CHAPTER FOUR

Phytostabilization: A Green Approach to Contaminant Containment

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Abstract

Phytostabilization involves the establishment of a plant cover on the surface of the contaminated sites with the aim of reducing the mobility of contaminants within the vadose zone through accumulation by roots or immobilization within the rhizosphere, thereby reducing off-site contamination. The process includes transpiration and root growth that immobilizes contaminants by reducing leaching, controlling erosion, creating an aerobic environment in the root zone, and adding organic matter to the substrate that binds the contaminant. Microbial activity associated with the plant roots may accelerate the degradation of organic contaminants such as pesticides and hydrocarbons to nontoxic forms. Phytostabilization can be enhanced by using soil amendments that immobilize metal(loid)s combined with plant species that are tolerant of high levels of contaminants and low-fertility soils or tailings. Although this technology is effective in the containment of metal(loid)s, the site requires regular monitoring to ensure that the stabilizing conditions are maintained. Soil amendments used to enhance immobilization may need to be periodically reapplied to maintain their effectiveness. We critically examine the applicability of this technology to manage metal(loid)s contaminated soils and identify fertile areas for future research.

1. Introduction

Phytoremediation comprises technologies that use higher plants to clean up and revegetate contaminated sites (Adriano *et al.*, 2004; Pulford and Watson, 2003; Robinson *et al.*, 2009). Many techniques and applications are included in the term phytoremediation. They differ in the process by which plants can remove, immobilize, or degrade contaminants. For example, the process in which plants are used to remove organic or inorganic contaminants from soil and water and store them in harvestable tissue is called phytoextraction, rhizoextraction, or phytofiltration. Similarly, the technique in which plants are used to remove contaminants through volatilization is called phytovolatilization (Moreno *et al.*, 2005). In phytostabilization, inorganic contaminants such as heavy metal(loid)s in the soil are immobilized, thereby minimizing their transport in water or dust. This technology may enhance the degradation of organic contaminants such as pesticides and hydrocarbons via microbial activity associated with the plant roots that accelerates the transformation of these contaminants into nontoxic forms (Berti and Cunningham, 2000).

Phytostabilization aims to contain contaminants within the vadose zone through accumulation by roots or precipitation within the rhizosphere. This prevents off-site contamination through their migration via wind and water erosion, leaching, and soil dispersion. Phytostabilization also refers to

Plate 1 **Organic amendments reduce metal toxicity in mine tailings (Moreno *et al.*, 2005).**

establishing a plant cover on the surface of the contaminated soils, which reduces their exposure to wind, water, and direct contact with humans or animals. Phytostabilization can be enhanced by using soil amendments that are effective in the immobilization of metal(loid)s and plant species that are tolerant of high levels of contaminants (Plate 1; Kumpiene *et al.*, 2007; Park *et al.*, 2011a; Vangronsveld *et al.*, 1995a).

Phytostabilization reduces the mobility, and therefore the risk, of inorganic contaminants without necessarily removing them from the site. This technology does not generate contaminated secondary waste that needs further treatment. It also enhances soil fertility, thereby achieving ecosystem restoration. However, since the contaminants are left in place, the site requires regular monitoring to ensure that the optimal stabilizing conditions are maintained. If soil amendments are used to enhance immobilization, they may need to be periodically reapplied to maintain their effectiveness (Bolan *et al.*, 2003a; Keller *et al.*, 2005).

While some organic contaminants undergo microbial or chemical degradation, inorganic contaminants such as metal(loid)s are immutable. Therefore, containment of metal(loid)s through phytostabilization is critical in managing contaminated sites. This review examines the various approaches to remediate contaminated sites; processes involved in phytostabilization of metal(loid)s; soil and plant factors affecting this technology; advantages and disadvantages; and enhancement of this technology using soil amendments.

2. The Importance of Bioavailability in Phytostabilization

Naidu *et al.* (2008a) defined the bioavailability of contaminants in soil as the fraction of the total metal(loid) in the interstitial pore water (i.e., soil solution) and soil particles that is available to the receptor organism. There is controversy in the literature regarding the definition and the methods for the measurement of bioavailability. Microbiologists often regard the concentration that can induce a change either in morphology or physiology of the organism as the bioavailable fraction, whereas plant scientists regard the plant available pool as the bioavailable fraction (Adriano *et al.*, 2004). Recent studies (e.g., McLaughlin *et al.*, 2000; Peijnenburg *et al.*, 2007; Vig *et al.*, 2003) indicate that the transformation of contaminants in soils is a dynamic process, which indicates that bioavailability changes with time.

A generic definition of *bioavailability* is the potential for living organisms to take up metal(loid)s through ingestion or from the abiotic environment (i.e., external) to the extent that the metal(loid)s may become involved in the metabolism of the organism (NRC, 2003). More specifically, it refers to the biologically available fraction (or pool) that can be taken up by an organism and can react with its metabolic machinery, or it refers to the fraction of the total concentration that can interact with a biological target (Vangronsveld and Cunningham, 1998). Bioavailability requires that the metal(loid)s come in contact with the organism (i.e., physical accessibility). Moreover, metal(loid)s need to be in a particular form (i.e., chemical accessibility) to enter biota. Bioavailable metal(loid)s are soluble and in an accessible form to the target organism.

Immobilization technologies minimize the bioavailability of metal(loid)s by allowing them to react with the soil for a longer period (aging; i.e., natural attenuation) or by adding soil amendments. Many studies have documented the effect of aging on the immobilization of metal(loid)s in soils (Lock and Janssen, 2003; Lothenbach *et al.*, 1999) and also the potential value of various organic and inorganic soil amendments in reducing the bioavailability of metal(loid)s in soil (Cheng and Hseu, 2002; Kumpiene *et al.*, 2007; Park *et al.*, 2011a). For example, various phosphate compounds have been found to be effective in the immobilization of Pb in soils (McGowen *et al.*, 2001), and USEPA recommends this technique for risk-based remediation of Pb-contaminated sites (USEPA, 2001) (refer to Section 7).

3. Phytostabilization Concepts

Most legislative schemes require that a soil be remediated if the total concentration of one or more contaminants (e.g., heavy metal(loid)s) is exceeded in a designated part (topsoil, subsoil) of the soil profile (Swartjes, 1999). Such a regulatory environment is not conducive to phytostabilization, since in an ideal phytostabilization operation, the total concentration of metal(loid) contaminants remain unchanged.

