At very high intracellular concentrations, plants catalyse redox reactions and alter the chemistry of these metal ions by converting it to less toxic forms. It is very evident in the case of metals with different oxidation states like As (Pickering et al. 2000) and Cr (Zayed et al. 1998). The metal can be detoxified by complexation with low molecular mass organic compounds during its uptake and transport. Different oxidation states of toxic elements have different uptake, transport and sequestration or toxicity characteristics in plants. Chelation of toxins by endogenous plant compounds can have similar effects on all of these properties as well. Citric, malic and oxalic acids have been implicated in the arrangement of processes, including differential metal tolerance, metal transport through xylem and vacuolar metal sequestration (Kramer et al. 2000; Shah and Nongkynrih 2007).

Two major types of heavy metal chelating peptides exist in plants—metallothioneins (MTs) and phytochelatins (PCs) which are involved in metal accumulation and tolerance. Plant PCs and MTs are rich in cysteine sulfhydryl groups, which bind and sequester heavy metal ions in very stable complexes in the cytosol which can be later sequestered into vacuole (Karenlampi et al. 2000; Cobbett and Goldsbrough 2002). PCs are small glutathione-derived, enzymatically synthesized peptides, which bind metals and are principal part of the metal detoxification system in plants (Goldsbrough 1999; Clemens 2001; Cobbett and Goldsbrough 2002; Yurekli and Kucukbay 2003; Fulekar et al. 2009). They have the general structure of (c-glutamyl-cysteinyl)n-glycine where $n = 2$–11 (Inouhe 2005). They are produced by the enzyme phytochelatin synthase (Sarma 2011). PC synthase is activated by various heavy metal ions with in vivo induction of PCs (Cobbett 2000).

MTs are gene-encoded, low molecular weights, metal-binding proteins, which can protect plants against the effects of toxic metal ions (Cobbett and Goldsbrough 2002; Fulekar et al. 2009; Jabeen et al. 2009; Sheoran et al. 2011). As many chelators use thiol groups as ligands, the sulphur (S) biosynthetic pathways have been shown to be critical for hyperaccumulator function (Pickering et al. 2003) and for possible phytoremediation strategies. Oxidative stress is one of the most common effects of heavy metal accumulation in plants, and the increased antioxidant capabilities of hyperaccumulators allow tolerance of higher concentrations of metals (Freeman et al. 2004).

By overexpression of natural chelators (PCs, MTs, and organic acids), not only metal ions' entrance into plant cell but also translocation through xylem is facilitated (Wu et al. 2010). Modification or over expression of GSH (glutathione) and PCS gene has significant potential for increasing heavy metal accumulation and tolerance in plants (Seth 2012). Studies are in progress to identify, isolate and characterize the biomolecules involved in the crossmembrane transport and vacuolar sequestration of heavy metals in plants. Advancement in such molecular studies will greatly help to improve our understanding of the complete mechanism of metal uptake, translocation and tolerance in plants, which in turn will help to enhance the efficiency of phytoremediation.

6.6 Aquatic Macrophytes Suitable for Phytoremediation

Aquatic macrophytes not only assimilate pollutants directly into their tissues, but they also act as catalysts for purification reactions by increasing the environment diversity in the root zone and promoting a variety of chemical and biochemical reactions that enhance purification (Jenssen et al. 1993; Vymazal 2002). They differ markedly in their potential to accumulate heavy metals (Rai et al. 1995; Wolterbeek and van der Meer 2002). The metal removal can be greatly enhanced by selecting appropriate plant species. Although the plants play a direct role in phytoremediation, their interaction with sediment microbes can play an equally important role by enhancing the efficiency of metal uptake by wetland plants (Olsen and Lorah 1998).

Aquatic macrophytes are broadly grouped into emergent, floating and submerged types. These three categories have varied phytoremediation capacities. The higher bioconcentration factor and translocation ability of heavy metals for free-floating macrophytes categorize them as efficient phytoremediators compared to emergent and submerged types (Ndeda and Manohar 2014). Plants like water hyacinth (*Eichhornia crassipes*), water lettuce (*Pistia stratiotes*), Duckweed (*Lemna minor*), Bulrush (Typha), vetiver grass (*Chrysopogon zizanioides*) and common reed (*Phragmites australis*) which possess the ability to remove heavy metals from aquatic systems have been studied in detail by many researchers and have been successfully implemented for the treatment of wastewater containing different types of pollutants (Lu et al. 2010; Dipu et al. 2011a, b; Girija et al. 2011; Akhtar et al. 2017).

During the last two decades, there have been many papers published/reviewed about aquatic macrophytes which remove toxic metals from polluted water (Maine et al. 2001; Miretzky et al. 2004; Hassan et al. 2007; Rai 2009; Sarma 2011; Ali et al. 2013; Mishra and Maiti 2017). Phytoremediation ability of most dominant aquatic macrophytes and their utilization for environmental clean-up are reviewed below.

6.6.1 Eichhornia crassipes *(Water Hyacinth)*

Eichhornia crassipes (Mart.) Solms, popularly known as water hyacinth, is an invasive aquatic perennial macrophyte belonging to the family Pontederiaceae. This erect free-floating macrophyte is a native of South America. It has rounded shiny green leaves, well-developed fibrous root system and very attractive purple flowers. It reproduces mainly through vegetative propagation (Verma et al. 2003). Fast-growing nature of this aquatic macrophyte presents quite contradictory effects—on the one hand, it is considered as a noxious weed affecting free navigation through waterbodies (Malik 2007) while on the other hand as an efficient bio cleaning agent to remove toxic metals from polluted ecosystem (Ebel et al. 2007; Rai 2016). The dry mass of the plant contains 5.2% N, 0.22% P, 2.3% K, 0.36% Ca, 280 mg kg^{-1} Fe, 45 mg kg^{-1} Zn, 2 mg kg^{-1} Cu and 332 mg kg^{-1} Mn (Koutika and Rainey 2015). The major characters that favour heavy metal accumulation by *E. crassipes* are expanded leaf area, profuse root system, unique survival capacity and stationary habitat (Baldantoni et al. 2004; Mishra and Tripathi 2008).

Among the seven species of water hyacinth,*Eichhornia crassipes* has been studied mostly for the purpose of phytoremediation (Tiwari et al. 2007; Melignani et al. 2015; Rai and Singh 2016) because of its rapid proliferation rate and high biomass production without showing much toxic symptoms (Malar et al. 2015; Melignani et al. 2015). It is listed as one of the most productive plants on earth and is considered one of the world's worst aquatic plants (Malik 2007).

E. crassipes is considered as a versatile phytoremediator because of its ability to decontaminate inorganic nutrients, toxic metals as well as persistent organic pollutants (Malik 2007; Ajayi and Ogunbayo 2012; Mishra and Maiti 2017). It successfully removed Cd, Ni and Fe from the polluted Ganges region of Ahmedabad, and the extent of accumulation was highest during the rainy season (Bais et al. 2015). It removed upto 600 mg As ha^{-1} day^{-1} under field conditions. The extensive removal of heavy metals by water hyacinth may be due to extensive adventitious root system, which absorbs these toxic substances from wastewaters (Alvarado et al. 2008).

E. crassipes is a good phytoextractor of Pb, Cu, Zn, Hg, Cd, Cr and Mn. Both root system and shoot system are involved in the removal of metals from the growth mediums like soil, sediment and water (Tiwari et al. 2007; Kumar et al. 2008; Rai 2009; Rai et al. 2010; Chatterjee et al. 2011; Fawzy et al. 2012; Gupta et al. 2012; Padmapriya and Murugesan 2012; Singh et al. 2012b; Patel 2012; Mishra et al. 2013; Sasidharan et al. 2013; Thampatti and Beena 2014). Several researchers reported the phytoremediation potential of *E. crassipes* for different heavy metals, viz. Hg (Skinner et al. 2007), Cu, Pb, Zn, and Cd (Liao and Chang 2004; Kumar et al. 2008; Rana et al. 2011), As (Islam et al. 2013), Pb (Xiaomei et al. 2004; Sukumaran 2013), Cu and Hg (Mishra et al. 2013), Cd, Ni, Fe and Mn (Khankhane et al. 2014), Fe and Cu (Ndimele et al. 2014), Cu (Preetha and Kaladevi 2014) Ni and Cr (Musdek et al. 2015), Zn and Cr (Swarnalatha and Radhakrishnan 2015), Fe (Thampatti et al. 2016) and, Mo, Pb and Ba (Romanova et al. 2016).

From a phytoremediation perspective, *E. crassipes* is a promising plant species for remediation of natural waterbodies/wastewater polluted with low levels of Zn, Cr, Cu, Cd, Pb, Ag and Ni (Odjegba and Fasidi 2007, Aina et al. 2012, Gupta et al. 2012, Rezania et al. 2015a, Prasad and Maiti 2016, Priyanka et al. 2017).

The heavy metal removing ability of water hyacinth has been widely utilized for the cleaning of waterbodies, drainage water and wastewater and contaminated as well as constructed wetlands. It had been utilized for the removal of Pb and Zn from paper industry effluent (Verma et al. 2005); Cr and Cu (Lissy and Madhu 2011) and Fe (Jayaweera et al. 2008) from wastewaters; Zn, Cu and Ni from drainage water (Hammad 2011) and industrial wastewater (Yapoga et al. 2013); Fe, Mn, Zn, Cu, Cd, Ni, Cr, Pb from composting water (Singh and Kalamdhad 2013); Fe, Al, Cd and Pb from wetland of Kuttanad (KAU 2009; Thampatti and Beena 2014), Cd (Ajayi and Ogunbayo 2012; Rai and Panda 2014); Fe, Al, Cd and Pb from freshwater lake (Meera 2017); and Cu from wastewaters from textile, pharmaceutical and metallurgical industries (Mokhtar et al. 2011). It can be effectively used for the treatment of aquaculture wastewater (Akinbile and Yusoff 2012).

E. crassipes varies in its ability to remove heavy metals from waterbodies. Liao and Chang (2004) ranked the heavy metal removal ability of water hyacinth as Cu > Zn > Ni > Pb > Cd. According to Shabana and Mohamed (2005) to treat one litre of wastewater contaminated with 1500 mg L^{-1}, As requires 30 g of dried water hyacinth root for a period of 24 h. Padmapriya and Murugesan (2012), during their study for the removal of heavy metals in aqueous solution using water hyacinth, found Langmuir and Freundlich models fitted well for the biosorption of all the metal ions.

Swain et al. (2014) recommended that the plant can be efficiently used to treat water contaminated with multimetal ions such as Cu and Cd where Cu accumulated mainly in shoot while Cd in root. Misbahuddin and Fariduddin (2002) and Alvarado et al. (2008) reported the phytoremediation potential of water hyacinth for As. About 73–98% of the metals assimilated by aquatic plants were accumulated in the roots, out of which nearly one-third to half portion adsorbed on root surface (Newete and Byrne 2016).

The detoxification mechanisms of the plant have also been reported by various researchers (Tokunaga et al. 1976; Gupta and Chandra 1998; Mishra and Tripathi 2009). The metal uptake capacity of water hyacinth and other aquatic macrophytes is affected by some biological and non-biological factors via plant species and different organs, season, pH, metal concentration and exposure time (Tokunaga et al. 1976). Jayaweera et al. (2008) reported that *E. crassipes* showed high phytoremediation efficiency for Fe and the Fe removal was mainly due to rhizofiltration and chemical precipitation of Fe $(OH)_3$ and Fe_2O_3. In addition, a key mechanism active efflux of Fe back to growth medium at intermittent period was observed by them in water hyacinth to prevent the Fe phytotoxicity. Kularatne et al. (2009) studied the removal mechanism of Mn by water hyacinth and reported that phytoextraction is mainly responsible for the removal of Mn, while the chemical precipitation mechanism was absent due to higher solubility of metal.

Li et al. (2015) tried to understand the molecular changes in water hyacinth on exposure to Cd stress and found that physiological and metabolic proteins were affected on exposure to Cd stress. However, analog proteins were induced to retain the corresponding functions, and water hyacinth could regain biomass much faster than *Pistia stratiotes*. In addition, some stress-resistant proteins like heat shock proteins (HSPs) and amino acids such as proline and post-translational modifications factors were found to be engaged in protection and repair of physiological and metabolic proteins. Consequently, the antioxidant enzymes significantly removed the excess reactive oxygen species which were formed in the plant body during Cd exposure.

Water hyacinth either as a live plant or as dead materials like dried root, activated carbon and ash derived from plant, acid-/alkali-treated plant and biochar was able for the sorption of contaminants from wastewater. The contaminants in the aqueous solution bind through the functional groups like alcohol, ketones, and aldehydes and other groups on the biosorbent surfaces at particular pH, and precipitation occurs (Ofomaja and Ho 2007). The biosorption was influenced by pH, dose of biomass, concentration of contaminants and temperature.

The high tolerance and affinity of *E. crassipes* for heavy metal accumulation are due to the high cellulose content and its functional groups including amino (–NH_2), carboxyl (–COO–), hydroxyl (–OH–), sulfhydryl (–SH) groups (Patel 2012). It contains several phytochemicals such as amino acids including glutamic acid, leucine, lysine, methionine, tryptophan, tyrosine, and valine, flavonoids including apigenin, azaleatin, chrysoeriol, gossypetin, kaempferol, luteolin, orientin and tricin which favour heavy metal absorption (Nyananyo et al. 2007).

The higher growth rate, pollutant absorption efficiency, low operation cost and renewability made *E. crassipes* as one of the ideal plant for phytoremediation of wastewaters (Isarankura-Na-Ayudhya et al. 2007). It is one of the most commonly used plants in constructed wetlands due to its fast growth rate and large uptake of nutrients and contaminants by root sorption, concentration and metabolic degradation (Guptha 1980). But the growth of water hyacinth poses a problem in the functioning of constructed wetlands due to its exotic invasive nature and rapid decomposition in comparison with other plants (Khan et al. 2000).

Since it is an invasive weed causing serious problems for navigation and irrigation, along with the implementation of phytoremediation technology, measures for controlling water hyacinth also should be carried out (Malik 2007). Its growth is limited by salinity, and hence in areas where there is saline water intrusion, its growth is arrested (Jafari 2010). It can also tolerate drought conditions and can survive in moist sediments for months (Center et al. 2002). However, this problematic aquatic weed, which is exceptionally difficult to control and eradicate from the waterbodies, has been routed for the phytoremediation of heavy metals due to its ability to remove metals from water. In the most recent years, the exploration of water hyacinth as the bioindicator for heavy metal removal present in the aquatic ecosystems has been demonstrated (Priya and Selvan 2014).

6.6.2 Pistia stratiotes *(Water Lettuce)*

Pistia stratiotes popularly known as water lettuce is a free-floating, small perennial aquatic macrophyte belonging to the family Araceae. It is widely distributed in the tropical and subtropical region of Asia, Africa and America. The active principles like alkaloids, tannins, flavonoids and phenolic compounds present in these aquatic plants help in their effective use for human therapy, veterinary (Lata 2010) and phytoremediation purposes (Aliotta et al. 1991; Kandukuri et al. 2009). It is capable of removing several heavy metals from water, including As (Farnese et al. 2014), and is commonly used as a phytoremediation agent for the wetland system (Prajapati et al. 2012).

The phytoremediation capacity of *P. stratiotes* for heavy metals like Pb, Cd, Cr and Co was assessed by Prajapati et al. (2012), Thilakar et al. (2012), Rijal et al. (2016) and Meera (2017). It is a very good phytoextractor of Pb, Cd, Cr and Co. Phytoremediation ability of *P. stratiotes* for heavy metals was reported by several researchers, viz. Cr, Cu, Fe, Mn, Ni, Pb and Zn (Lu et al. 2011); Cd and Pb (Vesely et al. 2011); Cu and Cr (Irfan 2015); Cr and Pb (Zhou et al. 2013); Cd (Das et al. 2014); lead(II) (Volf et al. 2014); and Hg, Cd, Mn, Ag, Pb and Zn (Ugya et al. 2015).

Metal accumulation of *P. stratiotes* in roots was about fourfold compared to that in leaves which clearly indicates the slow translocation rate of metals through the root system (Lee et al. 1991). Studies carried out to find out the phytoextraction ability of *P. stratiotes* for Al from acid sulphate soils of Kuttanad, India, revealed that it could survive under high levels of extractable Al up to 1000 mg kg^{-1} without affecting biomass production. Above 1000 mg kg^{-1}, it showed toxicity symptoms. Root accumulated more Al compared to shoot (KAU 2009). Meera (2017) also reported the Al extracting and accumulating ability of *P. stratiotes*, and Al was mainly accumulated in roots.

Sanità et al. (2007) reported the Cr phytoextraction ability of *P. stratiotes* and found an increase in the activity of antioxidant malondialdehyde and antioxidant enzymes superoxide dismutase and guaiacol peroxidase with increase in the concentration of Cr. Tewari et al. (2008) also observed an increase in antioxidant enzymes, guaiacol peroxidase, superoxide dismutase and level of lipid oxidation in Pistia for metal decontamination.

P. stratiotes is rated as a bioindicator of As in contaminated aquatic environments since it showed morphological, anatomical and physiological changes in response to increasing concentration of As (Farnese et al. 2013, 2014), and no such symptoms were produced under higher concentrations of other metals. It is more effective at lower concentrations.

6.6.3 Lemna Minor *(Duckweed)*

Duckweed is a small, free-floating aquatic plant belonging to the Lemnaceae family (Landolt 1998) consisting of five major genera: Lemna, Spirodela, Wolffia, Wolffiella and Landoltia. All of the species have flattened minute, leaf-like oval to round "fronds" of size about 1 mm to less than 1 cm across. Some species develop root-like structures in open water which either stabilize the plant or assist it to obtain nutrients where these are in dilute concentrations. It often forms dense floating mats in eutrophic ditches and ponds (Iqbal 1999; Driever et al. 2005; Elmaci et al. 2009; Patel and Kanungo 2017). The phytoremediation ability of duckweed depends on the growth conditions of the species, the type of pollutants and their concentrations.

Over the last 40 years, a great deal of research has been published on the use of duckweed to treat wastewater. It is highly suited to phytoremediation of heavy metals because of high reproductive rate, easy to culture and capacity to absorb a variety of metals principally through the fronds (Zayed et al. 1998; OECD 2002; Elmaci et al. 2009; Patel and Kanungo 2017). It was very effective in removing Cd, Se and Cu (Zayed et al. 1998; Hou et al. 2007; Khellaf and Zerdaoui 2009; Aina et al. 2012; Singh et al. 2012a, b; Chuudhary and Sharma 2014; Naghipour et al. 2015; Bokhari et al. 2016), Pb and Cr (Uciincii et al. 2013) and Se, As and rare-earth metals (Forni and Tommasi 2016) from contaminated water since it accumulates high concentrations of these elements. *L. minor* could effectively remove Cd (Wang et al. 2002), and Fe and Cu (Rai 2007) at low concentrations in laboratory experiments. It is a high phytoaccumulator of Cd and Pb (Verma and Suthar 2015) and Fe, Mn, Zn and Co (Amare et al. 2017).

6.6.4 Limnocharis flava *(L.) Buch (Velvet leaf)*

It is an emergent aquatic perennial herb native to Mexico and widely distributed in south and south east Asia belonging to the family Alismataceae. It grows in clumps with triangular-shaped leaves and hollow stem and produces three-lobed quite attractive yellow flowers. Reproduction is by seeds and vegetative means. Rapid rate of growth, huge biomass production and easy culture are the favourable factors that promote heavy/toxic metal alleviation property of this aquatic plant. It is a suitable aquatic macrophyte for the phytofiltration of low-level Cd contamination from water because it has higher bioconcentration factor, translocation factor, higher relative growth rate and biomass, and easy culture (Abhilash et al. 2009). It can change the hydrology of waterbodies by reducing the width of channels, thereby restricting water flow and creating silt traps.

It is a promising plant species for removal of Hg (Anning et al. 2013; Marrugo-Negrete et al. 2017); Fe and Mn (Anning et al. 2013; Kamarudzaman et al. 2012); Pb (Rachmadiarti et al. 2012); Cd (Rachmadiarti et al. 2012; Rijal et al. 2016); and Hg (Hui et al. 2017) from contaminated water and purification of aquaculture wastewater.

L. flava have been successfully proved to play an important role in the phytoremediation of contaminants through mechanisms such as phytoextraction, phytoaccumulation and rhizofiltration. Metal absorption by the plant increased with the exposure time according to first-order kinetics. The most functional part of *L. flava* as phytoremediation agent is the root, and the metals were mainly accumulated in roots (Wardani et al. 2017).

6.6.5 Hydrilla verticillata *(L.F.) Royle (Hydrilla or Star Vine)*

Hydrilla verticillata is a submerged, rooted aquatic plant that forms dense mats in a wide variety of freshwater habitats. It is usually a gregarious plant that frequently forms dense, intertwined mats at the water's surface. Approximately 20% of the plant's biomass is concentrated in the upper 10 cm of such a mat. Hydrilla has very wide ecological amplitude, growing in a variety of aquatic habitats. It tolerates moderate salinity up to 33% of seawater (Haller and Sutton 1975). It also grows well in both oligotrophic and eutrophic waters and even tolerates high levels of raw sewage. Sediments with high organic content provide the best growth, although it is found growing in sandy and rocky substrates (Mahler 1979).

H. verticillata effectively removed metals such as Pb (Gallardo et al. 1999), K, Na, Zn, Pb, Fe, Cd, Mg, Cu and Ca from contaminated water (Prusty et al. 2007; Kumar et al. 2008; Kameswaran and Vatsala 2017). Denny and Wilkins (1987) reported that shoots of *H. verticillata* are more efficient in phytoextraction of heavy metals. The sorption process followed first-order kinetics.

H. verticillata is a bioindicator of Cr pollution (Gupta et al. 2011). It removed Cd and Cr from solutions and accumulate them both in leaves and in roots. The removal was higher at low concentrations and decreased thereafter with increase in metal concentration. Long-term metal exposure adversely affected chlorophyll synthesis which indicates the inhibition of photosynthesis as a result of higher metallic concentration. Growth was not affected morphologically except dark brown and necrotic spots treated with the solution, which might be an early symptom of metal toxicity (Phukan et al. 2015).

Hassan et al. (2016) reported the phytoextraction ability of *H. verticillata* for Pb. Root accumulated more Pb than the stem and leaf. Even its non-living biomass could effectively remove Pb (II) from the aqueous solution containing a very low Pb (II) concentration by physical adsorption. Thampatti and Beena (2014) found *H. verticillata* as a good phytoextractor of Fe, Zn, Al and Cu from an acid sulphate wetland ecosystem.

6.6.6 **Monochoria vaginalis** ***(Burm.F.) (Oval Leaf Pondweed)***

It is an aquatic emergent weed seen usually as annual herb. But under continuous flooded conditions it may behave as perennial, characterized by long lanceolate to ovate leaves and showy blue to white bisexual flowers. It is widely distributed in freshwater habitats and belongs to the family Pontederiaceae. It is a common weed in rice fields and may reduce rice yield considerably. It is a rapidly growing, high biomass plant with an intensive root system and seems to be an ideal plant to clean up water and soil contaminant. This aquatic weed is well known for its phytoremediation potential for Cr, Cd and Cu (Kim et al. 2009).

All the plant parts of *M. vaginalis*, viz. leaves, rhizomes and roots, were identified as potential organs capable of accumulating Cu, Cr and Cd (Talukdar and Talukdar 2015). It is a promising phytoremediator for cleaning up of As-contaminated sites and is capable of accumulating Fe, Al and Pb in its shoot and root. The roots have higher metal accumulation potential (Mahmud et al. 2008).

6.6.7 Nelumbo nucifera *Gaertn (Indian Lotus)*

Nelumbo nucifera is a perennial emergent aquatic plant commonly seen in shallow waterbodies belonging to the family Nelumbonaceae. The large peltate leaves with long petioles float on the surface of water while the roots get anchored in the bottom of the waterbodies. The flower of this plant has got much-sacred value. The entire plant is having medicinal importance.

It hyperaccumulates heavy/toxic metals in its plant parts and thus alleviates the toxic effects of the polluted system in which it grows. Phytoaccumulation potential of lotus plant for Fe, Al, Pb and Cd was reported by Kumar et al. (2008), Kamal (2011) and Meera (2017). Metals were mainly accumulated in the root. Hyperaccumulation by *N. nucifera* for Mn was noticed in the leaves, Na in the petioles and Fe and Al in the rhizomes, without showing any toxicity symptoms (Obando 2012). The role of *N. nucifera* in reducing the hazardous effect of pollutants in wetland ecosystem was well substantiated. This ornamental plant tends to accumulate Cu, Cr, Pb, As and Cd (Hamidian et al. 2016). Its phytoextraction potential for Cd was reported by Mishra et al. (2009) and Kamal (2011); Sn, As and Cu by Ashraf et al. (2013), Meera and Thampatti (2016) and Rajoo et al. (2017).

6.6.8 Nymphaea nouchali *(Water Lilly)*

N. nouchali, a native of southern and eastern parts of Asia, belongs to the family Nymphaeaceae. It is a day-blooming nonviviparous plant with submerged roots and stems. Parts of the leaves are submerged, while others rise slightly above the surface. The leaves are large, rounded with darker underside. Flowers are highly attractive, violet or blue in colour and hence used as an ornamental plant. The epidermal glands on the submerged surface of leaf laminae, petioles and rhizomes act as metal accumulating sites. Accumulated metals get immobilized in the epidermal glands resulting in reduced translocation and high tolerance (Lavid et al. 2001).

Selective bioaccumulation of Zn and Pb was reported by Shuaibu and Nasiru (2011). Meera (2017) reported phytoextraction of Fe, Al and Cd by *N. nouchali.* The metals were mainly accumulated in roots showing a translocation factor less than one for all the three metals.

6.6.9 Trapa natans *(Water Chestnut)*

Trapa natans is a floating aquatic angiosperm that populates in natural wetlands. The plant spreads by the rosettes and fruits detaching from the stem and floating to another area on currents or by fruits clinging to objects, birds and animals.

T. natans have phytoremediative potential for Mn, and it is linked to induction of chelating phenolics in the floating leaves (Levin et al. 1990; Baldisserotto et al. 2004). Leaves are rich in phenolic compounds which include anthocyanin, and it plays a role in the mechanisms reducing the toxic effects of the metal (Levin et al. 1990; Hale et al. 2001). *T. natans* is Mn tolerant and is also characterized by Mn hyperaccumulation properties (Levin et al. 1990). In addition to the well-known ability to bioaccumulate Mn inside the fruit, it has been shown that *T. natans* exhibits peculiar Mn bioaccumulation inside specific tissues of the young floating lamina (Baldisserotto et al. 2004, 2007).

It was found to be very effective in improving physical, chemical and biological properties of municipal wastewater drained from activated sludge process plants. Treatment of wastewater with *T. natans* revealed that Cd, Cu, Fe, Mn and Zn were accumulated mainly in the leaves while Cr and Pb are in the roots (Kumar and Chopra 2018). *T. natans* accumulated Cu and Cd in the roots, shoots and fruits. But substantial amount of the metals was accumulated in the roots and shoots. However, both Cd and Cu were translocated to the fruits which are edible and thus showed a risk to contaminate the food chain and may also become hazardous for the human health if consumed (Rai and Sinha 2001; Bauddh et al. 2015).

6.6.10 Scirpus grossus *L. (Giant Bulrush)*

S. grossus is an emergent perennial tropical aquatic plant, belonging to the family Poaceae. It is a native of south east Asia and is widely distributed in the tropics and subtropics. It is a potential hyperaccumulator of Pb (Chuah et al. 2006; Tangahu et al. 2013; Marbaniang and Chaturvedi 2014). Tangahu et al. (2010) found a 100% survival of *S. grossus* up to the Pb concentration of 200 mg L^{-1} in sand culture study and 66.7% at a concentration of 350 mg Pb L^{-1} at the end of 7-week lead exposure. This effect increased with the increasing Pb concentration. Tangahu et al. (2013) rated *S. grossus* as a hyperaccumulator for Pb by carrying out sand culture studies. It can be used for the treatment of domestic wastewater (Jinadasa et al. 2006).

6.6.11 Bacopa monnieri *(Water Hyssop)*

It is a non-aromatic herb. The leaves of this plant are succulent, oblong and 4–6 mm thick. Leaves are oblanceolate and are arranged oppositely on the stem. The flowers are small, actinomorphic and white, with four to five petals. Its ability to grow in water makes it a popular aquarium plant. It can even grow in slightly brackish conditions. Propagation is often achieved through cuttings.

Potential of *Bacopa monnieri* to accumulate As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn has been reported by analysing the quantities of these elements in the naturally growing plants collected from different polluted areas of Kerala, India

(Hussain et al. 2010). *B. monnieri* cultivated in Hoagland medium artificially contaminated with micro-quantities of $HgCl_2$ and $CdCl_2$ revealed that its bioaccumulation potential is more for Cd than Hg. Absorption and translocation of Hg and Cd were proportional to the availability of the metal in the growth media and period of growth. The acidic pH enhanced the accumulation while basic pH significantly reduced the accumulation of Hg and Cd (Hussain 2007; Hussain et al. 2011). Phytoextraction ability of Bacopa for Cu, Cr, Fe, Mn and Pb was reported by Rai et al. (1995).

Thampatti et al. (2007) and KAU (2009) also revealed the phytoremediation potential of *B. monnieri* for Fe, Al, Zn and Cd. Fe and Zn were accumulated mainly in root and Cd and Zn in shoot portion. The metal extraction by the plants enhanced with increasing levels of the above metals in soil. The phytoremediation potential of *B. monnieri* has to be looked seriously since these plants possess high medicinal value and is an important ingredient of many ayurvedic preparations.

6.6.12 Hydrocotyle asiatica *(Asiatic Pennywort)*

Hydrocotyle asiatica an herbaceous, frost-tender perennial plant belongs to the family Apiaceae. It is native to wetlands in Asia. It is used as a culinary vegetable and as a medicinal herb. It is especially sensitive to biological and chemical pollutants in the water, which may be absorbed into the plant.

H. asiatica accumulates Fe, Al, Zn and Cd in both shoot and root. Fe and Zn were accumulated mainly in root and Cd and Zn in shoot portion. The metal extraction by the plants enhanced with increasing levels of the above metals in soil (Thampatti et al. 2007, 2016; KAU 2009; Thampatti and Beena 2014).

6.6.13 Phragmites australis *(Common Reed)*

It is an emergent aquatic macrophyte belonging to the family Poaceae. It is widely distributed in lakes, rivers and brackish waters across tropical and temperate regions of the world. It can withstand extreme environmental conditions, including the presence of toxic contaminants such as heavy metals (Ye et al. 1997; Baldantoni et al. 2004, 2009; Quan et al. 2007). This aquatic macrophyte can tolerate salinity upto 45 g L^{-1} (Cooper et al. 1996).

It acts as a biomonitor to assess the extent of pollution in its immediate environment (Bonanno and Giudice 2010) as indicated by the positive correlation between metal content in plant parts and that in water and sediment. The rate of metal accumulation was highest in roots and the lowest in leaves, suggesting low metal mobility within the plant.

Reed adsorbs many heavy metal ions from aqueous solution due to its high lignin and cellulose content (Srivastava et al. 1994). It can withstand toxic concentrations of heavy metals such as Zn, Pb and Cd (Bragato et al. 2006). It can be used in phytoremediation processes for As. The accumulation follows the order of root > rhizome > stem > leaves (Ghassemzadeh et al. 2008). It is a shoot accumulator for Cr, Fe, Mn, Ni, Pb and Zn and performed well in a laboratory comparison study with *Typha angustifolia* and *Cyperus esculentus*. Highest accumulation was observed for Fe (Chandra and Yadav 2011).

6.6.14 Azolla *Sp. (Water Velvet)*

Azolla is a floating aquatic fern and can grow in all kinds of fresh and wastewaters. It has nitrogen-fixing cyanobacterium *Anabaena* as symbiont. Different species of *Azolla* (*A. microphylla*, *A. pinnata* and *A. filiculoides*) can be used for treating Cr-contaminated wastewater. They grow well even under 10 μg Cr mL^{-1}. The metal accumulation varied from 5000 to 15,000 μg g^{-1} of biomass (Arora et al. 2006). Pectins present in the cell wall help to bind the heavy metals and aid in phytoremediation (Cohen-Shoel et al. 2002).

The capacity of Azolla to accumulate heavy metals like Cu, Cr, Ni, Hg and Zn (Rai 2008a; Rai and Tripathi 2009; Akinbile et al. 2016) enables the plant to be used in phytoremediation programme. *Azolla pinnata* could remove Hg and Cd from wastewater. Phytochelatin synthetase plays a key role in the detoxification of heavy metals, especially Cd absorbed by the plant, and increases tolerance (Liu et al. 2012). *A. filiculoides* is a high phytoaccumulator of Fe, Mn, Zn and Cu (Amare et al. 2017).

6.6.15 Colocasia esculenta *L. (Wild Taro)*

It is an emergent, perennial semi-aquatic macrophyte, native to south east Asia belonging to the family Araceae. It lives as a semi-aquatic-submerged plant which can be found commonly in swampy areas (Tumuhimbise et al. 2009). It grows to 1–1.5 m height and is characterized by large elephant ear-like leaves. This plant is fast emerging as a problematic aquatic weed in, India, but its higher growth potential enables the plant to be used in phytoremediation. It is a good phytoextractor of Pb and Cd and is very effective in the remediation of water polluted with lower concentrations of Pb and Cd (Bindu et al. 2009; Madera-Parra et al. 2015). Accumulated metals were bound to the root cells resulting in reduced translocation to the leaves. Reduction in biomass and chlorophyll production was noticed with increased concentration of metals and exposure time. The shoot portion of *C. esculenta* accumulated Zn at a rate more than 10,000 mg kg^{-1} with translocation factor > 1, confirming it as Zn hyperaccumulator (Chayapan et al. 2015).

C. esculenta showed phytostabilization potential for Cu, Pb, Mn, Fe and Zn (Mohotti et al. 2016). Similar results on remediation potential of this aquatic plant were given by Madera-Parra et al. (2015), Khatun et al. (2016) and Meera (2017).

It is considered as very effective in purification of aquaculture wastewater because of its ability to reduce the concentrations of Fe, Cd and P by greater than 50%, and accumulate Al, Fe and Cd at bioconcentration factor more than 1 (Hui et al. 2017).

6.6.16 **Echinochloa colona** ***(Jungle Rice L.)***

It is an emergent aquatic weed native to India widely distributed in tropical and subtropical regions, belonging to the family Poaceae. It is an erect herb with flat hairy stem and long, slender, alternate leaves. Flowers are bisexual, grouped together in a terminal spike or panicle, sessile, purple or brown, petals not visible (Khidir 1994). Kumar et al. (2008) reported its phytoextraction potential for Cd, Co, Cu, Ni, Pb and Zn. It is considered as a potential remediator of toxic pollutants like Cd, Cr and Pb (Subhashini and Swamy 2015; Amadi et al. 2018).

6.6.17 **Vallisneria natans** ***Lour (Eel Grass)***

It is widely distributed in tropical and subtropical regions of Asia, Africa and America and belongs to the family Hydrocharitaceae. It spreads by runners. This submerged aquatic plant is a good phytoextractor of Cd, Co, Cu, Ni, Pb, Zn, Cr, Fe and Mn (Kumar et al. 2008). Wang et al. (2009) reported its phytoextraction ability of metals from both water and sediment, rendering faster biocleaning of polluted ecosystem. Cr was accumulated in both root and shoot. It can be recommended for cleaning up of aquatic system polluted with As (Chen et al. 2015, 2017).

6.6.18 **Ipomoea aquatica** ***Forssk (Water Spinach)***

Ipomoea aquatic is a sprawling vine, annual or perennial, creeping on mud or floating on water. The stems are branched, hollow, rooting at the nodes and succulent when floating. Leaves are ovate-shaped, glabrous, alternate with long petioles and succulent when grown in water. Main source of reproduction is by vegetative means—stem rooting at nodes and also by stolons. It is native to Asia and now distributed throughout the tropical regions, belonging to the family Convolvulaceae.

It can be used for the removal of Cd, Co, Cu, Ni, Zn, Pb, Fe and Cr in polluted ecosystem (Prusty et al. 2007; Kumar et al. 2008). Phytoextraction potential of *I. aquatica* for Cu and Mn was proved by Mohotti et al. (2016). The suitability of this aquatic macrophyte for the purification of industrial effluents was confirmed based on the nutrient removal (99%) from palm oil mill effluent (Weerasinghe et al. 2008; Md Saat and Zaman 2017).

6.6.19 Nymphoides indica *L. (Marshwort)*

It is a perennial or annual herb with floating leaves, belonging to the family Gentianaceae. It occurs in a broad range of freshwater wetland types, including lakes, lagoons, swamps and margins of slow-flowing creeks and rivers (Calvert and Leissmann 2014). Meera (2017) reported *Nymphoides indica* as a phytoextractor of Fe, Al, Cd and Pb. The metals were mainly concentrated in root.

6.6.20 Salvinia molesta *D.S. Mitch. (Kariba Weed)*

It is a free-floating aquatic fern, native to south-eastern Brazil and characterized by dense mat-forming foliage. The fronds are in whorls of three with two floating and one submerged frond. *S. molesta* also called giant salvinia belongs to the family Salviniaceae. Its agricultural and ecological uses are already reported (Koutika and Rainey 2015).

The biosorption potential of *Salvinia* sp. for Cu was proved by Elankumaran et al. (2003) and Preetha and Kaladevi (2014). It could effectively remove Fe from contaminated water (Vandecasteele et al. 2005). Salvinia exhibits capacity for removing contaminants such as heavy metals, inorganic nutrients and explosives from wastewater. Properties such as high productivity, high sorption capacity and high metal removal potential establish Salvinia as an aquatic fern with immense potential for use in phytoremediation technologies (Dhir 2009).

The heavy metal removal and compartmentalization in *Salvinia* sp. are primarily a function of the presence of certain nutrients and chelants, with secondary dependence on environmental conditions (Olguin et al. 2003), though the mode of metal uptake varies depending upon the plant species and metal. The Cd uptake in salvinia occurs through biological mode while Cr and Pb follow the physical mode. Studies involving scanning electron microscopy microanalysis suggest direct sorption of heavy metals through leaves as they are in direct contact with the solution (Sune et al. 2007) and propose direct sorption as the main cause of increase in metal in the aerial parts (Maine et al. 2004).

High metal removal capacity of salvinia biomass has been attributed to great specific surface (264 m^2 g^{-1}) that is rich in carbohydrates (48.50%) and carboxyl groups (0.95 mmol g^{-1}) (Sanchez-Galvan et al. 2008). Proteins behave as important ligand atoms and also play an important role in metal sorption. The kinetics for the metal removal exhibit first-order rate, and equilibrium data fit well to both Langmuir and Freundlich's isotherms (Mukherjee and Kumar 2005).

Non-living biomass of salvinia exhibits equivalently high potential to remove heavy metals. The higher concentration of lipids and carbohydrates present on the plant surface acts as the cationic weak exchanger groups that contribute to metal sorption by ion exchange reactions. Sorption of heavy metals by dry biomass also follows the Langmuir isotherm (Schneider and Rubio 1999).

Many more native macrophytes possess hyperaccumulation and phytoremediation ability. But they have to be identified and their phytoremediation ability has to be estimated. Rather than using a single species, it is better to use consortium of aquatic macrophytes for the clean-up of an ecosystem. Farid et al. (2014) observed that cyclic phytoremediation using a series of aquatic plants found to be more effective than one single species.

6.7 Disposal of Phytoremediated Biomass

Harvesting and disposal of phytoremediated biomass is essential to prevent recycling of accumulated metals which are released during decomposition of wetland plants. The extent of uptake and how metals are distributed within plants greatly affect the residence time of metals in plants and the potential release of metals (Weis and Weis 2004). Hydrophytes such as *Ceratophyllum demersum*, *E. crassipes* and *Nuphar variegatum* undergo a more rapid decomposition compared with terrestrial species. Transfer and disposal of phytoremediated biomass is a noteworthy concern towards the effective usage of phytoremediation (Vajpayee et al. 2001; Dipu et al. 2011b; Raju et al. 2015). It is a big question that how to handle the phytoextracted biomass. Most common solution is burning. Such plants after burning can be either disposed as hazardous waste safely in specialized dumps or if economically feasible, processed for biorecovery of precious and semiprecious metals known as phytomining (Salt et al. 1998; Prasad 2003; Lone et al. 2008; Jadia and Fulekar 2008, 2009; Sheoran et al. 2011).

Conversion of the waste biomass to valuable materials such as compost (Sahu et al. 2002) or biogas (Rai 2007; Thilakar et al. 2012) is ideal for the recycling of phytoextracted metals in an eco-friendly manner. Composting and vermicomposting are the best-known processes for biological stabilization of green waste by transforming them into safer and more stabilized composts that can be used as a soil conditioner in agricultural applications (Gabhane et al. 2012). Composting results in efficient reduction of biomass (Cao et al. 2010). Composting of contaminated biomass of water hyacinth showed that heavy metals are largely confined to unavailable residual position, and the addition of FYM can further reduce the mobility of metals (Singh and Kalamdhad 2013). Reduced metal availability with composting was also reported by Reyes and Cuevas (2015). Application of water hyacinth compost resulted in higher yield for amaranthus, and there was no heavy metal accumulation (Sasidharan et al. 2013), while for tomato it had positively affected plant growth but not on tomato fruit production. Heavy metal concentration in tomato was below the MPL for Pb, Cu and Zn, and an application rate of 74 t ha^{-1} was found to be most promising (Mashavira et al. 2015).

The phytoextracted biomass of both *P. stratiotes* and *S. natans* was effectively used for the production of biofuels, viz. bio-ethanol and bio-methanol, using genetically engineered microbes. In this manner, pollution can be mitigated and aquatic ecosystem can be protected (Thilakar et al. 2012).

Uptake of heavy metals by plants and subsequent accumulation along the food chain is a potential threat to animal and human health. Addition of lime while composting the sewage sludge reduced the availability of heavy metals (Wong and Selvam 2006). Contaminated soil mixed with compost will result in less mobility of metals and become relatively unavailable for plant uptake. Humic and fulvic acids of the compost present complexation surfaces or ligands for effective binding of Cu (Fontanilla and Cuevas 2010). It resulted in minimal translocation of Cu to the shoot from roots (Reyes and Cuevas 2015).

Combustion of biomass under reduced oxygen conditions produces black-coloured carbon-rich residue "biochar". Because of the large surface area and CEC, both organic and inorganic contaminants get adsorbed on its surface resulting in reduced mobility in soil. Combined use of compost, manure and biochar can be the best mechanism for reducing pollution hazards in soil (Beesley et al. 2011). Houben et al. (2013a) suggested the conversion of phytoextracted biomass to biochar for its safe disposal and to the production of bioenergy. Meera (2017) was also of the same opinion. Houben et al. (2013b) recommended biochar application for *in-situ* metal immobilization. Use of biochar as an amendment in contaminated soil decreased the bioavailability of Cd, Pb and Zn to rapeseed. Liming was also effective in reducing the bioavailability of Cd, Pb and Zn. Wu et al. (2017) also reported that combined application of biochar and compost acted synergistically on soil remediation and plant growth in sunflower.

