Chapter 19
Use of Crop Plants for Removal of Toxic Metals

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Abstract Phytoextraction is an environmentally sound and cost-effective technology for cleaning up soils contaminated with toxic metals. The success of phytoextraction depends on the ability of plants to produce large amounts of biomass. In addition, plants must be tolerant to the target metals and be efficient to translocate metals from roots to the aboveground organs. The effectiveness of phytoextraction also depends upon site and metal species. However, the amount of metals extracted by plants is basically decided by (1) the metal concentration in dry plant tissues and (2) the total biomass of the plant. Certain varieties of high-biomass crops have been found to have the ability to clean up the contaminated soils. The major advantage of using crop plants for phytoextraction is the known growth requirements and well-established cultural practices. One of the most promising, and perhaps widely studied crop plant for the extraction of heavy metals is Indian mustard. Other crops like sweet sorghum, oat, barley, maize, and sunflower are also reported to accumulate toxic metals. As established cultural practices may not elicit the same plant response as observed under non-contaminated conditions, attention must be paid on developing suitable agronomic practices to optimize the growth of plants even under contaminated conditions. Further, a coordinated effort is required to collect and preserve germplasm of accumulator species where molecular engineering can play a key role in developing engineered plants capable of cleaning up contaminated soils and commercializing phytoextraction strategies.

Keywords Phytoextraction • Toxic metals • Contaminated soils • Crop plants

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19.1 Introduction

Since the Industrial Revolution, pollution of the biosphere with trace elements (heavy metals and metalloids) has accelerated dramatically. Many of these trace elements are toxic even at very low concentrations because of their nonbiodegradable nature, long biological half-life, and potential to accumulate inside the living bodies (Behbahaninia et al. 2009). Excessive deposits of heavy metals in agricultural soils may not only result in soil contamination but also lead to elevated heavy metal uptake by crop plants affecting quality and safety of foods (Muchuweti et al. 2006). Therefore, cleaning up of polluted soils is a subject of utmost concern to human beings. Most of the currently practiced remediation methods are primarily based upon civil engineering techniques whose cost is highly variable and depends on the contaminants of concern, soil properties, and site conditions (Lasat 2002). They are not only expensive but environmentally invasive, too. The search for an alternative remediation technique that is economically viable, environmentally sound, and equally protective of human health is thus urgently required. Strategies of this nature are classified under the generic heading of phytoremediation (Iskandar 2000; Iskandar and Kirtham 2001; Kabata-Pendias 2001), which is an emerging biotechnological application based on "green liver concept" and operates on the principles of biogeochemical cycling (Prasad 2004).

Phytoremediation consists of different plant-based technologies (Table 19.1), each having a different mechanism of action for the remediation of metal-polluted soils, sediment, or water. However, the terms phytoremediation and phytoextraction are often incorrectly used as synonyms, though phytoremediation is a concept, while phytoextraction is a specific cleanup technology (Prasad and Freitas 2003). Phytoextraction is in fact the most commonly recognized of all phytoremediation technologies and is the focus of the present review. Phytoextraction actually refers to a diverse collection of plant-based technologies that use either naturally occurring or genetically engineered plants for cleaning contaminated environments (Flathman and Lanza 1998).

While many plant species avoid uptake of heavy metals from contaminated soils, some characteristic plant species thriving in metal-enriched environments can accumulate significantly high concentrations of toxic metals, to levels that by far exceed the soil levels. These species are generally called hyperaccumulators and, among them, some crop plant species are also found. When phytoextraction is practiced, metal-accumulating plants are seeded or transplanted into metal polluted soil and are cultivated according to the established agricultural practices. The roots of established plants absorb metal elements from the soil and translocate them to the aboveground shoots where they accumulate. If metal availability in the soil is not adequate for sufficient plant uptake, chelates or acidifying agents may be used to liberate them into the soil solution (Huang and Cunningham 1996; Huang et al. 1997; Lasat et al. 1998). After sufficient plant growth and metal accumulation, the aboveground parts of the crop are harvested and removed from the contaminated site.