Regulators are now recognizing the influence of metal(loid) solubility and mobility on environmental risk. Consequently, there is an increasing adoption of a risk-based approach when assessing soil quality (Fernandez *et al.*, 2005; Naidu *et al.*, 2008b; Swartjes, 1999). Such risk-based regulatory systems are based on the effect of the contaminant, rather than on its total concentration in the soil (Naidu *et al.*, 2008b). Higher plants immobilize metal(loid)-polluted soils by affecting changes in the rhizosphere, which has distinct physical, chemical, and biological conditions. The rhizosphere is the few millimeters of soil surrounding the plant roots and influenced by their activity as well as the microbial assemblages associated with the roots. Functionally, the rhizosphere is a highly dynamic, solar/plant-driven microenvironment that is characterized by feedback loops of interactions between root processes, soil characteristics, and the dynamics of the associated microbial population (Adriano *et al.*, 2004; McGrath *et al.*, 2001). Soil characteristics such as pH and redox potential, nutrient status, the presence of contaminants, and physical properties all influence plant growth and the dynamics of microbial population (Marschner *et al.*, 2001). Most root exudates are ultimately responsible for many of the rhizosphere's unique characteristics. Root exudates stimulate microbial activity and biochemical transformations and/or enhancement of mineralization of metal(loid)s in the rhizosphere (Anderson *et al.*, 1993; Paterson, 2003). Between 10% and 40% of the total net C assimilated by crops is released in the form of soluble root exudates and insoluble materials such as cell walls and mucilage (Bolan *et al.*, 2011; Rasse *et al.*, 2005).

The chemical and biological reactions occurring in the rhizosphere play an important role in the bioavailability of metal(loid)s to plants. Plant roots change the physical, chemical, and biological conditions of the soil in the rhizosphere which, in comparison to bulk soil, is enriched with organic substances of plant and microbial origin, including organic acids, sugars, amino acids, lipids, coumarins, flavonoids, proteins, enzymes, aliphatics, aromatics, and carbohydrates (Chang *et al.*, 2002; Hinsinger *et al.*, 2005). Common organic acids in the rhizosphere are acetic, butyric, citric, fumaric, lactic, malic, malonic, oxalic, propionic, tartaric, and succinic acids. Organic acids in the rhizosphere affect the dynamics of metal(loid)s in soils via their effect on acidification, metal(loid)s chelation and complexation, precipitation, redox reactions, microbial activity, rhizosphere physical properties, and root morphology.

Plants may be identified and/or engineered that exude compounds capable of immobilizing contaminants using redox processes or precipitation of insoluble compounds in the rhizosphere. For example, Pb is precipitated as phosphate (Cotter-Howells and Caporn, 1996; Cotter-Howells *et al.*, 1994) and Cd forms complexes with sulfide (de Knecht *et al.*, 1994) in the roots and the rhizosphere of *Agrostis capillaris* and *Silene vulgaris*, respectively.

Plants reduce the mobility and transport of pollutants in the environment either by uptake or immobilization (Pulford and Watson, 2003). Phytostabilization can be enhanced by using soil amendments that are effective in the immobilization of metal(loid)s and is readily suited to the monitored natural remediation of contaminated sites, which is employed within the context of a carefully controlled and monitored site cleanup strategy to be able to achieve site-specific remediation objectives within a time frame that is more reasonable than that offered by other more invasive methods (Adriano *et al.*, 2004; Fig. 1).

Volatilization of contaminants into atmosphere via plants may be an important process in the phytostabilization of soils where high concentrations of organic contaminants are present (Ouyang, 2002; Schnoor *et al.*, 1995). Phytovolatilization has some potential to remediate soils contaminated with metal(loid)s that form volatile hydride and methyl compounds. Recent efforts have concentrated on developing transgenic species with increased potential for volatilizing Hg (Moreno *et al.*, 2005; Rugh *et al.*, 1998) and Se (de Souza *et al.*, 2002; Robinson *et al.*, 2009; Terry *et al.*, 2000). One drawback of volatilization is that there is no control on the final destination of the contaminants.

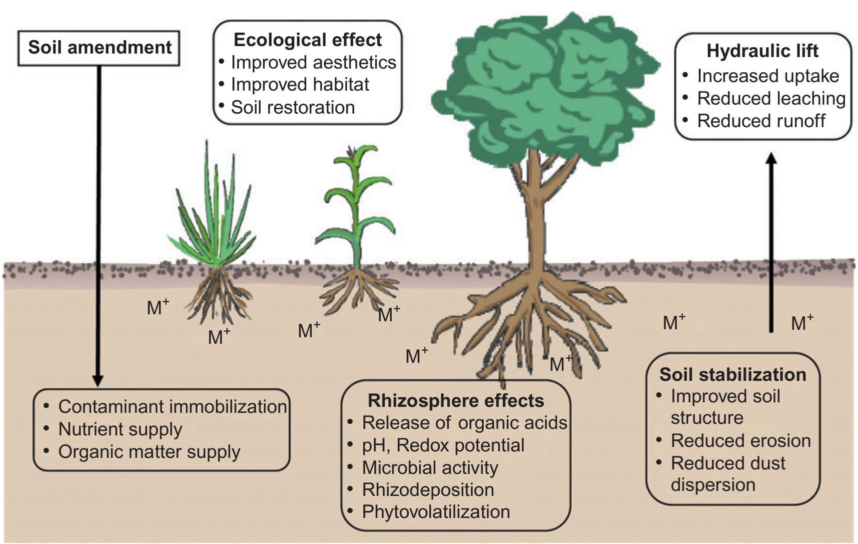

Figure 1 Schematic diagram illustrating the potential action of phytostabilization on contaminants in soil.

4. Processes Involved in Phytostabilization

Figure 2 shows the processes involved in reducing the mobility and bioavailability of contaminants. The most important of these are

- uptake and sequestration of contaminants in the root system;
- alteration of soil factors that influence the speciation and immobilization of contaminants (pH, organic matter, redox levels);
- root exudates that regulate the precipitation and immobilization of the contaminants;
- establishment of vegetation barrier that reduces the likelihood of physical contact with the soil by animals and humans;
- mechanical stabilization of the site to minimize erosion by wind and water;
- enhancement of evapotranspiration, thereby reducing the leaching of contaminants.