Biochar incorporation has reduced the availability of Cd and Pb in soil while increased the plant available P and K. This has resulted in the efficient partitioning of these metals in soil with biochar application and also resulted in more biomass production (Park et al. 2011). Comparative evaluation of biochar and ash of metal-contaminated waste showed phytotoxicity with respect to the availability of Cu and increased soil pH. But biochar was able to retain more Pb in soil compared to ash (Lucchini et al. 2014). Hence, care should be taken during large-scale applications of biochar or ash and is better to identify the source of the materials. Phytoextraction of heavy metals from soil through hyperaccumulators and converting it to biochar offers double extraction of heavy metals from soil and limits the leaching losses from soil (Paz-Ferreiro et al. 2014; Brendova et al. 2015).

Khan et al. (2000) suggested phytomining or the recovery of accumulated trace metals from hyperaccumulators, but the recovery of metals is very costly (Toet et al. 2005). According to Keller et al. (2005), incineration is a viable option to treat the phytoextracted biomass and it is possible to recover the metal from the residues. Ashing of phytoextracted biomass is a suitable option, but the ash should not be used in agriculture. The ash serves as a "commercial bio-ore" to return an economic profit, a process known as phytomining (Nicks and Chambers 1995, 1998; Anderson et al. 1999). If plants are incinerated, the ash must be disposed of in a hazardous waste landfill or to be stored in appropriate area that does not pose a risk to the environment (Chaney et al. 1997; Cunningham et al. 1995; Sas-Nowosielska et al. 2003; Reddy et al. 2005; Ali et al. 2013; Meera 2017).

Though many of the aquatic macrophytes are good phytoextractors of heavy metals, the absence of timely harvest will lead to the release of the metals back to the water and the process repeats. Such plants cannot be used as animal feed or biofertilizer. The safest option is to produce biogas rather than using as fodder (Jesus et al. 2014; Nsanganwimana et al. 2014).

Meera (2017) tested the disposal methods like ashing, composting, vermicomposting and biochar production using the phytoextracted biomass of *E. crassipes* containing Fe, Al, Cd and Pb, by applying this to amaranthus. Among the tested methods, the metal recovery from the processed biomass by amaranthus was highest for ash and least for biochar. Biochar retained the toxic metals within the growing medium itself, suggesting the biochar production from phytoextracted biomass is a good disposal method. Further studies are required to find out the retention time of each metal in the biochar form and its release pattern to growing medium or water.

To address the challenge of bioaccumulation of heavy metals in contaminated sites, the strategy accomplishing sustainable phytoremediation is another option. It is the need of the present and future. Sustainable phytoremediation can be achieved by using assisted spontaneous growth of vegetation (Pandey et al. 2015).

6.8 Merits and Demerits of Phytoremediation

Phytoremediation is a promising approach for remediation of heavy metal-contaminated soils but it has some merits and demerits which are presented below.

6.8.1 Merits

1. Low-cost and higher aesthetic value,
2. Safe for the removal of toxic organics and heavy metals,
3. Eliminates secondary wastes,
4. Generation of recyclable metal-rich plant residue,
5. Applicability to a range of toxic metals,
6. Minimal environmental disturbance and public acceptance,
7. Plants with increased metal accumulation properties may also be utilized to enhance crop productivity in areas with suboptimal metal levels, or as fortified food and feed (Guerinot and Sal 2001).

6.8.2 Demerits

1. It takes more time for the clean-up since the phytoremediation efficiency of most metal hyperaccumulators is usually limited by their slow growth rate and low biomass production.
2. It is better suited to sites with low to moderate levels of metal contamination because plant growth is not sustained in heavily polluted soils. There is a risk of food chain contamination in case of mismanagement and lack of proper care (Warrier 2012).
3. Safe disposal or recycling of the phytoextracted biomass is the most limiting factor that lessens the exploitation of phytoremediation as a major technique for environmental clean-up.
4. For wetlands, seasonal occurrence of plants is also a problem apart from biomass disposal.
5. Adaptation of the technology is limited due to restricted number of target metals that can be extracted, limited depth that can be accessed by the roots, decline in phytoextraction efficiency under increasing metal concentrations and the lack of knowledge on the agronomic practices and management (Keller et al. 2003; Robinson et al. 2003; Audet and Charest 2007).
6. Also, the complexity of hyperaccumulation has not been fully understood, either at the tissue or at the subcellular level.

However, much progress has been made on techniques of phytoremediation. Further studies in this area are still needed in order to provide more and better convincing evidence of the remediation performance of aquatic macrophytes in larger scales.

6.9 Future Thrust

Phytoremediation is a relatively recent technology and is perceived as cost-effective, efficient, novel, eco-friendly and solar-driven technology with good public acceptance. It is an area of active current research. New efficient metal hyperaccumulators are being explored for applications in phytoremediation and phytomining. Molecular tools are being used to better understand the mechanisms of metal uptake, translocation, sequestration and tolerance in plants. However, more thrust has to be given on the following topics:

1. Metal uptake by hyperaccumulators at cellular level,
2. Rhizosphere studies to examine antagonistic and synergistic effects of different metal ions in soil solution and polluted waters,
3. Microbial studies to examine the contaminant availability and uptake,
4. Phytoremediation research and application have to be validated based on field studies,
5. Identification of new macrophytes with good phytoremediation ability,

6. Exploitation of genetic engineering for better phytoremediation ability,
7. Use of hyperaccumulators for production of bio/green-nanomaterials.

In future aspects of phytoremediation, the utilization of invasive plants in pollution abatement technologies can contribute towards sustainable management in treating wastewater (Rezania 2015b). In spite of the many challenges, phytoremediation is perceived as a green remediation technology with an expected great potential.

6.10 Conclusion

Metal decontamination of aquatic systems through phytoremediation is an environment-friendly green technology involving aquatic macrophytes which offers a cost-effective means for cleaning up. A comprehensive understanding of the mode of metal uptake, transport, and trafficking across plant membranes and distribution, tolerance and sensitivity of plants, etc., under different environments are highly essential for the successful implementation of environmental clean-up programmes through phytoremediation. Aquatic macrophytes are widely employed for the restoration of metal-contaminated or degraded aquatic systems. But their full potential is yet to be open up. Another problem to be addressed is the safe disposal of the phytoextracted biomass. To face these challenges, a joint approach of scientists, environmental engineers and science administrators is needed.

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Chapter 7
Phytoremediation Using Aquatic Plants

Jonathan Fletcher, Nigel Willby, David M. Oliver and Richard S. Quilliam

Abstract Freshwaters are affected by a diverse range of pollutants which increase the demand for effective remediation. Aquatic phytoremediation is a nature-based solution that has the potential to provide efficient, spatially adaptable and multi-targeted treatment of polluted waters using the ability of macrophytes to take-up, sequester and degrade pollutants. This chapter considers the primary phytoremediation mechanisms that macrophytes employ to remove inorganic, organic and biological waterborne pollutants before highlighting some of the common macrophyte accumulators that have been studied. Three common macrophyte planting systems (i) constructed wetlands (CWs), (ii) wild macrophyte planting/harvesting and (iii) floating treatment wetlands (FTWs) are considered to understand how macrophytes are deployed for targeted aquatic phytoremediation. Important practical considerations for implementing aquatic phytoremediation include the use of invasive species, the optimal harvesting time and frequency for pollutant removal with macrophyte biomass, and the full extent of the role that microbial biofilms play in phytoremediation. In this chapter, these issues are unpacked and recommendations for future programmes of research and development are made. Finally, the opportunities to generate 'added value' from expanding aquatic phytoremediation in terms of the provision of ecosystem services and the potential for resource recovery are outlined.

Keywords Macrophytes · Phytoremediation · Floating treatment wetlands · Resource recovery · Ecosystem services · Diffuse pollution

7.1 Water Contamination and Water Security

Surface waters are vital for supporting people and ecosystems; however, freshwater availability is under increasing pressure due to a growing human population requiring access to safe water (Heathwaite 2010). Global freshwater resources comprise 2.5%

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of the total global water budget, although only 0.0072% (93,120 km^3) of the total global waters are available for drinking, energy, food production and the industry sector (Lawford et al. 2013; Zimmerman et al. 2008). Tilman et al. (2011) predict that crop production will need to increase by 100–110% by 2050 to feed the growing population, leading to a global freshwater deficit of approximately 2400 km^3 per year (Rockström et al. 2014).

Many surface waters are currently of sub-optimal standards due to a range of stressors impacting freshwaters such as point source and diffuse pollution, land-use change and climate change, which further compounds the challenge of providing water security (Ormerod et al. 2010; Berger et al. 2017). One of the major pressures on water quality in the UK is nutrient enrichment from diffuse pollution (Ulén et al. 2007), whereas elsewhere in countries such as China, additional issues of heavy metal pollution are also prominent (Cheng 2003). Interactions between different stressors in space and time can also lead to additive effects (Heathwaite 2010); for example, increased land-use change towards intensive agriculture and a potential increase in storm frequency may increase the delivery of nitrogen (N) phosphorus (P) and fine sediment to receiving water (Dunn et al. 2012).

Table 7.1 summarises the surface water pollutants that are of concern and where remediation solutions are being developed. Water pollutants can be broadly categorised as either organic, e.g. hydrocarbons, pesticides and algal toxins, or inorganic, e.g. metals or synthetic and manure-based fertilisers containing excess amounts of N and P, or biological, e.g. pathogens and algal toxins. The mobilisation and effects of different pollutants have been discussed extensively elsewhere (Heisler et al. 2008; Ohe et al. 2004; Liess and Carsten Von Der Ohe 2005; Edwards 2015; Lintelmann et al. 2003). However, different pollutants may have multiple sources; for example, N and P can be released from agriculture, aquaculture and urban wastewater streams.

Managing waterborne pollutants through in situ best management practices (BMPs) that target the source of pollution is the principal approach to improving water quality (Lam et al. 2011). However, lag times associated with the improvement of water quality and subsequent ecological recovery of receiving waters following mitigation may range from 1 to >50 years (Meals et al. 2010). The 'legacy effect' is one such component delaying water quality improvements in spite of BMPs being in place (Haygarth et al. 2014). Water bodies, such as those with long residence times, may become reservoirs for pollutants over time, meaning that although source management is in place, the receiving waters remain high in pollutant levels for significant amounts of time (Meals et al. 2010). Therefore, developing management systems that combine BMPs with other methods of remediating waters with high levels of pollutants, both at source and throughout the catchment, is needed to sustainably improve water quality.

The pollution of water with inorganic elements such as N, P and metals also provides an opportunity to recover elements as part of a 'circular economy' approach (Masi et al. 2017; Quilliam et al. 2015). Energy-intensive mining for macronutrients such as P and potassium (K) is exhausting finite supplies of nutrients for the production of agricultural fertilisers (Jones et al. 2013), whilst liquid fertilisers and

Table 7.1 Key pollutants impacting the aquatic environment, organised by pollutant category, type and providing examples of the pollutants, their sources and impacts

Pollutant category	Pollutant type	Example pollutant	Sources	Potential impacts
Organic	Persistent organic pollutants (POPs)/xenobiotics	Dioxins, organochlorides, polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls	Industry Agriculture	Toxicity Endocrine disrupting effects
	Pesticides	Glyphosate Hexachlorocyclohexane Fenhexamid Deltamethrin	Agriculture Aquaculture	Toxicity Endocrine disrupting effects
	Pharmaceutical and personal care products (PPCPs)	Antibiotics Hormones Pain relief medication	Domestic Agriculture Aquaculture	Endocrine disrupting effects Antibiotic resistance Destabilising microbial communities
	Algal toxins	Microcystin-LR	Cyanobacterial algal blooms	Acute/chronic toxicity
Inorganic	Nutrients	Nitrogen (N) Phosphorus (P) Potassium (K)	Agriculture Aquaculture Septic tank inputs	Nutrient enrichment/eutrophication
	Metalloid elements	Iron (Fe) Aluminium (Al) Lead (Pb) Nickle (Ni) Cadmium (Cd) Copper (Cu) Uranium (U)	Agriculture Industry (mining and combustion of fossil fuels) Al mobilisation through acid rain	Toxicity Endocrine disrupting effects
Microbial	Pathogens and parasites	*E. coli* O157 *Cryptosporidium parvum*	Agriculture Aquaculture Domestic	Human illness (intestinal infection)

nutrient-rich solid manures applied to agricultural land are readily transferred to receiving waters. Coupling systems that remediate water pollution and enable the capture of these resources may help close the loop on nutrient loss (Quilliam et al. 2015). Therefore, macrophyte phytoremediation has the potential to be employed for both the sustainable remediation of surface waters and as a management strategy for recovering nutrients.

7.2 Aquatic Phytoremediation

Aquatic phytoremediation is a phytotechnology used for the removal of pollutants from surface waters and the restoration of impacted water bodies (rivers, streams, lakes, ponds). Within surface waters, plants can be cultured to remove pollutants from both the water column and the sediment (Newete and Byrne 2016; Miretzky et al. 2004) and can be deployed at either the point source, or within waterbodies where diffuse pollution is problematic (Lu et al. 2011). Aquatic phytoremediation specifically uses macrophytes (i.e. freshwater adapted angiosperms, pteridophytes and ferns) for removing and degrading pollutants within aquatic environments (Rai 2009). This definition does not include microalgae species. Macrophytes can be broadly classified into three primary growth forms: floating, submerged and emergent (Fig. 7.1). Floating macrophytes occupy the water surface and include genera such as *Lemna* (duckweeds), *Hydrocharis* (frogbit) and *Nymphaea* (water lilies) which may be free-floating or rooted. Submerged macrophytes grow primarily below the water surface and may be anchored to the substrate, although *Ceratophyllum* (hornwort) is a widespread genus of unrooted submerged plants. Emergent macrophytes occupy the margins of water bodies and are rooted into the substrate but have significant shoot growth above the water level, e.g. *Typha* (reedmace) and *Phragmites* (common reed). These different growth forms facilitate the removal of pollutants from both the water column and the sediment depending on the way in which they are deployed (Newete and Byrne 2016).

Macrophytes have a significant capacity for uptake of nutrients and other substances from their growth medium and can thus lower the pollution concentration of a target water body (Dhote and Dixit 2009). Macrophytes can remove and degrade pollutants using the key mechanisms of rhizo/phytofiltration, phytoextraction, phytovolatilization and phytodegradation (Table 7.2). Emergent and floating macrophytes primarily take-up nutrients and other contaminants (whether from the substrate or water column) through their roots, whereas stem tissue can also be an important pathway for the removal from the water column for submerged macrophytes (Denny 1972; Gabrielson et al. 1984; Dhote and Dixit 2009). Specific mechanisms for pollutant removal and degradation by macrophytes depend primarily on the type of pollutant (nutrient, heavy metals, organic pollutants, biological) and the location of the pollutant within the surface water body (water column, lake or streambed sediment) (Miretzky et al. 2004; Padmavathiamma and Li 2007; Vymazal 2011; Xing et al. 2013; McAndrew et al. 2016; Polechońska and Samecka-Cymerman 2016). Different mechanisms for removing various classes of the pollutant from surface water systems by macrophytes are considered below.

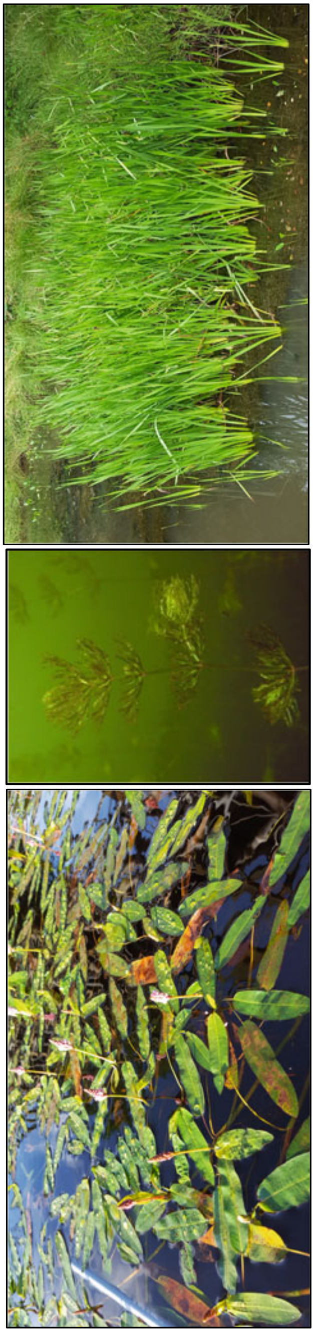

Fig. 7.1 Photograph examples of floating, submerged and emergent macrophyte life forms. From left to right: *Persicaria amphibia* (floating), *Ceratophyllum demersum* (submerged) and *Sparganium erectum* (emergent)

Table 7.2 Phytoremediation mechanisms

Mechanism	Medium	Contaminant category	Description	Accumulation part	Example genera
Rhizofiltration/phytofiltration	Water	Organics/inorganics/heavy metals	Extraction from contaminated water by adsorption/absorption	Shoots/roots	*Lemna*, *Hydrocharis*, *Eichhornia*
Phytoextraction/phytoaccumulation	Soil/water	Inorganics/heavy metals	Uptake by roots and translocation to upper parts	Shoots	*Juncus*, *Schoenoplectus*
Phytostablisation	Soil/sediment	Inorganics/heavy metals	Rendering contaminants immobile within soil matrix due to plant root action	Reduction in rhizosphere	*Chenopodium*
Phytovolatilization	Soil/sediment/water (less common)	Organics	Conversation of containments to volatile form	Atmospheric release	*Phragmites*
Phytodegradation	Soil/sediment/water	Organics/inorganics/microbiological	Degradation in rhizosphere through microbial degradation or by metabolism within plant	Degradation in rhizosphere/pollutant degraded in plant to less harmful metabolite	*Typha*, *Phragmites*, *Myriophyllum*

Adapted from Dhir (2013) and Rezania et al. (2016)

7.2.1 Macronutrients

It is important to note that elements targeted for phytoremediation may exist in a dissolved phase, or in a particulate phase adhered to suspended material in the water column or bound to sediment, which means there are different mechanisms for removal (Van der Perk 2006). Macronutrients, including N and P, are essential elements required in relatively large concentrations for plant metabolism (Hawkesford et al. 2011). Therefore, when aquatic system is enriched with N and P, phytoextraction (uptake and sequestration) is an important mechanism (Eid et al. 2012; Mkandawire and Dudel 2005). Particulate pollutants in the water column, such as P, can be stabilised by phytofiltration (Tanner and Headley 2011; Olguín and Sá Nchez-Galvá 2012), where plant roots may excrete exudates that assist phytoextraction of adsorbed elements (Jackson 1998; Verkleij et al. 2009; Akeel 2013). For N removal, phytodegradation may also be important in the water column and sediment as the oxygen and energy supplied to the root zone from macrophytes may support nutrient-degrading microbial communities, including the simultaneous presence of both nitrifying and denitrifying bacteria (Table 7.2) (Lu et al. 2018).

7.2.2 Micronutrients/Metals

Micronutrients are essential elements that are required by plants in relatively small quantities, e.g. to regulate redox reactions, metabolism and cell integrity (Broadley et al. 2011). Essential micronutrients include iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), molybdenum (Md) and boron (B); beneficial but non-essential micronutrients include sodium (Na), silicon (Si), cobalt (Co), selenium (Se); whilst there are elements that can be found in plant tissue but are not thought to be beneficial such as aluminium (Al) vanadium (V), titanium (Ti), lanthanum (La) and cerium (Ce) (Broadley et al. 2011) (Table 7.1). Some of these elements may be enriched by industrial pollution but can be reduced by phytoextraction through repeated harvesting of plant tissue, following uptake in the water column through hydroponic growth (e.g. in FTWs) or where plants are rooted in sediment (Ali et al. 2013) (Fig. 7.2). The efficiency of phytoextraction as a phytoremediation strategy depends upon the specific degree of essentiality of each element for plant metabolism and is determined by specific mechanisms for uptake and translocation into plant tissue (Dhir 2013). Hyperaccumulators are plants that have a high affinity for certain elements and through enhanced phytoextraction can sequester high concentrations of metals (Sarma 2011; Van der Ent et al. 2013). Phytofiltration is important for soluble and particulate pollutants with absorption/adsorption to plant roots (Olguín and Sá Nchez-Galvá 2012), and in some cases, metals can be bound and/or precipitated on the plant roots (Xian et al. 2010; Gomes et al. 2016) (Fig. 7.2).

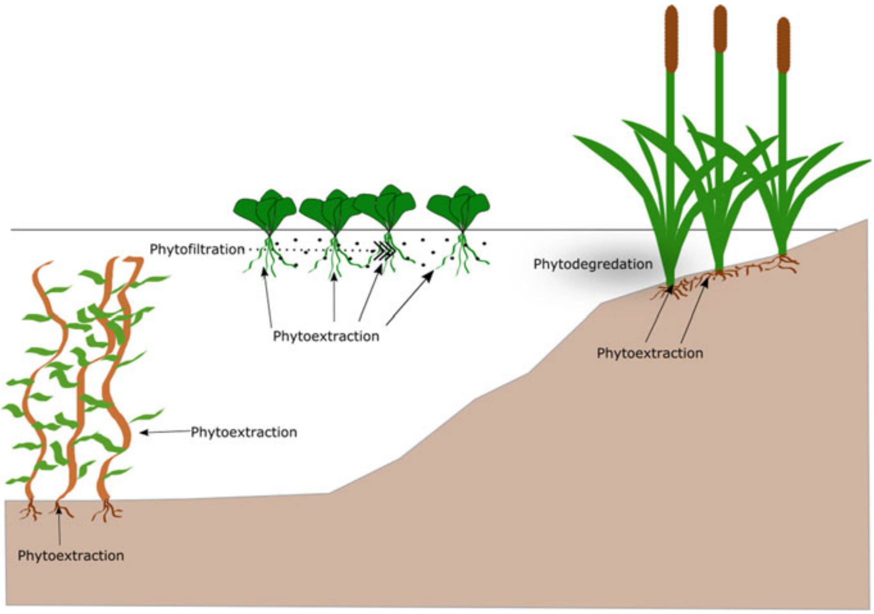

Fig. 7.2 Phytoremediation mechanisms used to degrade/remove waterborne pollutants, by growth form

7.2.3 Organic Pollutants

Organic pollutants are compounds containing carbon that are primarily synthetic, environmentally persistent and potentially toxic. They include products such as pesticides, solvents and pharmaceuticals and personal care products (PPCPs) (El-Shahawi et al. 2010) (Table 7.1). Phytometabolism and rhizodegradation within the water column and sediment are integral processes in the aquatic phytoremediation of organic compounds (Reinhold et al. 2010). Phytometabolism can occur if organic compounds are more hydrophilic meaning they pass more readily through the plant epidermis into plant cells (Lintelmann et al. 2003; Dettenmaier et al. 2009; Yamazaki et al. 2015) (Fig. 7.2). Sequestered compounds undergo chemical modification through oxidation, reduction or hydrolysis which makes them chemically more reactive within plant cells; the less harmful metabolite is then conjugated/bound to sugars, amino acids or glutathione to reduce its toxicity and hydrophobicity (Macek et al. 2000; Geissen et al. 2015). These bound metabolites may then be either stored within the vacuole or excreted from the plant or can become insoluble by being covalently bound within the cell wall (Zhang et al. 2014a, b). Rhizodegradation can take place within sediment, and more hydrophobic compounds can serve as a microbial carbon source where emergent macrophytes supply oxygen to the root zone (Fig. 7.2). The advantage of these two phytoremediation processes is that there is no need for repeated harvests to extract the pollutant and thus disturbance to the aquatic system is reduced.

7.2.4 Microbial Pollutants

Microbial water pollutants such as the bacteria *Escherichia coli* O157, the protozoan parasite *Cryptosporidium* spp. and viruses such as norovirus can cause harm to humans and animals (Haack et al. 2016; Fuhrimann et al. 2017) (Table 7.1). The ability of plants to directly take-up microbial pollutants is limited; however, there are some accounts of pathogens entering plant tissue through the process of internalisation, although whether this is an active or passive process is unclear and likely depends on the type of pathogen, plant and the local abiotic conditions (Hirneisen et al. 2012). The primary mechanisms for removal of microbial pollutants from water are either, chemical, e.g. oxidation, photodegradation, exposure to plant root biocides and adsorption to organic material and biofilms; physical, e.g. through filtration and sedimentation; or biological, e.g. predation, natural die-off, antibiosis and other biolytic processes (Decamp and Warren 2000; Karathanasis et al. 2003; Karim et al. 2004; Wand et al. 2006; Makvana and Sharma 2013). Macrophyte planting systems, particularly CWs, may promote these mechanisms and thus facilitate the degradation of microbial pollutants.

7.3 Macrophytes Used in Aquatic Phytoremediation

7.3.1 Macronutrients

Macrophytes uptake and sequester N primarily in the form of nitrate (NO_3^-) and ammonium (NH_4^+), whilst P is taken up as phosphate (PO_3^{4-}). Studies vary in their focus on total amounts (i.e. including particulate) versus the dissolved fraction of macronutrients, which makes comparing optimal macrophyte accumulator species challenging (Table 7.3). Macrophytes that have the greatest biomass production and/or fastest growth rates are some of the most effective nutrient phytoremediators (Kennen and Kirkwood 2015); for example, *Eichhornia crassipes*, *Lemna* sp. and *Typha latifolia* have growth rates of 60–110 t/ha/year, 6–26 t/ha/year and 8–61 t/ha/year, respectively (Gumbricht 1993).

Emergent species have received considerable attention in nutrient phytoremediation and are often deployed in CWs, with *Canna* spp. and *Cyperus* spp. showing some of the highest removal efficiencies for ammonium (NH_4^+) of between 74 and 100% (Table 7.3). *T. latifolia*, *Lolium multiflorum* and *Polygonum hydropiperoides*

Table 7.3 Removal efficiencies (%) of macrophyte species investigated in this review of nutrients phytoremediation

Species	Life form	Removal efficiency (%)						Macrophyte deployment	Experiment	References
		Total Nitrogen	Nitrate (NO_3)	Ammonia (NH_3)	Ammonium (NH_4)	Total phosphorus	Phosphate			
Canna sp.	Emergent	50			100			FTW	Mesocosm	Sun et al. (2009)
					42			FTW	Mesocosm	Ayaz and Saygin (1996)
Cyperus sp.	Emergent				33			FTW	Mesocosm	Ayaz and Saygin (1996)
		72			75			Constructed wetland	Constructed wetland	Kyambadde et al. (2004)
		57			63	54.09		FTW	Microcosm	Kansiime et al. (2005)
Polygonum hydropiperoides	Emergent	74				81		Direct planting	Mesocosm	Lang Martins et al. (2010)
Echinodorus cordifolius	Emergent		45		49.9	10.85		Direct planting	Mesocosm	Moore et al. (2016)
Ipomoea aquatica	Emergent	76						FTW	Mesocosm	Karnchanawong (1995)
		36–46				36–47		FTW	Mesocosms	Li et al. (2010)
		61.94			48	62		FTW	Mesocosm	Li et al. (2010)
Juncus effusus	Emergent	48		50		63		Constructed wetland	Constructed wetland	Coleman et al. (2001)
Leersia oryzoides	Emergent					51		Direct planting	Mesocosm	Tyler et al. (2012)
Limnocharis flava	Emergent			92			96	Constructed wetland	Constructed wetland	Kamarudzaman et al. (2011)
Lolium multiflorum	Emergent	81				90		FTW	Mesocosm	Xian et al. (2010)

(continued)

Table 7.3 (continued)

Species	Life form	Removal efficiency (%)						Macrophyte deployment	Experiment	References
		Total Nitrogen	Nitrate (NO_3)	Ammonia (NH_3)	Ammonium (NH_4)	Total phosphorus	Phosphate			
Miscanthidium violaceum	Emergent	57			47	41		Constructed wetland	Constructed wetland	Kyambadde et al. (2004)
Oenanthe javanica	Emergent	91		97		76		FTW	Mesocosm	Zhou and Wang (2010)
Panicum hemitomon	Emergent		60		54	28		Direct planting	Mesocosm	Moore et al. (2016)
Phragmites	Emergent				98			FTW	Mesocosm	Kintu Sekiranda and Kiwanuka (1997)
Saururus cernuus	Emergent		35		−3	−13		Direct planting	Mesocosm	Moore et al. (2016)
Scirpus atrovirens	Emergent			91			82	Constructed wetland	Constructed wetland	Kamarudzaman et al. (2011)
Scirpus validus	Emergent	25		25		48		Constructed wetland	Constructed wetland	Coleman et al. (2001)
Sparganium americanum	Emergent					14		Direct planting	Mesocosm	Tyler et al. (2012)
Thalia dealbata	Emergent		46		31	4		Direct planting	Mesocosm	Moore et al. (2016)
Typha angustifolia	Emergent	57				23		FTW	Mesocosm pots	Keizer-Vlek et al. (2014)
Typha latifolia	Emergent	62		62		81		Constructed wetland	Constructed wetland	Coleman et al. (2001)
						53		Direct planting	Mesocosm	Tyler et al. (2012)

(continued)

Table 7.3 (continued)

Species	Life form	Removal efficiency (%)						Macrophyte deployment	Experiment	References
		Total Nitrogen	Nitrate (NO_3)	Ammonia (NH_3)	Ammonium (NH_4)	Total phosphorus	Phosphate			
			32		17	12		Direct planting	Mesocosm	Moore et al. (2016)
Vetiveria zizanioides	Emergent	49		50		21		FTW	Mesocosm	Boonsong and Chansiri (2008)
Eichhornia crassipes	Floating		61–83					Direct planting	Mesocosm	Ayyasamy et al. (2009)
			92	81		67		Direct planting	Mesocosm	Kutty et al. (2009)
Pistia stratiotes	Floating	50				14–31		Direct planting	Ponds (storm water detention)	Lu et al. (2010)
			31–51					Direct planting	Mesocosm	Ayyasamy et al. (2009)
Salvinia molesta	Floating		18–36					Direct planting	Mesocosm	Ayyasamy et al. (2009)
Lemna gibba	Floating	97				99		Direct planting	Mesocosm-wastewater	Körner and Vermaat (1998)
			100	82			64	Sewage water system	Sewage water system	El-Kheir et al. (2007)
Ceratophyllum demersum	Submerged	42			65	73		Direct planting	Mesocosm	Dai et al. (2012)
Myriophyllum aquaticum	Submerged	88				94		Direct planting	Mesocosm	Souza et al. (2013)
			45		35	7		Direct planting	Mesocosm	Moore et al. (2016)

(continued)

Table 7.3 (continued)

Species	Life form	Removal efficiency (%)						Macrophyte deployment	Experiment	References
		Total Nitrogen	Nitrate (NO_3)	Ammonia (NH_3)	Ammonium (NH_4)	Total phosphorus	Phosphate			
Canna sp.	Emergent	50		100				FTW	Mesocosm	Sun et al. (2009)
				42				FTW	Mesocosm	Ayaz and Saygin (1996)
Cyperus sp.	Emergent			33				FTW	Mesocosm	Ayaz and Saygin (1996)
		72		75				Constructed wetland	Constructed wetland	Kyambadde et al. (2004)
		57		63		54.09		FTW	Microcosm	Kansiime et al. (2005)
Polygonum hydropiperoides	Emergent	74				81		Direct planting	Mesocosm	Lang Martins et al. (2010)
Echinodorus cordifolius	Emergent		45		49.9	10.85		Direct planting	Mesocosm	Moore et al. (2016)
Ipomoea aquatica	Emergent	76						FTW	Mesocosm	Karnchanawong (1995)
		36–46				36–47		FTW	Mesocosms	Li et al. (2010)
		61.94		48		62		FTW	Mesocosm	Li et al. (2010)
Juncus effusus	Emergent	48		50		63		Constructed wetland	Constructed wetland	Coleman et al. (2001)
Leersia oryzoides	Emergent					51		Direct planting	Mesocosm	Tyler et al.(2012)
Limnocharis flava	Emergent			92			96	Constructed wetland	Constructed wetland	Kamarudzaman et al. (2011)
Lolium multiflorum	Emergent	81				90		FTW	Mesocosm	Xian et al. (2010)

(continued)

Table 7.3 (continued)

Species	Life form	Removal efficiency (%)						Macrophyte deployment	Experiment	References
		Total Nitrogen	Nitrate (NO_3)	Ammonia (NH_3)	Ammonium (NH_4)	Total phosphorus	Phosphate			
Miscanthidium violaceum	Emergent	57		47		41		Constructed wetland	Constructed wetland	Kyambadde et al. (2004)
Oenanthe javanica	Emergent	91		97		76		FTW	Mesocosm	Zhou and Wang (2010)
Panicum hemitomon	Emergent		60		54	28		Direct planting	Mesocosm	Moore et al. (2016)
Phragmites mauritianus	Emergent			98				FTW	Mesocosm	Kintu Sekiranda and Kiwanuka (1997)
Saururus cernuus	Emergent		35		−3	−13		Direct planting	Mesocosm	Moore et al. (2016)
Scirpus atrovirens	Emergent			91			82	Constructed wetland	Constructed wetland	Kamarudzaman et al. (2011)
Scirpus validus	Emergent	25		25		48		Constructed wetland	Constructed wetland	Coleman et al. (2001)
Sparganium americanum	Emergent					14		Direct planting	Mesocosm	Tyler et al. (2012)
Thalia dealbata	Emergent		46		31	4		Direct planting	Mesocosm	Moore et al. (2016)
Typha angustifolia	Emergent	57				23		FTW	Mesocosm pots	Keizer-Vlek et al. (2014)
Typha latifolia	Emergent	62		62		81		Constructed wetland	Constructed wetland	Coleman et al. (2001)
						53		Direct planting	Mesocosm	Tyler et al. (2012)

(continued)

Table 7.3 (continued)

Species	Life form	Removal efficiency (%)						Macrophyte deployment	Experiment	References
		Total Nitrogen	Nitrate (NO_3)	Ammonia (NH_3)	Ammonium (NH_4)	Total phosphorus	Phosphate			
			32		17	12		Direct planting	Mesocosm	Moore et al. (2016)
Vetiveria zizanioides	Emergent	49		50		21		FTW	Mesocosm	Boonsong and Chansiri (2008)
Eichhornia crassipes	Floating		61–83					Direct planting	Mesocosm	Ayyasamy et al. (2009)
			92	81		67		Direct planting	Mesocosm	Kutty et al. (2009)
Pistia stratiotes	Floating	50				14–31		Direct planting	Ponds (storm water detention)	Lu et al. (2010)
			31–51					Direct planting	Mesocosm	Ayyasamy et al. (2009)
Salvinia molesta	Floating		18–36					Direct planting	Mesocosm	Ayyasamy et al. (2009)
Lemna gibba	Floating	97				99		Direct planting	Mesocosm-wastewater	Körner and Vermaat (1998)
			100	82			64	Sewage water system	Sewage water system	El-Kheir et al. (2007)
Ceratophyllum demersum	Submerged	42			65	73		Direct planting	Mesocosms	Dai et al. (2012)
Myriophyllum aquaticum	Submerged	88				94		Direct planting	Mesocosm	Souza et al. (2013)
			45		35	7		Direct planting	Mesocosm	Moore et al. (2016)

showed a high TP removal efficiency of 81–90% (Table 7.3). For floating macrophytes *E. crassipes*, *Lemna gibba* and *Pistia stratiotes* show good potential for nutrient removal: *E. crassipes* can remove up to 92% NO_3^- and 81% NH_3^- whilst *L. gibba* can remove 100% NO_3^- and 82% NH_3^- (Table 7.3). The same two species were also effective at removing total phosphorus (TP) (Table 7.3). Submerged plants have received less attention for their nutrient phytoremediation capacity (Table 7.3). This may reflect the difficulty of cultivating and harvesting submerged macrophytes, and the potentially lower biomass generated compared to emergent plants (Du et al. 2017). *Ceratophyllum demersum* and *Myriophyllum aquaticum* are potential candidates for the targeting of total nitrogen (TN) and TP with removal rates >41% (Table 7.3). *Potamogeton crispus* was deployed as part of a hybrid FTW experiment and was found to have enhanced effects over the FTW comprised of only emergent plants; however, the individual removal contribution from *P. crispus* was not quantified (Guo et al. 2014). Most submerged species are rooted in sediment and may also remove nutrients from the water column through foliar absorption (Eichert and Fernández 2011). Hence, they offer the dual ability to remove nutrients from water and sediment, allowing the simultaneous remediation of sediments that have a pollutant legacy and which may continue to release nutrients to the water column via internal loading even after external loads have been reduced. However, the disturbance caused during harvesting can re-suspend sediment-bound elements and alter the macrophyte-equilibrium state to a potentially undesirable phytoplankton-dominated state (Kuiper et al. 2017).

The phytoremediation potential of a macrophyte is influenced by biotic factors such as competition, predation and developmental stage (Quilliam et al. 2015) and abiotic factors such as temperature, pH, light availability, seasonality and nutrient loading (Ansari et al. 2014). For example, Ayyasamy et al. (2009) found that the removal efficiency of by *E. crassipes* increased between concentrations of 100 and 300 mg/l of NO_3^-, but decreased at higher concentrations of 400 and 500 mg/l of NO_3^-. Similarly, a mesocosm-based study of the effect of different temperature regimes on N and P removal by *Nasturtium officinale* and *Oenanthe javanica* found that maximum net accumulation of TN and TP occurred at an air temperature of 22 °C but deteriorated thereafter (Hu et al. 2010). Given the wide range of factors that may influence the ability of macrophytes to remove contaminants, understanding the performance of some of the key macrophyte accumulators under different environmental conditions is prudent in order to optimise species selection.

7.3.2 Metals

Macrophytes can also remove micronutrients [henceforth referred to as metals] (Rai 2009) from water and sediments, and hyperaccumulators are most appropriate for the phytoremediation of metals (Ali et al. 2013). The search for hyperaccumulator species has been one of the primary foci within the field given the widespread prevalence of past and current metal industrial effluents and the ecological risks they carry (Van der Ent et al. 2013); however, metal bioavailability can be reduced by sedimentation and adsorption to clay particles (Kumar et al. 2008). Studies based on mesocosm-scale CW experiments have been carried out on synthetic solutions with elevated metal concentrations in domestic and industrial wastewaters to assess the potential of macrophytes of different growth forms to act as hyperaccumulators (Fu and Wang 2011; Kamal et al. 2004; Rai 2009; Rezania et al. 2016) (Table 7.4). Many species also have the capacity to take-up multiple types of metals meaning that some species could be more beneficial in phytoremediation (Table 7.4).

Macrophytes that have often been cited as hyperaccumulators with high biomass potential are free-floating plants, such as members of the Lemnaceae (e.g. *Lemna minor*), *P. stratiotes*, *E. crassipes* and those from the genera *Salvinia* (Table 7.4). For example, *L. gibba* has been reported to concentrate between 14,000 mg/kg dry weight of Cd, whilst *E. crassipes* can concentrate 10,000 mg/kg Zn (Low et al. 1994; Mkandawire et al. 2004a, b). Furthermore, *T. latifolia* and *C. demersum* L. have also shown good potential (Osmolovskaya and Kurilenko 2005; Sunita and Bikram Singh 2015). The main limitation of macrophyte metal uptake is the toxicity of the target metal pollutant at higher concentrations (Landesman et al. 2011). However, detoxification mechanisms also allow species to avoid the negative effects of these metals (Deng et al. 2004); for example, more than 50% of the Ca, Cd, Co, Fe, Mg, Mn, and Zn recovered in the roots of *P. stratiotes* were actually attached to the external surfaces indicating the ability of the plant to exclude metals and thus maintain tolerable levels internally (Lu et al. 2011). Newete and Byrne (2016) also state that the extent of the root system affects the ability of macrophytes to remove metal pollutants, with fibrous root systems being superior due to their large surface area. Physio-chemical factors are also important for uptake and accumulation of metals with temperature, light, pH and salinity all having been shown to influence remediation performance (Rai 2009).

7.3.3 Organic Pollutants

Table 7.5 shows the wide range of studies that have been carried out in relation to the phytoremediation of organic pollutants and some of the key macrophytes that may be utilised. For pesticides, *L. minor* removed 95% of 2,4,5-trichlorophenol; whereas for isoproturon and glyphosate, *L. minor* its removal efficiency was poor (25% and 8%, respectively; Table 7.5). *E. crassipes* also shows good phytoremediation potential, removing up to 81% of ethion within a water mesocosm experiment (Table 7.5). The removal of DDT by macrophytes shows promise. For the DDT isomers *o,p′*-DDT and *p,p′*-DDT: *Spirodela oligorrhiza* can remove 66% and 50% respectively; whilst *M. aquaticum* can remove 76% and 82%, respectively (Gao et al. 2000). *Elodea canadensis* also has the ability to remove 48–89% of *p,p′*-DDT (Gao et al. 2000; Garrison et al. 2000). *L. gibba*, *Lemna minuta* and *P. crispus* have been demonstrated to be very efficient at removing phenols from water (Barber et al. 1995; Hafez et al.

Table 7.4 Key macrophyte metal accumulators reported in the literature

Species	Life form	Metals	References
Ceratophyllum submersum	Submerged	Ni	Kara (2010)
Ceratophyllum demersum	Submerged	Cr, Pb	Osmolovskaya and Kurilenko (2005)
Potamogeton natans	Submerged	U	Pratas et al. (2014)
Myriophyllum spicatum	Submerged	Co, Cu, Mn, Pb, Zn	Wang et al. (1996), Sivaci et al. (2004), Lesage et al. (2008)
Potamogeton pectinatus	Submerged	Cd, Cu, Mn, Pb, Zn	Rai et al. (2003), Singh et al. (2005)
Hydrilla verticillata	Submerged	As, Cu	Srivastava et al. (2011)
Limnocharis flava	Emergent	Cu, Fe, Hg, Pb, Zn	Anning et al. (2013)
Glyceria maxima	Emergent	Cu, Zn	Parzych et al. (2016)
Typha latifolia	Emergent	As, Cu, Ni, Zn	Ye et al. (1997), Ha et al. (2009), Manios et al. (2003), Qian et al. (1999)
Typha angustifolia	Emergent	Pb	Panich-pat (2005)
Elodea densa	Emergent	Hg	Molisani and Lacerda (2006)
Phalaris arundinacea	Emergent	Fe, Mn, Ni	Parzych et al. (2016)
Phragmites australis	Emergent	As, Hg	Windham et al. (2003), Afrous et al. (2011)
Scirpus maritimus	Emergent	As	Afrous et al. (2011)
Spartina alterniflora	Emergent	As	Carbonell et al. (1998)
Spartina patens	Emergent	Cd	Zayed et al. (2000)
Azolla filiculoides	Floating	Cd, Cr, Ni, Pb, Zn	Oren Benaroya et al. (2004), Arora et al. (2006), Taghi et al. (2005), Zayed et al. (1998)
Azolla caroliniana	Floating	As, Cr, Cu, Hg	Rahman and Hasegawa (2011), Bennicelli et al. (2004)
Pistia stratiotes	Floating	Cr, Cu, Hg	Miretzky et al. (2004), Molisani and Lacerda (2006), Maine et al. (2004)
Salvinia cucullata	Floating	Cd, Pb	Phetsombat et al. (2006)

(continued)

Table 7.4 (continued)

Species	Life form	Metals	References
Salvinia natans	Floating	Cr, Zn	Dhir et al. (2008)
Spirodela polyrhiza	Floating	As	Zhang et al. (2011a, b)
Eichhornia crassipes	Floating	Cd, Cr, Cu, Hg, Ni, Zn	Zhu et al. (1999), Hu et al. (2007), Molisani and Lacerda (2006), Low et al. (1994)
Lemna gibba	Floating	As, Cd, Ni	Mkandawire and Dudel (2005), Mkandawire et al. (2004a, b)

1998). However, *P. crispus* is less efficient at removing two PAHs, phenanthrene (removal 18–34%) and pyrene (removal 14–24%) (Meng et al. 2015).