Table 19.1 Types of phytoremediation techniques

Technique	Process	Medium
Phytoextraction	Accumulation of contaminants in shoots and subsequent shoot harvest	Soil
Rhizofiltration	Absorption/adsorption of contaminants in/on roots	Surface water
Phytostabilization	Root and root exudates reduce bioavailability of contaminant	Soil, groundwater
Phytovolatilization	Evaporation of contaminants through plant transpiration	Soil, groundwater
Phytodegradation	Plant-assisted microbial degradation of contaminants in rhizosphere	Soil, groundwater
Phytotransformation	Plant uptake and degradation of contaminants	Soil, groundwater, surface water
Removal of Aerial	Uptake of volatile contaminants by leaves	Air

(Compiled from Yang et al. 2005; Arthur et al. 2005; Solheim 2008)

19.2 What Merits Does It Have?

The phytoextraction is an environmental friendly green technology involving living plants. These plants act as solar-driven pumps, which can extract and concentrate particular elements from the environment (Raskin et al. 1997). Therefore, phytoextraction offers a cost-effective means for cleaning of metal-contaminated soils, because the cost of metal phytoextraction is only a fraction of that associated with conventional engineering technologies (Zhuang et al. 2009). This technology avoids dramatic landscape disruption as it remediates the soil *in situ*. Furthermore, no artificial materials are used, hence, preserving the ecosystem. In contaminated agricultural lands, metal removal and getting a harvest synchronously can be a key element of a new strategy for land management (Zhuang et al. 2009). However, some limitations avoid the wide application of this technology. The success of phytoextraction is primarily dependent upon the bioavailability of the contaminants of concern for plant uptake. Usually readily available metals in soil solution are free metal ions and soluble metal complexes and metals adsorbed to inorganic soil constitutes at ion exchange site. Therefore, phytoextraction is better suited for metals such as Zn and Cd, which occur primarily in exchangeable and readily bioavailable form, while the others need to be treated separately for making them bioavailable. Selection of plant species is of particular importance as most of accumulator species are slowly growing and produce little biomass over period of time. In addition, slow transport of metals from soil particles to root surface is another major factor limiting metal uptake into roots (Claus et al. 2007). Even after entering to the roots, many heavy metals form sulfate, carbonate, or phosphate precipitates and immobilize these metals in apoplastic (extracellular) and symplastic (intracellular) compartments. Apoplastic transport of metals is further limited by

Table 19.2 Advantages and limitations of phytoextraction with crop plants

Advantages	Limitations
Eco-friendly green technology involving living plants	Better suited for metals that are readily bioavailable
Low cost of implementation as compared to conventional means	Some metals need to be treated separately for making them bioavailable
Aesthetically pleasing and avoids dramatic landscape disruptions	Most of the identified species are slowly growing and produce little biomass over a period of time
No artificial materials are generally used	Long-term remediation effort, requiring many cropping cycles to decontaminate metal pollutants to acceptable levels
Applicable to a range of toxic metals and radionuclides	Depth of soil that can be cleaned or stabilized is restricted to the root zone of the plants being used
Eliminate secondary air- or waterborne wastes.	Applicable only to sites that contain low to moderate levels of metal pollution
Enhance regulatory and public acceptance	Potential contamination to food chain
Can get a harvest synchronously with metal removal	Results are variable
Known agronomic and crop management practices can be used	Climate dependent
Life cycle and biology of crop are well understood	
Easily implemented and maintained	

the high cation-exchange capacity of cell walls (Raskin et al. 1997). The highly insoluble nature of most of the hazardous metals interrupts their free movement in the vascular system of the plant. Therefore, translocating them to the aboveground shoots where their accumulation has taken place is also restricted. Phytoextraction is obviously a long-term remediation effort, requiring many cropping cycles to decontaminate metal pollutants to acceptable levels (Zhuang et al. 2009; Shukla et al. 2010). The depth of soil which can be cleaned or stabilized is restricted to the root zone of the plants being used. Depending on the plant, this depth can range from a few inches to several meters (Schnoor et al. 1995; Chen et al. 2000, 2003). This technology is applicable only to sites that contain low to moderate levels of metal pollution, because plant growth is not sustained in heavily polluted soils. The advantages and limitations of using crop plants for cleaning up contaminated soils are summarized in Table 19.2.

19.3 What Factors Decide the Success of Phytoextraction?

The effectiveness of phytoextraction is dependent upon many factors of which some are plant-, site-, or metal-specific characteristics. However, the amount of metals extracted by plants is basically decided by (1) the metal concentration in dry plant tissues and (2) the total biomass of the plant. Therefore, the product of these factors estimates the total amount of metal extracted from the contaminated soil

(Claus et al. 2007). The time required for remediation is dependent upon the type and extent of metal contamination, the length of the growing season, and the efficiency of metal removal by plants (Blaylock and Huang 2000). In addition, as this is essentially an agronomic approach, some agronomic practices, such as, plant selection, possibility of cultivation, fertilization and irrigation, etc., could also play a crucial role in successful cleaning of a contaminated site (Claus et al. 2007).