4.1. Contaminant removal

Although the removal of contaminants through plant uptake may not be the main process involved in phytostabilization, plant removal of contaminants may still play a role in this technology. Fässler *et al.* (2010) showed that

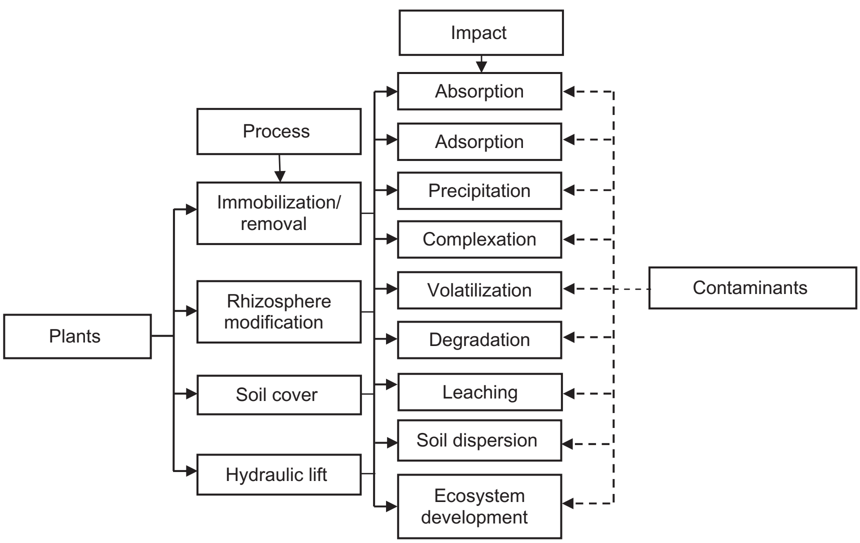

Figure 2 Processes involved in the phytostabilization of contaminants.

agricultural crops could enhance the phytostabilization of a metal-contaminated soil, while producing Zn-rich biomass that could be used as nutritious stock fodder. Poplars used in the phytostabilization of a B-contaminated sawdust pile extracted high concentrations of B (Robinson *et al.*, 2007). Here the biomass could be used as a B-rich mulch on nearby orchards that were deficient in this element. In both cases, the primary role of the plants was the stabilization of the site. The extraction of the metal(loid)s enhanced the value of the biomass.

Hyperaccumulating plants that are effective in the removal of metal(loid)s can be used to enhance this technology (Wong, 2003). Plants employ various mechanisms to take up metal(loid)s from soil (Table 1). For example, concentrations of phytosiderophores up to molar levels have been measured for nonsterile conditions in the rhizosphere of Fe-deficient plants (Romheld, 1991). Awad *et al.* (1994) found enhanced Fe mobilization up to a distance of 4 mm from the wheat roots and concluded that phytosiderophores are highly effective in Fe acquisition. Phytosiderophores also form chelates with Zn, Cu, and Mn and facilitate the solubilization of these metals in calcareous soils (Romheld, 1991; Shenker *et al.*, 2001). Grasses release phytosiderophores in response to Zn deficiency (Cakmak *et al.*, 1994; Walter *et al.*, 1994; Zhang *et al.*, 1991). Cakmak *et al.* (1996) demonstrated that the enhanced release of phytosiderophores correlates with Zn efficiency in wheat genotypes. Von Wiren *et al.* (1996) proposed two possible pathways for the uptake of Zn from Zn phytosiderophores in grasses: (1) via the transport of the free Zn cation and (2) the uptake of nondissociated Zn–phytosiderophore complexes. A defining feature of these metal(loid) transport systems is that they have poor specificity (Reid and Hayes, 2003). Therefore, nonessential metal(loid) ions with a similar size to nutrients may be taken up into the symplast and ultimately be translocated to the shoots. Khattak *et al.* (1991) and Peryea and Kammereck (1997) demonstrated that plants take up arsenate (AsO_4^{3-}) via the same physiological mechanism as phosphate (PO_4^{3-}). Similarly, Tl^+ may enter via the K^+ ion channel (Skulsky, 1991), Cd^{2+} may enter via either Ca^{2+} or Zn^{2+} transport system, and Ni^{2+} may enter along with Mg^{2+}.

Mench and Martin (1991) collected dissolved root exudates from two tobacco species (*Nicotiana tabacum*, *Nicotiana rustica*) and corn (*Zea mays*) to extract metal(loid)s from two soils. They observed increased extractability of Mn and Cu, while Ni and Zn remained recalcitrant. Root exudates from the tobacco species enhanced the solubility of Cd, and the amount extracted by the root exudates was in the range of Cd uptake in these plants grown on soil (*N. tabacum* > *N. rustica* > *Z. mays*). Therefore, increased solubility of Cd in the rhizosphere due to the release of organic exudates in the apical root zone can be viewed as a mechanism promoting Cd accumulation in tobacco.

Youssef and Chino (1989) found relatively lower concentrations of dissolved Cu and Zn in the rhizosphere soil being associated with higher pH.

Table 1 Selected references on the plant-based processes involved in the containment of contaminants

Contaminant	Substrate	Plant species	Containment process	Reference
Hg	Base metal tailings	*Brassica juncea*	Phytovolatilization and phytoextraction	Moreno *et al.* (2005)
Cr(VI)	Mineral soil	*Brassica juncea*	Reduction	Bolan *et al.* (2003b)
Cd	Variable charge soil	*Brassica juncea*	Phytoimmobilization	Bolan *et al.* (2003c)
Cu	Soil	*Brassica napus* L.	Chelation followed by uptake	Zeremski-Škoric *et al.* (2010)
Cu	Pasture soil	*Agrostis tenuis*	Chelation followed by uptake but resulted in Cu leaching	Thayalakumaran *et al.* (2003)
Pb	Hydroponics media	Alfalfa (*Medicago sativa*)	Chelation followed by uptake	López *et al.* (2005)
As	Orchard soil	Pome fruit trees	Phosphate-induced desorption followed by plant uptake	Peryea (1991)
As	Tailings	*Brassica Juncea*	Phytoextraction	Ko *et al.* (2008)
Mo			Phosphate-induced desorption followed by plant uptake	Neunhauserer *et al.* (2001)
Cd, Cr, Cu, Ni, Pb, Zn	Multimetal-contaminated soil	Canola (*Brassica napus*) and radish (*Raphanus sativus*)	Phytoextraction	Marchiol *et al.* (2004)
Pb, Cd, Cu	Artificially contaminated with 600 mg kg^{-1} Pb, 40 mg kg^{-1} Cd, and 100 mg kg^{-1} Cu	*Echinochloa crus-galli*	Root exudates-enhanced phytoextraction	Kim *et al.* (2010)
Cd, Cu, Pb, Zn	Mining soil	*Sedum alfredii*	Chelation followed by uptake	Liu *et al.* (2008)
Cd, Cu, Ni, Pb, Zn	Calcareous dredged sediment derived surface soil	*Brassic rapa*, *Cannabis sativa*, *Helianthus annuus*, *Zea mays*	Chelation followed by uptake	Meers *et al.* (2005)
Cd, Cr, Cu, Pb, and Zn	Multiply metal-contaminated soil,	*Brassica Juncea*	Chelation followed by uptake	Quartacci *et al.* (2006)

