Chapter 2
Phytoremediation of Agricultural Pollutants

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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

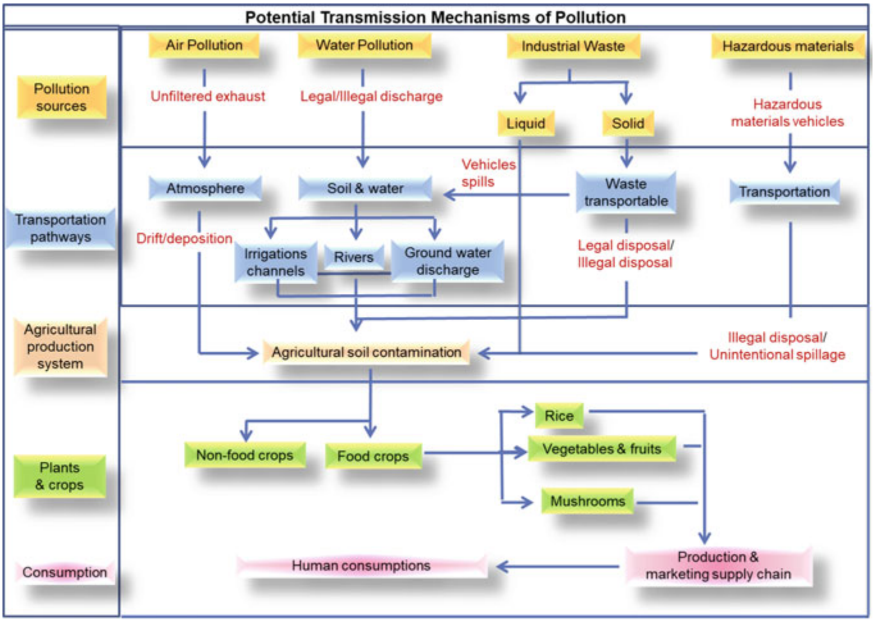

Fig. 2.1 Transmission mechanisms of pollution in agricultural environments (modified from Lin et al. 2017)

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

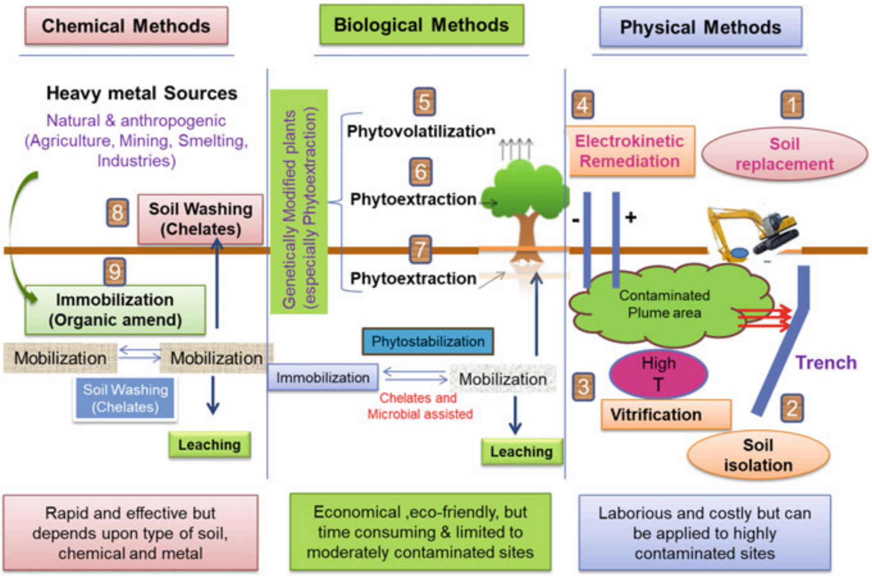

Fig. 2.2 Different soil clean-up methods (modified from Khalid et al. 2017)

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)

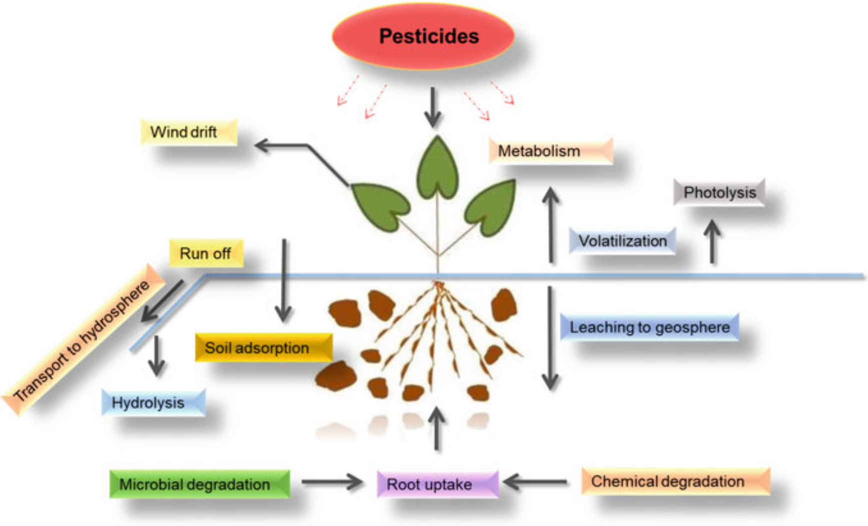

Fig. 2.3 Fate of pesticides in environment (modified from Ahemad and Khan 2013)