As a plant-based technology, the success of phytoextraction inherently depends upon several plant characteristics. The plant should have the ability to produce large amounts of biomass rapidly using standard crop production and management practices (Das and Maiti 2007) together with high efficiency of metal accumulation in shoot biomass (Blaylock et al. 1997; McGrath 1998; Shah and Nongkynrih 2007). Plants considered for use must also be tolerant to the targeted metal, or metals, and be efficient at translocating them after uptake by roots to the harvestable aboveground portions (Blaylock and Huang 2000). In addition to the high shoot biomass, a dense root system is important while growing under hardy conditions. Among the site-specific characteristics, the topography of the land should be acceptable and free from physical barriers, which otherwise could prevent the use of agricultural equipment and machineries. The distribution of metals in soil profiles and their movement in soils, which are primarily determined by many soil related factors, also contribute to the efficiency of metal removal by plants. In fact, a major factor limiting metal uptake into roots is the slow transport from soil particles to root surfaces (Claus et al. 2007). The accumulation of the metals in the surface layer of the soil seems to be related to the properties associated with high adsorption rate of the metals by soil solid phases (Behbahaninia et al. 2009). In this context, soil acidity, light texture, and structural features, such as soil cracks, can be considered as important factors (Smith 1996). Soil pH plays a key role in making the availability of elements in the soil for plant uptake (De Matos et al. 2001; Bambara and Ndakidemi 2010; Yobouet et al. 2010). According to Anton and Mathe-Gaspar (2005), higher temperature and lowering soil pH have resulted in increased cadmium and zinc contents of sorrel and maize shoots. Under acidic conditions, H^+ ions displace metal cations from the cation exchange complex (CEC) of soil components and cause metals to be released from sesquioxides and variable-charged clays to which they have been chemisorbed (McBride 1994).

19.4 Mechanisms of Phytoextraction

Proper understanding of the biological processes associated with metal acquisition, transport, and shoot accumulation is the key to formulate sound strategies for improving phytoextraction. In this context, why do plants absorb metals is the fundamental question to be answered. Plants need nutrients as they are among the key requirements for the growth and development of a plant. Some metals, such as Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, and Zn, are essential, serve as micronutrients, and are used for redox processes, to stabilize molecules through electrostatic interactions, as components of various enzymes, and for regulation of osmotic pressure (Bruins et al. 2000; Odjegba and Fasidi 2004). Many other metals have no biological role (e.g., Ag, Al, Cd, Pb, and Hg), and are nonessential (Bruins et al. 2000; Kamal et al. 2004) and potentially toxic to microorganisms. Therefore, it is understood that plants take some metals as they are essential nutrients. The literature on the mechanisms of root and plant cell uptake of elements like N, P, S, Fe, Ca, K, and possibly Cl is reported (Marschner 1995). However, little is known about how plants mobilize, uptake, and transport of most environmentally hazardous heavy metals, such as, Pb, Cd, Cu, Zn, U, Sr, and Cs. Nonessential metals, however, may effectively compete for the same transmembrane carriers used by essential metals (Thangavel and Subbhuraam 2004). Nutrient uptake pathways can also take up heavy metals that are similar in chemical form or behavior to the nutrients (Pivetz 2001). However, even for essential elements, plants keep maintaining the accumulation below their metabolic needs (<10 ppm) (Oyelola et al. 2009). Hyperaccumulator plants, however, can accumulate exceptionally high amounts of micronutrients. They not only accumulate excessively high levels of essential micronutrients, but can also absorb significant quantities of nonessential metals. Hyperaccumulators are capable of accumulating metals 100-fold higher (2% on the dry weight basis) than those typically measured in shoots of the common non-accumulator plants (Claus et al. 2007), and their metal tolerance has enhanced the interest of ecologists, plant physiologists, plant biologists and environmentalists to investigate the physiological and genetical factors responsible for metal uptake and tolerance in plants. Accumulator species have evolved specific mechanisms for detoxifying high metal levels accumulated in the cells, which allow bioaccumulation of extremely high concentration of metals (Yang et al. 2005). In fact, they do have their own mechanisms to absorb, translocate, and store the metals they need. In this regards, the structure and properties of cell membranes play a crucial role in metal absorption process. Because of their charge, metal ions cannot move freely across the cellular membranes and taking up metals into cells are mediated by membrane proteins with transport functions (Hooda 2007).