(*Continued*)

Table 1 (*Continued*)

Contaminant	Substrate	Plant species	Containment process	Reference
Pb	Artificially polluted by 800 mg Pb $(NO_3)_2$.	Maize (*Zea mays* L.)	Improved metal uptake by plant growth regulators (GA_3 and IAA) and EDTA	Hadi *et al.* (2010)
Cu, Pb, Zn	Paddy soils contaminated by several toxic metals under aerobic soil conditions	Rice (*Oryza sativa* L.), soybean (*Glycine max* [L.] Merr.), and maize (*Zea mays* L.)	Phytoextraction	Murakami and Ae (2009)
Cd	Unpolluted surface layer farmland soil spiked with Cd	*Solanum nigrum* L.	Improved plant growth and Cd uptake by fungi and citric acid	Gao *et al.* (2010)
U, Cd, Cr, Cu, Pb, Zn	Ra production site contaminated with Ra, U, and heavy metals	Mustard (*Brassica juncea*), ryegrass (*Lolium perenne*)	Chelation followed by uptake	Duqučne *et al.* (2009)
Hg	Tailings dam of the abandoned metal mine	*Brassica juncea*	Phytoextraction followed by phytovolatilization	Moreno *et al.* (2005)
Hg	Soil	Transgenic tobacco	Phytovolatilization	He *et al.* (2001)
Se	Se added soil	*Lycopersicon esculentum, Brassica oleracae, Festuca arundinacae, Medicago sativa, Astragalus bisulcatus*	Phytovolatilization	Duckart *et al.* (1992)
Se	Soil amended with dimethylselenoniopropionate, selenomethionine, sodium selenite, or sodium selenate	Indian mustard (*Brassica juncea* L.)	Phytovolatilization	de Souza *et al.* (2000)

Neng-Chang and Huai-Man (1992) observed that the impact of root activity on the rhizosphere pH was influenced by edaphic conditions. For example, the extractability of Cd by 0.1 M $CaCl_2$ was inversely correlated with the pH. In turn, the uptake balance between the anions and the cations influenced the rhizosphere pH. Thus, in terms of physiologically controlled mechanism, uptake of nitrate from fertilizer application could induce higher rhizosphere pH, limiting the solubilization of metals and their subsequent uptake. Whereas an increase in soil pH can increase the concentration of mobile metal(loid) species such as As^{5+} and Cr^{6+} and also increase the solubilization of organic matter, thereby releasing metal(loid)s that are associated with organic matter (Bolan *et al*., 2011; van Herreweghe *et al*., 2002).

The establishment of mycorrhizal fungi is a prerequisite for the success of any soil restoration program (Haselwandter and Bowen, 1996; Meier *et al*., 2011), and hence the relationships between roots and microorganisms in the rhizosphere need to be elucidated. Inoculation with specific mycorrhizal fungi has been considered to increase the uptake of nutrients and pollutants by phytoextractor species (Entry *et al*., 1996). Rogers and Williams (1986) found that inoculation of *Melilotus officinalis* and *Sorghum sudanense* with vesicular arbuscular mycorrhizae increased the uptake of ^{137}Cs by 30 Bq g^{-1} ash. The association of *Pteris vittata* with mycorrhizal fungi increased its capacity to uptake As up to 1031 mg As kg^{-1} dry weight compared to 527 mg As kg^{-1} in the nonmycorrhizal plants (Leung *et al*., 2010). Similarly, Díaz *et al*. (1996) reported increased mycorrhizal fungi enhanced plant metal tolerance (Schutzendubel and Polle, 2002) by absorbing metal(loid)s in their hyphal sheath and external mycelium. The hydrophobic fungal sheath may reduce metal(loid) access to the root. Fungal chelants may complex metal(loid)s reducing their bioavailability (Jentschke and Godbold, 2000). The mechanisms of plant nutrient uptake by the fungi and their subsequent translocation into the root may be more specific than the corresponding plant uptake mechanisms, reducing the amount of toxic metal(loid)s that enter the plant (Meier *et al*., 2011).

Results from greenhouse studies on the effect of mycorrhizae on contaminant uptake cannot be directly extrapolated to field conditions because of varying environmental conditions and time scale (short-term green house vs. long-term field conditions). Plant physiological and soil conditions in the field typically differ greatly, both spatially and temporally from those obtained in greenhouse experiments (Entry *et al*., 1996).

4.2. Soil cover

Vegetation acts as a sink for contaminants by uptake or assimilation, thus reducing the amount of contaminant available for transport to groundwater. Vegetative cover also plays a vital role in stabilization by reducing the water flux through the soil profile and mechanically stabilizing the soil through root growth. This reduces the movement of soil and the associated contaminants. Soil erosion potential is increased if the soil has no or sparse vegetative cover of plants and/or plant residues. Plant and residue cover protects the soil from rain-splash and slows the movement of surface runoff thereby increasing infiltration. Similarly, vegetation reduces the wind velocity, thereby mitigating the dispersion of soil and sediments. The vegetation-induced reduction in soil erosion is likely to reduce the movement of contaminants and subsequent off-site contamination (Table 2).

The major effects of vegetation on water and wind erosion include:

- interception of the direct impact of rainfall drops and wind;
- decreasing the velocity of runoff, and hence the cutting action of water and its capacity to entrain soil and sediment;
- root-induced compaction and increases in soil strength, aggregation, and porosity;
- enhancement of vegetation-induced biological activities and their influence on soil aggregation and porosity;
- transpiration of water, leading to the subsequent drying out of the soil;
- insulation of the soil against temperature variation which can result in cracking or "frost heave."

The erosion-reducing effectiveness of plant and/or residue covers depends on the type, extent, and quantity of cover (Fig. 3). Vegetation and residue combinations that completely cover the soil, and which intercept all falling raindrops at and close to the surface, are the most efficient in controlling soil erosion. Residual roots and earthworms are also important as these provide channels (biopores) that allow surface water to move into the soil, thereby reducing surface runoff and soil erosion (Bronick and Lal, 2005; McCallum *et al.*, 2004). Maintaining living ground covers, to provide the best protection against loss of soil because they slow down runoff water after rain, allows water to infiltrate into the soil and lessen evaporation losses. For example, vegetative cover in rehabilitated mined land increased infiltration rate and declined erosion from stimulated storm from 30–35 t ha^{-1} at 0% vegetative cover to 0.5 t ha^{-1} at 47% cover (Loch, 2000). Tree roots were found to increase soil strength by 2–8 kPa depending on species, while grass roots contributed 6–18 kPa, thereby decreasing the erosion potential of soils (Simon and Collison, 2002).