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

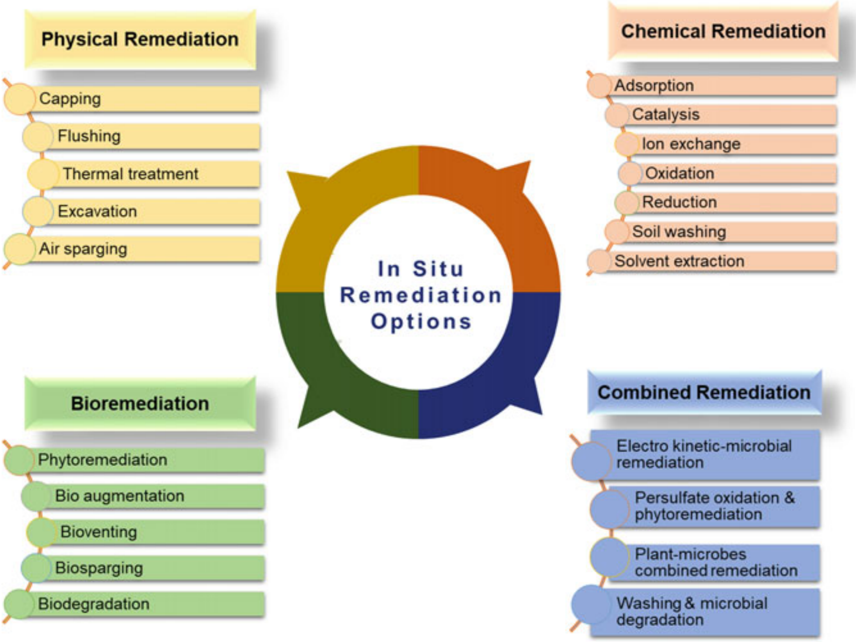

Fig. 2.4 In situ remediation options for soil and sediment contaminated with organic and inorganic pollutants (adapted from Song et al. 2017)

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)

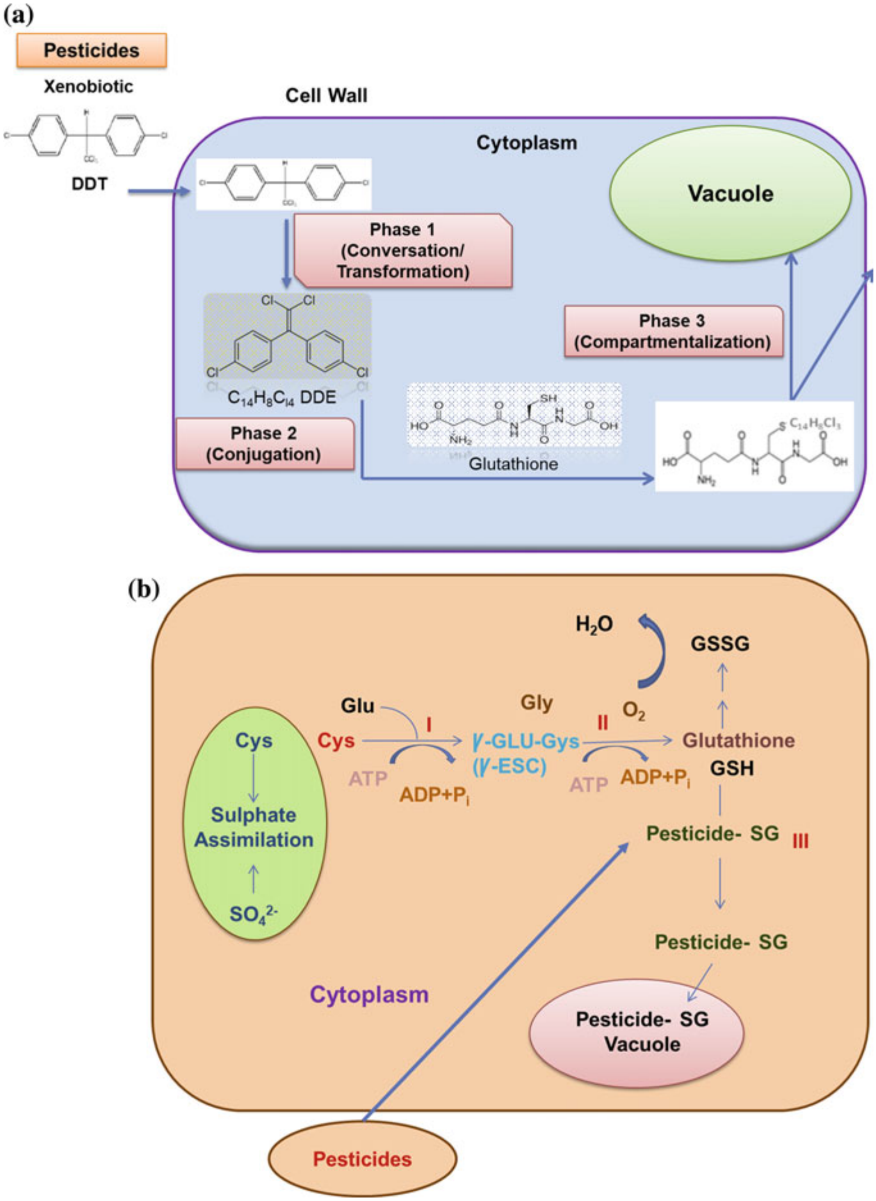

Fig. 2.5 Pesticide detoxification mechanisms in plant cell. **a** Modified from Singh and Singh 2017; **b** modified from Hussain et al. 2009. *Abbreviations* Cys, cysteine, γ-Glu-Cys, γ-L-glutamyl-L-cysteine, γ-ECS, γ-glutamylcysteine synthetase, GSH, glutathione, GSSG, oxidized glutathione

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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