There is great potential for phytoremediation of a wide variety of PPCPs such as anti-inflammatory, hormonal replacement and anticonvulsant products (Zhang et al. 2014a, b). CWs (Sect. 7.6.1) planted with *Phragmites australis* demonstrated very efficient removal of the hormones Estrone, 17 beta-estradiol and 17 alpha-ethinylestradiol from water (Table 7.5). In CWs, the water column/plant sediment matrix a depth of *circa* 7.5 cm provided more efficient PPCP removal than deeper depths of 30 cm (Zhang et al. 2014a, b). This highlights the importance of oxygen for the removal of waterborne hormone pollutants with vertical mixing from the surrounding atmosphere increasing the aeration of plant roots and (Zhang et al. 2014a, b). Plants such as *T. latifolia* with more extensive roots and rhizomes system may be favourable for deployment due to their capacity to oxygenate water (Makvana and Sharma 2013).

Scirpus validus displays mixed ability to remove anti-inflammatory pharmaceuticals with very efficient removal of naproxen, compared to very poor removal of diclofenac (Zhang et al. 2012, 2013a). *Typha angustifolia* removed 27–91% of anti-inflammatory drugs in a study by Zhang et al. (2011a, b). Chen et al. (2016a, b) found that there is large variability in planted rural CWs in terms of their removal efficiency of PPCPs with 11–100% removal of anti-inflammatories, 37–99% for β-blockers and 18–95% for diuretics. Understanding this variability and identifying macrophytes for the removal of PPCPs through laboratory studies and at the field scale is important given the need for low-cost removal solutions, especially in developing countries. There has been little focus on the use of novel macrophyte planting systems (e.g. FTWs) for the removal of organic chemicals, and future work on these systems would build flexibility into the deployment of different aquatic phytoremediation schemes for tackling the problem of PPCP pollution. Importantly, the distribution and storage of organic chemicals within plants, especially for PPCPs, requires further study in order to avoid the problem of transferring pollutant from one place to another (Sects. 7.8 and 7.9).

Table 7.5 Removal efficiencies of macrophyte species investigated in phytoremediation studies of organic pollutants

Organic pollutant	Species	Life form	Target pollutant	Experimental situation	Removal (%)	References
Pesticides	*Canna x generalise*	Emergent	Isoxaben, oryzalin	Mesocosm	n/a	Fernandez et al. (1999)
	Pontederia cordata	Emergent	Isoxaben, oryzalin	Mesocosm	n/a	Fernandez et al. (1999)
	Iris L. x 'Charjoys Jan'	Emergent	Isoxaben, oryzalin	Mesocosm	n/a	Fernandez et al. (1999)
	Eichhornia crassipes	Floating	Ethion	Mesocosm	81	Xia and Ma (2006)
	Juncus effusus	Emergent	Atrazine, lambda-cyhalothrin	Mesocosm	n/a	Bouldin et al. (2006)
	Ludwigia peploides	Emergent	Atrazine, lambda-cyhalothrin	Mesocosm	n/a	Bouldin et al. (2006)
	Lemna minor	Floating	2,4,5-trichlorophenol	Mesocosm	95	Tront and Saunders (2006)
			Isoproturon, glyphosate	Mesocosm	25, 8	Dosnon-Olette et al. (2011)
	Spirodela oligorrhiza	Floating	DDT (OP,PP-DDT)	Mesocosm	66, 50	Gao et al. (2000)
	Elodea canadensis	Submerged	DDT (OP,PP-DDT)	Mesocosm	31, 48	Gao et al. (2000)
	Myriophyllum aquaticum	Submerged	DDT (OP,PP-DDT)	Mesocosm	76, 82	Gao et al. (2000)
			Trifluralin, cycloxydim, atrazine, terbutryn	Mesocosm	n/a	Turgut (2005)
	Elodea canadensis	Submerged	DDT (OP,PP-DDT)	Mesocosm	89	Garrison et al. (2000)
POP	*Lemna gibba*	Floating	Phenol	Mesocosm	90	Barber et al. (1995)
	Lemna minuta	Floating	Phenol	Mesocosm	100	Paisio et al. (2018)
	Potamogeton crispus	Submerged	Phenol	Mesocosm	70–100	Hafez et al. (1998)

(continued)

Table 7.5 (continued)

Organic pollutant	Species	Life form	Target pollutant	Experimental situation	Removal (%)	References
			PAHs (phenanthrene and pyrene)	Mesocosm (sediment pots included)	18–34, 14–24	Meng et al. (2015)
PPCP	*Phragmites australis*	Emergent	Estrone, 17 beta-estradiol, 17 alpha-ethinylestradiol	Constructed wetland	68–84	Song et al. (2009)
	Scirpus validus	Emergent	Diclofenac	Mesocosm	1–7%	Zhang et al. (2012)
			Naproxen, carbamazepine	Constructed wetland	97–99, 53–60	Zhang et al. (2013a)
			Caffeine	Mesocosm	>99.7	Zhang et al. (2013b)
	Typha angustifolia	Emergent	Carbamazepine, naproxen, diclofenac, ibuprofen	Constructed wetland	27, 91, 55, 80	Zhang et al. (2011a, b)
	Pontederia cordata	Emergent	Triclosan, methyl triclosan and triclocarban	Constructed wetland	n/a	Zarate et al. (2012)
	Sagittaria graminea	Emergent	Triclosan, methyl triclosan and triclocarban	Constructed wetland	n/a	Zarate et al. (2012)
	Typha latifolia	Emergent	Triclosan, methyl triclosan and triclocarban	Constructed wetland	n/a	Zarate et al. (2012)

Note n/a refers to studies where the removal efficiencies are not reported

7.3.4 Microbial Pollutants

Most studies on the removal of microbial pollutants and their indicators of the presence (e.g. *E. coli*, faecal coliforms and faecal streptococci) are focused on macrophytes within CWs; therefore, the following examples will mainly refer to this planting type (see Sect. 7.6.1). Furthermore, most studies show that CW planting systems remove microbial pollutants from water via a combination of chemical, biological and physical mechanisms. A study of 12 CWs found that over a year vegetated CWs removed between 95–97% of faecal coliforms and 93–98% of faecal streptococci (Karathanasis et al. 2003). Similarly, in an experimental CW system, Makvana and Sharma (2013) demonstrated removal rates of 94%, 87% and 94% for *Salmonella*, *Shigella* and *Vibrio*, respectively. However, the removal of *Salmonella* and *E. coli* from water in unplanted control mesocosms versus mesocosms containing *T. latifolia*, *Cyperus papyrus*, *Cyperus alternifolius* and *P. australis* showed no significant difference in the removal rates (>98%) between the two treatments; furthermore, in general, unplanted mesocosms reached their maximum removal rate before the planted mesocosms (with the exception of the *C. alternifolius* mesocosm) suggesting that plants provide little additional benefit for removing biological pollutants over and above the effect of standing water conditions (Kipasika et al. 2016). Similarly, a review comparing *Lemna* sp. treatment ponds against unplanted treatment ponds showed that the latter had greater removal rates of *E. coli* facilitated by the greater exposure of the water to UV light and the subsequent photodegradation and microbial die-off (Ansa et al. 2015). However, Decamp and Warren (2000) have shown that gravel beds planted with *P. australis* remove *E. coli* more quickly compared to unplanted soil beds, possibly as a result of the impact of antagonistic root exudates from *P. australis* on *E. coli* survival.

The variability of the results obtained between planted and unplanted experiments suggests that for each treatment system different mechanisms of microbial pollutant removal become dominant. Within unplanted facultative systems or lagoons, it is likely that oxygenation and phytodegradation from UV light are the dominant methods of removal (Ansa et al. 2015). Conversely, biological and chemical processes may become more important within planted systems; for example, *P. stratiotes* facilitates the presence of protozoa by providing structural habitat, which can increase predation on *Salmonella* (Awuah 2006). Conversely, predation from protozoa seemed to have a negligible effect in systems planted with *Spirodela polyrhiza* (greater duckweed), highlighting that removal mechanisms are probably related to below-ground morphological attributes, with more extensive roots/rhizomes providing superior habitat for grazers (Awuah and Gyasi 2014). Increased root zone surface area also facilitates greater microbial biofilm growth which is thought to be a key removal structure for bacterial adsorption and predator microbial proliferation (Decamp and Warren 2000). Therefore, smaller grasses such as *Festuca arundinacea* may have limited potential for microbial pollutant removal compared to large emergent such as *T. latifolia* (Decamp and Warren 2000). Future research investigating the ability of different macrophytes to remove microbial pollutants from water, especially outside of CW systems, is clearly merited. Direct deployment of macrophytes for pathogen removal would be highly beneficial in developing countries where low-cost options for remediation could provide accessible water treatment.

Of the few experimental studies investigating the potential for macrophyte removal of microbial pollutants outside of CWs, Saeed et al. (2016) demonstrated a 72% reduction of *E. coli* in FTWs planted with *P. australis* and *Canna indica*. However, during times of high *E. coli* loading, induced by experimental 'shock phases' where hydraulic loading was increased between 5- and 14-fold to simulate low-frequency and high-magnitude discharge events, the removal of *E. coli* was reduced significantly to levels varying between 6 and 45%. The effect of hydraulic retention time is also important for pathogen survival and die-off (Reinoso et al. 2008) and may have implications for the use of phytoremediation (with FTWs) in lakes and rivers given the difference in hydraulic retention times.

7.4 Macrophyte Phytoremediation Communities

There has been considerable work focusing on the ability of individual plant species to remove single pollutants from water (e.g. Zhou and Wang 2010), with the design of CWs also focusing on monocultures of macrophytes (Kadlec 2009). Conversely, there has been a lack of studies that explicitly explore the ability of mixed plant assemblages to simultaneously take-up and degrade multiple pollutants (Koelbener et al. 2008). A plant community-based approach provides the opportunity to enhance the removal of both single pollutants, but also target multiple contaminants. Studies that have looked specifically at phytoremediation using plant communities have shown encouraging results (Fraser et al. 2004; Zhang et al. 2007; Liang et al. 2011; Türker et al. 2016). For example, an experiment testing the removal of N and P from four different emergent macrophytes in parallel (*Carex lacustris*, *S. validus*, *Phalaris arundinacea* and *T. latifolia*) found that microcosms planted with all four macrophytes in equal proportion, either matched or outperformed microcosms planted with a single species (Picard et al. 2005). Earlier studies also suggest that plant polycultures have a greater removal potential for heavy metals and can reduce biochemical oxygen demand (BOD) (Karpiscak et al. 1996; Scholes et al. 1999). However, Türker et al. (2016) reported that boron removal from mine effluent was more effective in native emergent monocultures compared to polycultures, although the opposite was true for NO_2^- removal. These results suggest that there are probably optimal plant combinations for particular pollutants and further experiments designed to identify these combinations would help to optimise the efficiency of phytoremediation.

To assemble appropriate plant combinations, there are several important factors to consider including the functional diversity of the community. It has been reported that simply increasing species diversity in a plant assemblage can increase nutrient removal, although polycultures containing more than three species showed no further benefit (Ge et al. 2015; Geng et al. 2017). A common theme among these studies is the importance of species identity in explaining variation in nutrient removal, where specific combinations can more effectively remove pollutants. Therefore, assembling appropriate plant communities is based around the complementary phytoremediation potential of individual species, and the interaction of those plants with others in the assemblage is potentially more important than simply increasing species richness per se. However, the effect of competition between plants is important to recognise as this may impact the community composition, and therefore the ability to remove the targeted pollutants from water (Zhang et al. 2007). In a mesocosm experiment, containing the submerged macrophytes *Stuckenia pectinata* (Sago pondweed), *Potamogeton natans* (broad-leaved pondweed), *P. crispus* (curled pondweed) and *Zannichellia palustris* (horned pondweed), it was found that *S. pectinata* reduced the biomass of the other species (Engelhardt and Ritchie 2001). Reducing the biomass of certain species will not necessarily compromise overall removal efficiency as uptake and sequestration potential will vary with species. However, this highlights the need to understand interspecific interactions in order to enhance removal efficiency, especially when considering targeting water bodies in a non-equilibrium state where conditions favour the dominance of one particular species (Engelhardt and Ritchie 2002).

A field study employing plant communities revealed some of the benefits of combining multiple macrophytes (Wang et al. 2009; Zhao et al. 2011). Nine macrophytes species (five floating, one submerged and three emergent) deployed on FTWs and planted on river banks outside Jiaxing City, China, demonstrated removal rates of TN and TP at 16–37% and 26–43%, respectively (Zhao et al. 2011). Although the removal rates were relatively low, it was also highlighted that the plant community-based approach allows for species within the community to compensate for deficits in the uptake of other species (Zhao et al. 2011). For example, the average P content of floating macrophytes was *ca.* 5.9 g/m^2, whereas emergent species including *C. indica and Pontederia cordata* with higher biomass accumulation stored P at a level of *ca.* 7.3 g/m^2. Similarly, a phytoextraction study with emergent species (*Carex flava*, *Centaurea angustifolia* and *Salix caprea*) allowed the impact of facilitation across increasing concentration gradients to be seen (Koelbener et al. 2008). Here, the willow *S. caprea* attenuated the toxic effect of Zn on the relative growth rate of *C. flava* by lowering the availability of Zn, thus mitigating the negative effect of Zn on the sedge (Koelbener et al. 2008). This highlights that competitive effects may not always be negative and may produce positive effects through 'over yielding'. The consequences of competitive interactions between candidate macrophytes evidently deserve particular attention within the field of plant community-based phytoremediation.

As well as the potential enhanced removal of pollutants from plant communities with macrophytes of different life forms (Koelbener et al. 2008), there may also be the potential for generating ecosystem services from polycultures. A 2-year study by Wang et al. (2009) explored the potential restoration of Lake Taihu and Lake Mochou by using a mosaic of macrophytes in successional stages highlighting the potential for spatial and temporal diversity in macrophyte deployment and the provision of ecosystem services. Floating and emergent macrophytes were first introduced to reduce light availability for algal growth, facilitating the introduction of submerged species leading to removal rates of TN and TP of 60% and 72% (Wang et al. 2009). The provision of ecosystem services due to the different plant life forms was highlighted as an advantage by Wang et al. (2009) as increased patches of vegetation provided refuge for zooplankton that subsequently grazed phytoplankton. The added value of diverse plant communities is a factor that requires quantification to espouse the benefits of aquatic phytoremediation over and above water treatment.

Plant community-based approaches provide the opportunity to build temporally more consistent treatment into phytoremediation by exploiting the differing phenology of plant species; polyculture systems can thus offer the most consistent water treatment option with the least susceptibility to seasonal variation (Karathanasis et al. 2003). However, the temporal dynamics of plant communities within the context of phytoremediation are under-researched, and there is a need to explore the assembly of plants, e.g. in terms of differing phenologies, to extend the growing season, especially in temperate regions where water treatment potential declines after senescence.

7.5 Issues in Utilising Invasive Macrophytes

The most effective phytoremediators have fast growth rates and high biomass accumulation; however, outside of their native range macrophyte species with these traits are often considered to be invasive, and given their potential for rapid colonisation, they can quickly outcompete native macrophytes (Chambers et al. 2008). Species that are invasive in the UK, such as *Azolla filiculoides* and *Hydrocotyle ranunculoides*, can clog waterways and have serious ecological impacts on native flora and fauna (Schultz and Dibble 2012). In the UK, the combined cost of controlling invasive plants, together with their economic impact, is estimated to be £1.7 billion per annum (The Great Britain Non-native Species Secretariat 2015). Therefore, there is a significant juxtaposition between using species of invasive plants in phytoremediation, and management strategies to control invasive species (Rodríguez et al. 2012). Given that in many cases the complete eradication of invasive aquatic macrophytes such as *E. crassipes* is unlikely, it may be more appropriate to exploit these macrophytes as part of an integrated management strategy that controls the spread of these species whilst at the same time effectively removing nutrients and metals, capturing suspended sediment, and harvesting the biomass for economic gain (Patel 2012; Yan et al. 2017). A similar parallel can be drawn with non-native and invasive zebra mussels (*Dreissena polymorpha*) which are often considered detrimental (Matsuzaki et al. 2009), but have also widely been reported to stabilise the clearwater state of shallow lakes through filtering phytoplankton and removing harmful cyanobacteria (Gulati et al. 2008).

Water bodies where invasive species are already present may be targeted for active harvesting allowing periodical regrowth for continued phytoremediation (Xu et al. 2014). However, there are important factors to consider including the containment of macrophytes to avoid transfer to other water bodies (e.g. via contaminated harvesting equipment or through downstream spread of fragments), including the most appropriate harvesting technique and the sustainability of exploiting such an ecological engineering systems (Rodríguez et al. 2012; Yan et al. 2017). The site-specific context will likely determine the appropriateness of active harvest of invasive aquatic plants (Yan et al. 2017). In terms of introducing macrophytes into a freshwater system for phytoremediation, it is inappropriate, and indeed possibly illegal, to deploy invasive species given the potential for ecosystem damage and long-term effects. In these circumstances, non-invasive or native plants should therefore be employed, unless containment of invasive plants can be ensured, such as in engineered CW systems.

7.6 Macrophyte Planting Systems

Macrophyte planting systems are effectively planting strategies that are employed to facilitate targeted phytoremediation of waters in different contexts in terms of point source and diffuse source treatment and restoration. The following section details the key aspects of the three main aquatic phytoremediation planting systems that have been developed: CWs, wild macrophyte harvesting and planting, and FTWs.

7.6.1 Constructed Wetlands

Phytoremediation has primarily been optimised for point source wastewater treatment in the form of CWs. CWs have been used for the treatment of a variety of effluents including urban storm water, sewage, mine-tailing drainage, storm water treatment, landfill leachate treatment systems and for wastewater polishing (Kivaisi 2001; Nivala et al. 2007; Tanner 1996; Vymazal 2009, 2011). CWs also show potential for treating wastewater containing emerging contaminants of concern including pharmaceuticals and other endocrine disrupters (Vymazal 2009).

CWs can be categorised as free water surface flow wetlands (FWSF) or sub-surface flow (SSF) wetlands (Dhir 2013) (Fig. 7.3). FWSF wetlands contain emergent, floating and submerged macrophytes growing in shallow ponds or lagoon waters over sandy or organic soils, which allows the influent contaminated water to slowly flow through the emergent macrophyte stems for maximum pollutant uptake and UV degradation (Kadlec 2009). SSF wetlands are the most common type of CW and comprise emergent macrophytes growing over a substrate of stone or gravel matrix enabling water to come in direct contact with plant roots, rhizomes and biofilms, which promote aerobic conditions (Vymazal 2011). Several processes including physical filtering of the water, biological processing of water by plants and microbial biofilms, and chemical changes due to redox state can assist in pollutant removal in SSF systems (Faulwetter et al. 2009). The average SSF CW system is 100 times smaller than the FWSF CW system (Kadlec 2009); therefore, FWSF is more common

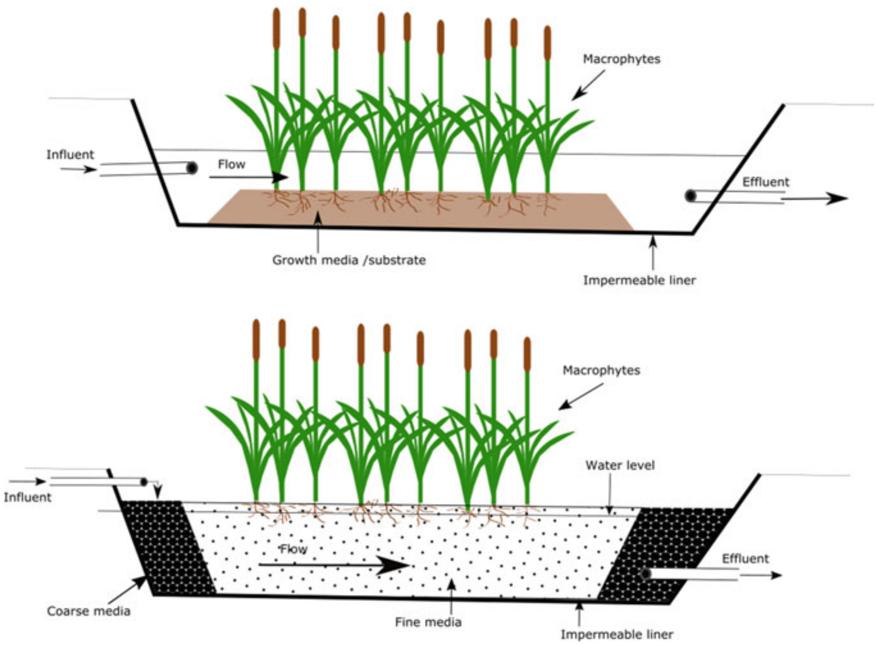

Fig. 7.3 Top: Key elements of a free water surface flow wetlands (FWSF) constructed wetland. Bottom: Key elements of a sub-surface flow (SSF) constructed wetland

in North America and Australia where a larger surface is available, whilst SSF wetlands are more common in Europe where land availability is more limited (Vymazal 2011). SSF wetlands are frequently used to ameliorate the concentration of biologically derived organic material as indicated by the lowering of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) from wastewaters (Vymazal and Kröpfelová 2009).

CWs are the most advanced form of macrophyte deployment within the umbrella of aquatic phytoremediation (Kennen and Kirkwood 2015). However, these systems can require high investment costs and they are restricted primarily to pollutant point sources where there is wastewater treatment such as tertiary sewage treatment and wastewater polishing before water enters a natural waterway (Patiño Gómez and Lara-Borrero 2012). This restricts the application of CWs for the treatment of water containing pollutants from diffuse sources. Although CWs have the potential to be utilised for treatment of a wide range of contaminants, their most widespread application has been for sewage wastewater-related contaminants, including BOD, COD, N and P, and often they are set up with crop monoculture to maximise plant uptake (Kadlec and Wallace 2009; Sundaravadivel and Vigneswaran 2001; Vymazal 2009).

CWs vary in level of design and engineering required for their development; FWSF wetlands are generally low tech gravity-fed systems, whereas SSF requires more construction and management to import the stone/gravel matrixes and also may include bunds to separate different treatments then requiring the use of electric pumps (Kadlec and Wallace 2009). In both types of CWs, there are high investments in construction and operational costs. CW can also become clogged with sediment, which impacts the functioning of the system and imposes additional costs for excavation and removal of contaminated sediments, and the subsequent reinstatement of macrophytes (Machado et al. 2016). According to design guidance for the treatment of urban wastewater and sewage, SSF CWs may require an area of around 5–10 m^2 of CW per person equivalent for adequate water purification (Tilley et al. 2014). Therefore, given the potentially large area required, CW-based phytoremediation may be unable to compete for limited land availability with other more profitable land uses. Furthermore, in countries where vector-borne diseases, such as malaria or dengue, are a public health issue the creation of open shallow wetland environments may be undesirable as it has the potential to provide ideal conditions for the propagation of mosquitoes and other disease vectors (Mwendera et al. 2017).

From both industry-based observations and from the available literature, the primary purpose of CWs is water treatment and wastewater polishing. This, however, ignores their potential to offer ecosystem services such as sequestering and harvesting nutrients for reuse, provisioning for biodiversity, pollination and carbon sequestration and thus underplays the overall value of CWs. There is great potential to develop different post-remediation 'streams' which have been relatively unexplored and which emphasise support for different ecosystem services (see Sect. 7.9.1). Aquatic phytoremediation is a promising technology for the treatment and remediation of polluted water with the operational point source-based CW systems in place; but given the limitations of these systems, including the lack of application for diffuse pollutants, investment costs and lack of ecosystem focus, there is an opportunity to further develop context-specific, sustainable phytoremediation that provides ecosystem services within wider environmental systems.

7.6.2 Wild Macrophyte Harvesting

Most aquatic phytoremediation planting systems involve the deliberate deployment (FTW) or engineering of planted systems (CWs). Harvesting of existing wild macrophytes from water bodies such as shallow lakes can also be a phytoremediation strategy and relies upon the opportunistic and timely removal of macrophyte biomass in order to manage waterborne pollutants such as N and P (Huser et al. 2016). A study of an urban shallow lake showed that harvesting an annual amount of 3600 kg dry weight of *E. canadensis* led to 16.4 kg P being removed from the system, equating to around 53% of the TP load removed (Bartodziej et al. 2017). Although the estimated cost of removal was $670 per kg of TP, which was more expensive than chemical flocculating treatment, this was still considerably less expensive than many catchment best management practices (Bartodziej et al. 2017). Macrophyte harvesting is often carried out in lakes and waterways to relieve navigation, drainage, aesthetic or recreational problems, rather than for phytoremediation purposes, but it is notable that nutrient export may be a collateral benefit of such harvesting. Other case studies have shown that macrophyte harvesting for nutrient removal does not reduce nutrient loading quite as favourably (Carpenter and Adams 1977; Morency and Belnick 1987), with Peterson et al. (1974) estimating that plant harvesting only removed 1.4% of TP loading.

The variation between these case studies is possibly a result of the levels of nutrient loading, with waters that receive extremely high inputs of nutrients leading to a poor offset by removal from plant harvesting (Bartodziej et al. 2017). Another source of variability for nutrient removal is the coverage of macrophytes across the particular water body; the reported optimal coverage of macrophytes ranges from 5 to 40% (Portielje and Van der Molen 1999; Dai et al. 2012; Xu et al. 2014). For environmental managers considering macrophyte harvesting as a mechanism for in-water nutrient management, it is crucial that a scoping study is carried out to determine the base balance of nutrient input/output and plant removal capacity and to identify the need for upstream best practices as part of an integrated management strategy.

The harvesting method itself is also an important element of harvesting wild macrophytes, e.g. removal by hand, or mechanically via specialised boats equipped with cutting or raking apparatus (Quilliam et al. 2015). Hand removal is labour and time-intensive, although it allows targeted macrophyte removal and minimises the disturbance. Conversely, mechanical removal allows more rapid and extensive removal but is non-selective and can lead to high levels of turbidity due to the re-suspension of sediments. This can impact invertebrates and fish by removing structural habitat and may ultimately drive the system from a desirable clearwater macrophyte-dominated state to a potentially unfavourable phytoplankton-dominated state (Dawson et al. 1991; Sayer et al. 2010; Habib and Yousuf 2016).

In some circumstances, it may be necessary to establish macrophytes in waterbodies by direct planting through seeding or transplanting propagules (e.g. tubers/root crowns) if there are no existing macrophytes, or if a particular species is required to target certain pollutants (Smart et al. 1998; Hilt et al. 2006). In addition to plant establishment, there is also scope to enhance macrophyte growth and biomass by engineering interventions such as the assembly of polytunnels over vegetation, or enclosures to reduce grazing losses.

7.6.3 Floating Treatment Wetlands

Within aquatic phytoremediation, one such novel ecological engineering solution that has been developed is the FTW. The premise of this system is that highly productive emergent macrophytes, such as *T. latifolia*, are planted within a growth medium, which is supported by a buoyant frame allowing the roots of the emergent macrophytes to be submerged in the water, thus enabling rhizofiltration, phytoextraction and phytodegradation to take place hydroponically (Nichols et al. 2016; Kiiskila

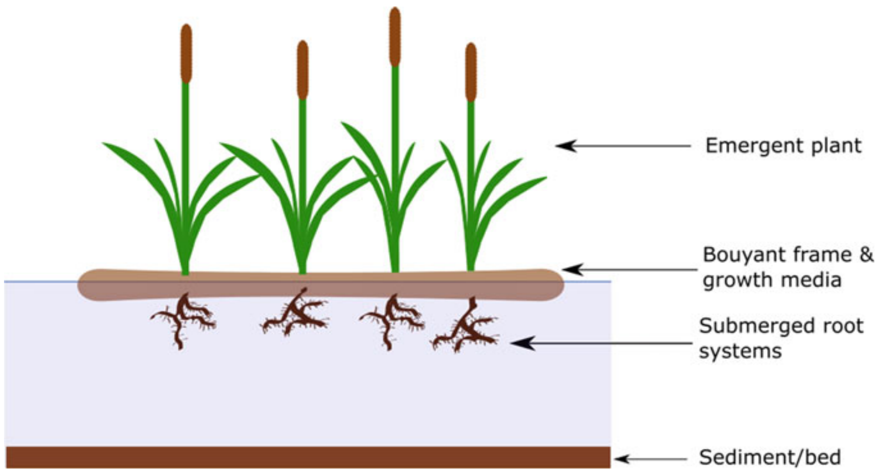

Fig. 7.4 Schematic view of a FTW

et al. 2017) (Fig. 7.4). Root uptake associated with FTWs is primarily applicable to water-soluble contaminants within the water column only, although sediment-bound pollutants can be physically filtered from the water column by plant roots (Tanner and Headley 2011). FTWs have recently gained increased attention and may also be referred to in the literature as artificial floating islands, integrated ecological floating beds, floating plant bed system and hydroponic root mats (Yeh et al. 2015).

FTWs can accommodate fluctuations in water levels, and the stability of materials used to construct the buoyant frame may include items such as polyvinyl chloride (PVC) pipes, foam sheets, bottles and bamboo (Ladislas et al. 2013; Wang et al. 2015; Pavlineri et al. 2017). However, it would be useful within the literature if qualitative information and design challenges were also reported to provide an idea of performance and usability of FTWs in practice, and although there are no reported incidences of FTWs capsizing or other failures during pilot tests, this may simply reflect publication bias.

Netting material or foam is generally used to support the growth medium in which the macrophytes are grown (Yeh et al. 2015). Material previously used as substrate includes peat, soil, cotton and coir fibre (Pavlineri et al. 2017). Furthermore, FTWs comprising foam with gaps to support pots have also been designed (Lynch et al. 2015). Growth media physically supports the planted macrophytes and provides nutrition, but the substrate can also enhance pollutant removal through the stimulation of microbial activity (Tanner and Headley 2011). Macrophytes may be established by transplanting of seedlings, cuttings or whole plants (Yang et al. 2008; Ning et al. 2014). An advantage of using FTWs rather than direct planting of macrophytes is the ease in which the biomass can be harvested from the frame, instead of having to remove plants from the sediment. The quick and simple method of harvesting afforded by growing plants in FTW facilitates recovering pollutants from plant biomass (Bartodziej et al. 2017). There is potential for quick re-planting of the FTW for continued remediation and biomass removal (Wang et al. 2015; Ge et al. 2016).

FTWs have been studied principally for their capacity to remove nutrients, but there have also been attempts to assess heavy metal, pathogen and phytoplankton removal (Borne 2014; Yeh et al. 2015; Jones et al. 2017; Kiiskila et al. 2017). FTWs have been deployed at a variety of different scales including microcosms, mesocosms, and as pilot trials within lagoons (Headley and Tanner 2008; Ladislas et al. 2013; Chang et al. 2014; McAndrew et al. 2016; Nichols et al. 2016; Kiiskila et al. 2017). Here the experimental polluted water used has included storm water, lake water, river water, sewage effluents, domestic wastewaters, refinery wastewater, acid mine drainage and livestock effluents (Zhu et al. 2011; Li et al. 2012; Borne 2014; Wang and Sample 2014; Abed et al. 2017; Kiiskila et al. 2017). Mesocosm-scale studies are the most prominent form of exploration into the effectiveness of FTW thus far (Chen et al. 2016a, b), although there have been a few examples of deployment at field scale, such as Zhao et al. (2012) who demonstrated that TN and TP concentrations could be reduced in a polluted Chinese river. Mesocosm studies with synthetically produced experimental water allow full control of all input parameters. However, they may not be representative of the real remediation performance given that polluted waters contain a multitude of chemicals and microbes which may influence remediation (Javadi et al. 2005). Therefore, further studies would benefit from testing the remediation of water sourced from the environment.

Only a small handful of field-scale experiments have been carried out that assess the usefulness of FTWs in successfully remediating pollutant-impacted waters (Zhu et al. 2012; McAndrew et al. 2016; Nichols et al. 2016; Olguín et al. 2017). Of the available studies that assess FTW performance within water bodies, including streams, urban and rural ponds, results focus on plant tissue element accumulation rather than the arguably more pertinent issue of water quality improvement (Zhu et al. 2012; Olguín et al. 2017; McAndrew et al. 2016; Nichols et al. 2016). Although plant tissue sequestration is extremely important for assessing the bioaccumulation potential of macrophyte species, it does not explicitly demonstrate water quality improvement; this can only be proven through monitoring water chemistry. Scaling up mesocosm-scale experiments to assess actual field-scale water quality improvement is challenging given the ideal of a control site with comparable water chemistry and abiotic and biotic conditions, or high-temporal resolution baseline water quality data for the experimental water body, both of which may be unavailable. Where there is a clear opportunity for upstream and downstream water quality sampling near the experimental FTWs, such as a stream, water quality changes are more likely to be attributed to the FTW intervention between these points (Olguín et al. 2017). Similarly, more field studies longer than 2 years, ideally up to 5–10 years, would lead to a better understanding of the longer-term performance of FTWs and, crucially, reveal the actual remediation time (Yang et al. 2006). Furthermore, the influence of inter-annual hydrological variability on FTW performance in terms of precipitation and evaporation could also be evaluated. Despite the paucity of scientific studies at the field scale, commercial companies now commonly offer FTWs as a water treatment

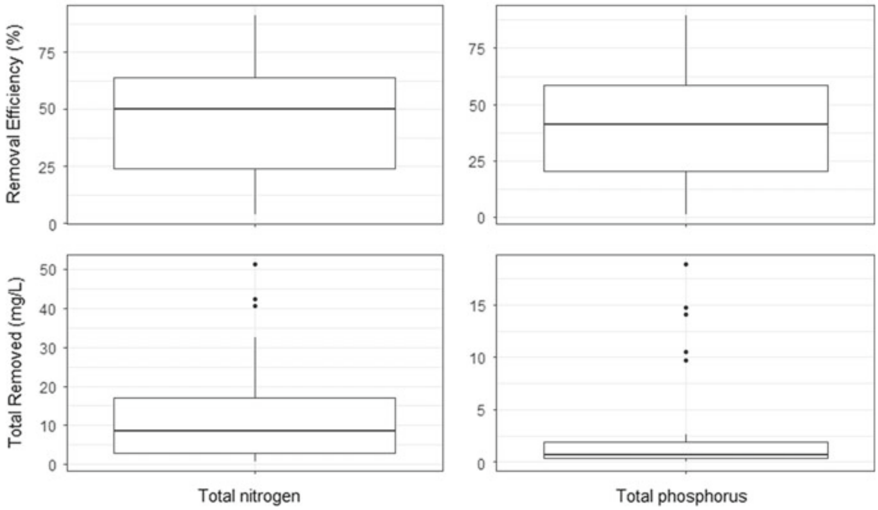

Fig. 7.5 Boxplots of removal efficiencies (%) and total removed (mg/l) of total nitrogen (TN) ($n = 44$) and total phosphorus (TP) ($n = 28$), raw data taken from literature reviewed by Pavlineri et al. (2017)

solution, and as part of the aesthetic enhancement of urban rivers. The phytoremediation research community must aim to keep pace with the private sector to corroborate industry-advocated benefits of FTWs and avoid any potential reputational damage to aquatic phytoremediation where expectations of these systems from stakeholders are not met (Kennen and Kirkwood 2015).

The remediation performance of FTWs is highly variable with reported minimum and maximum removal efficiencies for TN values being 0.71 mg/l (4%) and 51 mg/l (91%) and 0.06 mg/l (1%) and 18.85 mg/l (90%) for TP (Fig. 7.5). This high variability may be due to differences in FTW design, macrophyte species employed, and the chemical composition of the experimental water. A further example of variation in removal efficiency comes from Lynch et al. (2015) who compared two commercial FTWs (Beemat and Biohaven®) planted with the rush *Juncus effusus* that had been designed to treat storm water. It was found that Beemat FTW outperformed Biohaven® in both TN and TP removal (Lynch et al. 2015). The difference in removal may have been due to the difference in substrate (coir matting vs. sphagnum peat) or the physical design of FTW (Lynch et al. 2015). The growth medium is indeed an important source of variability within FTW design. Rice straw used as growth medium was found to enhance removal of TN, NH_4^+ and NO_3^- compared to plastic filling (Cao and Zhang 2014). Similarly, the FTW with straw filling had a greater total density of nitrifying and denitrifying bacteria which suggests that this organic material was providing both a habitat and a source of C for the growth of microorganisms, which were able to contribute to pollutant metabolism (Cao and Zhang 2014). Commercial FTWs are still an expensive management option, and there is currently a demand for more low-cost growth media that both provide a suitable substrate for macrophytes and enhances pollutant removal and such examples include biochar, activated carbons, coffee waste and green compost (Tran et al. 2015). To date, there has been no research incorporating these materials into FTWs to assess the potential for enhanced remediation and the potential value post-remediation.

Hybrid FTW planting systems are being developed in an attempt to enhance pollutant removal and ecosystem restoration (Guo et al. 2014; Li et al. 2010; Lu et al. 2015). Such systems integrate a new layer beneath the floating platform containing submerged macrophytes such as *P. crispus*, and/or bivalves such as freshwater clams (*Corbicula fluminea*) (Guo et al. 2014; Li et al. 2010) (Fig. 7.6). Photovoltaic solar panels have also been attached to the frames of FTW to power a submerged aerator to enhance oxygenation in the vicinity of the plant roots and associated microorganisms, thus increasing the nutrient degradation process (Lu et al. 2015) (Fig. 7.6). Whilst these hybrid systems appear to enhance pollutant removal from the water column compared to their macrophyte-only counterparts (Guo et al. 2014; Li et al. 2010), the added complexity may impact on the utility of FTW as a phytoremediation system. With the increasing complexity of FTW design, there is an increase in pollutant removal efficiency, cost and maintenance, but a there may also be a decrease in user uptake given the added management of submerged plants or solar PV systems. A focus on maximising removal efficiency over the simplicity of the system may create barriers for uptake by stakeholders such as farmers, land managers and government organisations looking for low-cost low maintenance treatment options, especially within developing countries. A useful exercise might be to compare the economics, maintenance requirements and user experience of hybrid versus conventional FTWs to determine when increasing FTW complexity is appropriate.

The coverage of FTW over the target water body is also important, as indicated by a meta-analysis showing that vegetation cover is significantly correlated with the removal of NH_4^- (Pavlineri et al. 2017). Although increasing FTW coverage reduces atmospheric diffusion, oxygen is supplied to water by emergent plants via root oxygenation (Xiao et al. 2016; Yeh et al. 2015). Furthermore, in eutrophic waters this coverage may inhibit algal primary productivity, which may be beneficial for mitigating the potential for occurrences of large algal blooms (Jones et al. 2017). The optimal coverage of FTWs has been reported as 10–25% (Marimon et al. 2013), although generally there is wide variation in the literature with values of between 100, 50 and 5–8% being reported as acceptable for water treatment (Pavlineri et al. 2017). McAndrew and Ahn (2017) also note that hydraulic retention time and plant productivity are important for determining removal efficiency. Surface cover therefore needs to be considered in tandem with hydrology and macrophyte selection. As the focus within the literature is on coverage, there has been no clear attempt to look at the different surface arrangements of FTW on the water surface at field scale. For example, targeting of an area, such as water inlet or outlet to a lake, may be more beneficial than increased FTW coverage over the target water body. Clearly, the coverage and area of FTW treatment are context-specific but there is likely to be significant potential in investigating spatially targeted phytoremediation.

Finally, the poor design and management of FTWs are a topic that is rarely discussed in the literature. FTWs have the potential to be pollutant sources should the

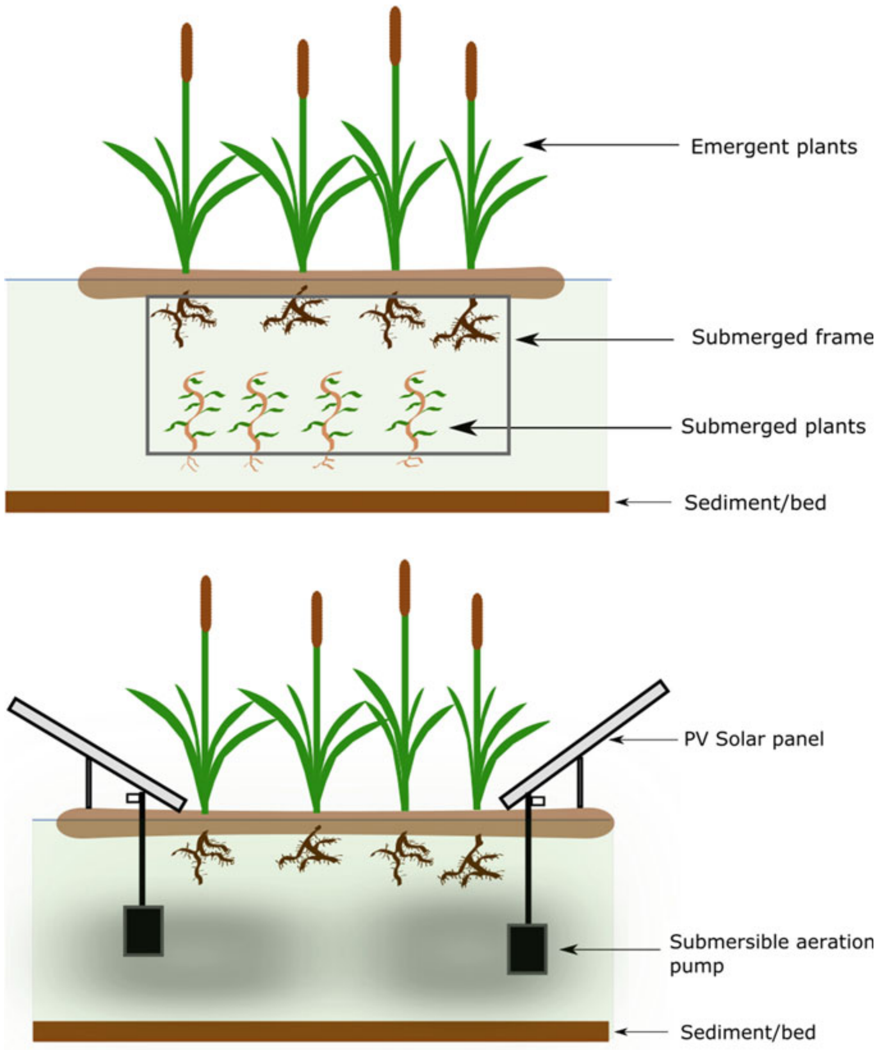

Fig. 7.6 Top, a schematic representation of a hybrid FTW including submerged vegetation. Bottom schematic representation of a FTW incorporating solar technology to power an aeration device

biomass not be continually harvested and removed, or if water birds attracted to the FTWs defecate into the water inputting nutrients and microbial contaminants (guanotrophication). Nutrient-rich growth media such as peat may also leach nutrients into the target water body compared to more inert coir fibre (Lynch et al. 2015). The placement of FTWs in watercourses must also be given full consideration as water birds and recreational users may also use the target water body. FTWs potentially slow the velocity of water in small water bodies such as ditches, which may conflict with farming interests where good drainage is required. As with any good catchment management practice, appropriate consultation with stakeholders is important for success.

7.7 Translocation and Element Storage in Macrophytes

Understanding how and where nutrients and other pollutants are distributed within macrophyte tissues is important to inform plant harvesting for the removal of pollutants. The recovery of nutrients is crucial for the value of post-harvest plant biomass, whilst ensuring correct plant parts are harvested for effective removal of heavy metal and organic pollutants from the planting system. Allometry of pollutants within plants varies according to species, but is also influenced by the environmental conditions in terms of nutrient availability (Barrat-Segretain 2001; Demars and Edwards 2007).