Lumber production is an important land use in New Zealand. Plantation forests of *Pinus radiata* cover some 6% of the land area. To prevent decay, lumber products are treated with biocides, with Copper Chromium and Arsenic (CCA) being the treatment of choice. Historically, pentachlorophenol (PCP) has been used. Boron is used to prevent sap stain. The use of these treatments has resulted in the contamination of sites used for wood waste disposal. Piles of wood waste, primarily sawdust, leach B, CCA, and PCP thus pose a serious environmental risk. One such pile, 3.6 ha and

Table 2 Selected references on the value of vegetative cover in reducing dust dispersion and erosion control

Plant species	Soil	Observations	Reference
Honey mesquite (*P. glandulosa*)	Semiarid area	Vegetative cover reduces wind erosion.	Hupy (2004)
Spontaneous plant communities *Piptatherum miliaceum Dittrichia viscosa*, *Helichrysum decumbens*, *Phagnalon saxatile*, *Sonchus tenerrimus*	Tailings	Plant communities reduce air borne and water erosion and may mitigate the spread of the contamination to the nearby areas.	Conesa *et al.* (2007)
Neyrudia reyaudinana, Imperta cylindraca, Rhus chinensis, and *Pteridium aquilium*	Lead/Zinc mine	Vegetation in mine tailings and disposal sites of dredged material will reduce erosion by water and wind.	Lan *et al.* (1997)
Smooth brome (*Bromus inermis* Leyss.) Red fescue (*Festuca rubra* L.) Perennial ryegrass (*Lolium perenne* L.) Alfalfa (*Medicago sativa* L.) Buckwheat (*Fagopyrum esculentum* Moench)	Coarse taconite iron ore tailing	Vegetative cover has improved depending on the type of municipal solid waste compost used and rate of application. Overall plant cover across all treatments has improved from zero prior to experimental manipulation to 83% after 4 years.	*Norland and Veith (1995)*
Lygeum spartum and *Piptatherum miliaceum, Cicer arietinum* (chickpea)	Mine tailings	Stabilization of the tailings using vegetation or other means would reduce both wind and water erosion.	Conesa *et al.* (2009)
Pioneer birch trees	The historical hard coal mining area-dumps	Vegetation on a dump surface protects from erosion and reduces the seepage water formation by evapotranspiration.	Willscher *et al.* (2010)
Rhodes grass (*Chloris gayana*) kikuyu (*Pennisetum clandestinum*)	Mine site	Erosion from the simulated storm was greatly reduced by vegetative cover, declining from 30–35 t ha^{-1} at 0% vegetative cover to 0.5 t ha^{-1} at 47% cover.	Loch (2000)

(*Continued*)

Table 2 (*Continued*)

Plant species	Soil	Observations	Reference
Rosmarinus officinalis, *Triticum aestivum,* natural-spontaneous vegetation	Hill slopes	The vegetative covers of *Rosmarinus officinalis* and natural-spontaneous vegetation reduced the soil losses by 99% and 98%, with respect to the *Triticum aestivum*, and the runoff losses by 94% and 96%, respectively. Also, the *Rosmarinus officinalis* and natural-spontaneous plants influenced infiltration by intercepting much of the rainfall water respect to the *Triticum aestivum*.	Zuazo *et al.* (2004)
Huisache (*Acacia* sp.), Mesquite (*Prosopis* sp.), Prickly Pear, or Nopal (*Opuntia* sp.), Cardon (*Opuntia imbricata*)	Semiarid area	Runoff was reduced by 87%, 87%, and 98% and soil loss by 97%, 93%, and 99% for *Acacia farnesiana*, *Prosopis laevigata*, and *Opuntia* sp., respectively, as compared to the Control.	Vásquez-Méndez *et al.* (2010)

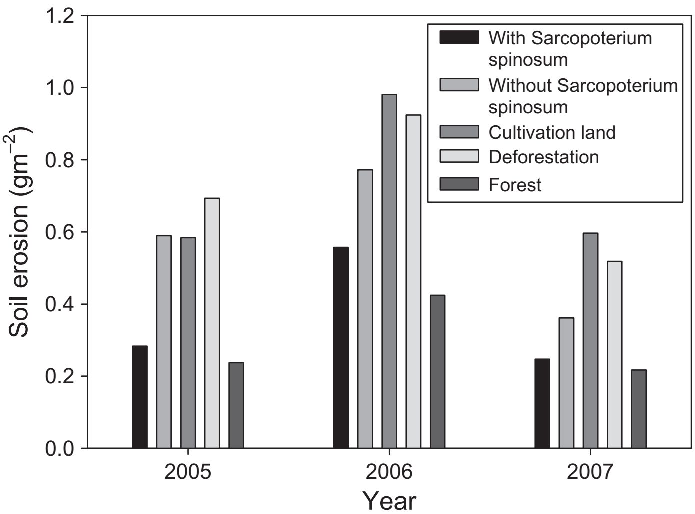

Figure 3 Total soil erosion (g m^{-2}) in different soil treatments: natural vegetation dominated by *Sarcopoterium spinosum;* natural vegetation where the *S. spinosum* was removed repeatedly; cultivation practices wherein all vegetative cover was removed and cleared; deforestation areas (cutting has been practiced on *Pinus halepensis* over the last 20 years); afforestation (*Pinus halepensis)* planted in 1960 (Mohammad and Adam, 2010).

located near the town of Kopu, New Zealand, was leaching high concentrations of B into local streams, resulting the degradation of ecosystems and fisheries. The presence of high B concentrations and a C:N ratio of 400 had prevented vegetation from establishing on the pile. Consequently, virtually all of the annual 1135 mm of rainfall resulted in leaching events. Saturated material occurred at depths as shallow as 20 mm, resulting in anaerobic conditions that reduced the rate of biodegradation of the wood waste and resulted in methane production.

Robinson *et al.* (2007) describes the phytostabilization of this pile using poplar trees. Poplar clones were selected that tolerate high B concentrations (Plate 2). The pile was heavily fertilized with nitrogen, and a collection pond to store any leachate was installed at the foot of the pile. After 3 years of growth, the trees have reduced leaching events from the pile during the Southern hemisphere winter (June–September). The holding pond collects most of this leachate, which is used for irrigation during the summer months. Occasional winter storms result in the holding pond discharging into the local stream. However, these storm events result in dilution of the contaminants to levels below the New Zealand Drinking Water Standard of 1.4 mg L^{-1}B.

Plate 2 Phytostabilization of timber treatment site in Kopu, New Zealand (Robinson *et al.*, 2007).