In soil, metals are found in different forms: (1) in solution as free metal ions and soluble metal complexes; (2) adsorbed to inorganic soil constituents on ion exchange sites; (3) precipitated such as oxides, hydroxides, and carbonates; (4) bound to soil organic matter; and (5) embedded in structures of silicate minerals. Plants do have several mechanisms to solubilize “soil-bound” metals and subsequent uptake (Raskin et al. 1997). Plant roots can solubilize soil-bound metals by acidifying their soil environment with protons extruded from the roots (Thangavel and Subbhuraam 2004). In the rizhosphere, root and microbial activities can influence the chemical mobility of metal ions and ultimately their uptake by plants as consequence of alterations of soil pH or dissolved organic carbon (Hinsinger and Courchesne 2007). Metal-chelating molecules can also be secreted into the rhizosphere to chelate and solubilize “soil-bound” metal (Yang et al. 2005; Hooda 2007). Some rhizosphere microorganisms also secrete plant hormones that increase root growth and thereby the secretion of root exudates (Hooda 2007). In this context, chelating compounds, termed phytosiderophores, have been studied in plants (Higuchi et al. 1999). Some plant roots are capable of reducing “soil-bound” metal ions by specific plasma membrane-bound metal reductases, which may increase metal availability (Thangavel and Subbhuraam 2004). For example, in response to iron deficiency, plants develop several biochemical and morphological reactions to ameliorate iron solubilization and uptake from the soil solution (Hell and Stephan 2003). The biochemical and physiological mechanisms induced in dicotyledonous plants under conditions of iron deficiency comprise three main processes (Babalakova et al. 2005). The first one includes an increased release of protons through the activation of plasmalemma P-type ATPase proton pump to acidify the surrounding solution, thus enhancing Fe(III)-containing compounds solubility (Espen et al. 2000). The second process is an obligatory reduction of ferric-chelates by a membrane-associated Fe(III)-chelate reductase to the more soluble ferro-complexes (Robinson et al. 1999). The third effect of short-term treatment with ionic and chelated copper on membrane adaptive biochemical response is an induction of the synthesis of a specific transporter for ferro-ions in plasmalemma of root cells (Hell and Stephan 2003). In addition, mycorrhizal fungi or root-colonizing bacteria can also be used in increasing the bioavailability of metals (Frey et al. 2000; Khan et al. 2000; Hooda 2007). Mobilized metals then enter the root cells by symplastic or apoplastic pathways (Solheim 2008). Most likely, entrance is via metal ion carriers or channels; however, specialized carriers could also exist for the transport of metal–chelate complexes (Solheim 2008).

The transmembrane structure facilitates the transfer of bound ions from extracellular space through the hydrophobic environment of the membrane into the cell (Lasat 2002). However, of all the adsorbed metals physically at the extracellular negatively charged sites of the root cell walls, only a part enters inside the cells. For success of phytoextraction, absorbed metals, however, should also be transported from roots to shoot, which is primarily controlled by how much water is released from leaves during transpiration and the pressure created by the roots (Welch 1995). Therefore, as the rate of transpiration increases, the internal movement of metal-containing sap from the root to the shoot also increases, allowing roots to absorb more moisture from the soil. Generally, a significant fraction of cell wall-bound metals cannot be translocated to the shoots and, thus, cannot be removed by harvesting shoot biomass (Lasat 2002). Apart from binding onto the cell wall, there are some other means also that determine metal immobilization into roots and subsequent inhibition of ion translocation to the shoot. Complexation in cellular structures of roots could also prevent translocation of metals to the aboveground parts (Lasat et al. 1998). In addition, some plants, coined excluders, possess specialized mechanisms to restrict metal uptake into roots (Lasat 2002). The excluders prevent metal uptake into roots avoiding translocation and accumulation in shoots. Though excluders have a low potential for metal extraction, they can be used to stabilize the soil, and avoid further contamination spread due to erosion (Dahmani-Muller et al. 2000). Most environmentally hazardous metals are too insoluble to move freely in the vascular system of the plant. Many forms like sulfate, carbonate, or phosphate precipitate by immobilizing these metals in apoplastic and symplastic compartments (Raskin et al. 1997; Ghosh and Singh 2005). However, plant species have unique abilities to tolerate, accumulate, and detoxify metals and metalloids (Danika and LeDuc Norman 2005). Several hundred plant species have so far been identified as hyperaccumulators of different metals (McGrath and Zhao 2003; McIntyre 2003; Ghosh and Singh 2005). Hyperaccumulators are found from a wide range of taxonomic groups (45 different families) (Baker et al. 2000) and geographic areas and possess a wide variety of morphologies, physiologies, and ecological characteristics (Pollard et al. 2002). The majority of them accumulate only one metal (Pollard et al. 2002) although a significant number show the ability to accumulate more than one (He et al. 2002; Yang et al. 2004; McIntyre 2003).