Typha domingensis, *E. crassipes*, *P. stratiotes* and *M. aquaticum* preferentially store N and P in the shoot compared to the roots or rhizome (Table 7.6), although nutrients can be translocated through the plants leading to temporal dynamism in element distribution driven by plant phenology and diurnal metabolism (Masclaux-Daubresse et al. 2010; Hawkesford et al. 2011; Eid et al. 2012). More than 50% of N can be stored in below-ground plant parts by the end of a growing season (Vymazal 2007). *P. australis* grown in either natural waters or a wastewater infiltration pond demonstrated a clear seasonal pattern in the translocation of nutrients from above-ground to below-ground parts as the end of the growing season approached (Meuleman et al. 2002). Early in the growing season, N and P concentrations are higher due to sink demand during active growth before concentrations decrease gradually through the season as plants begin to senesce.

Coinciding with the decrease in nutrient concentrations in above-ground biomass, below-ground concentrations of N and P increase, representing the preparation for plant senescence with nutrient storage in the roots and rhizomes for the following season's growth (Garver et al. 1988). Meuleman et al. (2002) suggested that harvesting during the winter meant that only 9% of N and 6% of P associated with nutrient loading was removed, whereas harvesting above-ground parts during peak nutrient storage in summer enhanced removal to 40–50% of N and P. Seasonality is important, although seasonal effects will differ between temperate, subtropical and tropical zones with macrophytes in the latter two zones showing less element translocation and therefore enabling multiple annual harvests (Vymazal 2007). Macrophytes may perform poorly if nutrient translocation to the rhizome is inhibited by harvesting during the active growing period (Tanaka et al. 2017), although the issue of nutrient allocation is less problematic for floating macrophytes and emergent macrophytes deployed in FTWs as the full plant can then be harvested (Wang et al. 2014).

Studies on element allocation tend to report absolute concentrations to determine if a species is a better above-ground or below-ground accumulator. The potential for pollutant uptake and removal by harvesting the areal parts is a function of both concentration and the biomass produced (Polomski et al. 2009). For example, although

Table 7.6 Plant allocations of pollutants in selected emergent, floating and submerged macrophytes

Species	Growth form	Plant allocation of pollutant		References
		Above-ground	Below-ground	
Cyperus riparia	Emergent	Cd, Ni, Zn		Ladislas et al. (2013)
Cyperus esculentus	Emergent	Cd, Cr, Cu, Fe, Mn, Ni	Pb	Chandra and Yadav (2011)
Glyceria maxima	Emergent	Cu, Fe, Mn, Ni, Zn		Parzych et al. (2016)
Juncus effusus	Emergent	Cd, Ni	Zn	Ladislas et al. (2013)
Phalaris arundinacea	Emergent	Cu, Fe, Mn, Ni, Zn		Parzych et al. (2016)
Phragmites australis	Emergent	Cu, Fe, Ni, Zn	Mn	Parzych et al. (2016)
		Cr, Cu, Mn, Ni, Zn		Duman et al. (2007)
Phragmites australis	Emergent	Cd, Cu, Zn	Cr, Fe, Mn, Pb	Chandra and Yadav (2011)
Schoenoplectus lacustris	Emergent	Cu, Ni, Pb, Zn		Duman et al. (2007)
Typha angustifolia	Emergent	Cd, Cr, Cu, Fe, Mn, Ni, Pb	Zn	Chandra and Yadav (2011)
Typha domingensis	Emergent	Ca, Cu, Fe, P, Zn	N	Eid et al. (2012)
Typha latifolia	Emergent	Cu, Fe, Ni, Zn	Mn	Parzych et al. (2016)
Eichhornia crassipes	Floating		N, P	Polomski et al. (2009)
Pistia stratiotes	Floating		N, P	Polomski et al. (2009)
	Floating	Al, Cd, Co, Cr, Cu, Fe, K, Mg, Na	Ca	Lu et al. (2011)
Micranthemum umbrosum	Submerged	Cd	As	Islam et al. (2013)
Myriophyllum aquaticum	Submerged		N, P	Polomski et al. (2009)

shoot concentration of N in *P. stratiotes* (13.93 mg/g) was greater than in *E. crassipes* (10.16 mg/g) in a study of nutrient recovery, the total areal shoot storage of N for *E. crassipes* was over four times higher due to its greater biomass (Polomski et al. 2009). This demonstrates that it is more effective to harvest plants with greater above-ground biomass and moderate tissue concentrations of the pollutant of interest, rather target plants with lower biomass but higher tissue concentrations (Duman et al. 2007; Vymazal 2016).

In eutrophic waters, light is commonly the limiting factor for growth and plants therefore tend to allocate nutrients to above-ground growth to maintain efficient light capture, whilst excessive nutrient availability negates the requirement for below-ground storage (Polomski et al. 2009; Lynch et al. 2015); this also maintain intra-specific competitive advantages in these environments and can be exploited as part of a phytoremediation management strategy. Where non-hyperaccumulator plants are grown in a substrate and where high concentrations of heavy metals and organic pollutants are present, physiological mechanisms within these plants often limit the transport of these compounds to above-ground tissue to mitigate damage to important cells, such as those responsible for photosynthesis (Zhu et al. 1999; Verkleij et al. 2009).

The preference for below-ground storage by emergent macrophytes has been demonstrated in multiple studies, as listed in Table 7.6. However, there are some occasions where metals are found at greater concentration in aerial parts, such as Pb in *Cyperus esculentus*, Zn in *Glyceria maxima*, Mn in *P. australis* and Cu in *P. australis* (Table 7.6), which suggests that specifically classing species as above-ground or below-ground accumulators of specific pollutants may be inappropriate. Furthermore, not all studies capture the full seasonal dynamics of nutrient or pollutant translocation and allometry under different concentration regimes, and therefore, to enable sound recommendations on harvesting during phytoremediation projects, further studies to characterise chemical allocation over time of key species should be carried out to ensure pollutant removal is appropriately targeted.

7.8 The Role of Microbial Activity in Aquatic Phytoremediation

There is debate within the phytoremediation literature as to the relative importance of macrophytes in removing pollutants compared to the independent microbial degradation. This perspective primarily comes from observations showing that unplanted CWs can match or outperform planted CWs in terms of pollutant removal (Cardinal et al. 2014). In addition to microbial activity, processes such as sedimentation in P stabilisation and removal, and the photodegradation of PPCPs have also been noted as important (Cardinal et al. 2014; Tanner and Headley 2011; Zhang et al. 2014a, b). Microbial activity is also an important factor for enabling phytodegradation of pollutants; however, the independent role of microbial communities is now receiving much more attention (Houda et al. 2014). Improved understanding of how microbial activity contributes to pollutant degradation is essential because it not only influences removal rates but may have implications for the value of harvesting plant biomass and post-remediation resource recovery if the actual plant uptake and sequestration (phytoextraction) of target pollutants is low.

There is an abundance of microorganisms associated with macrophyte roots that influence the removal and degradation of pollutants (Stottmeister et al. 2003; Faulwetter et al. 2009). These include bacteria that assist in nitrification and denitrification for the transformation and removal of excess N, and biological mineralisation of organic P (Valipour and Ahn 2016). These processes are integral to the efficient functioning of CWs but the role of macrophytes in facilitating and enhancing the metabolic processes of these microorganisms is still not well understood, although it is likely that the rhizosphere provides an energy source for microorganisms (Thijs et al. 2016). Redox state, dissolved oxygen content and temperature are common limiting factors for different microorganisms (Truu et al. 2009), and the potential for macrophytes to oxygenate the substrate surrounding their below-ground organs can also facilitate the growth of microbes in the rhizosphere (Pavlineri et al. 2017).

CWs are highly engineered, with multiple design elements that may influence the abundance and diversity of microorganisms. Consequently, carefully designed experiments are required to explore the potential role of the plant microbiome in phytoremediation. Applying this knowledge is particularly important for developing novel environmental engineering solutions such as FTWs. The formation of microbial biofilms on the underside of FTWs and plant roots has been suggested as a key removal pathway for nutrients and heavy metals (Tanner et al. 2011). Wang and Sample (2014) found that unplanted FTWs had similar removal efficiencies compared to those planted with monocultures of *P. cordata* and *Schoenoplectus tabernaemontani* (Fig. 7.7). In this study, and elsewhere, temperature was a key factor in the performance of FTW which has been related to changes in microbial activity (Van de Moortel et al. 2011; Wang and Sample 2014). In contrast, Zhang et al. (2014a, b) were unable to link microbial community traits associated with FTWs biofilm such as ribotype number and diversity index to the removal efficiency of pollutants.

Given the conflicting evidence on the relative importance of plants and biofilms in phytoremediation, a 'metaorganism' approach to phytoremediation is now required

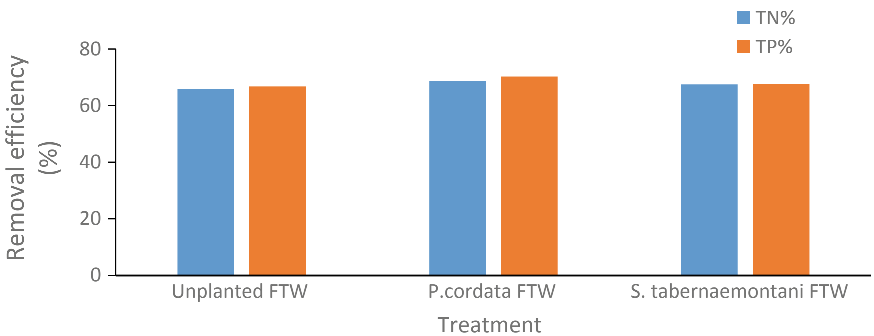

Fig. 7.7 Removal efficiencies of TN and TP for an unplanted FTW, a *P. cordata* planted FTW and an *S. tabernaemontani* FTW. Raw data taken from Wang and Sample (2014)

to appreciate the multitude of factors and process at work (Thijs et al. 2016; Feng et al. 2017). Further studies are required in these areas that employ suitable control treatments, along with adequate spatial and temporal characterisation of microbial communities for different macrophytes in monoculture and polyculture, and growth media. Furthermore, within these studies the mass balance of pollutant allocation should be investigated to fully assess where and how pollutants are being stored and translocated. Radio-labelled isotopes have been successfully employed to quantify the cycling of nutrients within CWs (Truu et al. 2009). However, such techniques have not been employed during FTW studies, where the application of radio-labelled isotopes would provide an opportunity to understand the biochemical cycling with these novel systems. Finally, after adequate characterisation of microbial communities and their relation to the plant and associated abiotic environment, there may be new opportunities to enhance the microbial community to promote pollutant removal (Glick 2003; Thijs et al. 2016).

7.9 Added Value of Aquatic Phytoremediation

7.9.1 Ecosystem Services

The process of phytoremediation has primarily been concerned with maximising the efficiency of water treatment, whilst the benefits of phytoremediation over and above remediation have essentially been overlooked. Clearly, water treatment is the primary ecosystem service in the provision of safe and clean water; however, the planting of vegetation within the environment creates new habitats for organisms (Zhu et al. 2011). For example, the presence of artificial floating islands improved the chick productivity of black-throated divers (*Gavia arctica*) by 44% in waterbodies with these structures (Hancock 2000), indicating a potential combined role for FTWs in water treatment and improved habitat connectivity. Similarly, a 15-year project investigating the environmental benefits of creating treatment wetlands to ameliorate mine-tailing effluents found that there were a high abundance and diversity of protozoa, higher plants, terrestrial animals and birds (Yang et al. 2006).

In addition to habitat provisioning, there is also the potential for facilitating pollination and carbon sequestration (Nesshöver et al. 2017). The capacity for the latter may depend on the post-remediation stage and the reuse of the biomass. Cultural services can also be provided by an improvement in the aesthetic appeal of an area with increased vegetation (Masi et al. 2017). This is most likely in urban waterways where FTW might provide attractive green infrastructure (Olguín et al. 2017). There is a need to quantify and assess ecosystem services associated with phytoremediation projects in order to better appreciate the multiple benefits generated from this form of water treatment.

7.9.2 Resource Recovery

The potential to generate large volumes of biomass through phytoremediation means that there are opportunities for resource recovery within the process (Gomes 2012). Post-remediation biomass reuse streams (PBRSs) are the disposal process and utilisation of the harvested plant tissues of macrophytes used for phytoremediation (Gomes 2012). As macrophytes are able to remove and assimilate metals, there is certainly potential for the recovery of metals such as gold, Cu and Ni (phytomining) (Anderson et al. 2005). To date, most research in this area has focused on terrestrial plants and soils contaminated through industrial mining (Rosenkranz et al. 2017). However, there may be potential to explore metal-contaminated waters and sediments of wetlands used to treat mine-tailing effluents. The usefulness of this process depends on the current market value of target metals and the economic benefits associated with this form of phytoremediation (Sheoran et al. 2009).

The use of macrophytes as biofuels is another possibility and is a feasible option to increase the value of phytoremediation if there is a market for biomass. An economic assessment by Jiang et al. (2015) found that high biomass production plants are required to make this a profitable venture. However, different options need to be considered in pre-treatment, such as de-wetting and briquetting, since fresh plant biomass comprises up to 90% water (Newete and Byrne 2016). Macrophyte biomass may also be used for animal feed, or to make compost or biochar (Quilliam et al. 2015; Tanaka et al. 2017). Quilliam et al. (2015) discussed in detail the issues with these PBRSs in terms of the transfer of pathogens, bio-magnification of heavy metals and propagation of invasive species. A phytoremediation decision-making system that couples the target pollutants, and the PBRS would allow the resource recovery options to be established early in the process (Song and Park 2017). For example, the remediation of a eutrophic lake would seem to link well with composting or animal feed PBRS given the potential for high nutritional content. However, if heavy metal or pesticide contamination also is identified, then a biofuel or phytomining PBRS may be more appropriate. Larger-scale pilot tests of aquatic phytoremediation are required, and these should explore the feasibility of using produced biomass in PBRSs.

7.10 Summary and Future Perspectives

This chapter has outlined the potential of aquatic phytoremediation to provide efficient, multi-targeted and sustainable remediation solutions for polluted waters. A summary of a proposed research agenda required to fulfil the potential of these systems is presented in Table 7.7. Given the wide range of organic, inorganic and biological pollutants that can impact surface waters, there is a need to steer phytoremediation towards a context-specific approach that allows the remediation of multiple water body types, and waters affected by a range of pollutants.

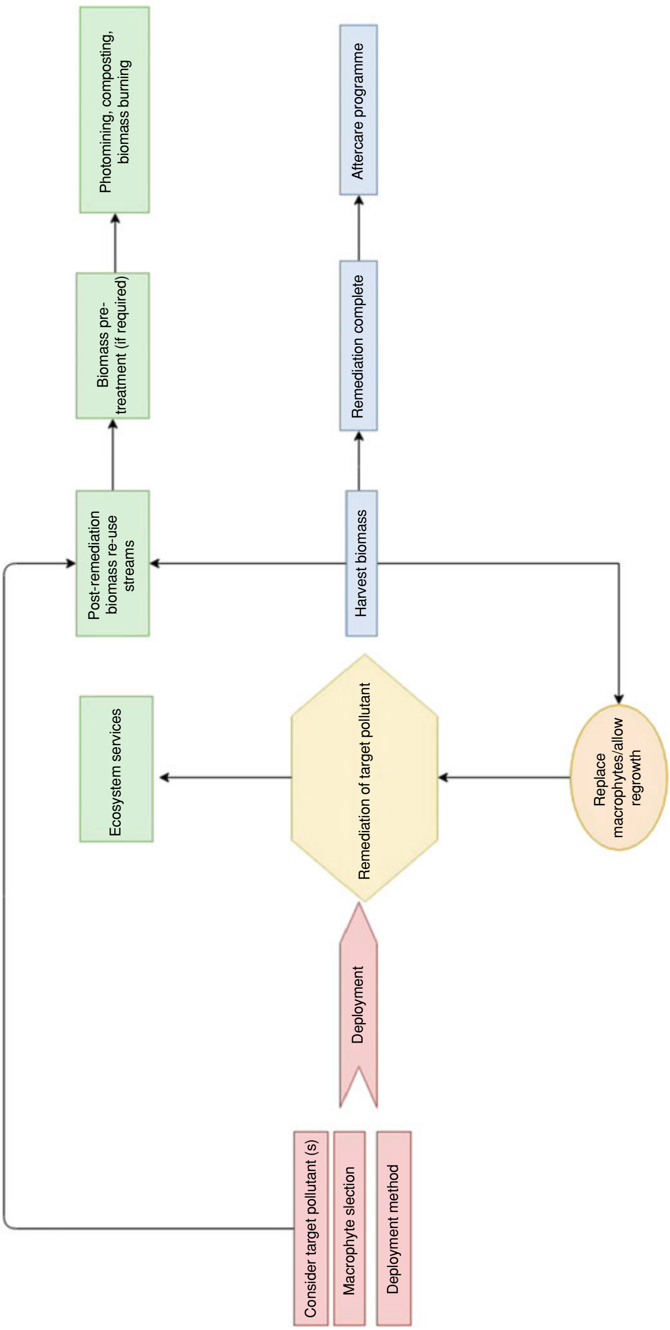

Fig. 7.8 Process diagram illustrating the proposed phytoremediation process in its entirety

Table 7.7 Summary of the aquatic phytoremediation research agenda required to deliver efficient, multi-targeted and suitable phytoremediation. Research areas, specific lines of investigation and their priority are highlighted

Research area	Lines of investigation	High priority (0–2 years)	Medium priority (2–5 years)	Low priority (5–10 years)
Identify new macrophyte accumulators for emerging pollutants	To what extent can macrophytes assimilate and degrade PPCPs and pathogens?			
Plant community-based remediation	Evaluate potential for multi-targeted remediation in plant polyculture incorporating temporal/Phenological differences and asses plant competitive effects			
Investigate the role of microbial communities on pollutant uptake/removal	Adopt a 'Metaorganism' approach to address the role of microorganisms and biofilms in phytoremediation by ensuring studies have suitable control treatments, assess spatial and temporal variation in microbial communities in order to fully characterise the bacteria by their functions Investigate how microbes can maximise the phytoremediation process by different plant associations and FTW growth media Mass balance studies required, potentially incorporating radiolabelled tracers			
Assess provision of phytoremediation to provide ecosystem services	Identify and quantify ecosystem services associated with phytoremediation to appreciate the value of method over and above water treatment			
Develop a system for macrophyte selection	Develop a suitable system for macrophyte selection to provide context-specific phytoremediation as a tool for environmental agencies and stakeholders			

(continued)

Table 7.7 (continued)

Research area	Lines of investigation	High priority (0–2 years)	Medium priority (2–5 years)	Low priority (5–10 years)
Identify accumulation zones of pollutants within macrophytes	Further studies into the allocation and translocation of pollutants within plants with temporal assessments of the optimum time to harvest biomass			
Explore novel ways of deploying macrophytes in the environment for phytoremediation	Explore new ways to deploy macrophytes into aquatic environment, especially by developing aquatic-aquatic attenuation and inducing growth in native flora Undertake large scale studies of FTWs that assess remediation and FTW surface spatial arrangement Assess stakeholder usability of novel phytoremediation methods			
Determine the effect of different growth media on pollutant removal	Assess influence of different FTW growth media e.g. biochar			
Determine post-remediation re-use streams for resource recovery	Investigate feasible options for resource recovery and identify' context-specific post-remediation biomass re-use streams that link with target pollutants e.g. biomass as fertilizers			
Testing macrophytes for individual accumulators	Continue testing new macrophytes for phytoremediation for inorganic, organic and biological pollutants. Focus on finding non-invasive plants.			

With the development of novel ways to deploy macrophytes, such as by FTWs, there are emerging options for spatial flexibility of applying phytoremediation, which is relatively inexpensive. Larger-scale pilot studies are required in this respect to assess the realistic opportunities for use. At present, there are a wide range of macrophytes of different growth forms that have been established as efficient accumulators of pollutants. A further focus is required to investigate the remediation potential of submerged species and to establish new accumulators that may be used. Importantly, some of the key hyperaccumulators are considered invasive and would be unsuitable to be deployed in natural surface waters. A proposed advancement for phytoremediation systems is to consider the benefits of a plant community-based approach that assembles polycultures of macrophytes with good accumulation capacity for different pollutants, enabling multi-targeted remediation. Here, the need for a logical system of macrophyte selection based on plant removal efficiencies and environmental tolerances, and target pollutant specifications, requires development.

The process of macrophyte phytoremediation still requires a deeper understanding of how to enhance removal efficiency and ensure sustainable harvesting of macrophytes. Understanding the spatial and temporal dynamics of pollutant translocation within macrophytes is crucial for permanent pollutant removal from water and for maintaining the economic value of different PBRSs. Furthermore, a 'metaorganism' approach needs to be considered in future phytoremediation studies to establish the role of plant-associated microbial communities. There may be untapped potential in manipulating these microbial communities for enhanced performance.

Finally, the focus of phytoremediation has been on the water treatment aspect, whilst there is growing recognition of the capacity of these ecological engineering strategies to provide ecosystem services such as carbon sequestration and biodiversity support. These benefits need to be better quantified to determine the added value of phytoremediation. With the waste management sector shifting towards a life-cycle approach, there are clear opportunities for resource recovery through identifying PBRSs such as composting, biofuel production and animal feed. These PBRSs require further exploration in terms of their safety, value and ability to link directly with the target pollutants removed (Fig. 7.8). A life-cycle approach needs to embed in prospective aquatic phytoremediation projects, to ensure that target pollutant(s) are being considered in tandem with the PBRS, whilst the frequency of harvest and replacement/regrowth of macrophytes is properly linked into the remediation of the target pollutant (Fig. 7.8).

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Chapter 8
Phytoremediation of Explosives

Stephen M. Via

Abstract The widespread use of civilian, industrial, and military munitions has led to pollution by explosive compounds in aquatic and terrestrial environments. Each step in the life cycle of a munition from production, transport, storage, distribution, and destruction can introduce explosives as pure liquid or solids via leaching, contaminant spills, trace particles, whole or partial unexploded and exploded ordnance. Remediating explosives is difficult because the behavior of any one explosive compound is rather difficult as a number of factors can vastly alter how it moves, where it binds, and how it is sequestered by organisms. The phytoremediation of explosives focuses largely on sequestering compounds in their parent forms or transforming and degrading the compounds to inert forms using inherent metabolic processes in the plants themselves.

Keywords Degradation · Explosives · Munitions · Nitrate esters · Nitroamines · Nitroaromatics · Phytoremediation · Ordinance · Secondary contamination · Sequestration · Tolerance

8.1 Explosive Compounds

8.1.1 The Explosives Issue

The result of widespread historical use of munitions as a part of civilian, industrial, and military endeavors, explosive compounds contaminate large portions of the globe (Fig. 8.1; Myler and Sisk 1991; Pichtel 2012; Kholodenko et al. 2014). Wartime and industrial activities are the largest contributors of explosives into the environment (Best et al. 1998; Just and Schnoor 2004; Pichtel 2012; Certini et al. 2013). Militaries have long depended on the utilization of explosives to assault and defend. Munitions containing reactive compounds have been long established as an effective tool of armies, with the use of gunpowder in battle tactics dates as far back as 969 CE in

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Fig. 8.1 Global map showing distribution of explosives. Country color represents particular levels of contamination (clean/no data, low, moderate, medium, heavy, and very heavy contamination). Contamination data obtained from EPA (2014), The Monitor (2013), Japan Air Raids.org. (2015), and THOR (2015). Modified from Via et al. (2016)

China (Kelly 2004). Throughout World War II (WWII), 2–2.7 million tons of bombs were dropped on Germany and occupied Europe. Given that these devices had a known failure rate of 5–15% (Eckardt 2012) there exsists roughly 27,000–300,000 unexploded ordnances (UXOs) across Europe (Abad-Santos 2012). The German government has stated that ~391,000 ha inside of its borders still need bomb removal operations to occur (Crossland 2008) with 3000 or more bombs under Berlin alone (Huggler 2015). More recent conflicts have also left staggering numbers of UXOs as well. The Pacific is littered with relic UXOS from not only WWII but both the Korean and Vietnam conflicts with Korea possessing 9100 ha of mined land outside the demilitarized zone (DMZ) (The Monitor 2009) and Laos containing over 750,000 tons of ordnance in its soils (Suthinithet 2010; Pichtel 2012). Just within the last 30 years, Iraq is estimated to have ~20 million landmines covering ~150 million ha (CISR 2013) and along the Syria–Turkey border there are an estimated 613,000–715,000 landmines present (HRW 2014). Today, 68 nations acknowledge some form of munitions issue within borders (Fig. 8.1). Even in the USA, a country that has not seen a major armed conflict on its soil since the 1860s, there are over 2000 Environmental Protection Agency Superfund sites and Department of Defense locations and numerous other areas with explosives contaminated soils (Jenkins et al. 2006; EPA 2014).

8.1.2 Sources

Explosive compounds enter the environment through a number of avenues; however, the largest contributor is by far military activities and industries. Every step in the life cycle of a munition from production, transport, storage, distribution, and destruction can introduce explosives as pure liquid or solids via leaching, contaminant spills, trace particles, whole or partial unexploded and exploded ordnance (UXOs). Abandoned UXOs range from bombs, to mortar rounds, to landmines (Fig. 8.2). Detonation does not mean that there are no contaminants left behind either. During a detonation event, the explosive compounds contained within the device do not entirely get consumed in the explosion. Residues, trace particles, and even whole portions of the munition/casing can be left behind, causing the release of these toxic chemicals into the surrounding area. This means that areas far removed from the actual conflict where munitions see use can possess elevated concentrations of contaminants. Beyond military activities the largest source of explosives contamination is industrial scale mining. Despite some types of mining having shifted away from large scale use of explosives they were heavily used in the past and are still used today (Kholodenko et al. 2014). Underground mining, for instance, has largely moved away from blast mining techniques while surface mining still relies heavily on them. Be it from historic of currently activing mining operations the potential for explsoives release is still present (Dick et al. 1983; Tiwary 2001). Contaminant releases from mining

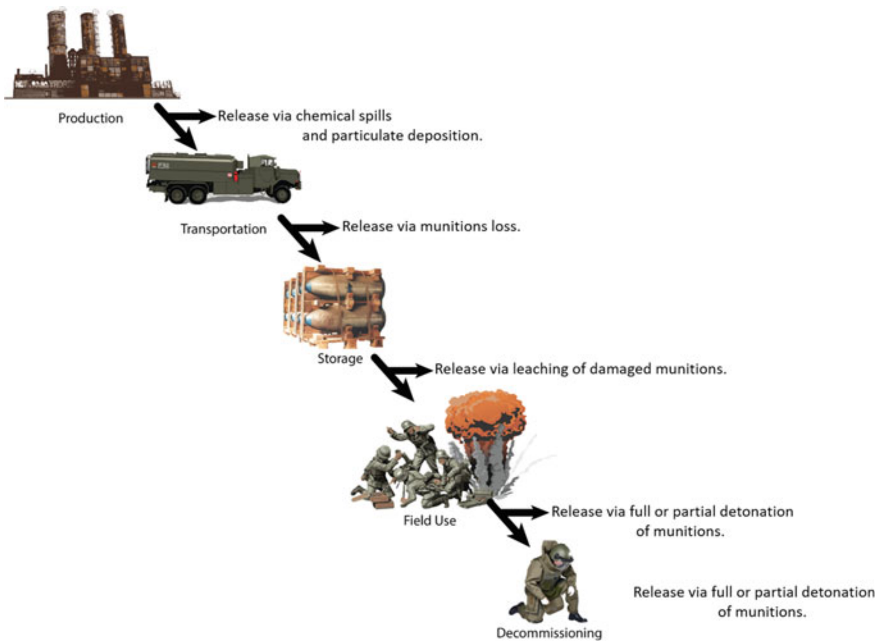

Fig. 8.2 Chain of potential sources of explosives contamination

operations are similiar to those of munitions. Leaching from stores, partial detonation of devices, and fractional residues playing a large role (Tiwary 2001). Additional sources that release explosives to a much smaller degree include fireworks, personal firearms, lacquers, paints, and even dyes (Hamilton 1921; Almog and Zitrin 2009).

8.1.3 Types of Explosive Compounds

Conventional explosive compounds can be grouped into three categories: (1) nitroaromatics, (2) nitroamines, and (3) nitrate esters. These groupings are based on structural differences of the associated compounds (Fig. 8.3). Nitroaromatics are characterized by their central aromatic ring with nitro groups attached at various points. Among these TNT is the only one which has seen large scale, long term, use. Other nitroaromatics can form during the degradation process of TNT and therefore can be present in contaminated areas; DNT and ADNT are the most common. Nitroamines are a smaller group of energetic compounds comprised of a central heterocyclic ring possessing N-nitro groups. Among nitroamines, RDX and HMX are the most widely used. Nitrate esters are esters of alcohols and nitric acid. These are the least toxic

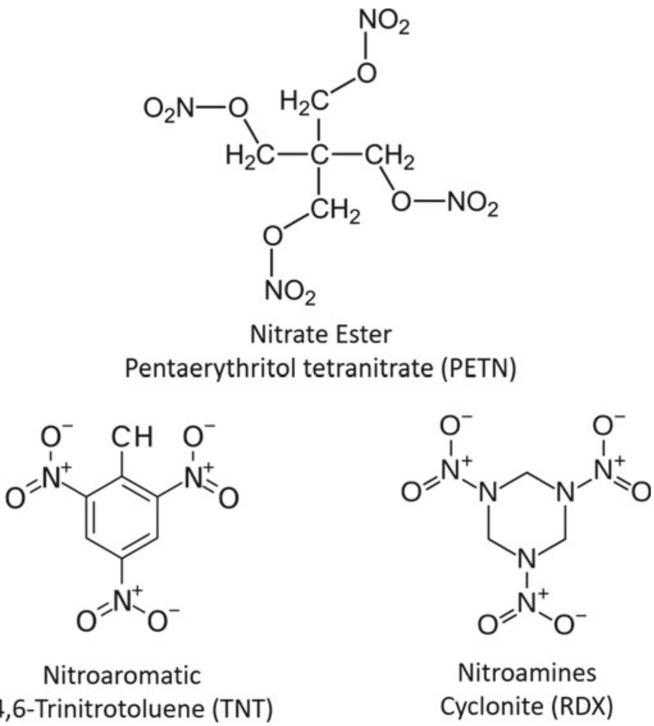

Fig. 8.3 Structural composition of common explosive compounds from the three different classes

explosive compounds used, with the most common examples being glyceryl trinitrate (nitroglycerin; GTN) and pentaerythritol tetranitrate (PETN).

Insensitive munition compounds and are largely comprised of a central aromatic or hetero-aromatic structure, high degree of hydrogen bonding, low oxygen balance, and have low free space due to efficient crystal packing (Pagoria 2016) reducing sensitivity to triggering stimuli. This reduces human risk when preparing, packaging, shipping, and deploying munitions as opposed to other compounds. While a great achievement for human safety, these compounds have only recently started to garner focus in ecotoxicological studies (Dontsova et al. 2014; Madeira et al. 2018). The most recent development in explosives is the persuit of "green" exlosives compounds which pose a lower risk environmentally.

Due to prolonged industiral reliance widespread use in major military conflicts of the last century, nitroaromatics and nitroamines comprise the largest proportion of explosive compounds currently in the environment (Via and Zinnert 2016). RDX and TNT containing munitions in particular have comprised the majority of those used to date and as such have garnered much of the focus in the literature.

8.1.4 Compound Behavior in the Environment

Predicting the behavior of any one explosive compound is rather difficult as a number of factors can vastly alter how it moves, where it binds, and how it is sequestered by organisms (Pichtel 2012). Explosive contaminants generally occur in the soil as particles or residues from munitions production or use and it is through dissolution into the soil that they are dispersed into the surrounding area (Pennington et al. 2008; Kalderis et al. 2011). Explosive compounds are mobile in solution and once they are in the environment do not remain at the point of release, rather they spread outward through the soil pore matrix (Pennington and Brannon 2002; Kiiskila et al. 2015; Taylor et al. 2015; Fig. 8.4). Variations in aqueous solubility of these compounds lead them to be stratified throughout the soil column (Pichtel 2012). Nitroamines have been shown to percolate deeper into the soil than nitroaromatics and nitrate esters but all compounds tend to appear at the highest concentrations within the first 15 cm from the surface (Pichtel 2012). Chemical releases input a single pulse of toxins into an area; however, the detonation of munitions and/or presence of UXOs can lead to long-term release patterns. The relatively low solubility of many common explosives leads to continuous release pulses into surrounding areas as munition and UXO particles degrade over time (Pennington et al. 2006; Taylor et al. 2015).

Contact with soil upon release can lead to sorption of explosive compounds to soil particles. Sorption occurrence and permanence are dependant on compound structure. Nitroaromatics are susceptible to binding with soil particles and is largely a reversible process. Nitroaromatics and nitrate esters are not readily sorbed to soils and when it does occur the bond is very difficult to break (Pennington and Brannon 2002). This is a factor that can be manipulated, however, to improve phytoremediation success. Absorption can be enhanced by the addition of sorption enhancing chemicals

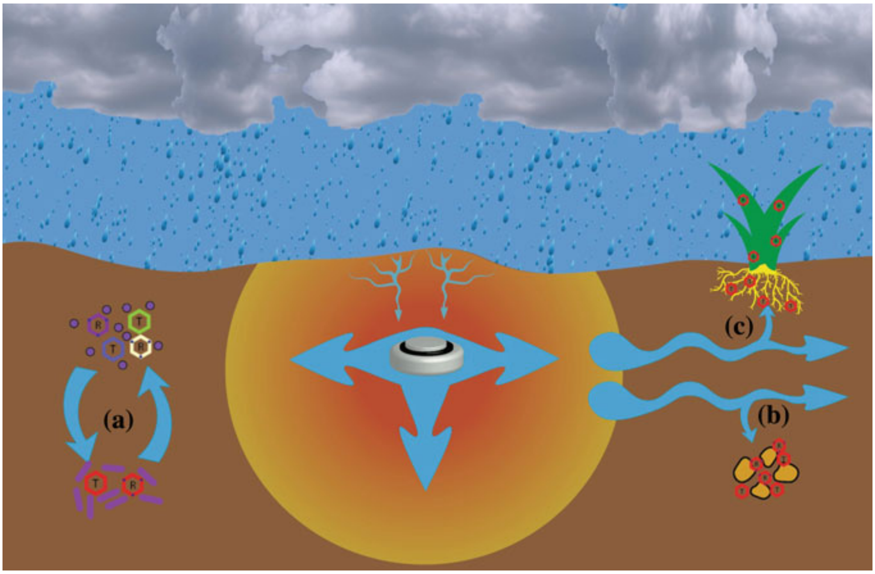

Fig. 8.4 Visualization of environmental behavior of explosive compounds in soils. Center icon represents a unexploded ordnance (UXO) and the color behind it represents the diffusion of contaminants. Water is denoted by blue arrows and contaminant presence outside of the central diffusion zone is indicated by colored pentagons. Region **a** represents microbial interactions and metabolism, **b** sorption to soil particles, and **c** uptake and sequestration by above and below-ground plant tissues

(Jung and Nam 2014) and desorption or release can be enhanced via surfactant additions (Pennington et al. 1995). Modulating soil binding can make more or less of the compound bioavailable to surrounding biota depending on the needs of the remediation plan.

8.2 Explosives and Vegetation

8.2.1 Contaminant Uptake

Plant–Contaminant interactions start with the uptake of contaminants, generally through the liquid solution in the soil pore matrix. Bioavailable explosive compounds in soil solution will enter plant roots unimpeded due to bulk flow water movement driven by leaf transpiration (Singh and Mishra 2014). Inside the root, the explosive compounds can travel between inter-membrane spaces (Ghosh and Singh 2005) eventually passing through the protective Casparian strip, onward into the xylem, and finally be deposited throughout the plant (Pilon-Smits 2005). Patterns of explosive compound contamination partitioning are largely conserved across species yet plant health and function responses are not (Via and Zinnert 2016).

8.2.2 Phytotoxicity

Explosive compounds are highly phytotoxic and can induce a wide range of stress responses in vegetation from impaired cellular function to morphological deformation. Responses to these contaminants vary based on species of plan, age at exposure, compound type, and concentration (Robidoux et al. 2003; Winfield et al. 2004; Just and Schnoor 2004; Vila et al. 2008; Ait Ali et al. 2014; Via et al. 2014). Morphological and physiological responses in vegetation to TNT presence appear at much lower concentrations than for RDX (Peterson et al. 1996, 1998; Pilon-Smits 2005; Vila et al. 2005; Zinnert 2012; Via et al. 2014). Impacts of exposure to explosives largely reflect compound localization in the plant. Nitroamines like RDX are predominantly bound to above-ground tissues causing significant damage to leaves (Winfield et al. 2004; Vila et al. 2007; Via et al. 2014) and impairs photosynthetic function (Thompson et al. 1998; Ait Ali et al. 2006; Zinnert 2012; Zinnert et al. 2013; Via et al. 2014). Common morphological changes induced by RDX are leaf necrosis, chlorosis, altered or disfigured leaf margins, reduced leaf size, and atypical bilateral symmetry (Winfield et al. 2004; Vila et al. 2007; Khatisashvili et al. 2009; Singh and Mishra 2014; Via et al. 2014; Fig. 8.5). Nitroaromatics like TNT are largely bound in below-ground tissues (Peterson et al. 1998; Vila et al. 2007; Khatisashvili et al. 2009; Singh and Mishra 2014) and result in impaired root growth, damage to existing root structures, as well as limited root functionality (Peterson et al. 1998; Gong et al. 1999; Krishnan et al. 2000; Vila et al. 2007; Khatisashvili et al. 2009; Singh and Mishra 2014). Nitrate esters have not undergone the extensive testing that other groups of explosives have, however, they has been shown to inhibit seed germination, seedling establishment, and early plant development (French et al. 1999).

Morphological responses have been more widely investigated than physiological ones but exposure to explosives can alter carbon assimilation, carboxylation,

(a) (b) (c)

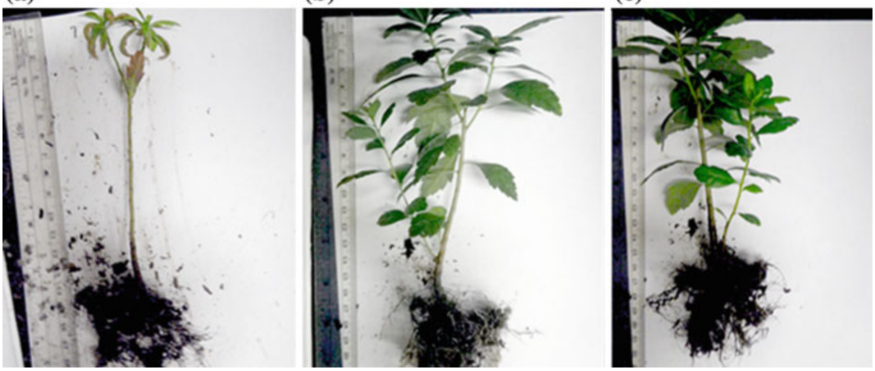

Fig. 8.5 Morphological impacts of RDX (**a**) and TNT (**c**) on vegetation relative to reference (**b**) individuals of *Morella cerifera* from Via et al. (2014)

gas exchange, electron use efficiency, and water relations (O'Leary 1981; Thompson et al. 1998; Dawson et al. 2002; Ait Ali et al. 2006; Zinnert 2012; Zinnert et al. 2012; Via et al. 2014). Stress tends to activate similar physiological response pathways in vegetation regardless of the stress source (Chapin III 1991); natural or anthropogenic. It is suggested, however, that there are distinct differences between natural and anthropogenic stress responses and that different classes of explosives alter physiology through different mechanisms. Woody plant species do not express curvilinear and highly-related responses in stomatal conductance and photosynthesis when exposed to TNT and RDX while this relationship is conservatively maintained under a range of natural stresses (Flexas et al. 1999; Zinnert et al. 2012; Via et al. 2014). The unique response induced by explosives may stem from a decoupling of physiological processes which are tightly linked under normal conditions. RDX and TNT induce similar reductions in carbon fixation in plants yet Ait Ali et al. (2006) and Via et al. (2014) suggest that despite commonalities among plant responses to explosives there are unique at play. These studies suggest that TNT impacts photosystem II (PSII) while RDX impacts the light-independent portion of photosynthesis as electron transport rate (ETR) and dark minimal fluorescence (F_o) in plants exposed to TNT did not show significant impairment (Ait Ali et al. 2006), a response observed under RDX exposure (Via et al. 2014), while TNT limited water relations and RDX induced dramatic increases in stomatal conductance for exposed individuals. Unfortunately, little outside of the impacts of TNT and RDX on plant physiology is understood. Phytotoxicity of explosives is compounded by the toxic effects of products of metabolic and light-induced degradation of RDX and TNT which can produce amino derivatives and other reduced compounds such as nitrous oxide, oxygen radicals, formaldehyde, and carbon monoxide (Spain 1995; Hawari et al. 2000; Halasz et al. 2002; Bernstein and Ronen 2012). Insensitive explosive compounds and nitrate esters have not been evaluated for physiological impacts on vegetation at this time.

8.2.3 Phytoremediation of Explosives

Phytoremediation of explosives contaminated soils and waters has been shown to be effective solution in laboratory conditions and show promise based on the relatively lmited field trials that have been done. Three main approaches are used for remediating explosives contaminated sites using vegetation: rhizofiltration, phytostabilization, and phytoextraction (Pilon-Smits 2005).

Rhizofiltration is the encouragement of bacterial communities to form and function at heightened levels of activity around the roots of plants in a region referred to as the rhizosphere (Pilon-Smits 2005). Generally, this zone extends for only a couple of centimeters from root structures but in species with broad-reaching fibrous roots could account for a considerable area. This zone of microbial activity is the first point where phytoremediation can begin acting on a contaminant. Efforts to harness microbes, such as those found in plant rhizospheres, for degradation of explosives have shown potential. Microbial metabolism can occur by removing extraneous methyl and nitrate groups as well as cleave the central rings (Hawari et al. 2000; Rylott and Bruce 2009; Rylott et al. 2011). It has been shown that wild-type microbial strains can undergo this process but a significant amount of work has been unertaken to improve upon these natural pathways via transgenic strains (Chatterjee et al. 2017; Rai et al. 2020). The rhizosphere relationship goes both wayshowever, as many microbes can influence plant growth and overall health just as much as the plant can have an impact on the bacteria and fungal communities. This region around the plant roots can be manipulated through microbial additions, introduction of endo- and ectosymbionts, and root (Kuiper et al. 2004; McGuinness and Dowling 2009).

Phytostabilization focuses on retaining compounds in a localized area and preventing them from being transported to other areas. Plants are particularly useful tools for this as contaminants that make it into the plant are generally subject to sequestration into cellular structures. Some species of vegetation are known to accumulate toxins in very high quantities, eventually containing a higher relative concentration in their bodies than in the surrounding environment. Some species do so to such an extent that they are known as hyperaccumulators. Vegetative species have an innate ability to bind foreign compounds (xenobiotics) into their cells in an effort to minimize cellular damage. Organic xenobiotics undergo three distinct phases post-uptake: transformation, conjugation, and finally sequestration. This process often described as the green liver model (Klein and Scheunert 1982; Sandermann 1994; Burken and Schnoor 1997; Hannink et al. 2002). Explosive contaminants undergo enzymatic transformation and conjugation with D-glucose, amino acids, or glutathione which can produce either soluble or insoluble products (Sens et al. 1999; Robidoux et al. 2003; Vila et al. 2008). Soluble products can be stored in the vacuole or bound to the cell wall. Insoluble products are sequestered into cell wall structures only (Burken et al. 2000; Lotufo et al. 2009; Rylott et al. 2011). Stabilization strategies for remediation show great promise for compounds like TNT which accumulate in below-ground tissues that are difficult to harvest.