The poplar trees accumulated high concentrations (>1000 mg kg^{-1}) of B in the leaves, while the concentrations of other contaminants, namely Cu, Cr, and As, were all <1 mg kg^{-1}. It was suggested that the trees be periodically coppiced and used as an organic B-rich mulch on nearby orchards that are deficient in this essential micronutrient. Such a strategy relies on only coppicing a fraction of the trees on the pile, so that hydraulic control is maintained.

4.3. Rhizosphere modification

Rhizosphere-induced changes in soil biochemical properties regulate the transformation, mobility, and bioavailability of metal(loid)s, thereby affecting the phytostabilization of contaminated sites. The major rhizosphere-induced biochemical properties that influence metal(loid) dynamics include acidification, release of organic acids, and increased microbial activity (Table 3).

Table 3 Selected references on processes involved in rhizosphere modification

Plant species	Substrate	Rhizosphere modification	Reference
Camellia japonica	Pasture soil	Decrease in pH, resulting in the dissolution of rock phosphate	Zoysa *et al.* (1997)
Clover	Pasture soil	Decrease in pH, resulting in the dissolution of rock phosphate	Bolan *et al.* (1996)
Brassica carinata	Metal-contaminated soil mixed with peat	Mobilization of metals in the rhizosphere by its acidification and complexation with organic acids present in root exudates	Quartacci *et al.* (2009)
Lupinus albus L.	Heavy metal-contaminated soil	Increase in water-soluble carbon and redox potential, resulting in the reduction of bioavailability, increase microbial activity	Martínez-Alcalá *et al.* (2010)
Thlaspi goesingense	Soil from serpentine site	Increase in DOC and water-soluble Ni concentrations	Wenzel *et al.* (2003)
Pteris vittata	As contaminated soil	Increase in DOC and pH, resulting in the increase in water-soluble As	Gonzaga *et al.* (2006)
Lolium perenne L.	Zn-contaminated soil	Increase in low-molecular-weight organic acids and amino acids, resulting in the increased available Zn fraction	Xu *et al.* (2007)
Thlaspi caerulescens	Agricultural topsoil where wastes from septic tanks had been applied regularly	Increase in DOC, resulting in the mobilization and complexation of Zn and Cd	Dessureault-Rompré *et al.* (2010)
Betula papyrifera	Contaminated soil from a Cu–Ni smelter	Decrease in pH and increase in DOC, resulting in the water and $BaCl_2$ extractable metal concentration	Legrand *et al.* (2005)

The major source of plant-based OH^-/H^+ fluxes affecting pH in the rhizosphere is related to the differential uptake of cations and anions by plant roots (Tang and Rengel, 2003). For example, plants receiving NH_4^+ will counterbalance the corresponding excess of positive charges by releasing equivalent amounts of H^+ in the rhizosphere, thereby decreasing rhizosphere pH. Apart from this, nitrogen transformation and nitrate leaching in the nitrogen cycle have been suggested to be major causes of soil acidification (Bolan and Hedley, 2003).

Acidification affects the solubility and speciation of metal(loid) ions in several ways, foremost of which include: (a) modification of surface charge in variable charge soils; (b) altering the speciation of metal(loid)s; and (c) influencing the redox reactions of the metal(loid)s (Adriano, 2001). Adsorption of metals almost invariably decreases with increasing soil acidity (or decreasing pH; Tiller, 1989; Yang *et al.*, 2006). Three possible reasons have been advanced for this phenomenon (Naidu *et al.*, 1994). First, in variable charge soils, a decrease in pH causes a decrease in surface negative charge resulting in lower cation adsorption. Second, a decrease in soil pH is likely to decrease hydroxy species of metal cations (MOH^{n+}) which are adsorbed preferentially over mere metal cation. And third, acidification causes the dissolution of metal(loid) compounds, resulting in an increase in their concentration in soil solution.

In the case of metalloids, such as As, the effect of soil acidity on adsorption is manifested through two interacting factors—the increasing negative surface potential on the plane of adsorption and the increasing amount of negatively charged As^{5+} species present in soil solution. While the first factor results in lower As^{5+} adsorption, the second factor is likely to increase adsorption. Thus, the pH effect on As^{5+} adsorption is largely influenced by the nature of the mineral surface. For example, in soils with low oxide content, increasing pH had little effect on adsorption, while in highly oxidic soils, adsorption decreased with increasing pH (Smith *et al.*, 1999).

Carbon compounds and nutrients are released by plant roots into the rhizosphere by "rhizodeposition" (Grayston *et al.*, 1997; Jones *et al.*, 2004). Rhizodeposits, which mostly consist of carbohydrates, carboxylic acids, and amino acids, are responsible for enhanced microbial growth (Aira *et al.*, 2010; Lynch and Whipps, 1990). The role of various compounds in root exudates has been examined for their potential impact on the biogeochemistry of metal(loid)s via complexation and redox reactions. Among the range of carboxylates exuded in the rhizosphere, malate, citrate, and oxalate are expected to have the most dramatic effect due to their implication in the complexation of metal(loid)s (Bolan *et al.*, 1996; Hinsinger, 2001).

In rhizosphere, some prokaryotic (bacteria, Archaea) and eukaryotic (algae, fungi) microorganisms excrete extracellular polymeric substances (EPS), such as polysaccharides, glycoprotein, lipopolysaccharide, soluble peptide, etc. These substances possess a substantial quantity of anion functional groups that can absorb metal(loid) ions. A number of microbes are involved in EPS production viz, *Bacillus megaterium, Acinetobacter*, *Pseudomonas aeruginosa*, sulfate-reducing bacteria, and Cyanobacteria (Satpute *et al.*, 2010). The cell wall of microbes also plays a major role in metal(loid) adsorption and redox reactions. The metal(loid)s uptake by stoichiometric interaction between functional groups of cell wall composition, including phosphate, carboxyl, amine as well as phosphodiester, has been well documented (Liu *et al.*, 2003; Schiewer and Volesky, 1995). Similarly, the higher rates of volatile Se produced from the vegetated plots with added methionine compared to bare irrigated plots have been attributed to additional microbial activity associated with plant roots (Banuelos and Lin, 2007).

4.4. Hydraulic control

Hydraulic control is the term given to the use of plants to control the migration of subsurface water through the rapid uptake of large volumes of water by the plants through transpiration. The plants are effectively acting as natural hydraulic pumps, which—when a dense root network has been established near the water table in the soil—can transpire large volume of water per day (e.g., 6 L of water $plant^{-1}\ m^{-2}\ d^{-1}$; equal to 2190 mm per year—Ashwath and Venkatraman, 2010). Terrestrial plants add 32×10^3 billion tones of water vapor to the atmosphere annually through transpiration—equivalent to about 30% of the precipitation that falls on land (Hetherington and Woodward, 2003). This fact has been utilized to decrease the migration of contaminants from surface water into the groundwater and drinking water supplies.