19.5 How to Enhance the Efficiency of Phytoextraction?

As many factors either directly or indirectly affect the efficacy of phytoextraction, it is important to employ an integrated approach in order to remove heavy metals from contaminated sites. Such integrated strategy may include selection of high-biomass-producing crops, identify plants that could grow in varying environmental conditions, selection of improved crop husbandry, innovative soil management practices, etc., to ensure high metal removal rates from contaminated soils (Nowack et al. 2006; Evangelou et al. 2007). Therefore, selection, breeding, and genetic engineering of metal accumulators can be considered as the key areas of practical significance. The bioavailability of metals for plant uptake can be altered in several means. For example, if the soil contains chelating agents, they can form soluble complexes with metals, thereby enhancing movement of metals in soil profile (Behbahaninia et al. 2009). To achieve this, use of different chelators has shown a dramatic increase in the metal mobility in soil substrate keeping metals as soluble chelate–metal complexes which become available for uptake by roots and are later on transported within the plants. Many chemical amendments, such as ethylene diamine tetra acetic acid (EDTA), diethylene triamine penta acetic acid (DTPA), nitrilotri acetic acid (NTA), and organic acids, have been used in pot and field experiments to enhance extraction rates of heavy metals and to achieve higher phytoextraction efficiency (Kayser et al. 2000; Thaylakumaran et al. 2003; Tandy et al. 2004; Ke et al. 2006; Wang et al. 2007; Wu et al. 2006; Zhuang et al. 2009). However, the effectiveness of different chelating agents is highly variable with the plant species and metal involved.

Though EDTA has been proved as one of the most efficient chelating agents in enhancing Pb phytoavailability in soil and subsequent uptake and translocation to shoots (Chen and Cutright 2001; Shen et al. 2002; Claus et al. 2007; Zhuang et al. 2009), it has failed, however, in enhancing some other metals such as Cd, Zn, and Cu accumulation in plants (Lai and Chen 2004; McGrath et al. 2006; Zhuang et al. 2009). Furthermore, there is enough evidence that suggest that some plant species had no remarkable response to the application of EDTA (Zhuang et al. 2005, 2007). When several heavy metals are present in the soil, interactions and subsequent inhibitory effects can play a role in responding to the added EDTA. Another key area to be considered is the physical features of the soil, because if the soil allows leaching of metal-chelating agents, it might possibly be a threat to groundwater contamination

(Nowack et al. 2006). Therefore, use of EDTA to enhance phytoextraction requires a critical assessment. Diethylene triamine penta acetic acid is another superior reagent used in extraction of metals, such as Cd, Pb, Zn, and Ni from contaminated soils (Behbahaninia et al. 2009). The DTPA extraction has frequently been found to correlate with amounts of metals taken up by the plants (Nouri et al. 2001). In a similar study, addition of thiosulfate and thiocynate salts to mine spoil has reportedly induced plants to accumulate Hg (Moreno et al. 2005) while chloride anions are shown to increase the Cd solubility in soils by forming relatively stable chloride ion complexes, for example, $CdCl^+$ and $CdCl_2$ (Weggler et al. 2004). According to Zhuang et al. (2005), inorganic agents like elemental sulfur or ammonium sulfate could also enhance metal accumulation. It has repeatedly been reported that the application of ammonium to soil could promote the phytoavailability of heavy metals from the contaminated soil (Xiong and Lu 2002; Zaccheo et al. 2006).

It seems that some soil applications (such as sludge) can produce soluble organic complexes with the heavy metals. These complexes are more mobile and possibly more readily taken up by plants than free metal ions (Shuman 2005; Senesi and Loffrdo 2005; Nouri et al. 2006). However, due to changing of their available forms to some unavailable forms such as fractions associated with organic materials, carbonates, or metal oxides (Walker et al. 2004), bioavailability of metals sometimes can be decreased by the organic amendments (Wei et al. 2010). Due to continuous loading of pollutants, heavy metals can be released into groundwater or soil solution, which are then available for plant uptake (Mapanda et al. 2004). Lowering in soil pH can weaken the retention ability of toxic metals to soil organic matter resulting in more available metal in soil solution for root absorption. In fact, many metal cations (e.g., Cd, Cu, Hg, Ni, Pb, and Zn) are more soluble and available in the soil solution at low pH (below 5.5) (Blaylock and Huang 2000). It could, therefore, be suggested that the phytoextraction process is enhanced when metal availability to plant roots is facilitated through the addition of acidifying agents to the soil (Brown et al. 1994; Salt et al. 1995). Possible amendments of acidification include NH_4-containing fertilizers, organic and inorganic acids, and elemental S.