Phytoextraction uses plants as pumps, pulling contaminated water from the soil, and depositing the toxins into their tissues. Compounds that are translocated into harvestable portions (above-ground tissues) of plants have the potential of being removed at the end of each growing season (Pilon-Smits 2005). In such instances, harvesting must be completed each season, if not plants can act as a new source of contaminant release, taking from within the soil and depositing it onto the surface through senescence of leafy and woody structures. Nitroamines and nitrate esters appear to behave in ways that allow them to potentially be effectively remediated through phytoextraction while the binding behaviors of nitroaromatics make it more problematic for them (Pilon-Smits 2005; Rocheleau et al. 2011).

One area of phytoremediation that has garnered lot of research attention has been in phytodegredation wherein the plant itself is responsible for the degredation or transformation of the compound. While not many, there are plants capable of transforming explosive compounds allowing transformation and metabolism of the compounds to occur. This phytodegradation is something that many studies have investigated and much effort has been spent to improve. Nitro group reduction can be the result of nitroreductases (Adamia et al. 2006; Makris et al. 2007b; Rylott and Bruce 2009; Rylott et al. 2011), oxophytodienoate reductases (OPRs), cytochromes P450 (Beynon et al. 2009; Rylott et al. 2011), and laccase activities (Schnoor et al. 1995). In the presence of TNT, nitroreductases can use flavin mononucleotide (FMN) or flavin adenine dinucleotide (FAD) as prosthetic groups and nicotinamide adenine dinucleotide (NADH) or nicotinamide adenine dinucleotide phosphate (NADPH) as reducing agents for this process (Bryant and DeLuca 1991). Nitroaromatic degradation can also utilize lactase enzymes in some cases (Schnoor et al. 1995). Nitroamine reduction primarily involves cytochrome P450, reductase, peroxidase, and glutathione S-transferases (GST) enzymes (Rylott et al. 2011). There is also evidence of compound transformation in plant tissues resulting from interaction with light termed phytophotolysis (Just and Schnoor 2004). While not a direct result of metabolism on the plant part this does introduce an additional avenue for potential degradation. Little is known about metabolism of nitrate ester explosives (Rylott and Bruce 2009) but in the presence of vegetation nitroglycerin can be transformed into dinitroglycerin (DNG) isomers (Rocheleau et al. 2011). Increasing the capabilities for plants to transform explosive compounds into neutral or less harmful forms would enable a much more efficient and less involved remediation procedure.

8.2.4 Transgenic and Wild-Type Species

Phytoremediation of explosives focused largely on sequestering and binding compounds in their parent forms or transform and degrade the compounds to inert forms using inherent metabolic processes in the plants themselves. Uptake and sequestration are by far more achievable goals when using wild-type varieties of plants but improved transformation and degradation of compounds have been achieved via genetically modified varieties (Vanek et al. 2006; Ibañez et al. 2015). Enzyme production for remediation of explosives is found in some wild-type vegetative species (Schnoor et al. 1995), however, the production of these enzymes can often be limited. In transgenic varieties, overexpression of genes can cause increased production of enzymes and efficacy of metabolism. For instance, overexpression of glycosyltransferases has been shown to increase detoxification of TNT contaminated conditions (Gandia-Herrero et al. 2008). Elevating the ability of vegetation to better serve as remediation tools using existing genes is promising in terms of capabilities and field applicability; however, transferring foreign genes into vegetative species has shown great potential as well.

A number of transgenic plant species designed for phytoremediation utilize microbial genes to better metabolize contaminants in their surroundings. *Nicotiana tabacum* (Tobacco) has been used in this way to handle pentaerythritol tetranitrate (PETN) and TNT via the additions of a PETN reductase gene from *Enterobacter cloacae* strain PB2 and bacterial nitroreductase gene (*nfsI*; Hannink et al. 2002). Poplar trees have also seen similar modifications to improve their remediation potential.

Van Dillewijn et al. (2007) incorporated nitroreductase gene (pnrA) from a strain of pseudomonas to great effect. Modifications to xenobiotic compounds through such means can have the additional benefit of reducing phytotoxic stress in the plants (Rylott and Bruce 2009; Van Aken et al. 2004). Rylott and Bruce (2009) used genetically modified *Arabidopsis thaliana* possessing bacterial gene xplA, the associated reductase xplB, and gene nfsI to remove explosives from TNT and RDX contaminated soils. These plants were the first of their kind to be tested and were capable of surviving at levels of contaminants that wild-type plants were not.

8.3 Field Applications

8.3.1 Suggested Species

Certain general characteristics are integral to making reliable and efficient bioremediators. The initial factor for species selection should be the ability of the species to tolerance the contaminant in the remediation area and can it survive the environmental conditions there. Attributes other than tolerance that make for an effective bioremediator include rapid growth, ease of care, and its ability to uptake or transform target contaminants (Pilon-Smits 2005; Best et al. 2008). Those species which produce large quantities of above-ground biomass are sought after for phytoextraction projects and those with dense, fibrous root structures, such as grasses, are often preferred for rhizo- and phytostabilization and transformation (Pilon-Smits 2005; Best et al. 2008). Species with nitrogen-fixing capabilities are also very useful in remediation activities as they require less input of fertilizers (EPA 2001) and can potentially utilize nitro compounds attached to the explosives compound central rings (Labidi et al. 2001; Khan et al. 2015). It can be difficult to glean suggested species from the literature based on uptake capabilities as some studies publish the proportion of contaminants removed from the system, some report only tissue concentrations post-uptake, and types of growing media vary widely.

There is little standardization across the historic and current literature for reported values of remediation success, The general consensus is though, that plant species of grass, sedge, and weedy broadleaf taxonomic groups show the most promise. These groups of plants excel in terms of tolerance and sequestration of explosive compounds for both terrestrial and wetland communities (Tables 8.1 and 8.2). Rapid growth rate and dense root system make these types of plants species real contenders as potential remediators for explosives (Pilon-Smits 2005). Other broad stroke recommendations can be made looking at functional traits of many plants as well (Via et al. 2016). Annuals are far more resistant to explosives-induced stress compared to perennials (Schnoor et al. 1995; Quist et al. 2003; Zhang and Chu 2013), monocots are largely more tolerant than dicots (Winfield et al. 2004; Vila et al. 2007; Panz et al. 2013), and herbaceous and vine species appear to have greater tolerance than woody species as well (Via et al. 2016, b; Table 8.3). Tolerance trends among large taxonomic groups

Table 8.1 Suggested species for phytoremediation of RDX and HMX based on literature findings. Removal potential is listed as high (75–100%), moderate (50–75%), and low (<50%) based on percent contaminant removed from growing media. Uptake is reported as high (80–100+%), moderate (50–80%), or low (<50%) depending on relative concentration in plant tissues compared to those of growing media

Contaminant	Functional group	Genus	Removal	Uptake	System	References
RDX	Submerged	*Ceratophyllum*	-	High	Aquatic	Best et al. (1997b), Kiker et al. (2000)
RDX	Algae	*Charales*	High	-	Aquatic	Best et al. (1997a)
RDX	Graminoid	*Cyperus*	-	High	Wetland	Price et al. (1997)
RDX	Herbaceous	*Lactuca*	-	High	Terrestrial	Price et al. (1997)
RDX	Submerged	*Myriophyllum*	-	High	Aquatic	Best et al. (1997a, b)
RDX	Graminoid	*Oryza*	-	Low	Wetland	Vila et al. (2007)
RDX	Graminoid	*Phalaris*	High	Moderate	Wetland	Best et al. (1997b), Sikora et al. (1998)
RDX	Woody	*Populus*	-	High	Terrestrial	Thompson et al. (1999)
RDX	Submerged	*Potamogeton*	Low	Low	Aquatic	Best et al. (1997a)
RDX	Woody	*Robina*	-	Moderate	Terrestrial	Schneider et al. (1995)
RDX	Herbaceous	*Sagitaria*	-	Low	Wetland	Schneider et al. (1995) Best et al. (1997b)
RDX	Herbaceous	*Solidago*	-	High	Terrestrial	Schneider et al. (1995)
RDX	Submerged	*Stuckenia*	High	High	Aquatic	Best et al. (1997a)
RDX	Graminoid	*Triticum*	-	High	Terrestrial	Vila et al. (2007)

(continued)

Table 8.1 (continued)

Contaminant	Functional group	Genus	Removal	Uptake	System	References
HMX	Herbaceous	*Brasica*	Low	High	Terrestrial	Groom et al. (2002)
HMX	Herbaceous	*Medicago*	Low	High	Terrestrial	Groom et al. (2002)
HMX	Submerged	*Myriophyllum*	High	High	Aquatic	Bhadra et al. (2001)
HMX	Graminoid	*Phalaris*	High	-	Wetland	Sikora et al. (1998)
HMX	Woody	*Populus*	Moderate	-	Terrestrial	Yoon et al. (2002)
HMX	Graminoid	*Triticum*	Low	High	Terrestrial	Groom et al. (2002)

may be the result of altered mechanisms and behaviors where water usage and growth are concerned. Generalizations on ability can provide a good starting point when planning a remediation project, however, species-specific responses and capabilities vary greatly and should be investigated and selected base on site criteria (Pilon-Smits 2005; Meagher 2000; Yadav et al. 2016; Bari et al. 2017).

8.3.2 Field Knowledge

Current understanding of phytoremediation of explosives comes from laboratory studies, and few field studies have been undertaken (Hawari et al. 2000; Green and Hoffnagle 2004; Travis et al. 2008). Nitroamines, like RDX and HMX, have not had as much success with field remediation but Nitroaromatics have (Schnoor 2011; U.S. Army Corps of Engineers 2016). This has been attributed to the high mobility of nitroamine compounds resulting in them flushing from the system before the plants have time to interact with them (Schnoor 2011). To date, only three long-term studies have been reported in the literature. One at Milan Army Ammunition Plant in Tennessee (Milan Plant; Lorion 2001), another at Eglin Air Force Base in Florida (Eglin AFB; Schnoor 2011), and the third at Iowa Army Ammunition Plant in Iowa (Iowa Plant; Best et al. 1998; US Army Corps of Engineers 2016). Experiments at the Milan and Iowa Plants showed significant removal of TNT via constructed wetlands (Lorion 2001; US Army Corps of Engineers 2016). Small-scale wetland systems at the Iowa Army Ammunition Plant filtered effluent at the site and outflow water

Table 8.2 Suggested species for phytoremediation of TNT based on literature findings. Removal potential is listed as high (75–100%), moderate (50–75%), and low (<50%) based on percent contaminant removed from growing media. Uptake is reported as high (80–100%), moderate (50–80%), or low (<50%) depending on relative concentration in plant tissues compared to those of growing media

Explosive	Functional group	Genus	Removal	Uptake	System	References
TNT	Woody	*Abutilon*	High	-	Wetland	Chang et al. (2003)
TNT	Herbaceous	*Alisma*	High	-	Wetland	Best et al. (1997b)
TNT	Graminoid	*Bromus*	Low	Low	Terrestrial	Zellmer et al. (1995)
TNT	Graminoid	*Carex*	High	-	Wetland	Best et al. (1997b)
TNT	Herbaceous	*Catharantus*	High	-	Terrestrial	Hughes (1997)
TNT	Submerged	*Ceratophyllum*	High	-	Aquatic	Best et al. (1997b)
TNT	Algae	*Charales*	High	-	Aquatic	Best et al. (1997a)
TNT	Herbaceous	*Cicer*	Moderate	-	Terrestrial	Adamia et al. (2006)
TNT	Herbaceous	*Dipsacus*	Low	Low	Terrestrial	Zellmer et al. (1995)
TNT	Submerged	*Egeria*	High	-	Aquatic	Best et al. (1997a)
TNT	Graminoid	*Eleocharis*	High	-	Wetland	Best et al. (1997a)
TNT	Submerged	*Elodea*	High	-	Aquatic	Best et al. (1997a)
TNT	Herbaceous	*Glycine*	High	-	Terrestrial	Adamia et al. (2006)
TNT	Herbaceous	*Helianthus*	Moderate	-	Terrestrial	Adamia et al. (2006)
TNT	Graminoid	*Heteranthera*	High	-	Terrestrial	Best et al. (1997a)
TNT	Graminoid	*Hordeum*	High	-	Terrestrial	Adamia et al. (2006)
TNT	Graminoid	*Juncus*	High	-	Wetland	Nepovim et al. (2005)
TNT	Graminoid	*Lolium*	High	-	Wetland	Adamia et al. (2006)

(continued)

Table 8.2 (continued)

Explosive	Functional group	Genus	Removal	Uptake	System	References
TNT	Herbaceous	*Medicago*	High	-	Terrestrial	Zellmer et al. (1995), Adamia et al. (2006)
TNT	Submerged	*Myriophyllum*	High	-	Aquatic	Best et al. (1997a, b), Hughes (1997), Pavlostathis (1998), Wang et al. (2003)
TNT	Herbaceous	*Nicotiana*	High	-	Terrestrial	Hannink et al. (2002)
TNT	Graminoid	*Phalaris*	High	-	Wetland	Best et al. (1997b)
TNT	Graminoid	*Phragmites*	High	-	Wetland	Nepovim et al. (2005), Vanek et al. (2006)
TNT	Herbaceous	*Pisum*	High	-	Terrestrial	Adamia et al. (2006)
TNT	Herbaceous	*Polygonum*	-	-	Wetland	Schneider et al. (1995)
TNT	Algae	*Portieria*	High	-	Aquatic	Cruz-Urib and Rorrer (2006)
TNT	Submerged	*Potamogeton*	High	-	Aquatic	Best et al. (1997a)
TNT	Herbaceous	*Sagitaria*	High	-	Wetland	Schneider et al. (1995), Best et al. (1997b)
TNT	Submerged	*Stuckenia*	High	-	Aquatic	Best et al. (1997a)
TNT	Graminoid	*Triticum*	High	-	Terrestrial	Scheidemann et al. (1998)
TNT	Herbaceous	*Typha*	High	-	Wetland	Best et al. (1997b)

(continued)

Table 8.2 (continued)

Explosive	Functional group	Genus	Removal	Uptake	System	References
TNT	Submerged	*Vallisneria*	High	-	Aquatic	Best et al. (1997a)
TNT	Graminoid	*Vetiveria*	High	High	Terrestrial	Makris et al. (2007a), Das et al. (2010)

Table 8.3 General selection criteria based on plant function groups indicated in literature as being effective remediators (Table 8.1 and 8.2). Symbols in the central squares indicate positive (+) or neutral/negative (−) characteristics. Symbols are read left to right with first being the term to the left, the middle symbol refers to the top term, and the right symbol to the right side term

	Annual	Perennial	
Monocot	+ + +	+ - +	Herbaceous
Dicot	- + -	- - -	Woody

explosives concentrations were below EPA human health advisory level (0.002 mg/l; McCutcheon and Schnoor 2004). The only recorded large-scale implementation of phytoremediation of explosives contamination was at Eglin AFB. Groundwater at the base was contaminated with TNT, RDX, and HMX, and *Paspalum notatum* was chosen as the primary remediation species for the study. Over 18 months it was observed that TNT was transformed to varying degrees in both planted and unplanted soils. RDX and HMX, on the other hand, were not effectively remediated, likely due to migration deeper into the soil causing reduced bioavailability for plant uptake (Schnoor 2011).

8.3.3 Phytoremediation Potential and Future Directions

Addressing areas contaminated with a single contaminant allows for very precise tailoring of approaches allowing for surrounding climate, land-use, and soils, as well as contaminant type and concentration to be taken into consideration. Site-specific variability in concentration represents a large hurdle to overcome to predict ecological impacts of explosives. For instance, soil concentrations for RDX can range from 0.7 to 74,000 ppm dry soil and TNT from 0.08 to 87,000 ppm (Best et al.

2008, 2009). A majority of the data available on remediation of explosives comes from studies which focus on a single contaminant. This complicates the applicability of laboratory findings to field predictions as explosive compounds are rarely ever found as isolated contaminants. Secondary or parallel contamination involving other explosive compounds, heavy metals, and a variety of other compounds is common and most often comes in the form of other explosives. This is due to munitions and ordnance predominantly containing multiple compound to ensure the desired result or blast is achieved (National Research Council 2004; Pichtel 2012).

Given the inherent complexities in remediating contaminated systems and our current understanding of plant–explosive interactions there is great potential for the use of phytoremediation on contaminated sites. Gaps in field data, particularly, that of long-term large-scale efforts are something that need to be rectified to establish optimal phytoremediation strategies in terms of both efficacy and cost. Phytoremediation of explosives is a good option for surface and shallow soil as well as shallow groundwater remediation. This approach to decontaminating sites has shown great promise for the removal of nitroaromatics and nitrate esters but nitroamine removal has been limited. Nitroaromatics are not readily taken out of contaminated soils due to their mobility, but may be remediated effectively using bioreactors or constructed wetlands for effluent discharge sites (Sikora et al. 1998; Truu et al. 2015). Taking our current understanding into consideration phytoremediation of explosive compounds shows great potential, but requires substantial investment into field application. Laboratory results are essential to the basic understanding of any process, but when moving to the field a plethora of confounding factors can drastically alter plant responses. Understanding these complications is critical to propelling remediation technologies and their use forward.

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Chapter 9
Phytoremediation Using Native Plants

Anthony E. Futughe, Diane Purchase and Huw Jones

Abstract The unprecedented growth in industrialization has significantly increased pollution in the environment causing public health concerns. The remediation of various contaminated environmental matrices presents a global challenge. Phytoremediation using native plants can serve a dual purpose of site remediation and ecological restoration. Native plants provide an ideal residence for microbial community in their rhizosphere with enzymatic ability to accumulate, stabilize, biodegrade or volatilize various inorganic and organic contaminants. A case study that compared a native plant, *Chromolaena odorata*, from crude oil-polluted land in Nigeria against a referenced plant, *Medicago sativa*, for polycyclic aromatic hydrocarbons (PAHs) remediation is presented in this chapter. It was observed that the native plant thrived, tolerated and degraded PAHs better than the reference plant but with no significant difference in PAH degradation. The use of plants is well suited to its natural contaminated area and solar-driven, prevents erosion and eliminates secondary airborne and waterborne waste but with some challenges. Phytoremediation using native species may be effective and efficient than its non-native counterparts, and it is ecologically safer, cheaper, aesthetically pleasing, socially acceptable and easier to cultivate. Native plants in phytoremediation can be further enhanced and improved using molecular techniques to optimize the harvest time, reduce growth duration and increase biomass production and root depth.

Keywords Ecological restoration · Heavy metals · Microbial community · Native plants · Phytoremediation · Polycyclic aromatic hydrocarbons · Rhizosphere

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9.1 Introduction

The unprecedented growth in oil production, transportation, military activities, agriculture, chemical and mining industries has significantly increased the already intensive generation of pollution to the environment (air, soil, water and biota). These pollutants such as metals and metalloids, persistent organic pollutants [hydrocarbons (HCs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pesticides, organic solvents, dioxins, furans] and radionuclides are released either accidentally (e.g. through oil and brine spills during exploration, production or transport of petroleum, chemical storage tank leakage, mining and processing of metals) or deliberately (e.g. through pesticides, military activities and fossil fuel combustion), causing serious environmental issues and adverse human health effects (Sciacca and Oliveri Conti 2009; Miri et al. 2016; Gerhardt et al. 2015, 2017; Kaushal et al. 2015; Jesus et al. 2015). The remediation of polluted sites presents enormous global challenges. Various physico-chemical remediation techniques are used such as soil incineration or excavation, and transfer to landfill may be able to reduce substantial quantities of pollutants, but these technologies consume energy and water, generate waste by-products, cause atmospheric pollution and may have negative impact on the quality of life. In addition, many techniques are expensive and labour intensive and result in extensive alteration to the physical, chemical and biological features of the treated sites (Futughe 2012).

For close to 300 years, plants' ability to remove pollutants from impacted sites has been recognized and its merits are also acknowledged (McCutcheon and Schnoor 2003). The use of plants over time has evolved to the construction of treatment in landfarming of waste, wetlands or even tree planting to mitigate air pollution. In more recent years around the world, as the damaging effects from decades of industrial economy and extensive chemical usage grew, so did interest in finding sustainable technologies such as phytoremediation that could remediate residual pollutants (McCutcheon and Schnoor 2003). Phytoremediation is a relatively inexpensive eco-friendly alternative, using plants and their associated micro-organisms to extract, immobilize, contain and/or degrade pollutants in soil, water or air (Cunningham et al. 1996; Bennett et al. 2003; Greipsson 2011; Ali et al. 2013; Barcelo and Poschenrieder 2003; Cunningham et al. 1995; Ghosh and Singh 2005; Pilon et al. 2000; Prasad 2003). It can be an effective strategy for onsite and/or in situ removal or stabilization of various pollutants including HCs, PAHs, PCBs, solvent (e.g. trichloroethylene (TCE)), munition waste (e.g. 2,4,6-trinitrotoluene (TNT)), metals and metalloids, salt (NaCl) and radioisotopes (Gerhardt et al. 2015, 2017; Kaushal et al. 2015; Jesus et al. 2015) present in the environment as shown in Table 9.1.

An extensive body of the literature has shown the ability of selected non-native plants to remediate polluted sites (e.g. Reilley et al. 1996; Jordahl et al. 1997; Nedunuri et al. 2000; Chen et al. 2003; Chekol et al. 2004; Rentz et al. 2005), and larger quantities of contaminants such as heavy metals and metalloids can be

Table 9.1 Phytoremediation applicability

Organic		Inorganic		Materials	
Halogenated VOCs	Y	Metals	Y	Gravel > 2 mm	Y
Halogenated SVOCs	Y	Radionuclides	Y	Sand 0.06–2 mm	Y
Non-halogenated VOCs	Y	Corrosives	Y	Silt 2–60 μm	Y
Non-halogenated SVOCs	Y	Cyanides	Y	Clay < 2 μm	Y
Organic corrosives	N	Asbestos	Y	Peat	Y
Organic cyanides	N	**Miscellaneous**			
PCBs	Y	Explosives	Y		
Pesticides/herbicides	Y				
Dioxins/furans	Y				

Source Nathanail et al. (2007), FRTR (2007), CL:AIRE (2001), Khan et al. (2004)
Key
Y = usually or potentially applicable
N = not applicable

bio-accumulated in the tissue of some plants. However, in establishing an effective phytoremediation plant community, a significant factor is to search for native plant species that develop well in the polluted area and which are also effective in removing the contaminants of interest. One of the important advantages of using native plant species for phytoremediation is avoiding the use of non-native and potentially invasive new plant species that could be a threat to the plant regional diversity. However, few field trials have taken advantage of using native plant diversity in phytoremediation, resulting in poor plant colonization and soil conditions at contaminated sites (Mendez and Maier 2008). The use of native plant species for phytoremediation can serve the dual purpose of remediation as well as native habitat restoration/reclamation, especially for microbe-assisted phytoremediation which may be required after successful remediation.

Non-native plants need to be established and managed, often require frequent irrigation and application of fertilizers and pesticides, and seldom lead to the restoration of the natural ecosystem by themselves. One of the most attractive propositions of phytoremediation is allowing native plants to naturally restore the habitat since it has arguably more advantages than its planted/managed counterparts as presented in Table 9.2. Generally, the use of plants incurs mowing cost, replanting, pruning and harvesting; however, native plants may not require replanting as they are already growing on the site. They have the added benefit of not disturbing the soil if the accumulation of potentially toxic pollutants occurs in easily harvestable plant parts (mainly shoots), and it also contributes to restoration of the site (Marrugo-Negrete et al. 2016; Nedunuri et al. 2010). According to Henry (2006), if native plants can remediate a site similar to managed non-native plants while simultaneously establishing a plant community comparable to that existing in the vicinity, the result will be both site remediation and ecological restoration. This chapter reviews the phytoremediation associated mechanisms, the merits of native plants

Table 9.2 Some merits of native plant over non-native plants in phytoremediation

Native plant species	Non-native plant species
• More cost effective as replanting may not be required	• Incur additional cost due to planting, irrigation, fertilization and pesticide treatments
• Little or no soil disturbance	• Minimal soil disturbance
• Results in both site remediation and ecological restoration	• Do not lead to ecological restoration by themselves
• Includes ecological features of social and aesthetic value, recovery of soil quality, functionality and sustainability	• Often carries the potential ecological risk burden by displacing or hybridizing with native species
• Usually do not pose ecological risk as they are ecologically friendly and self-sustaining	• Ecological risks need to be minimized; e.g. genes can be introduced to prevent propagation or to render a species overly sensitive to abiotic stressors such as temperature changes or chemicals. Or prevented from successfully competing outside the contaminated site
• Usually adapt to stressors such as temperature variation, nutrient, precipitation, herbivory, plant pathogens, competition by weed species, etc.	• Usually affected by stressors such as temperature variation, nutrient, precipitation, herbivory, plant pathogens, competition by weed species that adapts better to the site

over non-native plants in phytoremediation and current applications in different contaminated sites using native plants for phytoremediation of inorganic pollutants (metals and metalloids) and organic pollutants (persistent organic pollutants) with a case study on PAH-contaminated soil and discusses the prospects as well as challenges of this remediation technique and the future development of native plants in phytoremediation.

9.2 Mechanisms of Phytoremediation

Phytoremediation approaches encompass a group of mechanisms and techniques that may immobilize, stabilize or degrade contaminants in the rhizosphere, sequester or degrade within the plant or volatilize (Cunningham et al. 1995; Horne 2000). The various mechanisms employed within the field of phytoremediation are phytostabilization or phytoimmobilization, phytodegradation, phytoextraction (especially for the application of soil, sediment and sludge), rhizofiltration, rhizodegradation, hydraulic barrier control, vegetative caps and constructed wetland, especially for water application (Adams et al. 2000; Barcelo and Poschenrieder 2003; Prasad 2003, 2004). These mechanisms in addition to the unique characteristics of individual plant species, especially native species, can be a formidable option for clean-up of contaminants.

Figure 9.1 presents a simplified overview of the phytoremediation mechanism in some basic essential processes such as phytostabilization and phytoextraction for inorganic contaminants and phytodegradation, rhizodegradation and phytovolatilization for organic contaminants (USEPA 2000; Prasad and De Oliveira Freitas 2003). Plant root exudate reduces or eliminates contaminant mobility from the contaminated soil to the environment by demobilizing, stabilizing and binding them in the substrate or roots, a process referred to as **phytostabilization**. This mechanism transforms soil heavy metals or metalloids to less toxic forms, without removing them from the soil (Adams et al. 2000; Chaney et al. 1997; Cunningham and Berti 2000; Prasad 2004). Certain plant species have used absorption and accumulation by roots, adsorption onto roots or precipitation within the root zone to immobilize both organic and inorganic contaminants in the soil, sediment, sludge and groundwater (USEPA 2000; Prasad and De Oliveira Freitas 2003). Specific plant species can absorb and remove

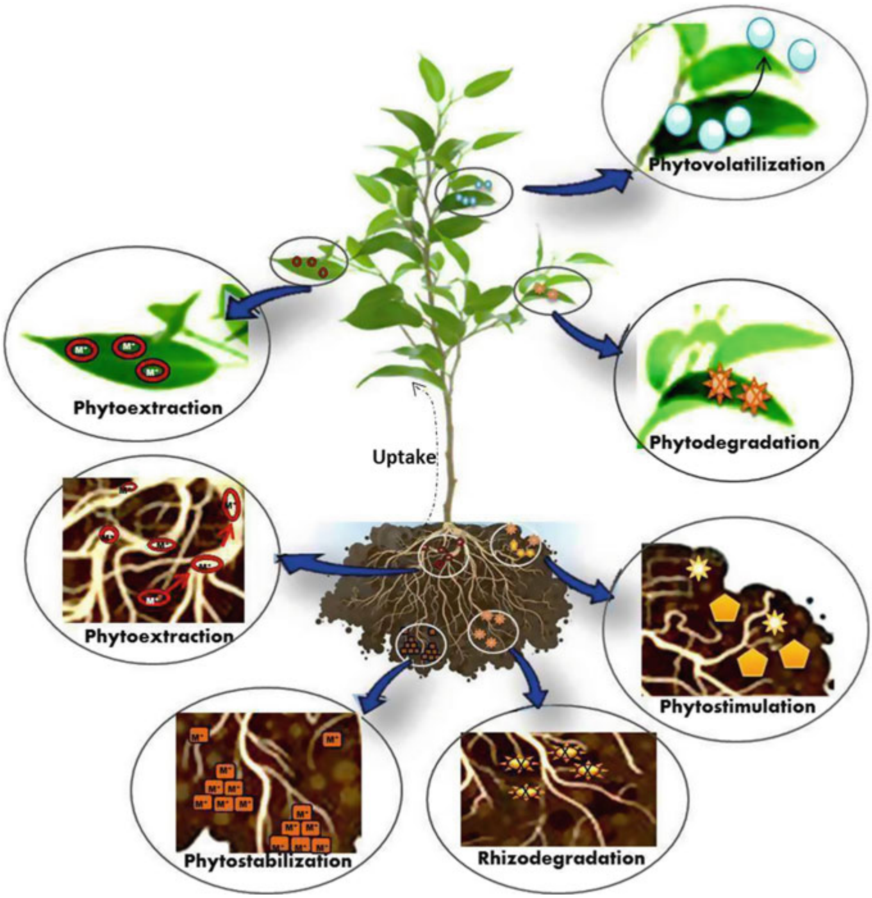


Fig. 9.1 A simplified overview of the phytoremediation mechanisms

heavy metals, metalloids, radionuclides and organic contaminants from soils, sediments and sludge medium and "uptake" them into harvestable root and shoot tissue through a process known as **phytoextraction**. The plant parts storing contaminants are removed and destroyed or recycled (USEPA 2000; Prasad and De Oliveira Freitas 2003; Cunningham et al. 1995; Vassilev et al. 2004). **Phytovolatilization** is a process in which plants absorb contaminants from soil, groundwater, sediment or sludge and subsequently volatilize the contaminants or it is less harmful modified forms into the atmosphere while **phytodegradation** is the breakdown of contaminants taken up by plants through metabolic processes within the plant or externally by the effect of compounds synthesized by the plants. This process is relevant to complex organic compounds such as hydrocarbons, PCBs, PAHs, pesticides, organic solvents, dioxins and furans that are degraded or mineralized into simpler or basic molecules such as CO_2 and H_2O (Adams et al. 2000). **Rhizodegradation** on the other hand is the breakdown of contaminants in the soil through microbial activity that is stimulated by the presence of the root zone. Micro-organisms feed on the organic contaminants for nutrition and energy. **Phytostimulation** is a process whereby natural substances such as sugar, alcohol, amino acids, organic carbon in addition to O_2 through dense root mass released by the plant roots stimulate micro-organisms for the biodegradation of contaminants (USEPA 2000; Prasad and De Oliveira Freitas 2003). **Rhizofiltration** is a process whereby plant roots take up metals, metalloids, radionuclides and/or excess nutrients from groundwater, surface water and wastewater through the adsorption or precipitation onto plant roots or absorption of contaminants that are in solution surrounding the root zone into the roots (USEPA 2000; Prasad and De Oliveira Freitas 2003; Adams et al. 2000; Chaney et al. 1997). **Hydraulic control** is a process whereby the roots of plant avoid migration of leachate towards groundwater or receiving waters. It is not necessary to install an engineered system as the roots are in contact with a greater volume of soil than a pumping well (Adams et al. 2000).

9.3 Inorganic (Heavy Metal and Metalloid) Contaminated Sites

Biologically, a series of metals and in some cases metalloids are described as "heavy" because it is a term that is synonymous with being toxic to plants and animals even in low concentrations (Rascio and Navari 2011). Metals and metalloids have been spread worldwide, and their origin consists of natural and human activities with the latter being the most common contribution to soil, air and water contamination (Pfeifer et al. 2000; Tanhan et al. 2007; Alkorta et al. 2004; Khan et al. 2008; Wuana and Okieimen 2011). It has been reported that more than 10 million contaminated sites exist globally with over 50% of these sites contaminated with heavy metals and metalloids (He et al. 2015). A significant amount of these heavy metal and metalloid contaminated sites are found in developed countries such as USA, Australia, Germany, Sweden, France and China due to their higher industrial activities (Foucault et al. 2013; Goix et al. 2014; Agnello et al. 2015). It has been estimated that about 600,000 ha of land especially brownfield sites is contaminated with heavy metals and metalloids in the USA, and the US EPA has designated more than 50,000 priority heavy metal and metalloid contaminated sites awaiting immediate clean-up (Ensley 2000). Similarly, different countries in Europe have several heavy metal and metalloid contaminated agricultural sites situated close to mining areas (Foucault et al. 2013; Goix et al. 2014). Currently, about 1,170,000 potentially contaminated sites have been identified in 27 European countries and this is estimated to about 45% of the number of possible sites for the 33 EEA members together with six EEA cooperating countries (Liedekerke et al. 2014). Approximately, one-third of 342,000 contaminated sites have been identified for the EEA-39 with 15% of the estimate remediated (Liedekerke et al. 2014). In the Netherlands and Belgium, the Campine area (700 Km^2) is polluted by atmospheric deposition of Pb, Zn and Cd (Meers et al. 2010). High-level heavy metal and metalloid contaminated soils in Germany have been taken out of food production about 10,000 ha of agricultural land (Lewandowski et al. 2006), and a survey supported by the European Commission has reported that about 17.3 billion euros per year is lost as a result of contaminated soil (Khalid et al. 2017).

In China, the situation of soil pollution by metal and metalloids is more severe. Approximately, 4 mha of arable land which accounts for about 2.9% of China's arable lands has been moderately or severely polluted (Khalid et al. 2017). In a survey carried out from 2005 to 2013, the Ministry of Land Resources of China and the Ministry of Environmental Protection of China jointly reported that heavy metals and metalloids have exceeded the environmental quality standard for soil in 16.1% farmland soils with more than 19.4% sites exceeding environmental quality standard for agricultural soil on more than 2.4 million square mile of land across mainland China (The New York Times 2014). Hongbo et al. (2011) reported that over 20,000,000 acres of farmland (about 25% of total arable farmland area) in China is contaminated with heavy metals and metalloids including Pb, Cd, Cr, Sn and Zn. There is 10,000,000 tons loss of crop output yearly in China due to heavy metal and metalloid pollution (Hongbo et al. 2011). In less developed countries like Pakistan, India, Bangladesh, Nigeria, etc., high levels of heavy metals and metalloids are also reported in soil (Khan et al. 2015; Isimekhia et al. 2017).

Arguably, one of the most currently considered serious environmental problems is heavy metal and metalloid contaminated soil due to their persistence and toxicity impacting greatly the use of land (Becerril Soto et al. 2007). Studies abound indicating that the soil is a sink of heavy metals and metalloids, for instance, through atmospheric deposition of particles emitted by urban and industrial activities (Fabietti et al. 2009), vehicle exhaust (Hernandez et al. 2003) and agricultural activities (Fabietti et al. 2009) among other sources (see Fig. 9.2). The accumulation of metals and metalloids in soils may produce undesirable changes in their properties (Navarro-Aviñó et al. 2007), and its remediation presents a technological challenge for both industries and government institutions, with phytoremediation being an alternative that contemplates soil conservation by harnessing the potential of plants particularly native plants to transform or eliminate the accumulating contaminants in their tissue

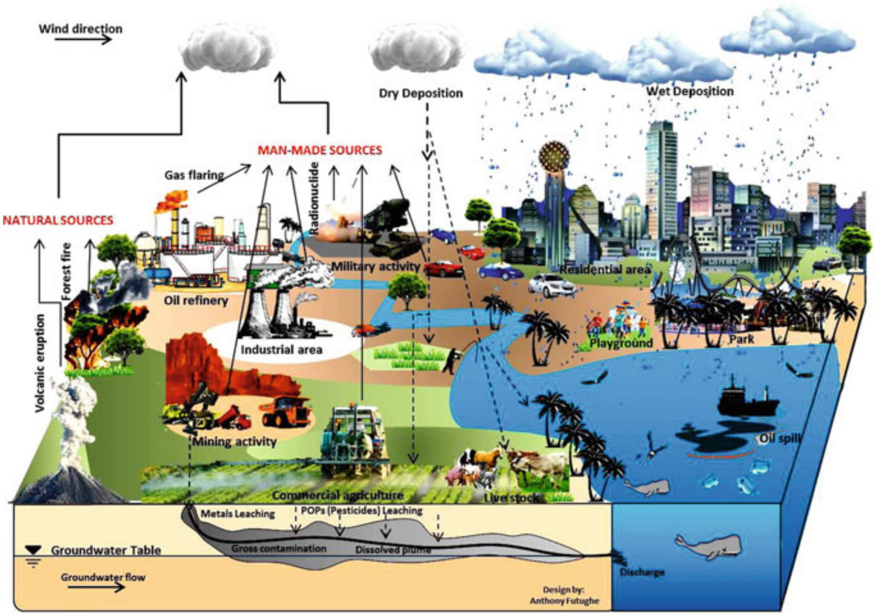


Fig. 9.2 A typical conceptual site model of pollution in the environment

(Alvarez and Illman 2006). This technique has many merits over traditional decontamination technology, especially when the plants used are native or non-invasive, as positive results obtained include ecological features of social and aesthetic value, in addition to elimination of heavy metals and recovery of soil quality, functionality and sustainability even though it requires long-term application (Alvarez and Illman 2006). Despite the use of phytoremediation technology in many parts of the world, studies related to the use of native plants are relatively scarce.

9.3.1 Current Application of Native Plants in Phytoremediation of Inorganic (Heavy Metal and Metalloid) Contaminated Sites

According to Calvachi (2002), native plants are species that can be found in a wide geographical location around the world enhancing biodiversity of ecosystems and represent evolution and residence across millennia. These species are constitutive elements that support the regulation of the ecosystem, preserve equilibrium and have the ability to adjust to the biogeographic conditions of their growth habitat (Ojasti 2001). A survey of natural vegetation on heavy metal- and metalloid-rich sites is an efficient approach for identifying potential native plant species with high bioaccumulation factors and the ability to hyperaccumulate (in their shoot) for easy harvest and/or tolerate potentially harmful heavy metals and metalloids (Poschenrieder et al. 2001; Bech et al. 2002; Ginocchio and Baker 2004; Freitas et al. 2004; Pratas et al. 2005; Conesa et al. 2006; Moreno-Jimenez et al. 2009; Liu et al. 2014). The spontaneous vegetation especially in heavily contaminated mining areas is a result of a strong environmental pressure for the selection of tolerance mechanisms which allow these plants to grow under the stressful prevailing conditions at these sites (Fernández et al. 2017). Numerous reports have shown that native plants from contaminated sites have either higher resistance by more efficient exclusion or higher accumulation and tolerance to potentially harmful concentrations than those from non-contaminated sites (Macnair 1993; Schat et al. 2000). According to McGrath et al. (1993), field trial results in which several hyperaccumulators were grown in polluted soils reduced Zn from 440 to 300 g/g, the established threshold by the Commission of the European Community (Commission of the European Communities 1986). Many native plant species have been identified with the ability to tolerate and accumulate heavy metals and metalloids in impacted mines, for example, *Agrostis capillaris* (Watkins and Macnair 1991), *Agrostis castellana* and *Agrostis deliculata* (De Koe and Jaques 1993), *Agrostis truncatula* (Garcia-Sanchez et al. 1996), *Cynodon dactylon* and *Amaranthus hybridus* (Jonnalagadda and Nenzou 1997), *Bidens cynapiifolia* (Bech et al. 1997), *Dittrichia graveolens*, *Herniaria hirsuta* and *Verbascum blattaria* (Shallari et al. 1998), and *Pteris vittata* (Ma et al. 2001). The above studies show that collecting/using native plant species on contaminated soils is an effective way for selecting potential phytoremediation plants (Del Rio et al. 2002).

The use of native plants for phytoremediation and restoration of Mediterranean metal-enriched areas has been reported due to their metal tolerance and adaptation to local conditions (Boukhris et al. 2015; Mendez and Maier 2008; Parraga-Aguado et al. 2014; Baker et al. 2010; Marchiol et al. 2013). Heckenroth et al. (2016) reported that some native plant species including *Coronilla juncea* and *Globularia alypum* for shrubs, and *Biscutella laevigata*, *Lobularia maritima, Piptatherum caerulescens* and *Silene vulgaris* for perennial grass and forbs showed significant positive correlations with the metal and metalloid contamination levels that suggested their higher tolerance to pollution compared well to the other plants of the community. According to Chandra et al. (2018), growing native weeds and grasses such as *Argemone mexicana, Saccharum munja, C. dactylon*, *Pennisetum purpureum, Chenopodium album, Rumex dentatus, Tinospora cordifolia, Calotropis procera* and *Basella alba* on organo-metallic polluted site mixed with androgenic and mutagenic compounds showed potential phytoextraction with high accumulation and translocation indexes. There was high accumulation of Fe, Zn, Cu, Mn, Ni and Pb in their root and leaves compared to the shoot. Plants with bioconcentration factor (BCF) and transfer factor (TF) both greater than one (TF and BCF > 1) have the potential to be used for phytoextraction (Raskin and Ensley 2000; Yoon et al. 2006). Majority of the plants was found with a BCF and TF > 1 for various metals, and as a result these native weeds and grasses suggest strong evidence for hyperaccumulation tendency from complex polluted sites. Diez et al. (2016) carried out the phytoremediation potential of some native plant species characterized by rapid growth on Hg-contaminated soil at a gold mine. Root accumulation of Hg was reported in all the native plants in addition to leaf accumulation, especially from the atmosphere. Five native plants had a TF > 1 suggesting their ability to translocate Hg from roots to shoot. Native plant species such as *Jatropha curcas, Phyllanthus niruri, Ricinus communis* (Euphorbiaceae), *Capsicum annuum* (Solanaceae) and *Piper marginatum* (Piperaceae) are common herbs, shrubs and sub-shrubs in mining area and established themselves after several months of mining activity (Reyes et al. 2006).

Some recent studies of heavy metal and metalloid contaminated sites using native plant species for phytoremediation are presented in Table 9.3. However, competition between species should be avoided and care should be taken to avoid introduction of species with invasive potentials and a greater ability to grow that might become a threat for less competitive native species. Some of the selected tolerant native plant species, especially those with reduced heavy metals and metalloid translocation, i.e. the fast-growing herbaceous and small shrubs, could be applied as nurse species or ecosystem engineers (Jones et al. 1994) in order to promote a later establishment of a more diversified plant community (Markham et al. 2011; Parraga-Aguado et al. 2014). Others could serve as a filter for heavy metal and metalloid by reducing leaching and run-off and the subsequent metal availability for less tolerant native species (Affholder et al. 2013, 2014; Testiati et al. 2013), thus improving the soil quality by nutrient and/or organic matter input by these engineer species within the rhizosphere (Barea et al. 2011; Cortina et al. 2011; Krumins et al. 2015; Ottenhof et al. 2007; Wenzel et al. 1999; Wong 2003).