Plants regulate the movement of contaminants through leaching and surface runoff by controlling the flow of water in soils (i.e., hydraulic control). For example, phytostabilization (i.e., phytocapping) of contaminated sites involves placing a layer of soil material and growing dense vegetation on top of the soil layer (Chen *et al.*, 2007; Venkatraman and Ashwath, 2007). The water holding capacity of the soil layer allows it to act as a "sponge" to reduce infiltration during rain events, particularly when plants are inactive. During the growing season, the evapotranspiration activity of the plants and soil surface acts as a "bio-pump" that reduces the moisture content of the soil layer during rain and irrigation events. For an effective site water balance, it is important that appropriate plant species are chosen and the soil growing conditions including depth and fertility optimized. Trapping and consuming water in the root zone result in less volume of water to act as a vehicle to carry contaminants beyond the grasp of roots, thereby leading in their leaching to groundwater (Clothier and Green, 1997). Barton *et al.* (2005) noticed that phytostabilization of a landfill site containing coal waste using loblolly (*Pinus taeda*) and Virginia (*Pinus* *virginiana*) has resulted in a decrease in the drainage volume by facilitating water loss through transpiration.

Contaminants move in soils by diffusion and mass flow processes (Grifoll and Cohen, 1996). Solutes diffuse through soils and aquifer materials in response to differences in energy from one point to another. These energy gradients may be caused by differences in concentration or temperature within the system. The principal process of movement of contaminants in soils and groundwater is mass flow. Dissolved constituents in water move through the soil, with the water acting as a carrier of the contaminants. Plant-induced hydraulic control influences both these transport processes, thereby regulating the movement of contaminants in soils (Robinson *et al.*, 2006).

Some of the metal(loid)s are essential for both microorganisms and higher plants and their physiological uptake involves both active and passive processes (Huang, 2004). Both microorganisms and higher plants exhibit specific mechanisms for the uptake of metal(loid)s that involve carrier systems associated with active ionic influxes across the cell membrane. Metabolically active processes are slower than passive absorption, demanding the presence of suitable energy source and ambient conditions. It has often been observed that an increase in transpiration rate results in higher metal(loid)s uptake, especially those elements that are taken up via passive process (Tables 4 and 5). For example, Liao *et al* (2006) and Grifferty and Barrington (2000) observed an increase in Pb and Zn uptake by lettuce and wheat, respectively, with an increase in transpiration rate. In these studies, high-transpiration rate produced significantly larger quantity of transpiration stream of water to drive water-soluble Zn and Pb uptake across plasma membranes in roots than low transpiration did (Fig. 4A and B).

5. Factors Affecting Phytostabilization

Soil, plant, contaminant, and environmental factors determine the successful outcome of phytostabilization technology in relation to both the remediation and revegetation of contaminated sites.

5.1. Soil factors

As the establishment of vegetation is critical to phytostabilization, the physical, chemical, and biological properties of soils which control plant growth determine the successful outcome of this technology. Further, soil properties also regulate the dynamics of metal(loid)s thereby affecting their stabilization in soils.

Table 4 Selected references on the effect of transpiration on the uptake of metal(loid)s

Plant species	Metal(loid)s	Observations	Reference
Lettuce	Pb: $Pb(NO_3)_2$ solutions of different concentrations (100, 200, and 300 mg L^{-1} of Pb) were added to the quartz sand.	Pb uptake by lettuce increased with an increase in transpiration rate.	Liao *et al.* (2006)
Wheat	Zn: Pots were irrigated using a fertilized solution with five different levels of: 0, 2, 10, 25, and 50 mg L^{-1}.	Zn uptake increased with an increase in transpiration rate.	Grifferty and Barrington (2000)
Wheat	Zn, Cd: Two types of sands with a low and high fertility with solutions containing various levels of Cd/Zn (0/0, 0.01/0, 0.10/0, 0.50/0, 0/25, 0.01/25, 0.10/25, 0.50/25, and 0.50/50 mg L^{-1}).	Shoot Zn and Cd levels of wheat plant increased with higher transpiration rates.	Salah and Barrington (2006)
Buckwheat (*Fagopyrum esculentum* L.)	Zn, Cu: Pots received irrigation treatments containing Zn (0 and 25 mg L^{-1}) and Cu (0, 5, 10, and 15 mg L^{-1}).	Plant Cu and Zn uptake increased with transpiration rates.	Tani and Barrington (2005)
Phytolacca americana	Cd: Zn and Mn smelter and Cu mine tailing.	There was a significantly positive relationship between the shoot Cd concentration and the leaf transpiration of *P. americana*.	Liu *et al.* (2010)
Sedum alfredii	Cd: Contaminated soil due to mining activities.	Inhibition of transpiration rate in the hyperaccumulating ecotype of *S. Alfredii* has no essential effect on Cd accumulation in shoots of the plants.	Lu *et al.* (2009)
Atriplex halimus subsp. *schweinfurthii*	Cd: Modified Hoagland nutrient solution containing cadmium chloride ($CdCl_2$; 0, 50, 100, 200, and 400 μM).	Increased $CdCl_2$ decreased chlorophyll concentration, transpiration, and root hydraulic conductivity.	Nedjimi and Daoud (2009)
Wheat seedlings (*Triticum durum*)	Cd: Hoagland–Arnon nutrient solution containing 0.04 mM of cadmium acetate.	Cadmium treatment led to an inhibition of growth rate, transpiration, and ion uptake by wheat seedlings.	Veselov *et al.* (2003)

Table 5 Selected references on using plants for hydraulic control

Plant species	Transpiration rate	Attributes for phytostabilization application	Reference
Buckwheat	The change in volumetric water content in the presence of plant was smaller than that of the control with rainfall.	The total amount of Pb in the leachate was strongly correlated with the amount of leachate. During the cultivation period, the total amount of Pb leached in the control was 1.28 mg per container, while in the presence of buckwheat, the total amount of Pb was ~22.7% of the control. Moreover, with buckwheat cultivation, Pb polluted leachate resulting from rainwater was prevented.	Honda *et al.* (2007)
Willow	Average amplitude in the 6-year-old willow cover system was 9.2 mm d^{-1} (1.5–16.9 mm d^{-1}) and amplitudes in other treatments (systems) ranged from 1.8 to 2.8 mm d^{-1}.	Phytoremediation effectiveness in establishing hydraulic control was tested using a sine wave function to describe diurnal, plant-mediated max–min water table amplitudes.	Kline (2008)
Tectona grandis	The reforested land has the highest steady infiltration rate due to better soil structure and more macropores created by root activity and high organic matter content. The soil water retention was highest in the reforested soil.	Increased infiltration and water retention will decrease surface run off and conserve soil and water, restoring the hydrological balance.	Mapa (1995)
Willow tree (*Salix* spp.)	200 L d^{-1}	Plants having these characteristics may provide an inexpensive alternative to mechanical pump and treat systems for contaminated ground water in shallow aquifers.	Gatliff (1994)