Fertilization, on the other hand, can enhance the growth of the plants resulting in high biomass, which has also been used in increasing the efficiency of phytoextraction (Wei et al. 2010). For example, Wei et al. (2010), in a study with *Solanum nigrum*, reported that the application of urea has enhanced the efficiency of phytoextraction. After application of natural N-P-K fertilizer, particularly at the early stage of growth, the biomass of common reed *(Phragmites australis)* was increased by twofold compared to control plants that subsequently improved phytoextraction of Ni and Zn by 2–3-folds (Claus et al. 2007). In addition, fertilizers with high content of NH_4^+ have the additional benefit of lowering the soil pH, leading to an increase in plant uptake of metals. According to Zaccheo et al. (2006), soils amended with $(NH_4)_2SO_4$ and $(NH_4)_2S_2O_3$ led to an increase in metal availability due to decreased soil pH. The addition of NH_4NO_3 and $(NH_4)_2SO_4$ to soil, however, did not increase Zn and Cu accumulation in three sorghum varieties (Zhuang et al. 2009). The contradictory reports on the effect of ammonium fertilization on phytoextraction are basically due to the degree of solubilization of metals under different soil pH levels. Generally, Zn and Cd can easily be solubilized at pH values of conventional soils, whereas the solubilization of Pb and Cu occurs at lower pH (Schmidt 2003). Therefore, metal availability in soil can be manipulated by the proper ratio of NO_3 to NH_4 used for plant fertilization.

19.6 Promising Crop Plants

Many studies have indicated that certain varieties of high-biomass crops display heavy metal tolerance and/or ability to cleaning up the contaminated soils. In this regard, Kumar et al. (1995) evaluated several fast-growing Brassicas such as Indian mustard (*Brassica juncea* L. Czern), black mustard (*Brassica nigra* Koch), turnip (*Brassica campestris* L.), rape (*Brassica napus* L.), and kale (*Brassica oleracea* L) for their ability to tolerate and accumulate metals. Indeed, Indian mustard is one of the most promising, and perhaps most studied, non-hyperaccumulator plant for the extraction of heavy metals from contaminated sites (Prasad and Freitas 2003). Upon further screening, it was found effective in sorbing particularly divalent cations of toxic metals (Salt and Kramer 2000). In a similar study, Dushenkov et al. (1995) observed that the roots of Indian mustard are effective in the removal of Cd, Cr, Cu, Ni, Pb, and Zn as also reported by others (Ebbs and Kochian 1998; Prasad and Freitas 2003). In a recent investigation, the leaves of sorghum plants have been found very effective in the removal of Pb, while the removal of Cd, Zn, and Cu was maximum by stems (Zhuang et al. 2009). Sweet sorghum (*Sorghum bicolor* L.) a hardy, C4 grass widely used as a forage crop (Buxton et al. 1998; Unger 2001) and as a great promising energy plant, has also shown to display a potential removing ability also due to its fast-growing and high-biomass production capacity. Zhuang et al. (2009) have used three varieties of sweet sorghum to evaluate the phytoextraction efficiency of heavy metals. Their results revealed that even when grown in the contaminated soil, sorghum plants can extract more than 0.05 kg/ha of Cd in a single crop and the removal of Pb and Zn was 0.35 and 1.44 kg/ha, respectively. Similar findings for sorghum plant were also reported by Marchiol et al. (2007) who calculated the values of 0.38 kg/ha for Pb and 1.22 kg/ha for Zn in an alkaline, industrial-polluted soil. These reports confirmed the findings of An (2004) who also reported the ability of sweet sorghum to accumulate metal elements. According to Madejón et al. (2003), compared to sorghum plant, sunflower (*Helianthus annuus* L.) could extract significantly greater amount of Zn (2.14 kg/ha), when the roots were also considered in calculations. Studies conducted with hydroponic solutions revealed that sunflower can remove Pb (Dushenkov et al. 1995), U (Dushenkov et al. 1997a), ^{137}Cs, and ^{90}Sr (Dushenkov et al. 1997b). Claus et al. (2007) have used sunflower, maize (*Zea mays* L.), and rape (*Brassica napus*) to assess the removal of Cd, Cu, Ni, Zn, Cr, and Pb from a contaminated site. According to their findings, rape plants bioconcentrated up to 40 ppm Cr and Pb. Even though maize produced the largest biomass, the total amount of metals taken up by this plant was lower than sunflower and rape plants. Metal removal capacity of different plants has also been studied in various cultural practices by Keller et al. (2003) and Ciura et al. (2005) using maize as the test plant, while Madejón et al. (2003) and Soriano and Fereres (2003) tested sunflower and barley respectively for assessing their metal-removing potential.