9.4 Organic (POPs) Contaminated Sites

Many persistent organic pollutants (POPs) are relatively inert and prevalent globally. Examples of POPs include petroleum oil, hydrocarbons (e.g. aliphatic, aromatic, polycyclic aromatic hydrocarbons (PAHs); benzene, toluene, ethylbenzene and xylene (BTEX); chlorinated hydrocarbons like polychlorinated biphenyls (PCBs), trichloroethylene (TCE) and perchloroethylene; nitroaromatic compounds; organophosphorus compounds), solvents and pesticides (e.g. organochlorines). POPs have high toxicity and low biodegradability; they are persistent and soluble in lipids and can bio-accumulate in the environment (Pies et al. 2007; Sun et al. 2016; UNEP 2007). Their high stability is related to their aromatic ring structure, carbon–chlorine bond and other chemical arrangements (UNEP 2007). Large amounts of these compounds may persist for up to 20 years (Table 9.4) in soil, and part of these may serve as a secondary emission source to atmospheric, surface and groundwater pollution (Bidleman and Leone 2004; Tao et al. 2008; Cabrerizo et al. 2011; Zhang et al. 2013a, b; Zhong and Zhu 2013). Soil also receives these compounds by industrial effluents, sewage, sediment and air and by direct contamination during use (USEPA 2002). Most POPs under normal environmental conditions are recalcitrant as a result of the difficulty to degrade biologically, and their residues especially in agricultural soils can enter the food chains and consequently present a potential risk to public health via tropic transfers (Fantke and Jolliet 2015; Liu et al. 2016). Seepage and run-off

Table 9.3 Summary of some native plant species used in phytoremediation of heavy metal and metalloid contaminated sites

Native plant species	Global distribution/location	Metal and metalloid pollutants	Uptake mechanism and media (substrate)	Removal efficiency	Benefit/comment	References
Family: Amaranthaceae *Chenopodium album*	India	Fe, Zn, Cu, Mn, Ni, Pb	Phytoextraction (organo-metallic polluted site)	BCF and TF for Zn, Cu and Ni were found > 1	Hyperaccumulation properties of heavy metals from organo-metallic polluted site mixed with androgenic and mutagenic compounds	Chandra et al. (2018)
Family: Asclepiadaceae *Calotropis procera*	India	Fe, Zn, Cu, Mn, Ni, Pb	Phytoextraction (organo-metallic polluted site)	BCF and TF for Zn, Cu and Ni were found > 1	Native plant showed hyperaccumulation potential for Zn, Cu and Ni	Chandra et al. (2018)
Family: Asteraceae *Baccharis sarothroides*	North America, USA	Cu, Pb, Mn, Mo, Cr, Vn, Zn, As, Ni, Co	Phytoextraction (mine)	TF > 1 for Cu, Mo, Cr and Zn	Potential hyperaccumulator Very efficient in transporting metals and metalloids from root to shoot	Gardea-Torresdey et al. (2008)
Cousinia sp.	Iran	Zn	Phytostabilization (soil)	TF = 0.14; BCF = 1.00	Most efficient for phytostabilization of Zn	Lorestani et al. (2011)
Chondrilla juncea	Iran	Zn	Phytostabilization (soil)	TF = 0.13; BCF = 1.03	Had potential for phytostabilization	

(continued)

Table 9.3 (continued)

Native plant species	Global distribution/location	Metal and metalloid pollutants	Uptake mechanism and media (substrate)	Removal efficiency	Benefit/comment	References
Bidens triplinervia *Senecio* sp.	Spain, Peru	Cu, Fe, Mn, Zn and Pb	Phytoextraction (mine)	TF < 1 TF > 1	Phytostabilization potential of Pb and Zn Hyperaccumulator of Cu, Fe, Mn, Zn and Pb in greater proportion	Bech et al. (2012), Duran (2010)
Family: Basellaceae *Basella alba*	India	Fe, Zn, Cu, Mn, Ni, Pb	Phytoextraction (organo-metallic polluted site)	BCF and TF for Zn, Cu and Ni were found > 1	Potential hyperaccumulator	Chandra et al. (2018)
Family: Brassicaceae *Lepidium bipinnatifidum*	Venezuela, Colombia, Ecuador, Peru, Bolivia, Brazil, Spain and Argentina	Pb	Phytoextraction (mine)		Accumulator of Pb	Duran (2010)
Family: Cyperaceae *Carex* spp.	Colombia, New Zealand, France, Spain and Ireland	Cd, Zn, Ni, Al, Co, Cr, Ni, Pb, Cu	Phytoextraction (wetland)	BCF (root/water) shows better bioavailability of Ni in water	Zn and Ni accumulated in plant tissues, particularly in the root system	Ladislas et al. (2014), Matthews et al. (2005), Walker et al. (2004)

(continued)

Table 9.3 (continued)

Native plant species	Global distribution/location	Metal and metalloid pollutants	Uptake mechanism and media (substrate)	Removal efficiency	Benefit/comment	References
Eleocharis sp.	Colombia, Costa Rica, Central and South America, Mexico, Brazil and Argentina	As	Rhizofiltration (water)	89–99% As removal from treated water	Able to accumulate and tolerate significant amounts of As	Litter et al. (2012)
Kyllinga brevifolia	Colombia, Tropical America, Paraguay, India, Malaysia, the Philippines and China	U, Th, Sr, Ba, Ni and Pb	Phytoextraction (radioactive waste)	TF > 1	Accumulated high concentrations of U in its aerial parts	Hu et al. (2014)
Family: Euphorbiaceae *Phyllanthus niruri*	Columbia	Hg	Phytoextraction (soil)	TF = 1.12; BCF = 0.59; AF = 0.66	Suitable for phytoremediation of Hg due to high Hg transfer from root to shoot	Diez et al. (2016)
Euphorbia macroclada	Iran	Cu, Fe	Phytostabilization (soil)	TF = 0.34, 0.39; BCF = 1.33, 1.10, respectively	Most suitable for phytostabilization of Cu and Fe	Lorestani et al. (2011)
Family: Euphorbiaceae *Phyllanthus niruri*	Columbia	Hg	Phytoextraction (soil)	TF = 1.12; BCF = 0.59; AF = 0.66	Suitable for phytoremediation of Hg due to high Hg transfer from root to shoot	Diez et al. (2016)

(continued)

Table 9.3 (continued)

Native plant species	Global distribution/location	Metal and metalloid pollutants	Uptake mechanism and media (substrate)	Removal efficiency	Benefit/comment	References
Euphorbia macroclada	Iran	Cu, Fe	Phytostabilization (soil)	TF = 0.34, 0.39; BCF = 1.33, 1.10, respectively	Most suitable for phytostabilization of Cu and Fe	Lorestani et al. (2011)
Family: Fabaceae *Inga edulis*	Colombia	Hg	Phytoextraction (soil)	TF = 1.21; BCF = 0.28; AF = 0.34	Suitable for phytoremediation of Hg due to high Hg transfer from root to shoot	Diez et al. (2016)
Family: Gramineae *Saccharum munja* *Cynodon dactylon* *Pennisetum purpureum*	India	Fe, Zn, Cu, Mn, Ni, Pb	Phytoextraction (organo-metallic polluted site)	BCF and TF for Zn, Cu and Ni were found > 1	Hyperaccumulation properties of metals from organo-metallic polluted site mixed with androgenic and mutagenic compounds	Chandra et al. (2018)
Family: Juncaceae *Juncus* spp.	Colombia, Venezuela, Brazil, Austria, Australia, and common to a large number of countries	Cd, Zn, Ni, Al, Co, Cr, Ni, Pb, Cu	Phytoextraction (soil)	Very effective in accumulating Pb	Show great potentials for Cu, Pb, Cd tolerance	Archer and Caldwell (2004), Johnston and Proctor (1977), Wenzel and Jockwer (1999)

(continued)

Table 9.3 (continued)

Native plant species	Global distribution/location	Metal and metalloid pollutants	Uptake mechanism and media (substrate)	Removal efficiency	Benefit/comment	References
Family: Lamiaceae *Hyptis capitata*	Colombia, neotropics; introduced in tropical Asia and Pacific, Australia	Cd, Cu	Phytoextraction/rhizofiltration (water)	Accumulator of Cd and Cu	Demonstrates the utility of hairy roots for screening plant species	Nedelkoska and Doran (2000)
Plectranthus sp.	Colombia	Hg	Phytoextraction (soil)	TF = 1.73; BCF = 0.33; AF = 0.57	Suitable for phytoremediation of Hg due to high Hg transfer from root to shoot	Diez et al. (2016)
Ziziphora clinopodioides	Iran	Zn	Phytoextraction (soil)	TF = 0.12; BCF = 1.06	Most efficient for phytostabilization of Zn	Lorestani et al. (2011)
Family: Melastomataceae *Clidema* sp.	Columbia	Hg	Phytoextraction (soil)	TF = 1.43; BCF = 0.36; AF = 0.51	Suitable for phytoremediation of Hg due to high Hg transfer from root to shoot	Diez et al. (2016)
Family: Menispermaceae *Tinospora cordifolia*	India	Fe, Zn, Cu, Mn, Ni, Pb	Phytoextraction (organo-metallic polluted site)	BCF and TF for Zn, Cu and Ni were found > 1	Potential hyperaccumulators	Chandra et al. (2018)

(continued)

Table 9.3 (continued)

Native plant species	Global distribution/location	Metal and metalloid pollutants	Uptake mechanism and media (substrate)	Removal efficiency	Benefit/comment	References
Family: Oenotheraceae *Ludwigia* spp.	Colombia, South America; introduced in South Asia and Australia, India, Tanzania	Cu, Pb, Cr, Zn, Cd, Ni and Hg	Phytoextraction (wetland)	The removal efficiency was 99.7, 63.7, 44.9 and 32.6% for Hg, Fe, Cu and Zn, respectively	Less tolerance to toxicity. Plant died at the end of the experiment	Kamal et al. (2004), Das and Maiti (2008), Mganga et al. (2011)
Family: Papaveraceae *Argemone mexicana*	India	Fe, Zn, Cu, Mn, Ni, Pb	Phytoextraction (organo-metallic polluted site)	BCF and TF for Zn, Cu and Ni were found > 1	Native plant shows hyperaccumulation properties of heavy metals from site	Chandra et al. (2018)
Family: Plantaginaceae *Plantago* sp	Colombia, Spain	Pb, Zn, Cu, Cd, As	Phytoextraction (soil)	Zn and Pb accumulators	Can be considered as a promising species	Del Río et al. (2002)
Family: Polygonaceae *Rumex dentatus*	India	Fe, Zn, Cu, Mn, Ni, Pb	Phytoextraction (organo-metallic polluted site)	BCF and TF for Zn, Cu and Ni were found > 1	Potential hyperaccumulators	Chandra et al. (2018)
Rumex pulcher	Spain	Pb, Zn, Cu, Cd, As	Phytoextraction (soil)	Zn, Pb and Cu accumulators	Can be considered as a promising species	Del Río et al. (2002)

(continued)

Table 9.3 (continued)

Native plant species	Global distribution/location	Metal and metalloid pollutants	Uptake mechanism and media (substrate)	Removal efficiency	Benefit/comment	References
Family: Potamogetonaceae *Potamogeton paramoanus* *Potamogeton pectinatus*	Colombia, Venezuela to Bolivia–Colombia, common to a large number of countries, Turkey	Potamogeton Cd, Pb, Cr, Ni, Zn y Cu Accumulator of Cd, Pb, Cr, Ni, Zn y Cu	Phytoextraction (marsh)	Ni and Pb were accumulated by plants at a higher rate from bottom sediments than from water	Can be used as a biological indicator	Demirezen and Aksoy (2004)
Family: Solanaceae *Solanum nigrum*	Africa, Eurasia, Spain	Pb, Zn, Cu, Cd, As	Phytoextraction (soil)	Pb, Zn, Cu and As accumulators	Can be considered as a promising species	Del Río et al. (2002)
Capsicum annum	Colombia	Hg	Phytoextraction (soil)	TF = 1.19; BCF = 0.83; AF = 1	Suitable for phytoremediation of Hg due to high Hg transfer from root to shoot	Diez et al. (2016)

Key:
BCF = Bioconcentration factor
TF = Translocation factor

Table 9.4 UNEP POP classification and persistence

Pesticides	Persistence (half-lives)
Aldrin	5 years
Chlordane	5 years
Dichlorodiphenyltrichloroethane (DDT)	1–3 years
Dieldrin	Years
Endrin	12–15 years
Heptachlor	Up to 2 years
Mirex	Up to 10 years
Toxaphene	100 day–12 years
Hexachlorobenzene (HCB)	2.7–22.9 years
Industrial chemicals or by-products	
Polychlorinated biphenyls (PCBs)	0.91–7.25 years
Polychlorinated dibenzo-p-dioxins (dioxins)	More than 20 years
Polychlorinated dibenzo-p-furans (furans)	More than 20 years

Sources WWF (2005), ETOXNET (2001), USEPA (2005)

of POPs owing to their mobility and continuous cycling of volatilization and condensation have resulted in their presence in fog, rain and snow (Dubus et al. 2000). About 1.7–8.8 million metric tons of oil is released yearly into water bodies globally, and more than 90% of this oil pollution is directly linked to accidents due to human failures in addition to deliberate activities such as waste disposal (Zhu et al. 2001) (see Fig. 9.2).

9.4.1 Current Application of Native Plants in Phytoremediation of Organic (POPs) Contaminated Sites

9.4.1.1 Pesticides and PCBs

Organochlorine pesticides are one of the most important POPs prioritized by United Nations Environment Programme (UNEP) and banned or restricted by the Stockholm Convention in May 2001 (UNEP 2001) (see Table 9.4). These compounds such as dichlorodiphenyltrichloroethane (DDT) and its metabolites p,p′-dichlorodiphenyldichloroethylene (p,p′-DDE) and hexachlorocyclohexane (HCH) are very effective in controlling pests (Li et al. 2001; Liu et al. 2015) and eradicating malaria in agriculture and public health, respectively, for decades. However, they bioaccumulate along the food chain and remain in the environment making water and food undesirable for consumption (Mcleod et al. 2014). However, these pesticides are still in use in many developing countries, especially in Africa (Emoghene and Futughe 2016). Although most have been banned for decades and other restricted, pesticides remain ubiquitous in the environment globally even in remote parts of rapidly developed countries like China (He et al. 2013; Huang et al. 2014). South America, historically, is considered to be the continent with the greatest use of DDT, lindane and toxaphene (D'Amato et al. 2002). Organochlorine pesticides specifically DDT, HCH, heptachlor, aldrin, dieldrin and endrin had been extensively used in Brazil to control pest and increase food production (D'Amato et al. 2002). Its use has been banned in Brazil since the 1980s, but the long half-life causes these compounds to persist in the environment (D'Amato et al. 2002; Connell et al. 1999). Currently, in the fight against etiologic vectors particularly malaria and leishmaniosis, the use of DDT is still allowed (D'Amato et al. 2002). Most developing countries, especially Nigeria, are currently relying heavily on pesticides to prevent and/or control crop-threatening disease (Emoghene and Futughe 2016). It was reported that the re-emission of some pesticides such as DDT from soil is a dynamic process that may be affected by the properties of the soil. Previous studies indicated that DDTs have higher volatility in soils with increased temperatures and lower organic contents (Kurt-Karakus et al. 2006; Zhang et al. 2012). It has become necessary to study the bioavailability of pesticides, particularly in polluted area to assure the quality of agricultural products as uptake through plant root has since being established (Fantke and Jolliet 2015).

Polychlorinated biphenyls (PCBs) are a group of compounds synthesized commercially by direct chlorination of biphenyls. PCBs are toxic and carcinogenic and degrade slowly. Due to their dielectric nature, they are widely used in transformer fluids. Other uses include hydraulic fluids, plasticizers, adhesives, lubricants, flame retardants, etc. Some of the congeners of PCBs such as polychlorinated dibenzo-p-dioxins (dioxins) and polychlorinated dibenzo-p-furans (furans) with lateral chlorine substitutions at positions 2, 3, 7 and 8 are recalcitrant chemicals with known human carcinogens (Kaiser 2000). Through its wide-scale usage and continuous disposal, PCBs are introduced into the environment and its sink is the soil from where it spreads and contaminates groundwater and surface water in the atmosphere and even in the polar regions (Graham and Ramsden 2008; Andersson 2000). According to Bhandary (2007), the degree of chlorination and isomeric substitution pattern of the biphenyl molecule determines the degradation and transformation of PCBs in the environment. However, several studies have shown that plants provide an ideal residence for microbial community in their rhizosphere with enzymatic ability to biodegrade pesticides or PCBs (Zhao et al. 2003; Mandelbaum et al. 1995; Radosevich et al. 1996; Struthers et al. 1998) and proposed the use of plants (native plants) for pesticide or PCB degradation (see Fig. 9.3 for a typical plant–microbial degradation mechanisms).

Rissato et al. (2015) used a dicotyledonous plant, *R. communis* (castor bean) belonging to the family of Euphorbiaceae, which includes a large number of native species in the tropical region from Ethiopia, Africa (Aserse et al. 2012), to promote the degradation of 15 POPs including hexachlorocyclohexane (HCH), DDT, heptachlor

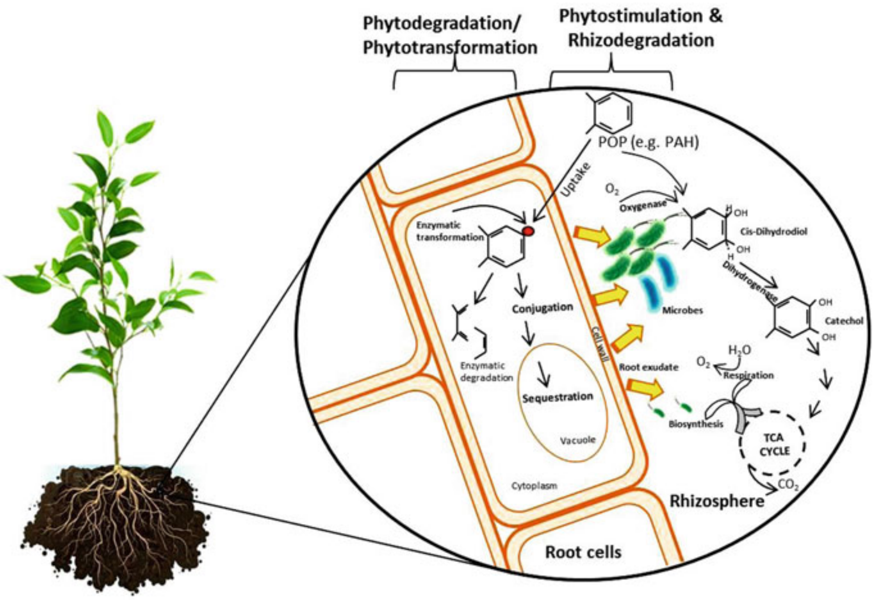


Fig. 9.3 A typical plant–microbial POP degradation mechanisms of phytoremediation

and aldrin. The result showed up to 70% clean-up which confirms the importance of using native vegetation in phytoremediation of pollutants. Romeh (2014) used a very familiar perennial weed, *Plantago major* L., commonly found by roadsides, in meadows, lawns, wastelands and canal water to remediate cyanophos insecticide in water. *P. major* L. significantly reduced cyanophos in water by 11.0% and 94.7% during 2 h and 9 days of exposure as compared with 0.8% and 36.9% in water without the plantain. Examples of phytoremediation of pesticides such as DDT and its metabolites, PCBs, HCH, alachlor, chlordane, metolachlor, atrazine among other, POPs using native plants are presented in Table 9.5.

9.4.1.2 Hydrocarbons and PAHs

Crude oil is made up of very complex chemical mixture of hydrocarbons containing more than 17,000 compounds (Marshall and Rodgers 2004) including polycyclic aromatic hydrocarbons (PAHs). Many of these hydrocarbons are toxic, mobile and environmentally persistent (Farrell-Jones 2003). PAHs are the most damaging among various hydrocarbons as they are potentially carcinogenic and/or mutagenic, ubiquitous and environmentally persistent and their occurrence in food presents a threat to public health (Abdulazeez 2017). Higher levels of PAHs are found in urban soils and roadside soil with very high concentration reported in contaminated sites. Generally, PAH range varies from 1 μg to 300 g/kg soil depending on contamination sources

Table 9.5 Examples of native plant species used in phytoremediation of organic (POPs) contaminated sites

Native plant species	Global distribution/location	POPs	Uptake mechanism and media (substrate)	Removal efficiency	Benefit/comment	References
Family: Asteraceae *Chromolaena odorata*	Americas, Caribbean, Nigeria and other African countries	PCBs, hydrocarbons	Phytoextraction and phytodegradation (soil)	BCF and TF < 1 for PCBs BCF > 1 for hydrocarbons	Native *C. odorata* was able to phytoextract PCBs into its root comparable to other known plants. *C. odorata* thrived at highest concentration > 8000 mg/kg	Anyasi and Atagana (2014), Atagana and Anyasi (2017)
Family: Cyperaceae *Fimbristylis littoralis*	Africa, Europe, Asia	PAH	Phytodegradation (soil)	Up to 92% of total PAHs were removed after 90 days from 42.4 mg/kg at day 0	Potential phytoremediation for crude oil-contaminated site	White (2001), Nwaichi et al. (2015)
Family: Fabaceae *Lathyrus sylvestris* (flat pea) *Medicago polymorpha* (burr medic)	Mediterranean, West and Central Asia	PCBs	Rhizodegradation and phytodegradation (soil) Rhizodegradation and phytodegradation (soil)	Highest amount, 32.7 (±0.3)%, was recovered by flat pea; recovery levels in amended soil ranged from 20.5% to 39.2%	Highest PCB dissipation was in planted and amended soils	Dzantor and Woolston (2001)

(continued)

Table 9.5 (continued)

Native plant species	Global distribution/location	POPs	Uptake mechanism and media (substrate)	Removal efficiency	Benefit/comment	References
Family: Euphorbiaceae *Ricinus communis*	Ethiopia and Brazil	DDTs, DDE, HCHs, heptachlors, aldrin, chlorpyrifos, transchlordane, diclofopmethyl, methoxychlor	Phytoextraction (soil)	25–70%	The highest BCR values were found when *Ricinus communis* was used for the uptake of diclofopmethyl, methoxychlor, transchlordane, aldrin, p,p′-DDT and o,p′–DDT	Rissato et al. (2015)
Family: Plantaginaceae *Plantago major*	Most European countries, including UK and Egypt	Cyanophos	Phytodegradation/rhizodegradation (water)	Over 90%	*Plantago major* L. significantly reduced cyanophos in water by 11.0% and 94.7% during 2 h and 9 days of exposure as compared with 0.8% and 36.9% in water without the plantain	Romeh (2014)
Family: Poaceae ***Phalaris arundinacea*** (reed canary grass)	Europe, Asia, North Africa and North America	PCB	Rhizodegradation and phytodegradation (soil)	Highest amount, 32.7 (±0.3)%, was recovered by flat pea; recovery levels in amended soil ranged from 20.5 to 39.2%	Highest PCB dissipation was in planted and amended soils	Dzantor and Woolston (2001)

(continued)

Table 9.5 (continued)

Native plant species	Global distribution/location	POPs	Uptake mechanism and media (substrate)	Removal efficiency	Benefit/comment	References
Family: Urticaceae *Urtica dioica*	USA, Canada, Europe, Asia, Africa and South America	PCBs	Phytodegradation	After four months, up to 33% of the less chlorinated biphenyls had been removed	Findings suggest that remediation by stinging nettle could have a much wider range of applications than previously thought	Viktorova et al. (2017)
Family: Typhaceae *Typha latifolia* **Family: Poaceae** *Phragmites* spp.	North and South America, Europe, Eurasia and Africa	HCB	Rhizodegradation and phytodegradation (sediment)	Plant species increase the degradation of HCB. After 125 days, no HCB was detected	Phragmites was best at improving microbial activity	Ma and Pardue (2005)

Key:
BCF = Bioconcentration factor
TF = Translocation factor

such as fossil fuels, gasification and liquefaction of coal, incineration of waste, wood treatment processes among others (Bamforth and Singleton 2005). Incomplete combustion of organic materials releases about 100 different PAHs that are ubiquitous pollutants. PAHs are rarely used industrially apart from a few used in medicine, dyes, plastics and pesticides (USEPA 2008). Some PAHs can be transformed through metabolism into mutagenic, carcinogenic and teratogenic agents, e.g. dihydrodiol epoxides at the site of entry which bind to and disrupt DNA and RNA, paving the way to tumour formation (Wild and Jones 1995). The US EPA has listed sixteen PAHs in a priority control list in which seven such as benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DahA), indeno[1,2,3-cd]pyrene (InP) and benzo[g,h,i]perylene (BghiP) are confirmed to be carcinogenic (Harvey 1991) and should therefore be the target on this basis. However, due to their lower bioavailability, they present less danger than some more mobile pollutants (Cmkovic et al. 2006).

The presence of plants enhances the biodegradation of hydrocarbons in soil by assisting higher hydrocarbon-degrading microbial communities in the rhizosphere (Siciliano et al. 2003), increasing PAH bioavailability, by influencing PAH desorption from the soil and by polymerization actions, e.g. humification to stabilize hydrocarbons (Wild et al. 2005; Harvey et al. 2002). Phytostimulation and/or rhizodegradation is the main pathway of phytoremediation of hydrocarbons due to the catabolic activities of proliferated microbes as a result of the presence of plant roots within the dynamic region of the rhizosphere (Wild et al. 2005; Siciliano et al. 2003) (see Fig. 9.3). The genetic composition of the plant (or native plant), its root system, exudate pattern and components of cell wall may give some plants the advantage over others as better phytoremediators (Siciliano et al. 2003; Philips et al. 2006).

Atagana and Anyasi (2017) recently carried out an assessment of native plants at petroleum-contaminated sites for phytoremediation potential in South-Eastern Nigeria. A total of 28 native plants sampled include *Chromolaena odorata, Aspilla africana, Chrysocoma ciliata, Dimorphotheca sp., Cosmos bipinnatus, Teraxacum sp.* from the Asteraceae family (most dominant native plants at the site); *Orinus longiglumis, Paspalum scrobiculatum, Paspalum vaginatum, Chloris babata* from the Gramineae family; *Cyperus rotundus, Cyperus esculentus, Carex stricta, Scirpus cespitosus* from the Cyperaceae family among other native plant family such as Leguminoceae, Malvaceae, Euphobiaceae, Pteridophyte, Onagraceae, Sterculiaceae, Melastomaceae, Vitaceae, Anacardiaceae and Annonaceae. They reported that at high concentration of total petroleum hydrocarbons (TPH) in the soil, *C. odorata, A. africanus, C. ciliate, C. bipinnatus, P. vaginatum, C. babata, E. atrovirens, B. acuminate, U. chamae* survived while *C. odorata, B. acuminate* and *U. chamae* showed the ability to thrive at the highest TPH contaminated site with contamination range from 214 to 8011 mg/kg. In their conclusion, the screened native plants especially *C. odorata* demonstrated potential for hydrocarbon-contaminated sites in Nigeria. *C. odorata* has also been shown to remediate heavy metals (Tanhan et al. 2007), PCBs (Anyasi and Atagana 2014) and radionuclide pollutants (Tang and Willey 2003; Singh et al. 2009). Table 9.5 presents examples of current studies on hydrocarbons and PAH phytoremediation with native plant species.

9.4.2 A Case Study on PAH-Contaminated Soil Using a Native Plant from the Niger Delta, Nigeria

Since the advent of oil discovery in Nigeria in 1956, the Niger Delta region has been suffering from the intense detrimental environmental consequences associated with oil development. Present-day industrial activities release substantial amounts of crude oil, heavy metals and refined products into the natural environment particularly in the region as a result of events such as vandalization of oil pipelines by local inhabitants; corrosion due to ageing pipelines; oil blowout from flow station; sabotage coupled with oil theft and illegal bunkering; inadequate care in loading and offloading of oil vessel, etc. PAHs were chosen as the pollutants of concern because they are part of the persistent organic pollutants (POPs) with two or more fused benzene rings (Oluseyi et al. 2011) and are highly lipophilic and ubiquitous in the environment (Sun et al. 2009; Wang et al. 2012). Phenanthrene, fluoranthene and benzo[a]pyrene (Fig. 9.4) were the targeted PAH contaminants in this case study because they are common pollutants but with contrasting molecular weights and associated different physico-chemical properties. PAH environmental occurrence is highly dependent on their molecular weight, and low molecular weight PAHs with 2–3 fused rings, such as phenanthrene (3 fused rings), occur in the atmosphere in the vapour phase whereas multi-ringed PAHs (5 rings or more), such as benzo[a]pyrene, are bound to particles, while PAHs with four rings such as fluoranthene are partitioned between vapour and particulate phases depending on temperature (Harner and Bidleman 1998; Howsam et al. 2000).

The most thriving and dominant native plant, *C. odorata* (Fig. 9.5a) colloquially known as Awolowo, Akintola or Queen Elizabeth weed, was sampled with their seeds from the Bomu Manifold contaminated land at K-Dere, Gokana Local Government Area (Ogoniland), Cross River State, Nigeria (Fig. 9.5b–c). The Bomu Manifold covers an area of 5000 m^2 with two distinct gates large enough to provide heavy machinery access, and it is surrounded by a 3-m-high wire mesh fenced and guarded by armed army personnel and Shell Petroleum Development Company (SPDC) (Fig. 9.5c). Majority of the pipes and manifold infrastructure are above ground, while pipes run below ground outside the manifold area. Visible heavy polluted crude oil was found inside the fence which was seeping through the fence and contaminating additional 19,000 m^2 of land outside the manifold as there was no

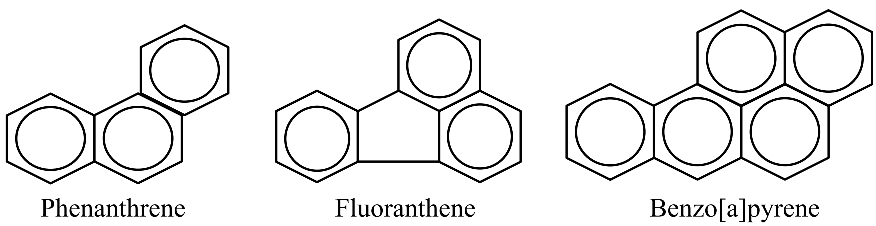


Fig. 9.4 Structures of PAHs of concern

(a)

(b)

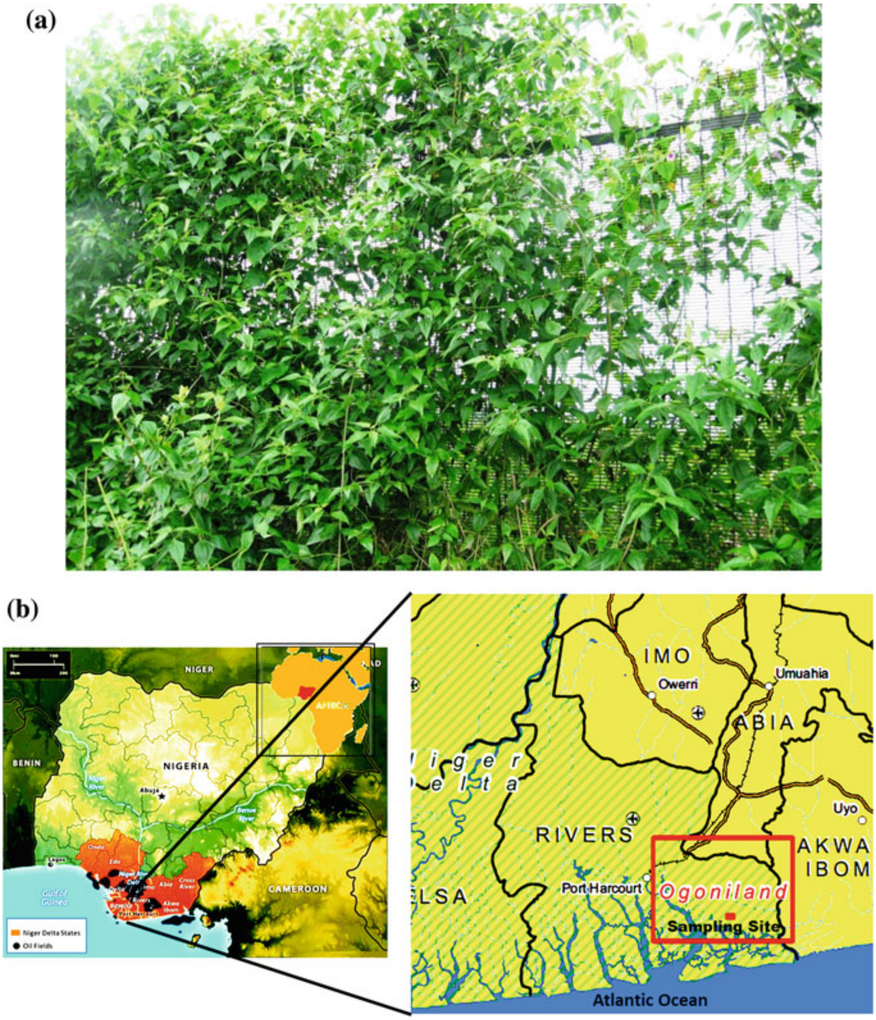


Fig. 9.5 **a** Thriving and dominant native *Chromolaena odorata* at the 3-m-high perimeter fence. **b** Niger Delta, Nigeria, showing Ogoniland where Bomu Manifold is located. *Sources* Modified from UNEP (2011) and Stratfor (2016). **c** Bomu Manifold, K-Dere, Cross River State, where plant sampling took place. *Source* Modified from UNEP (2011)

trench or perimeter drainage system around the manifold. Off this, some 9000 m^2 is highly polluted with concentration of crude oil overwhelming the soil surface resulting in a strong oily smell. An old flow station, reportedly blown during the Biafran War and later decommissioned, is located 150 m to the east (UNEP 2011).

In this bench-scale study, air-dried soil from Sonning Farm (University of Reading, Berkshire, UK) was artificially contaminated with a mixture of PAHs (phenanthrene, fluoranthene and benzo[a]pyrene) using partial spiking protocol according to

(c)

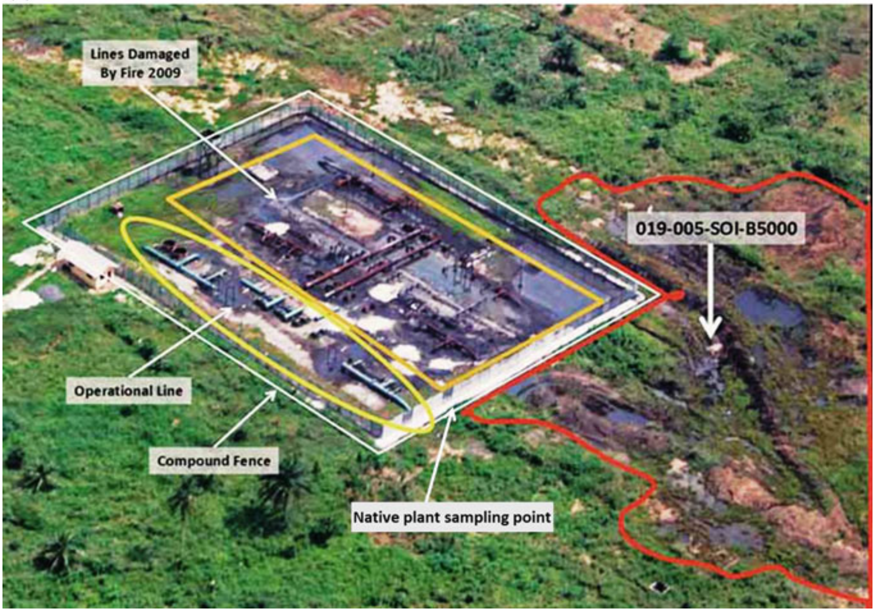


Fig. 9.5 (continued)

Jacobsen et al. (2002). Spiked soils with 60 mg/kg (20 mg/kg each) and 120 mg/kg (40 mg/kg each) as a baseline from the literature reviews in the Niger Delta (Ayodele et al. 2015) were used for the plant screening. Artificially contaminated soils were amended with or without a commercially synthesized rhamnolipid biosurfactant (500 mg/kg or 1000 mg/kg) (Table 9.6) with a critical micelle concentration (CMC) and half maximal effective concentration (EC_{50}) of 105 g/L and 0.1 g/L, respectively. Four weeks old native *C. odorata* from the region's contaminated soil was screened against a commercially available plant, *Medicago sativa* (Alfalfa), of the same age for their PAH tolerance over 28 days. Alfalfa was chosen as a reference plant as reports have shown its phytoremediation potentials (Fan et al. 2008;

Table 9.6 Experimental design of plant screening with codified treatments

Treatment	Vegetated		Un-vegetated
	C. odorata	*M. sativa*	
Control	A	F	K
PAHs (60 mg/kg)	B	G	L
Biosurfactant (500 mg/Kg) + PAHs (60 mg/kg)	C	H	M
PAHs (120 mg/kg)	D	I	N
Biosurfactant (1000 mg/kg) + PAHs (120 mg/kg)	E	J	O

Bonfranceschi et al. 2009; Peralta-Videa et al. 2004; Li and Yang 2013; Ding and Luo 2005; Ouvrard et al. 2011; Zhang et al. 2013a, b). The benchtop experiment was carried out inside Stewart's electric heated propagator to simulate the subtropical condition in the Niger Delta region at average temperature of 20 °C with 2 short lengths of white fluorescent tubes hung above it, supplying a photoperiod of 10 h light. Plants received water daily by gently spraying with artificial rainwater (0.01 M of $CaCl_2$) to prevent leaching. The location of the pots was randomly changed daily within propagator chamber. Plant mortality rates over the 28-day experimental time were recorded by counting live and dead plants differentiated by visual inspection. At the harvested time, plant height, taking into account change in growth difference, and root length from the base of the stem to the longest root tip of plant were measured.

The result of the plant screening showed that native *C. odorata* plants were able to grow to a mean height range of 5.83 ± 3.01 to 13.00 ± 0.91 cm at 28th day from an original mean height range of 3.50 ± 0.58 to 4.75 ± 1.50 cm in the transplanting week. In contrast, *M. sativa* group has a mean height range of 5.50 ± 0.71 to 10.13 ± 1.38 cm from an original mean height range of 4.00 ± 0.00 to 5.00 ± 1.73 cm, but there was a significant increase in native *C. odorata* height compared to *M. sativa* ($p < 0.05$) suggesting that the native *C. odorata* grew better in all the treatment soils than the reference *M. sativa* (Fig. 9.6a). In terms of both plant biomasses, the shoot and root could not be determined separately due to the relatively short growth periods resulting in the development of tender plants; however, the dry biomass of the whole plants (combination of shoot and root) from both groups was determined as shown in Fig. 9.6b and there was a statistical significant decrease with some evidence against the H_0 ($p < 0.05$) in the dry biomass of *M. sativa* when compared to the native *C. odorata* with *p*-value of 0.04 and a *T*-value of 2.26 suggesting that there is very likely a genuine difference in the dry biomass means of the two plants. This also shows that native *C. odorata* performed significantly better than *M. sativa* under similar conditions. However, *M. sativa* has increased root lengths with statistical difference ($p < 0.00$) in relative comparison with *C. odorata* fibrous root with very strong evidence against the H_0 ($p < 0.05$) (Fig. 9.6c). Plant root systems can be grouped into two main categories: tap root as seen in *M. sativa* and fibrous root systems as seen in *C. odorata* (Holm et al. 1977 and Henderson 2001). Tap root systems are characterized by an enlarged central root that penetrates down into the soil, with lateral roots branching off this central axis. Fibrous root systems, being finer and more profuse, offer a superior means of increasing the total rhizoplane surface area m^{-3} of soil when compared to a tap root system. The larger rhizoplane surface area of a fibrous root system would be advantageous in the establishment of an active microbial population (Aprill and Sims 1990) and may penetrate the soil deeply. The fibrous root structure of *C. odorata* may be an added advantage over *M. sativa* despite its short root length for phytoremediation particularly in stimulating rhizosphere micro-organisms to enhance degradation of PAHs. The presence of growing root systems in the soil environment can be viewed as an effective means of increasing and distributing soil organic matter throughout the soil. The proliferation of plant roots also serves as a means of distributing soil micro-organisms through the soil as

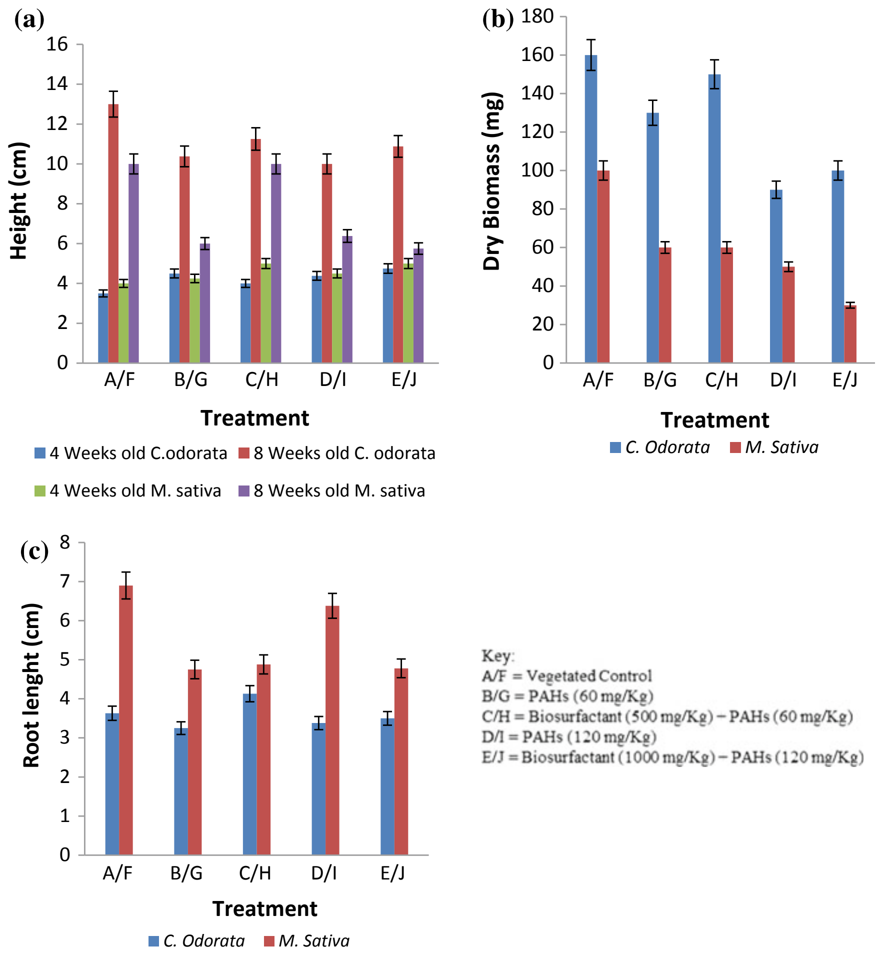


Fig. 9.6 **a** Mean growth of *Chromolaena odorata* and *Medicago sativa* from seedlings (4 weeks old) to harvest (8 weeks old). **b** Dry biomass of *Chromolaena odorata* and *Medicago sativa* after 56 days of growth. **c** Root length of *Chromolaena odorata* and *Medicago sativa* after 56 days of growth. Error bars represent the standard deviation of two sampled pots

they are carried with growing root tips. Therefore, the probability of contact between microbes and a toxic compound is enhanced (Aprill and Sims 1990).

PAHs were drastically reduced especially in biosurfactant amended soils of both plants (Fig. 9.7). There was a significant difference between the un-vegetated control groups, *C. odorata* and *M. sativa* (vegetated groups), with very strong evidence against the H_0 with a *p*-value of 0.00 (Fig. 9.8). But in terms of phytoremediation potentials, the reference plant, *M. sativa* (Alfalfa), was not better than the preferred fibrous root native plant, *C. odorata*. As shown in Fig. 9.9 using a Tukey simultaneous 95% confidence interval where *M. sativa* and *C. odorata* do not contain zero

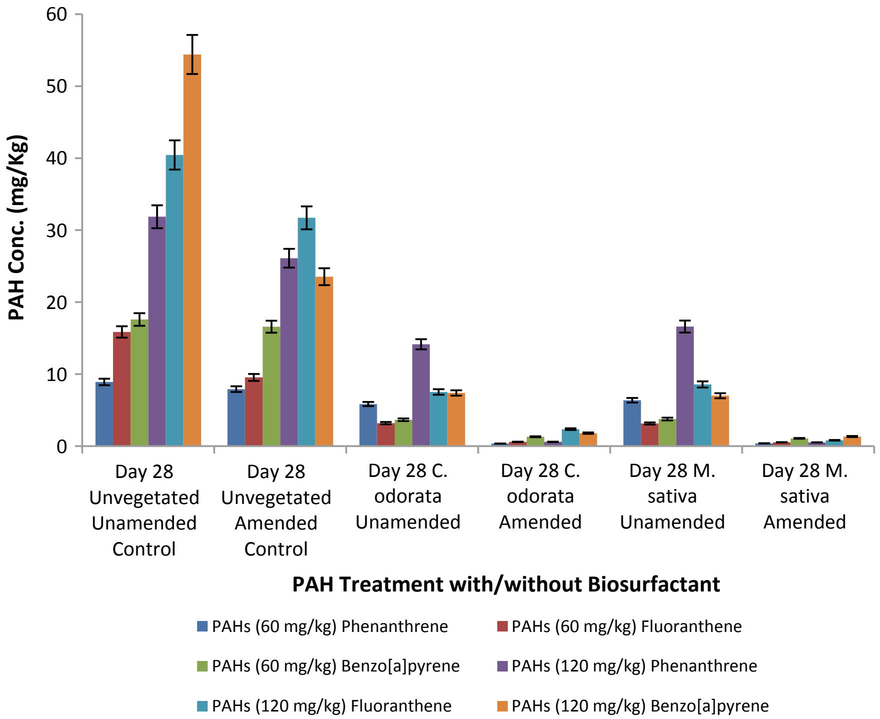


Fig. 9.7 Effect of biosurfactant on PAH mixture reduction in screened soil treatments of *Chromolaena odorata* and *Medicago sativa* after 28 days. Error bars represent the standard deviation of two sampled pots

meaning their corresponding means are significantly different from the un-vegetated control which contained zero. In addition, there was no statistical significant difference between the native *C. odorata* and the referenced *M. sativa* in terms of enhanced phytoremediation potentials. This demonstrates that both plants especially the native *C. odorata* enhanced with biosurfactant were responsible for the significant reduction of PAHs in the study. Thus, the native *C. odorata* showed a more thriving and tolerant nature in PAH contaminated soil in almost all parameters measured compared to the referenced *M. sativa* which is a proven and well-established phytoremediation plant. This study which is sustainable, environmentally friendly and cost effective opens up new possibilities for phytoremediation especially in the Niger Delta using native plant species such as *C. odorata* with the added advantages of social and aesthetic value, improved soil quality, functionality and ecological restoration of one of the world's largest deltas and wetlands.

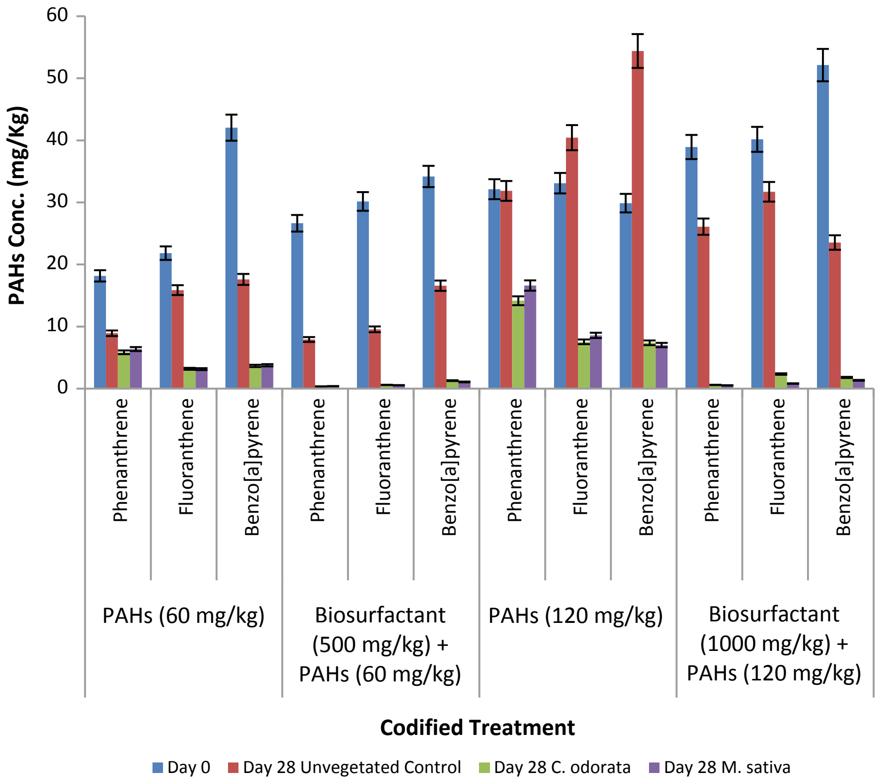
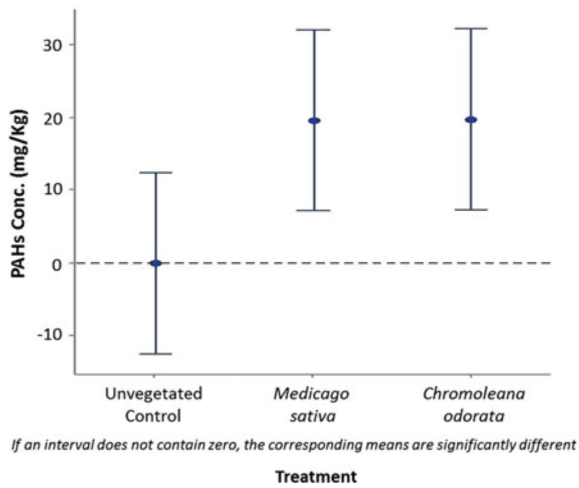


Fig. 9.8 Mean concentrations of total PAH mixtures in screened soil treatments of un-vegetated soil control, *Chromolaena odorata* and *Medicago sativa* with or without biosurfactant after 28 days. Error bars represent the standard deviation of two sampled pots

Fig. 9.9 Tukey simultaneous 95% confidence interval plot comparing treatment differences of Day 0 and 28 of un-vegetated control, *M. sativa* and *C. odorata* with 9.57, 29.21 and 29.09 mg/kg means, respectively, with or without biosurfactant



9.5 Prospects and Challenges of Native Plants in Phytoremediation

The use of native plants in phytoremediation is well suited to its natural contaminated area, solar-driven and aesthetically pleasing, has a favourable public perception, prevents erosion, eliminates secondary airborne and waterborne waste and provides striking prospects compared with traditional methods. However, it also has some challenges. It is arguably the most cost effective of all treatments as plants are already adapted to the environment and little or no management cost is incurred other than marginal costs for harvesting. No additional CO_2 is released into the atmosphere if harvested biomass is burned except that originally assimilated by the plant during growth. It is a CO_2 neutral and potentially profitable technology especially when plant biomasses are used for heat and energy production. One of the most outstanding prospects of using native plants is the simultaneous remediation of a site and establishment of similar floristic diversity in addition to recovery of site quality, functionality and sustainability. However, its relatively slow pace has become a major challenge because it requires several years or even decades to clean up impacted sites. The depth of the root systems of some native plants, the solubility and availability of pollutants and the adjacent penetration of pollutants into media and trophic chain can be detrimental to its usage.

9.5.1 Future Development of Native Plants in Phytoremediation

Area of improvement of native plants' performance in phytoremediation lies in the advancement of molecular techniques such as genetic engineering to optimize the harvest time, reducing growth cycle duration and engineering of native plant species with high biomass production, increased root depth, high toxicity tolerance, more metal–metalloid accumulation and sublime POP degradation. A number of experiments have shown the feasibility of engineering higher extractive and degradative abilities in plants through genetic modification (Hooda 2007; Song et al. 2003; Becher et al. 2004; Van de Mortel et al. 2006). Current floristic communities in contaminated sites should be exploited for potential heavy metal–metalloid hyperaccumulators and screened for new effective organic contaminant degraders, which will require more fundamental research knowledge on the natural detoxification/degradation mechanisms of native plants. As shown in the case study, low solubility and availability of pollutants in contaminated sites can be increased by amendments with biosurfactant so as to make it more effective, time saving and economically competitive. Phytoremediation can also be advanced especially with native plants using other integrated technology such as soil solarization which is a non-chemical soil treatment that uses radiation from the sun and a thin transparent film normally made of polyethylene to heat up the soil temperature. This process was initially intended as a treatment method for soil-borne pathogen control (Katan et al. 1976); however, research has shown that solarization has other effects on soil characteristics that can influence the performance of plants, such as enhancing nutrient concentration (Chen et al. 1991) and soluble organic matter content (Chen et al. 2000). According to Emoghene and Futughe (2011), *Amaranthus viridis* plants grown on solarized plots performed better than their non-solarized counterparts in all the growth parameters measured in addition to increased microbial population in post-solarization compared to pre-solarization. The use of native plant species is emerging as a simpler, more cost effective, more environmentally friendly and more self-sustaining alternative to non-native plants in phytoremediation.

9.5.2 Conclusion

Native plants growing on various contaminated sites globally are potential phytoremediators which can remediate a broad range of inorganic and organic pollutants and may drastically increase the technology's application globally. The case study concludes that *C. odorata* performed equally well as the reference plant, *M. sativa* (Alfalfa), in terms of phytoremediation potentials. Phytoremediation using native plant species has been proven to be an effective and efficient approach especially when enhanced with biosurfactant than its non-native counterparts because it is ecologically safer, cheaper, aesthetically pleasing, socially acceptable and technologically simpler.

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Chapter 10
Municipal and Industrial Wastewater Treatment Using Constructed Wetlands

Vivek Rana and Subodh Kumar Maiti

Abstract High rate of urbanization and industrialization in recent years is generating very large amount of wastewater. Inadequate wastewater treatment options may lead to the discharge of untreated wastewaters (containing organic matter, inorganic and organic chemicals, toxic substances, and disease-causing agents) into the aquatic environment, thereby deteriorating their quality. These toxic chemicals such as heavy metals draw our concern towards their remediation due to their harmful effect on human metabolism and ecosystem as a result of their high persistence in the environment. Constructed wetlands are being widely used for treating many classes of contaminants such as heavy metals, domestic and industrial wastewater, textile dye effluents, pesticides, petroleum hydrocarbons, explosives, radionuclides, etc. This treatment method overcomes the shortcomings of conventional wastewater treatment methods as it is a cost-effective, non-intrusive and eco-centric technology. This chapter reviews and provides an insight into constructed wetland technology employed for efficient remediation of difficult-to-treat wastewaters.

Keywords Constructed wetlands · Environmental pollution · Industrial wastewater treatment · Phytoremediation

Abbreviations

BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
CW	Constructed Wetlands

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FWSCW	Free Water Surface Constructed Wetlands
HRT	Hydraulic Retention Time
HSSFCW	Horizontal Sub-surface Flow Constructed Wetland
SSFCW	Subsurface Flow Constructed Wetland
STP	Sewage Treatment Plants
TOC	Total Organic Carbon
TSS	Total Suspended Solids
VFCW	Vertical Flow Constructed Wetland
VSSFCW	Vertical Sub-surface Flow Constructed Wetlands

10.1 Introduction

Wetlands are defined as areas that are inundated or saturated with surface or groundwater, saline or fresh, which support vegetation typically adapted for living in saturated soil conditions (Metcalfe et al. 2018). They are characterized by distinguished vegetation (aquatic plants) and are adapted to the unique hydric soils. Wetlands exist in every climatic zone (from polar to tropical regions) and include marshes, peatlands, mangrove forests, rivers, lakes, deltas, and floodplains. Being an important component of the ecosystem, urban wetlands offer vital services such as water purification, filtration, retention of nutrients, flood control, groundwater recharge, and providing habitat for a variety of species (Gibbs 1993; Boyer and Polasky 2004; Rana et al. 2016). They play an important role in regulating biogeochemical cycles (carbon, nitrogen, and sulfur cycles) in the atmosphere. With increasing population and industrialization, the total area covered by wetlands has decreased substantially due to anthropogenic activities (Hansson et al. 2005). Wetlands act as "sinks" to metals, as they offer processes such as sedimentation and adsorption of pollutants. The metals in dissolved and particulate form are reduced in wetlands due to the presence of organic matter, divalent ion (Fe), and clay. In addition, carbonates, phosphates, and Fe/Mn oxides also promote the immobilization of metals.

The economic value of a wetland depends upon its functioning. Wetland functions are not necessarily of economic worth but the value derives from the existence of a demand for wetland goods and services due to these functions. *Use-value* of a wetland means indirect or direct utilization of wetland goods and services by humans. However, *non-use* value of a wetland is associated with benefits derived simply from knowledge that a resource such as an individual species or an entire wetland is maintained (Turner et al. 2000). It is independent of use, although it is dependent upon the essential structure of the wetland and functions it performs.

The diversity of wetlands depends upon their method of formation, geographical location, and altitude. The flow of water in to and out of the wetland system is driven by the climate and configuration of its catchment area. The storage capacity of the system is regulated by landscape and geology. This hydrological cycle influences the rates at which gases diffuse through water, the reduced or oxidized (redox) state of

Table 10.1 Different levels of wastewater treatment (Adopted from Metcalf and Eddy 2003)

Treatment level	Description
Preliminary	Removal of wastewater constituents such as rags, sticks, floatables, grit, grease that may hamper operation and maintenance of various treatment processes
Primary	Removal of a portion of the suspended solids and organic matter from the wastewater
Advanced primary	Enhanced removal of suspended solids and organic matter from the wastewater, typically accomplished by chemical addition and filtration
Secondary	Removal of biodegradable organic matter and suspended solids. Disinfection is also included in the definition of conventional secondary treatment
Secondary with nutrient removal	Removal of biodegradable organics, suspended solids, and nutrients (nitrogen, phosphorus, or both)
Tertiary	Removal of residual suspended solids (after secondary treatment), usually by granular medium filtration or micro-screens. Disinfection is also a type of tertiary treatment. Nutrient removal is often included in this definition
Advanced	Removal of dissolved and suspended materials remaining after normal biological treatment when required for various water reuse applications

nutrients and their solubility which thereby affecting the salinity of the water. These factors indicate the diversity of flora and fauna that sustain in a wetland and species diversity and composition, in turn, regulates the recycling of nutrients and pollutants in wetlands (Gupta et al. 2020).

Municipal wastewater represents the spent water supply of communities. Before discharging the wastewater into natural water streams, it undergoes various levels of treatment which are enlisted in Table 10.1.

10.1.1 Phytoremediation: A Green Technology

Phytoremediation refers to the use of plants to remove, destroy, or sequester hazardous contaminants from media, such as soil, water, and air (Prasad 2003; Rana and Maiti 2018a). It encompasses the use of various technologies to reduce, degrade, or immobilize harmful intoxicants in the environment, primarily of anthropogenic origin, with an objective to remediate contaminated sites and wastewater treatment by employing plants (Mukhopadhyay and Maiti 2010). Phytoremediation is being used in different decentralized wastewater treatment systems such as constructed wetlands for treating municipal and various industrial wastewater efficiently (Daverey et al. 2019).

Phytoremediation operates through various processes: phytoextraction, rhizofiltration, phytostabilization, phytodegradation, and phytovolatilization. The remediation of pollutants can take place either individually or in combination by these processes (Ali et al. 2013). Phytoremediation is being widely used for treating many classes of contaminants such as metals, pesticides, petroleum hydrocarbons, explosives, and radionuclides (McCutcheon and Schnoor 2003). Phytoremediation overcomes the shortcomings of conventional wastewater treatment methods as it is a solar-driven, cost-effective, non-intrusive, and environment-friendly technology.

10.1.1.1 Phytoextraction

Phytoextraction (also known as phytoaccumulation, phytoabsorption, or phytosequestration) is defined as the process that utilizes plant roots for the uptake of pollutants from soil or water and their translocation to and subsequent accumulation in above-ground biomass, e.g., shoots or any other harvestable part of the plant (Bhargava et al. 2012). Microbe-assisted phytoextraction enhances the uptake of metal ions by plants.

10.1.1.2 Rhizofiltration

Rhizofiltration is the technique of utilizing plant roots to absorb, precipitate, and concentrate toxic metals from polluted effluents. Rhizofiltration technique has been used for the remediation of uranium and metals such as Pb, Cd, and Zn (Lee and Yang 2010; Duresova et al. 2014).

10.1.1.3 Phytostabilization

Phytostabilization is the immobilization of pollutants in the soil to dampen the biological availability of the pollutants and to reduce the possibility of further environmental degradation by transportation to other environmental components through the air or by leaching into the underground water table. Phytostabilization mainly focuses on sequestering metal ions and other pollutants near the root area instead of plant tissues (Lee 2013).

10.1.1.4 Phytodegradation

Phytodegradation, also known as phytotransformation, is the uptake, metabolization, and degradation of organic pollutants with the help of enzymes such as dehalogenase and oxygenase generated by plants and is independent of rhizospheric microorganisms. This technique has been used for treating pollutants of organic nature such as dyes (Muthunarayanan et al. 2011).

10.1.1.5 Phytovolatilization

Phytovolatilization encompasses the release of contaminants into the air through leaves after taking up the contaminated water. This technique could be used for remediation of organic pollutants and the uptake of some metals such as Hg, Se, and As (Ali et al. 2013).

10.1.2 Ramsar Convention for Conservation of Natural Wetlands

Ramsar Convention is an inter-governmental treaty that provides the framework for national action and international cooperation for the conservation and wise use of wetlands and their resources. On February 2, 1971, in the Iranian town of Ramsar, 18 nations signed this remarkable treaty. It was the first of the modern instruments seeking to conserve natural resources on a global scale. The need to sign this treaty on an international level was because: (i) many wetlands shared international boundaries, thus the circulation of water in atmosphere was truly international; (ii) fish hatching in wetlands included shares in two or more countries; (iii) migratory birds crossed international boundaries to rest, feed, and breed; and (iv) there must be international arrangements for the provision of technical and financial aid to conserve wetlands in developing countries (Matthews 1993). As of 2016, the Ramsar Convention included 2266 sites of international importance. The country with the highest number of sites is the United Kingdom with 170 wetland sites, and the country with the greatest area covered with wetlands is Bolivia, with over 140,000 km^2. The countries signing this treaty commit to (i) work towards the wise use of the wetlands to be conserved under this treaty; (ii) include suitable wetlands in the list of Wetlands of International Importance (Ramsar list) and ensure their effective management; and (iii) cooperate on transboundary wetlands, shared wetland systems, and shared species. In India, there are 26 wetland sites which are designated as Ramsar sites.

10.1.3 Flora in Natural Wetlands

Macrophytes are large plants that may dominate in wetlands or littoral zones of lakes and streams. Lakes, rivers, and marshes comprise of two types of macrophytes: (i) free-floating and (ii) rooted (Fig. 10.1).

Rooted macrophytes divide the shoreline into distinct zones and assist in removing nutrients from the sediments and water column. From the shallow to the deeper water, three different types of plants are there: (i) floating-leaved plants, with leaves that grow from the vegetative portions near the bottom of the wetland until floating at the surface; (ii) emergent plants, with all or part of their vegetative and sexually

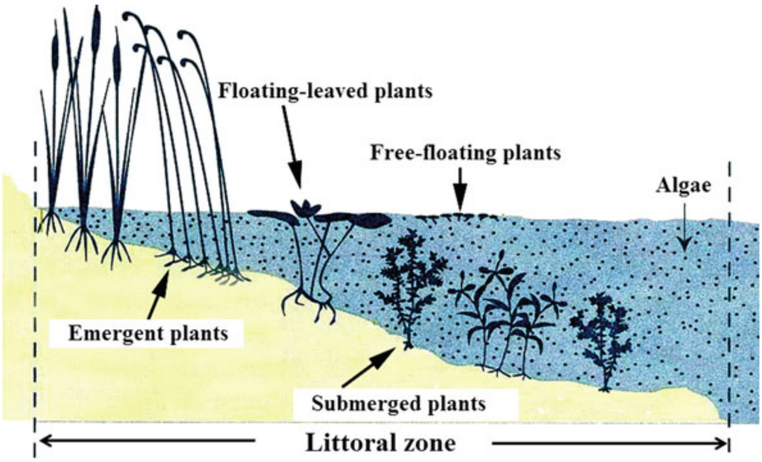

Fig. 10.1 Different types of macrophytes found in littoral zone of wetlands (Courtesy of the Minnesota Department of Natural Resources, the USA)

reproductive parts above the water surface; and (iii) submerged plants, that have all portions of the plant underwater, or the weed is dependent upon water for support. The list of some of the macrophytes which are commonly found in wetlands is shown in Table 10.2.

10.1.4 Biogeochemical Cycles in Natural Wetlands

10.1.4.1 Carbon Cycle

Wetlands are one of the largest biological pools of carbon and play a vital role in driving global carbon cycles by acting as natural carbon sinks (Mitra et al. 2005). Wetlands cover a mere 6–8% of the land and freshwater surface; however, they contribute about 12% of the global carbon pool (Mitsch and Gosselink 2007). Carbon in wetlands exists as plant biomass carbon, dissolved carbon, particulate carbon, microbial biomass carbon, and gaseous products such as CH_4 and CO_2. The mass balance of carbon in wetlands depends on the (i) carbon input contributed by organic matter production and (ii) carbon output contributed by decomposition of organic matter, methanogenesis, etc. The storage of carbon in the wetlands is dependent on its topography, landscape, morphology, hydrologic regime, vegetation, temperature and pH, salinity and moisture of the soil.

Methane is generated through different pathways: (i) diffusion, which includes the transmission of CH_4 through the soil and water to the atmosphere; (ii) plant mediated, which encompasses aerenchyma possessing tissues for direct transport of gases between atmosphere and plant roots; (iii) ebullition, which encompasses the

Table 10.2 List of some macrophytes commonly found in wetlands

Scientific name	Family	Common name
Floating macrophytes		
Commelina benghalensis L.	Commelinales	Benghal dayflower, tropical spiderwort
Enhydra fluctuans Lour	Asteraceae	Water spinach, watercress
Hydrocharis dubia (Blume) Backer	Hydrocharitaceae	–
Ipomoea aquatic Forssk.	Convolvulaceae	Water spinach, water convolvulus
Pistia stratiotes L.	Araceae	Water cabbage, water lettuce
Salvinia auriculata Aubl.	Salviniaceae	Eared watermoss, butterfly fern
Salvinia molesta D.Mitch.	Salviniaceae	Giant salvinia
Salvinia natans (L.) All.	Salviniaceae	Floating fern, floating moss
Trapa natans L.	Lythraceae	Buffalo nut, devil pod
Emergent macrophytes		
Cabomba aquatica Aubl.	Cabombaceae	Aquarium plant
Colocasia esculenta (L.) Schott	Araceae	Taro
Cyperus alternifolius Rottb., 1772	Cyperaceae	Umbrella papyrus, umbrella sedge
Cyperus esculentus L. *Euryale ferox* Salisb.	Cyperaceae Nymphaeales	Hufa sedge, nut grass Fox nut, gorgon nut
Leersia hexandra Sw.	Poaceae	Southern cutgrass, club head cutgrass
Monochoria hastata (L.) Solms	Pontederiaceae	–
Scirpus grossus L.f.	Cyperaceae	Bulrush, deer grass
Typha latifolia L.	Typhaceae	Broad-leaf cattail
Typha angustifolia L.	Typhaceae	Narrow-leaf cattail
Submerged macrophytes		
Cabomba caroliniana A. Gray	Cabombaceae	Carolina fanwort, fish grass
Elodea canadensis Michx.	Hydrocharitaceae	Canadian waterweed or pondweed
Hydrilla verticillata (L.f.) Royle	Hydrocharitaceae	Waterthyme, hydrilla
Najas graminea Del.	Hydrocharitaceae	Rice-field water-nymph
Ottelia alismoides (L.) Pers.	Hydrocharitaceae	Duck-lettuce
Potamogeton crispus L.	Potamogetonaceae	Curled pondweed, curly-leaf pondweed
Ruppia maritima L.	Ruppiaceae	Beaked tasselweed, widgeon grass
Utricularia vulgaris L.	Lentibulariaceae	Greater bladderwort, common bladderwort
Vallisneria Americana Michx.	Hydrocharitaceae	Wild celery, water celery

release of trapped CH_4 in the vacuoles of the soil through popping up the CH_4 pockets as a result of the built-up pressure over the time (DelSontro et al. 2016).

The consumption of O_2 by microorganisms living in warm, moist conditions is more than its diffusion from the atmosphere leading to the characterization of wetlands as an anaerobic platform for fermentation. Two types of bacteria belonging to the domain *Archaea* play a significant role in the global carbon budget: (i) methanotrophs and (ii) methanogens. Methanogens are obligate microorganisms degrading the organic matter by utilizing CO_2 as the energy source in the absence of alternative electron acceptors (Fe^{3+}, NO_3^-, and SO_4^{2-}). The reduction of CO_2 is carried out either with molecular H_2 or through fermentation by acetoclastic methanogenesis encompassing the fermentation of acetate and H_2–CO_2 into CH_4 and CO_2 as shown in Eqs. (10.1) and (10.2). Active methanotrophs in aquatic environments including wetlands are quantified using various conventional and novel techniques such as determination of gene transcripts, DNA-based stable-isotope probing (SIP), quantitative PCR (Q-PCR), pyrosequencing (Deng et al. 2016).

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{10.1}$$

$$HC_3 - COOH \rightarrow CH_4 + CO_2 \tag{10.2}$$

The methane flux in wetlands is a function of the relative activities of methanotrophs and methanogens. Methane flux is also dependent upon several other factors such as the water table of the area, temperature, plant community composition, and substrate availability (Yun et al. 2015). The decaying plant organic matter and root exudates released in the rhizosphere increases the substrate pool for the methanogens. Moreover, the O_2 transferred to the rhizosphere through the aerenchyma of the plants growing in the wetlands increases the oxidation of CH_4 by methanotrophs (Whalen 2005). Contrary to that, the aerobic methanotrophs can feed upon CH_4 for carbon and energy utilization.

The organic matter content within wetland systems is impacted by processes such as biodegradation, photochemical oxidation, sedimentation, volatilization, and sorption. Some of these mechanisms provide natural organic matter accumulation via microbial and/or vegetative decay. Moreover, the accumulation of organic matter is a potential energy source for microbial communities. Dissolved organic matter degradation is expected to occur via heterotrophic uptake by aerobic and anaerobic bacteria, and degradation by ultra-violet light. Several authors have reported on dissolved organic matter transformations in algae, forest vegetation, wetland plant material, microbial groups, and soils. Dissolved organic matter from plant exudates appears more dominant during warm months with active plant growth.

10.1.4.2 Nitrogen Cycle

The nitrogen transformation includes the conversion of inorganic to organic compounds and organic compounds back to inorganic form. Bacteria (known as ammonifiers) convert organically bound N to ammonia and the process is known as ammonification (Vymazal 2007). The optimum temperature and pH for ammonification are 40–60 °C and 6.5–8.5, respectively. The ammonification process encompasses oxidative and reductive deamination in oxidized and reduced soil layers, respectively, which can be written as Eqs. (10.3) and (10.4).

$$\text{Amino acids} \rightarrow \text{Imino acids} \rightarrow \text{Keto acids} \rightarrow NH_3 \text{ (oxidative deamination)} \tag{10.3}$$

$$\text{Amino acids} \rightarrow \text{Saturated acids} \rightarrow NH_3 \text{ (reductive deamination)} \tag{10.4}$$

Chemotrophic bacteria (nitrifiers) perform oxidation of ammonium to nitrate with nitrite as an intermediate in the reaction sequence and the reaction is known as nitrification [Eqs. (10.5), (10.6), and (10.7)]. Nitrification is a two-step process in which the first step includes oxidation of ammonium-N to nitrite-N by strictly chemolithotrophic (strictly aerobic) bacteria such as *Nitrosomonas europaea*. The second step includes oxidation of nitrite-N to nitrate-N by facultative chemolithotrophic bacteria such as *Nitrobacter winogradskyi* and *Nitrococcus mobilis* (Paul and Clark 1996).

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O \tag{10.5}$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \tag{10.6}$$

$$NH_4^- + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \tag{10.7}$$

After O_2 depletion, the reduction of nitrate is carried out by two processes: nitrate-ammonification in which nitrate is reduced to NH_4^+ by nitrate-ammonifying bacteria such as *Bacillus vireti* (Mania et al. 2014) and denitrification in which nitrate is reduced to N_2 or N_2O by denitrifying bacteria such as *Acidovorax*, *Azoarcus*, *Bradyrhizobium*, *Ochrobactrum*, *Paracoccus*, *Pseudomonas*, *Mesorhizobium*, *Ensife*r, and *Thauera* via intermediates nitrite, nitric oxide, and nitrous oxide (Song et al. 2000).

Microbial denitrification is considered as the dominant and long-term mechanism of nitrate-nitrogen removal from wastewater especially when the constructed wetland system is subjected to high nitrate loading (Lin et al. 2002). In constructed wetlands, the nitrogen transformation directly/indirectly depends upon the temperature, soil material types, operation strategies, and redox conditions in the wetland bed. Nitrogen fixers such as symbiotic actinomycetes and asymbiotic heterotrophic bacteria convert gaseous N_2 to ammonia in the presence of nitrogenase enzyme. In anaerobic ammonium oxidation (ANAMMOX), autotrophic bacteria convert ammonia to N_2 gas with nitrite as the electron acceptor. Apart from conventional nitrogen transformation mechanisms in wetlands (natural/constructed), new techniques such as completely autotrophic nitrogen removal over nitrite (CANON), single reactor high-activity ammonia removal over nitrite (SHARON), simultaneous partial nitrification, ANAMMOX and denitrification (SNAD) have also gained attention as novel biological nitrogen transformation processes (Chang et al. 2013).

10.1.4.3 Sulfur Cycle

The sulfate-reducing bacteria (SRB) present in the wetlands are strict anaerobes and sensitive to low temperatures which utilize on mole of sulfate to generate one mole of sulfide along with alkalinity Eq. (10.8).

$$SO_4^{2-} + 2CH_2O + 2H^+ \rightarrow H_2S + 2H_2O + 2CO_2 \tag{10.8}$$

In constructed wetlands, the sulfur dynamics are dependent on biotic and abiotic factors such as the presence of SRB, availability of organic matter, precipitation as metal sulfides (Wu et al. 2013). The sulfide produced in anoxic zones by SRB is transported to the oxic zones and then may oxidize back to polysulphides, elemental sulfur, thiosulfate, tetrathionate, or sulfate by biological pathways which is evident by the presence of sulfur compounds such as elemental S which can be generated by oxidation, by chemolithotrophic microbes using electron acceptors such as oxygen or nitrate. Moreover, anoxygenic phototrophic bacteria may associate sulfide oxidation with CO_2 reduction in some micro-zones of constructed wetlands. However, the generated elemental S can again convert back to sulfide by sulfur-reducing bacteria.

10.2 Constructed Wetlands: Decentralized Wastewater Treatment Technology

Phytoremediation is being widely used for treating many classes of contaminants such as metals, pesticides, petroleum hydrocarbons, explosives, and radionuclides. Phytoremediation overcomes the shortcomings of conventional wastewater treatment methods as it is cost-effective, non-intrusive, and environment-friendly (Roongtanakiat et al. 2007).

Constructed wetlands are engineered wastewater treatment systems that have been designed to work on the natural processes encompassing wetland vegetation, soils, and their associated microbial assemblages. They are constructed considering the merits of many of the same processes that work in natural wetlands but bound to work in a more controlled environment (Vymazal 2013; Rana and Maiti 2018b). Constructed wetlands have become a popular alternative to traditional wastewater treatment technologies which accounts for their low cost of installation and maintenance, and optimum climatic conditions for ponds found in tropical areas (Kivaisi 2001). The conventional wastewater treatment technologies lag in the treatment applicability due to expensive installation, power consumption, formation of by-products while using chemical treatment methods (Robinson et al. 2001). Constructed wetlands also have other merits related to environmental safeguards such as advancement of biodiversity, bioaccumulation, and methylation of metals, rendering habitat for wetland organisms and wildlife, rationing climatic and hydrological functions. Constructed wetlands have been used for the: (i) treatment of septic tank and Imhoff tank effluents from housing complexes and (ii) tertiary treatment of effluents from aerated lagoons and conventional STPs. In western countries, constructed wetlands have been used to treat storm waters, industrial, mining, and agricultural wastes. Constructed wetlands were first developed in 1960 by Dr. K Seidel in Germany. By 1995, over 200 units had been installed in Europe (Mainly in Denmark, Germany, and the United Kingdom) and another 200 units in the USA. In India, only 50–60 units were reported to be installed by the year 2005 which existed mostly in Tamil Nadu and Auroville, Puducherry. A schematic diagram of a constructed wetland is shown in Fig. 10.2.

They are in wide usage as a recognizable and attractive treatment technology for domestic sewage (El Hamouri et al. 2007; Sutar et al. 2019). Moreover, their application has also been extended to various difficult to treat wastewaters such as pharmaceutical wastewater, textile wastewater, sugarcane molasses stillage, landfill leachate, tannery wastewater, pulp and paper mill effluent, and electroplating wastewater (Zainith et al. 2019). Toxic pollutants are released into the aquatic environment by natural and anthropogenic sources which pose a serious threat to

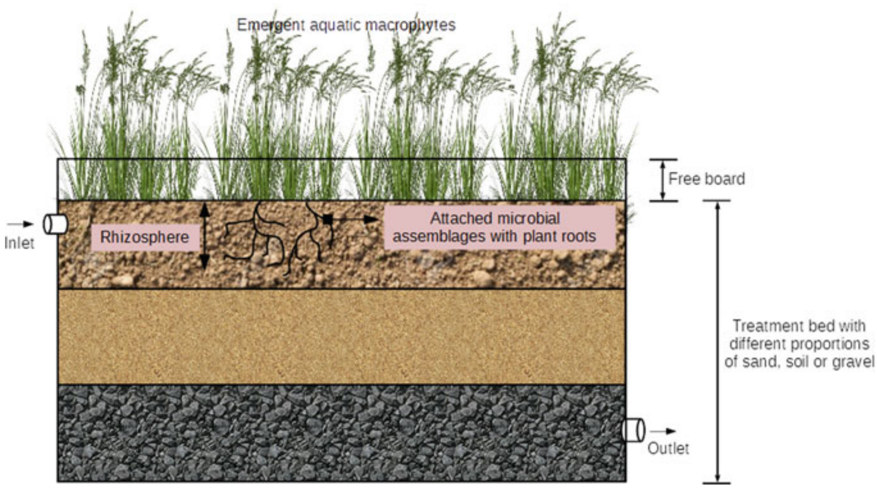

Fig. 10.2 Schematic diagram of a constructed wetland

mankind. These pollutants may be organic or inorganic encompassing metals, dyes, and landfill leachate. The presence of metals and its components that are essential for the sustainability of an ecosystem is ubiquitous in the environment but their non-biodegradable, immutable, and almost indefinite persistent nature leads to the presence of these metals in an excess amount which may result in chronic and acute poisoning to the receivers. High concentrations of these metals found in the human body adversely influence nervous, cardiovascular, respiratory, gastrointestinal, hepatic, renal, hematopoietic, immunological, and dermatological systems. The toxic nature of Cd is attributed to its exceptionally high biological half-life in the human body (10–30 years) (Bernard and Lauwerys 1986). Cadmium toxicity affects the immune system, leads to bone deformities accompanying renal dysfunction. Mercury is transported by water into the aquatic ecosystem and is considered relatively lipid-soluble due to its low water solubility. Mercury toxicity devastates the nervous system by interfering with the production of energy and impairing cellular detoxification processes causing cell death or cellular malfunction (Rice et al. 2014). Lead also interferes with a number of body functions and primarily affects the central nervous system, hematopoietic, hepatic, and renal system producing serious disorders in the body. Chromium toxicity affects the immune system and may lead to immunosuppression or immune stimulation. Chromium also causes lung cancer, nasal irritation, and nasal ulcer and hypersensitivity reactions like contact dermatitis and asthma (Shrivastava et al. 2002).

National Environmental Engineering Research Institute (NEERI) at Nagpur (India) developed a constructed wetland that was exclusively designed for the treatment of municipal, urban, agricultural, and industrial wastewater. The treatment system was based on plants such as *Pennisetum purpureum* Schumach, 1827, *T. latifolia*, *Phragmites* sp., and *Iris pseudacorus* L. Moreover, some ornamental and flowering plants such as *Duranta erecta* L. were used for wastewater treatment as well as for aesthetic purposes. Depending upon land availability, NEERI constructed sub-surface Phytorid technology in parallel or series modules. The treatment bed consisted of simple materials such as gravel, stones, and crushed bricks. The treatment system was divided into three zones: (i) inlet zone, which consisted of crushed bricks and stones of different sizes; (ii) treatment zone, which comprised the same media with plantation, and (iii) outlet zone. This technology demonstrated a reduction of 70–80% total suspended solids, 78–84% BOD, 70–75% nitrogen, 52–64% phosphorus, and 90–97% fecal coliform. The treated water was used for various purposes such as municipal gardens, fountains, and irrigation. The total area requirement for the treatment system is approximately 35 m^2 for a wastewater flow rate of 20 m^3/day. This technology has been transferred to General Techno Services, Technogreen Environmental Solutions, Pune, BIOUMA, Goa, and Devi Agencies, Aurangabad, and implemented to reuse water and benefit the local people.

The advantages of using constructed wetlands with emergent vegetation are:

i. Rhizomes of the reeds grow vertically and horizontally in the treatment bed (soil, sand, or gravel), opening up “hydraulic pathways”;

ii. Wastewater BOD and nitrogen are removed by bacterial activity; aerobic treatment takes place in the rhizosphere, with anoxic and anaerobic treatment taking place in the surrounding soil;
iii. Oxygen passes from the atmosphere to the rhizosphere via the leaves and stems of the reeds through the hollow rhizomes and gets out through the roots;
iv. Suspended solids in the sewage are aerobically composted in the above-ground layer of vegetation formed from dead leaves and stems; and
v. Nutrients and metals are removed by plant uptake.

Based on the water surface, the constructed wetlands are generally of two types: (i) free water surface type, and (ii) submerged flow type. The submerged flow type constructed wetlands can be horizontal or vertical depending upon the wastewater flow regime. Submerged flow wetlands are preferred over free water surface wetlands due to: (i) relatively easy installation; (ii) inexpensive; and (iii) discouragement to the possibility of mosquito breeding that is likely with a free water surface wetland. Constructed wetlands are composed of media bed and vegetation that grows upon the media. The treatment media is composed of natural materials, such as gravel, sand, soil, etc. A list of materials used in different types of constructed wetlands is shown in Table 10.3.

10.2.1 Merits and Demerits of Constructed Wetlands

Constructed wetland systems offer a green and sustainable treatment of wastewaters; however, they are characterized by some disadvantages too (Arceivala and Asolekar 2006). Constructed wetland systems used for wastewater treatment are advantageous in the following ways (Singh et al. 2019):

i. Installation, operation, and maintenance of constructed wetlands are comparatively inexpensive to other treatment options;
ii. They constitute simple construction and operation. There is no skilled labor required for the construction, operation, and maintenance of constructed wetlands;
iii. Only periodic on-site labor is required for operation and maintenance of constructed wetlands, instead of continuous monitoring in other treatment options;
iv. They utilize natural processes for wastewater treatment;
v. They reduce excess sludge production; and
vi. They enable reuse and recycling of water.

However, there are also some limitations to the use of constructed wetlands which are as follows:

i. A large land area requirement is a constraint for constructed wetlands. They require a large land area for the same level of treatment by traditional

Table 10.3 Different types of treatment media used in constructed wetlands

Treatment media	Constructed wetland type	Type of wastewater treated	References
Gravel: Rock chips of charnackite type	Sub-surface	Domestic wastewater	Bindu et al. (2008)
1. Gravel (D_{10}: 15 mm) 2. Composite filling: Round ceramsite + blast furnace granulated slag + soil + sawdust (Ratio 3:3:2:1)	Sub-surface vertical flow	Cadmium-spiked synthetic wastewater	Gao et al. (2015)
Gravel (ϕ: 25 mm and porosity (η): 38.6%)	Horizontal sub-surface flow	Synthetic landfill leachate	Madera-Parra et al. (2015)
Fine sand (ϕ: 2 mm)	Free-surface flow	Diesel-spiked synthetic wastewater	Al-Baldawi et al. (2013)
1. Fine sand (ϕ: 2 mm) 2. Gravel (ϕ: 1–5 mm) 3. Gravel (ϕ: 10–20 mm)	Sub-surface flow	Diesel-spiked synthetic wastewater	
Gravel (0.2–2.24 mm)	Vertical flow	Phosphorus-spiked synthetic wastewater	Li et al. (2013)
Gravel	Sub-surface flow	Mercury-spiked synthetic wastewater	Gomes et al. (2014)

technologies which render them unsuitable for treating large volumes of wastewater;

ii. Treatment time is comparatively higher than other treatment technologies;
iii. The performance of constructed wetlands is driven by environmental factors, for example, the efficiency is reduced in colder climate;
iv. The longer time period is required before the vegetation is fully established and optimum treatment efficiency is acquired;
v. The dynamics of the treatment process are unclear which leads to inaccurate design and operation criteria;
vi. They require a minimum base water flow as they can tolerate temporary water level drawdowns but not complete drying; and
vii. The biological components are intolerant to shock loads due to toxic pollutants.

10.2.2 Mechanisms of Pollutant Removal in Constructed Wetlands

Constructed wetlands resemble natural wetlands and include mineral or organic soil underneath vegetation. The vegetation encompasses emergent or floating macrophytes which, collectively with media bed, assist in removing the pollutants from wastewater. The basic processes driving the removal of pollutants are physical, chemical, and biological. The physical processes include sedimentation and filtration; chemical processes include sorption, photo-oxidation, and volatilization; and biological processes encompass the conversion of organic matter to CO_2 by using carbon as an energy source. The various pollutant removal mechanisms that are active in constructed wetlands are shown in Table 10.4.

Biochars increase plant growth, metal immobilization, and pH reduction in constructed wetlands (Zhang et al. 2013). They sorb metals and increase the metal removal efficiency of constructed wetlands (Cui et al. 2016; Kizito et al. 2017). Apart from metals, biochar also improves the overall efficiency of a constructed wetland system. Gupta et al. (2015) treated synthetic wastewater and reported that the wetland with biochar was more efficient as compared to the wetland with gravels alone with an average removal rates of 91.3% COD, 58.3% TN, 58.3% NH_3, 92% NO_3-N, 79.5% TP, and 67.7% PO_4. Enhanced nitrogen removal was also observed by using plant-based biochar in constructed wetlands (Li et al. 2018).