In addition to Indian mustard, Zn has also been removed successfully by oat (*Avena sativa* L.) and barley (*Hordium vulgare* L.) with the established cultural practices (Ebbs and Kochian 1998). Some more reports are also available on Indian mustard, oat, maize, barley, sunflower, and ryegrass (Salt et al. 1998; Shen et al. 2002; Meers et al. 2005; Komárek et al. 2007). Moreover, fast-growing willows (*Salix viminalis*) and poplars (*Populus* sp.) are excellent producers of biomass and have characteristics that make these species promising for phytoremediation application (Vervaeke et al. 2003). Keller et al. (2003) reported that *Nicotiana tabacum* L. has the ability to produce 12.6 t/ha of biomass, which could extract 1.83 kg/ha of Zn, 0.47 kg/ha of Cu and 0.042 kg/ha of Cd. Potentially promising crop plants with respective metals are given in Table 19.3.

Table 19.3 Potentially promising crop plants for phytoextraction

Metal	Species	Reference
Pb	*Lycopersicon esculentum*	Cornu et al. (2007) and Oyelola et al. (2009)
	Sorghum bicolor	Marchiol et al. (2007) and Zhuang et al. (2009)
	Helianthus annuus	Madejón et al. (2003), Marchiol et al. (2007), and Claus et al. (2007)
	Zea mays	Ciura et al. (2005) and Claus et al. (2007)
	Hordeum vulgare	Soriano and Fereres (2003)
	Brassica juncea	Ebbs and Kochian (1997) and Prasad and Freitas (2003)
	Brassica napus	Claus et al. (2007)
	Pisum sativum	Huang et al. (1997)
	Amaranthus cruentus	Oyelola et al. (2009)
Cd	*Sorghum bicolor*	Zhuang et al. (2009)
	Helianthus annuus	Turgut et al. (2004), Claus et al. (2007), and Marchiol et al. (2007)
	Zea mays	Ciura et al. (2005) and Claus et al. (2007)
	Hordeum vulgare	Soriano and Fereres (2003)
	Brassica juncea	Zavoda et al. (2001), Keller et al. (2003), and Prasad and Freitas (2003)
	Nicotiana tabacum	Keller et al. (2003)
	Brassica napus	Claus et al. (2007)
Zn	*Sorghum bicolor*	Madejón et al. (2003), Marchiol et al. (2007), and Zhuang et al. (2009)
	Helianthus annuus	Madejón et al. (2003), Marchiol et al. (2007), and Claus et al. (2007)
	Zea mays	Ciura et al. (2005) and Claus et al. (2007)
	Hordeum vulgare	Ebbs and Kochian (1998) and Soriano and Fereres (2003)

(continued)

Table 19.3 (continued)

Metal	Species	Reference
	Brassica juncea	Kumar et al. (1995), Keller et al. (2003), and Prasad and Freitas (2003)
	Nicotiana tabacum	Keller et al. (2003)
	Brassica napus	Claus et al. (2007)
	Avena sativa	Ebbs and Kochian (1998)
Cr	*Helianthus annuus*	Zavoda et al. (2001), Turgut et al. (2004), and Claus et al. (2007)
	Brassica juncea	Kumar et al. (1995) and Zavoda et al. (2001)
	Zea mays	Claus et al. (2007)
	Brassica napus	Claus et al. (2007)
Cu	*Sorghum bicolor*	Zhuang et al. (2009)
	Helianthus annuus	Madejón et al. (2003), Marchiol et al. (2007), and Claus et al. (2007)
	Zea mays	Brun et al. (2001), Ciura et al. (2005), and Claus et al. (2007)
	Hordeum vulgare	Soriano and Fereres (2003)
	Brassica juncea	Prasad and Freitas (2003)
	Nicotiana tabacum	Keller et al. (2003)
	Brassica napus	Claus et al. (2007)
	Lycopersicon esculentum	Cornu et al. (2007) and Oyelola et al. (2009)
	Amaranthus cruentus	Oyelola et al. (2009)
Ni	*Helianthus annuus*	Zavoda et al. (2001), Turgut et al. (2004), and Claus et al. (2007)
	Brassica juncea	Kumar et al. (1995) and Zavoda et al. (2001)
	Zea mays	Claus et al. (2007)
	Brassica napus	Claus et al. (2007)
Cs	*Brassica oleracea*	Lasat et al. (1997)
	Phaseolus acutifolius	Lasat et al. (1997)
	Brassica juncea	Lasat et al. (1997)