Table 10.4 Wastewater pollutant removal mechanisms in constructed wetlands

Pollutant	Removal mechanism
Total suspended solids	Sedimentation and filtration
Soluble biodegradable organic matter	Microbial degradation (aerobic, anoxic, and anaerobic), adsorption, and plant uptake
Nutrients	
Nitrogen	Ammonification (mineralization), nitrification/denitrification, nitrate-ammonification, plant/microbial uptake, media adsorption/ion exchange, ammonia volatilization, and ANAMMOX
Phosphorus	Media adsorption, plant and microbial uptake, sedimentation, and precipitation
Metals	Adsorption and cation exchange, complexation, precipitation/co-precipitation, oxidation and hydrolysis, plant uptake, microbial oxidation/reduction (microbial-mediated processes), and sedimentation
Pathogens (microbial population)	Sedimentation, filtration, natural die-off, predation, UV irradiation, excretion of antibiotics by roots of macrophytes, and adsorption
Organic xenobiotics	Sedimentation, volatilization, biodegradation, adsorption, plant uptake, photolysis, and chemical reactions

10.2.3 General Design Considerations for Constructed Wetlands

For the creation of successful constructed wetlands, Mitsch and Cronk (1992) suggested the following guidelines: (i) simple designing; (ii) minimum maintenance; (iii) system designing using natural energies (such as gravity flow); (iv) system designing for peak loading condition and not average loading; (v) integrating the design with natural topography of the site; and (vi) designing for performance optimization. Arceivala and Asolekar (2006) had given some process design norms for the construction of sub-surface flow constructed wetlands for treating raw domestic wastewaters in India which is shown in Table 10.5.

For designing macrophyte beds with the horizontal flow, two key aspects have to be kept in mind: (i) organic removal parameters, and (ii) hydraulic flow considerations.

10.2.3.1 Organic Removal in Constructed Wetlands

BOD removal has been approximated by first-order plug-flow kinetics. On the basis of the European design and operations guidelines, Green and Upton (1994) reported Eqs. (10.9) and (10.10) based on first-order kinetics as also used in Severn Trent, the United Kingdom, for the design of constructed reed beds for polishing wastewater treated effluents from small communities.

$$C_t = C_0 e^{-Kt} \tag{10.9}$$

Table 10.5 Process design norms for the construction of sub-surface flow constructed wetlands for treating raw domestic wastewaters in India (Adopted from Arceivala and Asolekar 2006)

Parameter	Typical values	
	European literature	Recommended for India
Area requirement, m^2/person[a]	2.0–5.0	1.0–2.0
BOD_5 loading rate, g/m^2-day[b]	7.5–12.0	17.5–35.0
Detention time, days	2–7	2–3
Hydraulic loading rate, mm/day	(Must not exceed hydraulic conductivity of the bed)	
Depth of bed, m	–	0.6–0.9
Porosity of bed, % (typical)	–	30–40
First-order reaction constant, K_T/day	–	0.17–0.18
Evapotranspiration losses, mm/day[c]	10–15	>15

[a]Constructed wetlands may be suitably downsized when wastewater is pre-treated
[b]Based on raw sewage BOD = 50 g/person-day and 30% reduction in pre-setting
[c]1.0 mm/day = 10 m^3/ha-day

Since t is a function of bed area, we can also write

$$A = \frac{Q(\ln C_0 - \ln C_t)}{K_{\mathrm{BOD}}} \tag{10.10}$$

where A = bed area, m^2; Q = average flow, $\mathrm{m}^3\ \mathrm{day}^{-1}$; C_0 = inlet 5-day BOD, $\mathrm{mg\ L}^{-1}$; C_t = outlet BOD_5, $\mathrm{mg\ L}^{-1}$; $K_{\mathrm{BOD}} = \mathrm{BOD}_5$ reaction constant, day^{-1}.

10.2.3.2 Hydraulic Considerations in Design

The dimensions of the reed bed can be calculated by two assumptions in applying Darcy's law: (i) hydraulic gradient is equivalent to a slope of 5% and (ii) hydraulic conductivity will stabilize at around $1 \times 10^{-3}\ \mathrm{m\ s}^{-1}$ ($86.4\ \mathrm{m\ day}^{-1}$) as the reed bed is fully established. In India, values up to $500\ \mathrm{m\ day}^{-1}$ have been reported.

The cross-sectional area of the reed bed can be calculated as

$$A_{\mathrm{c}} = \frac{Q}{K_{\mathrm{f}} \frac{\mathrm{d}H}{\mathrm{d}S} \times 86{,}400} \tag{10.11}$$

where A_{c} = cross-sectional area of the bed, m^2; Q = average flow, $\mathrm{m}^3\ \mathrm{day}^{-1}$; K_{f} = hydraulic conductivity, $\mathrm{m\ s}^{-1}$; $\mathrm{d}H/\mathrm{d}S$ = slope = $\mathrm{m\ m}^{-1}$.

10.2.4 Potential Plants for Wastewater Treatment

Based on the response of plant species to metal concentrations, they are primarily classified into three categories: (i) metal excluders (which prevent metals from entering their aerial parts over a broad range of metal concentrations); (ii) metal indicators (accumulate metals in their above-ground tissues and the metal levels in the tissues of these plants generally reflect metal levels in the rhizosphere); and (iii) metal accumulators (usually referred to as hyperaccumulators that concentrate metals in their above-ground tissues to levels far exceeding those present in the rhizosphere or in non-accumulating species growing nearby) (Memon and Schroder 2009). Plants act as solar-driven pumps that can extract metals from the environment with which they interact (Garbisu and Alkorta 2001). In addition, constructed wetlands that employ plants for the treatment of wastewater are found effective in treating organic matter, nutrients, and pathogens. Aquatic macrophytes are preferred over terrestrial plants for the treatment of wastewater due to their faster rate of growth, larger biomass production, relatively higher pollutant uptake ability, and better pollutant removal due to direct contact with the wastewater. A number of aquatic plant species encompassing free-floating species such as *Eichhornia* sp., *Lemna* sp., *Spirodela* sp., and *Salvinia* sp., submerged species (*Potamogeton* sp.), and emergent species such as *Typha* sp., *Phragmites* sp., *Vetiveria* sp., and *Juncus* sp. are well known to be employed for phytoremediation.

Duckweed belongs to Lemnaceae family that grows in stagnant and slow-flowing water in many parts of the world except Arctic and Antarctic regions (Zhao et al. 2014). Duckweed encompasses four main genera of Lemnaceae: *Lemna, Spirodela, Wolffia, and Wolfiella* and is considered as the smallest and fastest-growing flowering plant on earth. Duckweeds possess high removal efficiency for dissolved nutrients (especially nitrogen and phosphorus), suspended solids, and organic matter. A comparative study between *Lemna gibba* L. and *Lemna minor* L. to accumulate boron from secondary wastewater was carried out by Tatar and Obek (2014) and reported that *Lemna gibba* L. is more prone to accumulate boron in comparison with *L. minor.* Moreover, the study carried out by Sekomo et al. (2012) revealed that textile wastewater laden with metals such as Cr, Zn, Pb, Cd, and Cu was also treated by duckweeds, making it suitable for metal uptake from contaminated wastewaters. *Typha* sp. is one of the eleven flowering plant species classified under family Typhaceae widely distributed in parts of the northern hemisphere. *Typha* sp. is commonly known as "cattails" which describes its characteristic inflorescence. Cattails are familiar wetland plants used for wastewater treatment and have an ability to adapt to diverse climatic conditions and are particularly found in wet soil, marshes, swamps, and shallow fresh and brackish waters. *T. latifolia* has reduced COD, BOD, total suspended solids, ammoniacal nitrogen, nitrate nitrogen, and phosphorus (Ciria et al. 2005). Similarly, *Typha domingensis* Pers. was found to remediate textile effluents and metals. Species of *T. latifolia* were studied for uptake and removal of various metals such as Cr, Zn, Mn, Co, and Cd and for treatment of effluents generated from aluminum smelters. *Canna indica* L., a perennial rhizomatous herb, belongs to the family Cannaceae. *C. indica* grows naturally along creeks, lakes, and open swamps and is often used as an ornamental plant in parks and streets which makes its use as a phytoremediation species possible. *C. indica* plant was used individually and in combination with other plant species to remediate domestic wastewater. Individually, this species was able to satisfactorily remove total nitrogen, ammonia nitrogen, and BOD_5 (Li et al. 2013). *Azolla* sp. is a fast-growing nitrogen-fixing pteridophyte that freely floats on water and is considered as an excellent plant species for removal, disposal, and recovery of metals from polluted aquatic ecosystems (Arora et al. 2006). Reed (*Phragmites* sp.) belongs to gramineous perennial herbaceous plants in aquatic ecosystems possessing the ability to absorb metal pollutants such as Cu, Zn, Pb, and Cd; and thus is important in wastewater treatment. Reeds are large perennial grass found in wetlands distributed throughout temperate and tropical regions of the world.

Shukla et al. (2011) evaluated the metal uptake capability of *Terminalia arjuna* (Roxb.) Wight and Arn., *Prosopis juliflora* (Sw.) DC., *Populus alba* L., *Eucalyptus tereticornis* Sm., and *Dendrocalamus strictus* (Roxb.) Nees by growing selected plants on tannery sludge dumps of Common Effluent Treatment Plants. After one year of study period, a reduction in the concentration of Cr (70.22%), Ni (59.21%), Cd (58.40%), Fe (49.75%), Mn (30.95%), Zn (22.80%), Cu (20.46%), and Pb (14.05%) in the tannery sludge was observed. Some of the plants, which are generally used for wastewater treatment, are listed in Table 10.6.

Table 10.6 Emergent wetland plants used for treatment of different types of wastewater

Plant species	Family	Wastewater treated	Performance	References
Typha sp.	Typhaceae	Pharmaceutical wastewater	80% removal of clofibric acid after 21 days of exposure to a solution spiked with 20 μgL^{-1} clofibric acid	Dordio et al. (2009)
Typha sp.	Typhaceae	Pharmaceutical wastewater	82% of carbamazepine (an epilepsy drug)	Dordio et al. (2011)
Cyperus alternifolius Rottb., 1772	Cyperaceae	Urban wastewater	Removal of 652 kg BOD_5 ha^{-1} d^{-1} and 1869 kg COD ha^{-1} d^{-1}	Calheiros et al. (2008)
Typha angustifolia L.	Typhaceae	Textile wastewater	60% color removal was found in 14 days of exposure	Nilratnisakorn et al. (2007)
Canna indica L.	Pontederiaceae	Domestic wastewater	In combination with *Pontederia cordeta* L., it has shown 62.8% COD removal, 12.8% TN removal, and 51.1% TP removal	Chang et al. (2012)
Colocasia esculenta (L.) Schott	Araceae	Landfill leachate	–	Madera-Parra et al. (2015)

Mishra et al. (2008) investigated the capacity of aquatic macrophytes [*Eichhornia crassipes* (Mart.) Solms, *L. minor*, and *Spirodela polyrhiza* (L.) Schleid.] for the uptake of metals (Hg and As) for the treatment of open-cast coal mine effluent generated at Northern Coalfields Limited (NCL), Singrauli (India). The results indicated that *E. crassipes* possessed the highest uptake capacity for Hg and As followed by *L. minor* and *Spirodela polyrhiza* (L.) Schleid. Zojaji et al. (2015) reported uptake of Cr, Zn, and Cu using *Populus deltoides* W. Baltram ex Marshall, with enrichment coefficients of 0.18, 1.11, and 1.35, respectively. Primarily, constructed wetlands are categorized as free water surface constructed wetlands (FWSCW), sub-surface flow constructed wetlands (SSFCW), and hybrid wetlands. SSFCW may be further classified into the vertical sub-surface flow (VSSF) and horizontal sub-surface flow

(HSSF) systems depending upon the flow regimes they follow. Various suitable plant species that are being used in combination or individually in engineered wetlands for the phytoremediation of toxic pollutants present in the wastewater are enlisted in Table 10.7.

In a study conducted by Morari and Giardini (2009), two vertical flow constructed wetlands (VFCWs) were constructed and planted with *T. latifolia and Phragmites australis* (Cav.) Trin. ex Steud. and the observed treatment efficiency was higher (>86%) for COD, BOD, N, and K while lower (<47%) for Na and Mg. In Czech Republic, a similar study in a horizontal sub-surface flow constructed wetland for the treatment of municipal sewage using *P. australis* demonstrated that highest concentrations in plants were observed for Al, Fe, Mn, Ba, and Zn while the lowest concentrations were those of Hg, U, and Cd (Vymazal et al. 2009). Secondary treated municipal wastewater was also treated by Sharma and Brighu (2014) using VFCWs planted with *C. indica* and *Phragmites australis* (Cav.) Trin. ex Steud. resulting in better aerobic conditions and removal of nitrogenous compounds such as NH_4-N, TKN, and NO_3^- in mesocosms planted with *C. indica* than treatment beds planted with *P. australis*. Moreover, treatment beds having gravel as the media have been

Table 10.7 Treatment efficiencies of constructed wetlands for different wastewaters

Type of wastewater	Removal performance	Wetland design and operation			References
		Plant species	Flow regime	HLR	
Winery wastewater	TSS: 86.8%; BOD_5: 74.2%; COD: 73.7%; TKN: 52.4%	*Phragmites australis* (Cav.) Trin. ex Steud. and *Juncus effusus* L.	VFCW[a] followed by HFCW[b]	19.5 mm/d	Serrano et al. (2011)
Olive mill wastewater	COD: 70%; TKN: 75%	*Phragmites australis* (Cav.) Trin. ex Steud	VFCW	–	Herouvim et al. (2011)
Synthetic wastewater	TSS: >44%; BOD_5: >80%	*Typha angustifolia* L.	HFCW	–	Weerakoon et al. (2013)
Domestic Wastewater	NO_3–N: 97%; TN: 46.6%	*Cyperus alternifolius* Rottb., 1772	VFCW	20.78 mm/d	Bilgin et al. (2014)
Polluted river water	COD: 39.3 ± 12.1%; NH_4–N: 62.1 ± 8.8%; TN: 45.8 ± 15.4%; TP: 57.7 ± 8.3%	*Iris sibirica* L.	VFCW	–	Gao et al. (2014)

VFCW[a] Vertical Flow Constructed Wetlands, *HFCW*[b] Horizontal Flow Constructed Wetlands known to show better oxygenation capacity to oxidize the organic matter while superior filtration and adsorption properties were observed while using sand as the media. Nitrogen in wastewater poses a serious threat to the aquatic life due to the potential of eutrophication in aquatic systems. A hybrid constructed wetland was designed by Ye and Li (2009) to enhance nitrogen removal during domestic wastewater treatment in China. The designed plant increased the nitrification rate by providing passive oxygen creating a cascade-type current and the reported average removal rates as 89% for total suspended solids, 85% for COD, 83% for ammoniacal nitrogen, 83% for total nitrogen, and 64% for total phosphorus.

Morvannou et al. (2014) dealt with the modeling of the fate of nitrogen during the treatment of domestic raw wastewater using a VFCW and demonstrated that the ammonium was adsorbed onto the organic matter during the feeding period and characterized the presence of heterotrophic biomass mainly in the sludge layer (first 20 cm), whereas autotrophic biomass was located in the first 50 cm of the VFCW (sludge and 30 cm biomass).

Advanced oxidation processes can be combined with the constructed wetlands for the treatment of wastewaters to increase their efficiency and foster the reuse of treated water. Horn et al. (2014) investigated the combination of constructed wetlands with photocatalytic ozonation for a university sewage treatment plant. The treatment efficiency with the constructed three-stage sub-surface flow sequence planted with *Hymenachne grumosa* (Nees) Zuloaga had the following characteristics: a constructed wetland (CW-1) built inside the greenhouse and another constructed wetland (CW-2) built-in outdoors with a UV/TiO_2/O_3 reactor in between the two systems to improve the quality of wastewater for reuse. The treatment efficiency after the photocatalytic ozonation of the effluent from CW-1 increased as follows: BOD_5 (88.7%); COD (62.1%); total Kjeldahl nitrogen (27.6%); ammoniacal nitrogen (27.1%); and total phosphorus (63.4%). A hybrid system encompassing a horizontal sub-surface flow (HSSF) CW preceded by two VSSFCW working in parallel was constructed by Comino et al. (2013) to treat gray wastewater and demonstrated that the system was able to bear the subjection to high hydraulic and organic variations and reduced COD efficiently even at three times the pollutant concentration and with an inlet flow four times higher than the designed specifications.

Complex wastewaters emanating from leather industry were treated with five wetland plants by Calheiros et al. (2007), namely *C. indica, T. latifolia, P. australis, Stenotaphrum secundatum* (Walter) Kuntze, and *Iris pseudacorus* L. and the treatment performance at hydraulic loading rates of 3 and 6 cm d^{-1} was assessed. COD reduction of 41–73% for an inlet organic loading varying between 332 and 1602 kg ha^{-1} d^{-1} and BOD_5 reduction of 41–58% for an inlet organic loading varying between 218 and 780 kg ha^{-1} d^{-1} was reported. Moreover, *P. australis* and *T. latifolia* were the only plants that were able to establish successfully. Another study conducted by Ong et al. (2009) for the treatment of dye wastewater using up-flow constructed wetland reactors planted with *P. australis* reported that COD concentration drastically decreased at the aeration points in the reactor and supplemented aeration led to increased removal of organic pollutants. Tee et al. (2015) reported an increase in dye removal efficiency by incorporating baffles in HSSF constructed wetlands to facilitate up-flow and downflow conditions to achieve aerobic, anoxic, and anaerobic conditions sequentially in the same wetland bed. The planted baffled unit was found to achieve 100, 83, and 69% dye removal against 73, 46, and 30% for the conventional unit at HRT of five, three, and two days, respectively.

The root properties such as root porosity, radial oxygen loss (ROL), and Fe plaque formation are important parameters for the selection of wetland plants. Wetland plants grown in waterlogged conditions own a strategy to cope with the anaerobic environment by forming extensive aerenchyma tissue which provides low resistance to the passage of oxygen from the aerial parts of the plant to their roots. The excessive oxygen diffuses from the roots into the rhizosphere resulting in its oxidation. The oxidation of the rhizosphere leads to the precipitation of As on wetland plant's root surface. Due to the release of oxygen by wetland plants, reduced soluble iron reacts with it to form a smooth regular reddish precipitate on root surfaces. A substantial amount of Fe is transferred to the plaque during the process of ROL and rhizosphere oxidation which develops a well-defined zone of ferric hydroxide accumulation in the rhizosphere. The Fe plaque can sequester metals on root surfaces and so influence metal uptake and tolerance by wetland plants. A study carried out by Yang et al. (2014) revealed that wetland plants possessing high porosity and high ROL from their roots tend to have high Fe, Mn, and Zn concentrations on root surfaces and in their rhizosphere. Cheng et al. (2014) illustrated that ROL-induced Fe plaque would promote Pb and Cd deposition on root surfaces. Plants improve Fe uptake by excreting protons by a plasma membrane H^+-ATPase which acidifies the rhizosphere and reduces Fe^{3+} to more soluble Fe^{2+}.

10.2.5 Textile Wastewater Treatment in Constructed Wetlands

Widespread use of dyes in the paper, leather, and tannery industries generate a substantial amount of wastewater and their presence in wastewater affects all forms of life. A total of fifteen percent of the dyes produced globally are lost during the dyeing process and are released in the textile effluents. Azo dyes are characterized by strong—N=N—nature which is the most common chromophore of reactive dyes. Azo dyes' structural stability compels their recalcitrant nature toward biodegradability (e.g., activated sludge) or physical/chemical treatment methods (e.g., flocculation and coagulation) and results in the transfer of azo dyes from wastewater to the sludge, leading to additional disposal problems. Various garden plants like *Aster amellus* L., *Cosmos bipinnatus* Cav., 1791, *Chrysanthemum cinerariifolium* (Trevir.) Vis. pyrethrum, *Cuphea hyssopifolia* Kunth and *Cortaderia selloana* Schult. and Schult.f. Asch. and Graebn. (Pampas grass) effectively treat a wide array of textile wastewater up to varying extents. Hu et al. (2010) reported Congo Red dye removal from textile wastewater by cattail roots as they are porous in structure and have a large surface area. The use of cattails for dye wastewater treatment demonstrated that the removal of Congo Red increased with increasing adsorbent dosage, i.e., cattail roots and decreased with increasing temperature over the operating conditions (20–40 °C). Adsorption dynamics analysis indicated that pseudo-second-order equation fitted well to the adsorption of Congo Red on cattail root ($R^2 > 0.99$). The role of sunflower, a flowering garden plant, in removing some azo dyes hydroponically was assessed by Huicheng et al. (2012) and demonstrated a decolorization of 62.64% of average percent of three azo dyes (Evans Blue, Bismark Browny, and Orange G) at 100 mg/L within four days. Another study was carried out by Nilratnisakorn et al. (2007) using narrow-leaved cattail (*Typha angustifolia* L.) and observed a maximum decolorization of 60% of Reactive Red 141 in 14 days. Moreover, it was reported by Nilratnisakorn et al. (2007) that *T. angustifolia* can grow well under caustic conditions and can withstand stress due to salts as they have high plant weight and extensive roots undergoing special mechanisms such as salt accumulation in roots by shedding older leaves and by the formation of metal complexes in the form of Ca, Fe, and Si bonded to dye molecules.

Patil and Jadhav (2013) used *Tagetes patula* L. (flowering plant) for the degradation of Reactive Blue 160 (textile dye) and reported 90% decolorization within four days. Inthorn et al. (2004) studied the treatment of dye wastewater using narrow-leaved cattail (NLC) powder as an adsorption media after pre-treatment with distilled water (DW-NLC), a mixture containing 37% formaldehyde and 0.2 N sulfuric acid (FH-NLC) or 0.1 N NaOH (NaOH-NLC) and reported that the highest removal of dye was observed with FH-NLC treatment. Khandare et al. (2011) evaluated the removal of a sulfonated azo dye, Remazol Red, by *Aster amellus* L. and the study revealed a reduction of BOD (75%), COD (60%), and total organic carbon (54%) after 60 h. However, Bulc and Ojstršek (2008) reported removal efficiency of COD (84%), BOD_5 (66%), TOC (89%), N_{total} (52%), $N_{organic}$ (87%), SO_4^{2-} (88%), TSS (93%), and color (90%) in a constructed wetland planted with *P. australis*.

Davies et al. (2005) constructed a VFCW planted with *P. australis* to remove an azo dye [Acid Orange 7 (AO7)] and reported degradation of AO7 dye and its aromatic amines, after 120 h in contact with H_2O_2, and removal of 3.2–5.7 mg AO7 g^{-1} *P. australis* was obtained for 40 mg AO7 L^{-1} (8 mg AO7 g^{-1} *P. australis*). The potential of duckweed (*L. minor*) for the degradation of C.I Acid Blue 92 (AB92) has been evaluated by Khataee et al. (2012) and observed the considerable potential of *L. minor* for the phytoremediation of AB92 depending upon temperature, initial dye concentration, and weight of the plant. Sekomo et al. (2012) constructed a lab-scale system, each system consisting of three ponds in series and seeded with algae (natural colonization) and duckweed (*L. minor*) with a hydraulic retention time of seven days under different light regimes. The observations revealed that both the systems were unsuitable for the removal of metals due to low and negotiable differences in the removal efficiencies of duckweeds and algae for metals.

10.2.6 Landfill Leachate Treatment in Constructed Wetlands

A landfill is one of the most widely adopted methods globally for the disposal of municipal solid waste. A landfill containing a wide range of organic molecules of both natural and xenobiotic origin is highly variable and heterogeneous in nature and landfill leachate is difficult to be co-treated with conventional municipal wastewater treatment plants due to its low biodegradability, high nitrogen content, and other possible toxic components. Phytoremediation of landfills appears economically viable option which has been practiced in many countries with varying degrees of success and found out to be less harmful to human health. As a practice of merging traditional forestry with waste management, the treatment of leachate was conducted by Justin and Zupancic (2009) in which irrigation of *Salix purpurea* L. was done by reusing leachate after treatment through a constructed wetland and it was found that these leachate acts as a good fertilizer for landfill vegetative cover if applied under controlled conditions. As an alternative to conventional clay cover on landfills, phytocapping seems to be a sustainable alternative owing to its cost-effectiveness, less technical expertise requirement, prevention of the percolation of water into the piled waste, thus reducing the amount of leachate generation. *Populus* sp. is suitable for phytoremediation because of its high water usage, fast growth, and deep root system, and *Populus* sp. clones irrigated with landfill leachate designed by Zalesny et al. (2009) exhibited greater height, diameter, and number of leaves of *Populus* sp. Justin et al. (2010) used *Salix viminalis* L. and *Salix purpurea* L. for the treatment of municipal solid waste landfill leachate and demonstrated a 155% increase in above-ground biomass, compared to control water treatments and an average mass load of 2144 kg N ha^{-1}, 144 kg P ha^{-1}, 709 kg K ha^{-1}, 1010 kg Cl ha^{-1}, and 1678 kg Na ha^{-1}. *Salix* sp. is an excellent candidate for phytoremediation due to its large biomass, high metal tolerance, and accumulation capacity and demonstrated that a significant clonal difference in Mn tolerance and accumulation among *Salix* clones was observed (Yang et al. 2015). Moreover, the phytoextraction potential of Mn varied 5.8-fold among *Salix* clones due to which a scope for the improvement in Mn removal efficiency can be expected. Willows (*S. viminalis*) are known to have considerable oxygen transfer capacity (195.7 g O_2 m^{-3} h^{-1} $kg^{-1}{}_{\text{root wet mass}}$) so that oxidation of the organic matter present below-ground can take place (Randerson et al. 2011). Akinbile et al. (2012) also reported significant removal of metals from leachate in a SSFCW planted with *Cyperus haspan* L.

10.2.7 Treatment of Organic Pollutants in Constructed Wetlands

Organic pollutants enter into the environment through various sources such as spills (fuel and solvents), military activities (explosives and chemical weapons), agricultural activities (pesticides and herbicides), industries (chemical and petrochemical), and wood treatment. The treatment of organic pollutants such as explosives and pesticides through phytoremediation has been a concern among various researchers. Explosives such as research department explosive (RDX) and trinitrotoluene (TNT) have been treated by transgenic plant species *Arabidopsis thaliana* (L.) Heynh. (Rylott et al. 2011). Benzene, toluene, ethylbenzene, and xylene (BTEX), an organic solvent consisting volatile organic compounds released by petroleum derivatives, was removed from wastewater using HSSFCW (offering more than 60% removal for HRT higher than 100 days) planted with *T. latifolia* and *P. australis* (Ranieri et al. 2013). Al-Baldawi et al. (2013) carried out the treatment of petroleum hydrocarbons by *S. grossus* and reported a higher remediation potential of SSFCW in comparison with FWSCW. Naphthalene, a polyaromatic hydrocarbon, was found to be reduced by *E. crassipes* (Nesterenko-Malkovskaya et al. 2012).

10.2.8 Metal Removal in Constructed Wetlands

The increasing presence of metal ions in aquatic systems has become a significant environmental problem in both industrialized and developing countries. The various anthropogenic sources of common metals found in wastewater are enlisted in Table 10.8.

Table 10.8 Anthropogenic sources of common metals found in wastewater

Metal	Anthropogenic sources	References
As	Tannery, electroplating, pesticides, fertilizers, smelting, landfilling paints/chemicals, and mining	Lievremont et al. (2009)
Cd	Manufacturing of cadmium–nickel batteries, phosphate fertilizers, pigments, stabilizers, alloys, and electroplating industries	Mortaheb et al. (2009)
Cu	Electroplating, agricultural run-off, mining, electrical and electronics, iron and steel production, nonferrous metal industry, printing and photographic industries, and metalworking and finishing processes	Nadaroglu et al. (2010)
Hg	Solid waste incineration, coal and oil combustion, and pyrometallurgical processes	Wang et al. (2004)
Ni	Nickel plating, colored ceramics, electroplating, batteries manufacturing, mining, and metal finishing and forging	Sud et al. (2008)
Cr	Electroplating, leather tanning, metal finishing, nuclear power plant, textile industries, and chromate preparation	Tripathi et al. (2011)
Pb	Combustion of coal, processing and manufacturing of lead products, manufacturing of lead additives such as tetraethyllead (TEL) for gasoline	Acharya et al. (2009)
Zn	Mining, smelting, steel making, fossil fuel combustion, phosphate fertilizer, manure, sewage sludge, pesticides, motor vehicles, and galvanized metal	Fuge (2004)

Because of their high solubility in the aquatic environment, metals are highly prone to be absorbed by living organisms and lead to their bioaccumulation by entering into the food chain. Their ingestion beyond permissible concentration may lead to serious health problems. Although several treatment methods such as chemical precipitation, coagulation–flocculation, flotation, ion exchange, and membrane filtration can be employed to remove metals from contaminated wastewater, they have inherent limitations in practical application. Hyperaccumulation of metals by plants involves several steps, including metal transport across plasma membranes of root cells, xylem loading, and translocation after facilitative radial symplastic passage through the roots and across the epidermis (Clemens et al. 2002), detoxification, and sequestration of metals at the whole plant and cellular level. The general mechanism for metal detoxification encompasses the distribution of metals to apoplast tissues like trichome and cell walls, reduced uptake or efflux pumping of metals at the plasma membrane followed by chelation of the metals in the cytosol by various ligands such as organic acids, amino acids, and peptides (phytochelatins and metallothioneins). Thereafter, repairing of stress-damaged proteins and sequestration of metal-ligand complex into the vacuole takes place (Yang et al. 2005). An efficient translocation of metal ions from roots to shoots requires mobile metal-binding chelators in cytosol and xylem with efflux activities to pump toxic metals out of the root cells into the xylem (Clemens 2006).

Metal-chelating compounds such as catecholates, hydroxamates, and organic acids were found out to be released by ectomycorrhizal fungi collected from *Pinus radiata* D. Don. Various chemicals secreted in the plant root zone mediate multipartite interactions in the rhizosphere, where plant roots continually respond to and alter their immediate environment. Hyperaccumulator species may release metal-chelating root exudates which enhance metal uptake, translocation, and resistance. Plant growth affects the pH, redox conditions, and dissolved organic carbon content in the rhizosphere and thus affects the distribution of metals within the chemical species and their mobility in the plant's rhizosphere. Moreover, they oxidize Fe present in rhizosphere and cause co-precipitation of metals, thereby reducing metal mobility in the rhizosphere. Various plant species are known to successfully remediate metals present in industrial wastewaters as shown in Table 10.9. Principal metal chelators in plants such as phytochelatins, metallothioneins, organic acids, and amino acids endow metal detoxification by buffering cytosolic metal concentrations (Shah and Nongkynrih 2007).

10.2.8.1 Siderophores

Siderophores are high-affinity iron-chelating compounds released by gramineous plants as well as microorganisms to acquire/sequester iron that is accumulated in mineral phases as iron oxides and hydroxides. These form strong complexes with Fe^{3+}, which are highly soluble over a wide pH range and hence can be taken up by active transport. It was reported by Ma et al. (2011) that phytosiderophores typically have a lower affinity for iron than microbial siderophores. In their metal-binding

Table 10.9 List of plant species used for metal removal from industrial wastewater

Nature of wastewater	Plants vegetated	Metals removed	References
Industrial effluent	*Ecchornia crassipes* (Mart.) Solms; *Typha latifolia* L.	Cd, Pb, Cu, As	Sukumaran (2013)
Municipal wastewater	*Phalaris arundinacea* L.	Cd, Cr, Cu, Ni, Pb, Zn	Brezinova and Vymazal (2015)
Landfill leachate	*Typha latifolia* L.; *Phragmites australis* (Cav.) Trin. ex Steud.	As, Cd, Cr, Cu, Pb, Zn, Ni	Grisey et al. (2012)
Artificial wastewater	*Canna indica* L.; *Typha angustifolia* L.; *Cyperus alternifolius* Rottb., 1772; *Alternanthera hiloxeroides* Griseb. *Zizania latifolia* (Griseb.) Turcz. ex Stapf; *Echinochloa crus-galli* (L.) Beauv; *Polygonum hydropiper* L. (1753); *Isachne globosa* (Thunb.) Kuntze; *Digitaria sanguinalis* (L.) Scop.; *Fimbristylis miliacea* (L.) Vahl;	Cu, Cr, Co, Ni, Zn Zn	Yadav et al. (2012) Liu et al. (2007)
Swine wastewater	*Typha domingensis* Pers., *Eleocharis cellulosa* Torr.	Cu, Zn	Jorge et al. (2012)
Synthetic wastewater	*Typha domingensis* Pers.	Zn, Ni, Cr	Mufarrege et al. (2015)

sites, siderophores have either α-hydroxycarboxylic acid, catechol, or hydroxamic acid moieties and thus can be classified as hydroxycarboxylate, catecholate, or hydroxamate-type siderophores. Various phytosiderophores such as mugineic acid, deoxymugineic acid, epi-hydroxymugineic acid, avenic acid are released by plants out of which mugineic acid is the very first detected phytosiderophore. However, many siderophores have shown negative or no increase in the metal uptake capacity of plants which indicates their dependency on the type of plant and other factors affecting metal uptake capability. Metal cation uptake capacity by siderophores varies in accordance with their valency as reported by Dimkpa et al. (2009b); in that trivalent metal ions have shown more competitiveness for siderophore binding. Various siderophores produced by rhizospheric microbes that assist in increasing metal availability and mobility are listed in Table 10.10.

Table 10.10 List of siderophores assisting in increasing metal mobility and availability

Microbial metabolites	Microorganisms	Microbial origin	Plant cultivated	Effect on metal uptake by plants	References
Ketogluconates	*Pseudomonas aeruginosa*	Tannery air environment (Karachi, Pakistan)	–	Solubilization of Zn	Fasim et al. (2002)
5-ketogluconic acid	*Gluconacetobacter diazotrophicus* PAl5	Center of Advanced Studies in Agricultural Microbiology, Tamil Nadu Agricultural University (India)	–	Solubilization of Zn	Saravanan et al. (2007)
Desferrioxamine B, desferrioxamine E, coelichelin	*Streptomyces tendae* F4	Uranium mine, Wismut (Eastern Thuringia, Germany)	Sunflower	Enhanced Cd solubility and availability to plants	Dimkpa et al. (2009a)
Pyoverdine, pyochelin and alcaligin E	*Pseudomonas aeruginosa, Pseudomonas fluorescens, Ralstonia metallidurans*	VITO, Flemish Institute for Technological Research (Belgium)	Maize	Enhanced Pb and Cr uptake by plants though increasing their mobility	Braud et al. (2009)
Desferrioxamine B, desferrioxamine E, coelichelin	*Streptomyces acidiscabies* E13	International Max Planck Research School (Munchen)	Cowpea	Enhanced uptake of Al, Cu, Fe, Mn, Ni, U	Dimkpa et al. (2009b)

10.2.8.2 Metal-Binding Cysteine-Rich Proteins

Plants ubiquitously synthesize cysteine-containing metal-binding ligands namely, metallothioneines, phytochelatins, and glutathione. Metallothioneines are low molecular weight cysteine-rich metal-binding peptides containing thiol group while phytochelatins are naturally occurring cysteine-rich non-ribosomal peptides composed of only three amino acids, namely Glu, Cys, and Gly, with Glu and Cys residues linked through a γ-carboxymide bond. These are produced by glutathione by enzyme phytochelatin synthase PCS (γ-glutamylcysteine dipeptidyl transpeptidase). Glutathione (GSH), L-Glutamyl-L-cysteinyl-glycine, is considered as the most important non-protein thiol present in all living organisms consisting of three amino acids (Glu-Cys-Gly) and the cysteine thiol group of the active site is responsible for its biochemical properties (Mendoza-Cózatl et al. 2005). Metallothioneins and phytochelatins comprise of amino acids and form thiolate complexes through binding with metals which is energy-intensive and requires significant amount of amino acids (especially cysteine), growth limiting elements sulfur and nitrogen from the plant as the level of metal accumulation rises. Phytochelatins, synthesized using glutathione as a substrate by enzyme PC synthase that is activated in the presence of metal ions, contain strongly nucleophilic sulfhydryl groups and thus can react with many toxic species within the cell, such as free radicals, active oxygen species, cytotoxic electrophilic organic xenobiotics, and metals (Singh and Tripathi 2007). Apart from metal detoxification, phytochelatins facilitate metal homeostasis in plants which are responsible for metal availability in plant cells. Glutathione conjugates with metal ions or electrophilic xenobiotics through nucleophilic cysteine thiol moiety and sequesters in the vacuoles of the leaves of the plants. In addition, histidines are known to have a high affinity for transition metal ions such as Zn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}. Zn^{2+} bears resemblance to Cd^{2+} because of its position in the periodic table.

10.2.8.3 Organic and Amino Acids

The organic acids and amino acids such as citric, malic, and histidine are exudated by plants (due to the reactivity of metal ions with S, N, and O) and play an important role in metal detoxification and tolerance (Clemens 2001). These acids release H^+ ion while the COO^- binds to the cationic positive charge and forms metal–ligand complex. In addition, organic acids may chelate with metals in the cytosol where the ions can be transformed into non-toxic or less toxic form (Clemens 2001). The Cd- and Zn-citrate complexes are pervasive in leaves; however, malate is more ample. Moving from roots to leaves, citrate, and histidine are the principal ligands present in the xylem sap for Cu, Ni, and Zn. Ethylenediamine disuccinate and nitrilotriacetic acids are natural aminopolycarboxylic acids produced by many microorganisms which play an important role in enhancing the phytoavailability and phytoextraction of metals. The root-induced chemical changes on metal uptake have been observed by Kim et al. (2010) using Indian mustard (*Brassica juncea* (L.) Czern.) and sunflower (*Helianthus annuus* L.) and it was found that metal uptake and bioavailability increased with increasing rhizospheric pH and dissolved organic carbon. Moreover, Kim et al. (2010) also reported that the influence of root-induced dissolved organic carbon on metal solubility is a function of pH as well as total metal loading. It was reported by Javed et al. (2013) that organic acids exudation by the roots of *Eriophorum angustifolium* Honck. increases the rhizospheric pH and is a suitable plant for remediation of acidic metal-polluted soils. High concentrations of citric, malic, and malonic acids were found in the hairy roots of the plants *Thlaspi caerulescens* J. Presl and C. Presl and *Alyssum bertolonii* Desv., which are Cd and Ni hyperaccumulators, respectively. Citric acid has shown an enhancement in Cr uptake by *Parthenium hysterophorus* L. (UdDin et al. 2015). Synthetic acids like ethylenediaminetetraacetic acid increase the mobility of various metals such as Cu, Pb, Cd, and Zn.

10.2.8.4 Biosurfactants

Biosurfactants are biological complexing agents produced by yeast or bacteria from various substrates including sugars, oils, alkanes, and wastes (Mulligan 2009). They are capable of improving metal mobility, leading to enhanced phytoremediation. They are amphiphilic in nature, having a polar (hydrophilic) and a non-polar (hydrophobic) moiety. The hydrophobic part of the molecule is based on long-chain fatty acids, hydroxy fatty acids, or α-alkyl-β-hydroxy fatty acids while the hydrophilic portion can be a carbohydrate, amino acid, cyclic peptide, phosphate, carboxylic acid, or alcohol. Metals are transferred from one chemical state to another by biosurfactants, which changes their mobility and availability. The anionic biosurfactants form ionic bonds with metals and create complexes and these metal–biosurfactant bonds are stronger than the metal bond with the medium from which the metal is to be removed. As a result, the metal is desorbed from the medium due to the lowering of surface tension and the precipitation of the biosurfactants out of the complexes takes place (Singh and Tripathi 2007). However, the cationic biosurfactants replace the same charged metal ions by competing for some of the negatively charged surfaces (ion exchange). In addition, metal ions can also be removed by the formation of micelles by the biosurfactants in which the hydrophilic portion binds to metals and increases the mobility of metals. The entrapment of metal ions in the micelles increases bacterial tolerance and resistance toward a high concentration of metals. The potential of environmentally compatible di-rhamnolipid biosurfactant produced by *Pseudomonas aeruginosa* strain BS2 to treat metals in soil artificially contaminated with multi-metals was evaluated and di-rhamnolipid selectively removed Cd and Pb in the soil with more uptake of Cd, and the corresponding uptake efficiency was reported as Cd = Cr > Pb = Cu > Ni (Juwarkar et al. 2008). Various other researchers have evaluated biosurfactant-induced increment in the availability and mobility of metals which are enlisted in Table 10.11.

Table 10.11 Biosurfactant-induced increment in the availability and mobility of metals

Microorganisms	Microbial origin	Effect on metal uptake by plants	References
Bacillus sp. J119	Nanjing (China)	Enhanced Cd uptake	Sheng et al. (2008)
Candida lipolytica	Culture collection (Brazil)	Removal of 96% of Zn and Cu, and reduction in the concentration of Pb, Cd, and Fe	Rufino et al. (2012)
Pseudomonas sp. LKS06	Rhizosphere of Cd-hyperaccumulator *Solanum nigrum* L. grown in tailings	Uptake of Pb and Cd	Huang and Liu (2013)

10.3 Recent Development of Constructed Wetlands in India

According to Central Pollution Control Board, Government of India (CPCB 2009), the total wastewater generation from Class I cities (no. of cities 498, population greater than 1.0×10^5) and Class II (no. of cities 410, population between 5.0×10^4 and 9.9999×10^4) towns in the country is approximately 35,558 and 2696 million liters per day (MLD), respectively. However, the installed sewage treatment capacity in Class I cities and Class II towns is just 11,553 and 233 MLD, respectively, thus leading to a gap of 26,468 MLD in sewage treatment capacity. To reduce this gap, there is a need for a sustainable wastewater treatment alternative against conventional treatment methods. The use of constructed wetlands for the treatment of sewage in India is increasing day by day in rural as well as peri-urban India (Singh et al. 2019; Sutar et al. 2019). Several researchers are working on pilot-scale studies to implement constructed wetland technology to a large scale in India. Yadav et al. (2018) developed a "French system" vertical flow constructed wetland for domestic wastewater treatment and achieved COD and BOD removal up to 90 and 84%, respectively. Gray water was treated by constructed wetlands and reused for gardening and toilet flushing (Gupta and Nath 2018). Moreover, it is also applied to treat livestock wastewater (Rajan et al. 2019). For nitrogen and phosphorus removal from wastewater, pilot-scale plants are being tested for the development of a full-scale application (Nandakumar et al. 2019). Verma and Suthar (2018) treated dairy wastewater and reported that *Typha* biomass can be used as a potential feedstock for renewable energy operations. In India, constructed wetland technology is being studied widely by researchers on pilot-scale but very few large-scale studies are being applied.

10.4 Conclusion

An increase in wastewater generation mandates the utilization of an alternative treatment option to bridge the gap between wastewater generation and its treatment. Domestic and industrial wastewater treatment using constructed wetlands is an increasingly attractive option since it is effective with relatively low energy demands when compared to current physical and chemical alternatives. The efficiency of hyperaccumulators in heavy metal remediation is improved multifold by the secretion of siderophores, organic acids, biosurfactants, and metal-binding cysteine-rich proteins by plants. Despite the critical function of these biomolecules in the treatment of an array of environmental contaminants, the biogeochemical factors that affect their activity are poorly understood. Unraveling the exact mechanisms of how these molecules assist in facilitating heavy metal uptake by plants offers a low-cost and sustainable solution for remediation of toxic and recalcitrant pollutants. Also, in India, the escalation of pilot-scale studies to the large-scale applications may reveal the long-term applicability of constructed wetland technology.

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