19.7 What Aspects Need More Investigations?

Though, phytoextraction has been intensively investigated over the years, only a scanty of information is available on the usage of crop plants for the metal removal from contaminated sites. The prime advantage of using common crop species for phytoextraction is the known growth requirements and well-established cultural practices. Although some crop species were found to accumulate heavy metals while producing high biomass in response to established agricultural management (Ebbs and Kochian 1998), growth and yield performances may vary widely under contaminated conditions (Blaylock et al. 1997), and even established cultural practices sometimes may not elicit the same plant response as observed under non-contaminated environment. The fundamental aim of the agronomic research is to enhance the growth and yield performance. But in general, no attention is paid on how to enhance metal accumulation in the tissues of crop species. However, with the merits of phytoextraction, it is necessary to develop suitable agronomic practices to optimize the growth of crop plants even under contaminated conditions. In this context, research must be focused on agronomic practices such as crop establishment (planting season, spacing, establishment method), irrigation (frequency, amount, method), fertilization, weeding (method and frequency), and other cultural practices including mulching, pruning, pest and disease control, and harvesting (method and time) to increase the efficiency of phytoextraction. Among the different agronomic practices, the composition, frequency, and method of application of fertilizers need to be assessed thoroughly in order to find potential crop species. Furthermore, over dosage and/or frequent application of certain plant nutrients can limit/suppress the absorption of the target element. To make phytoextraction economically viable, the cost of fertilization should also be considered while formulating fertilizer mixtures.

Another factor that makes phytoextraction successful is the biomass and ability of plants to accumulate metals within the tissues (Blaylock et al. 1997; McGrath 1998). Increased plant biomass can obviously take up and store more metals. Well-developed root system can provide more surface area to take up metals and the aboveground components should be ready to store them. However, increase in aerial and belowground biomass cannot be achieved simultaneously, because plants generally tend to develop more roots under stressed conditions, which negatively affect the aboveground biomass. Since conclusive reports on these aspects are still lacking, scientists need to address these issues seriously. The majority of phytoextraction research has focused on finding the ideal metal-accumulating plant species and the means by which metals can be removed from soils. Once any promising crop species is identified, genetic factors responsible for their hyperaccumulating nature should be investigated. Despite recent advances in biotechnology, little is known about the genetics of metal hyperaccumulators. Particularly, the heredity of relevant plant mechanisms, such as metal transport and storage (Lasa et al. 2000) and metal tolerance (Ortiz et al. 1992, Ortiz et al. 1995), must be better understood. Bioengineering of plants capable of cleaning up contaminated soils could be the next step that has been successfully performed for several species. Manipulation of genes involved in the biosynthesis of metal sequestering compounds and subsequent introduction and expression of the engineered genes into desirable plant species might attract plant growers to adopt phytoremediation strategies (Prasad and Strzalka 2002). Meanwhile, Chaney et al. (1999) proposed the use of traditional breeding approaches for improving metal hyperaccumulator species and possibly incorporating significant traits, such as metal tolerance and uptake characteristics, into high-biomass-producing plants. Further, it is important to collect and preserve germplasm of accumulator species. The USDA-ARS Plant Introduction Station maintains a worldwide collection of *B. juncea* accessions that are known metal accumulators, and the seeds are distributed to public and private research institutions at no cost (Prasad and Freitas 2003).

19.8 Conclusion

Since it evidently does indicate several benefits, phytoextraction can be considered as one of the most preferred methods for restoring metal contaminated environments. In order to exploit the full potential of phytoextraction, a comprehensive understanding is needed on as to how metal uptake, transport, and trafficking across plant membranes and distribution, tolerance, sensitivity, etc., take place under different cultural practices. Furthermore, phytoextraction should be viewed as a long-term remediation solution because many cropping cycles may be needed over several years to reduce metals to acceptable regulatory levels. Taking all these into consideration, it could be concluded that phytoextraction with crop plants is still in the research and developmental phase, which requires further attention.

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