Grass and forest cover	With a continuous and invariant input of ^{90}Sr to the soil (37 kBq m^{-2} $year^{-1}$), both the predicted annual and cumulative hydrologic flux of ^{90}Sr from the soil were reduced by 16% under forest cover, relative to losses under grass cover, due to greater evapotranspiration by the forest. Mean leaching losses were 67 cm under the forest cover and 86 cm under the grass cover due to modeled differences in evapotranspiration.	Over a period of 30 years, and under various management strategies, the model predicted that $<15\%$ of the ^{90}Sr initially present in soil at a contaminated site was lost through hydrologic transport and $<53\%$ was lost by radioactive decay. Phytostabilization may be important in the management of radioactive land.	Garten (1999)
Willow (*Salix viminalis*)	Perennial root system of *Salix viminalis* lowers the risk of leaching.	Concentrations of P, K, Ca, Mg, S, Mn, Zn, Cu, Ni, and Cd increased significantly with height, which was assumed to be mainly a consequence of increasing bark proportions.	Sander and Ericsson (1998)

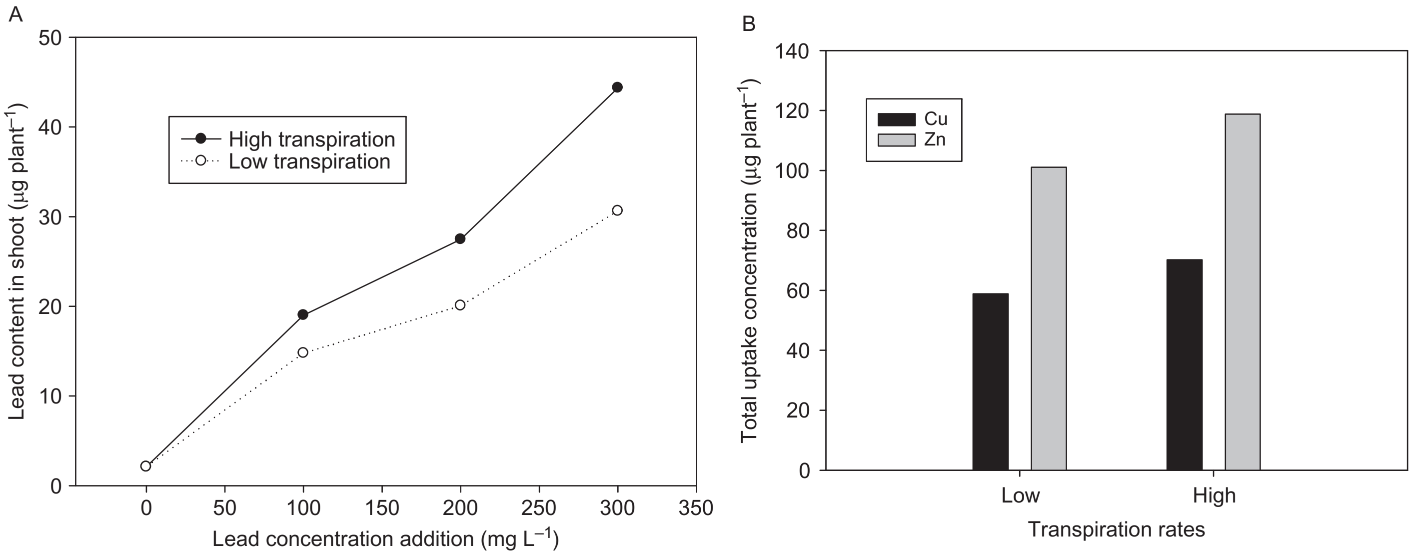

Figure 4 (A) Effect of transpiration on Pb uptake by lettuce (Liao *et al.*, 2006). (B) The mass of Cu and Zn extracted by buckwheat under low- and high-transpiration rates (Tani and Barrington, 2005).

Often, contaminated sites are not conducive for plant growth due to metal(loid) toxicity, lack of nutrients and microbial activity, and poor physical properties. For this reason, the phytostabilization of contaminated sites may require the amendment of the soils to stimulate plant growth. Some of the common amendments used to improve the soil conditions include biosolids, lime, and green waste. Some of these amendments used for improving the soil properties also enhance the efficiency of phytostabilization by altering the solubility and bioavailability of contaminants (see Section 7). For example, biosolids are generally applied to the cultivated land, given that it contains a wide range of nutrients and carbon, thereby improving the soil conditions for crop production. However, it has been recognized that the long-term application of biosolids to cultivated land has potential detrimental effect in terms of food safety due to the contaminants such as heavy metal(loid)s contained in the biosolids. Therefore, the application of biosolids to contaminated sites for phytostabilization performance will be more socially acceptable. Moreover, the contaminants in the biosolids could be also remediated by the plants.

Soil plays a significant role in controlling the immobilization and bioavailability of contaminants in the environment, thereby affecting the phytostabilization of contaminated sites. The primary soil factors influencing the immobilization and bioavailability of contaminants include soil pH, soil organic matter, cation and anion exchange capacities (AECs; available charged sites on soil surfaces), texture (clay content), and soil type.

Soil pH is one of the key parameters influencing the sorption of both inorganic and ionizable organic contaminants given that it controls virtually all aspects of contaminant and biogeochemical processes in soils. These processes include solubility, precipitation, speciation, and sorption as well as microbial activity. In most variable charge soils such as the strongly weathered tropical soils and less-weathered Andisols, increasing soil pH results in an increase in the number of negatively charged sites with a concomitant decrease in the positively charged sites (Auxtero *et al.*, 2004; Bolan *et al.*, 1999; Naidu *et al.*, 1994, 1996). In addition to its effect on surface chemical properties, soil pH also controls the speciation of contaminants. For metals, the net charge of the metal complexes and their precipitation/dissolution reactions are directly impacted by soil pH (Zeng *et al.*, 2010).

Organic contaminants and most metal(loid)s bind strongly to organic matter in soils, thereby reducing their bioavailability. Organic contaminants preferentially partition to the nonpolar domain of organic matter relative to the polar aqueous phase (Chiou *et al.*, 1984; Poerschmann and Kopinke, 2001), while the organic acid functional groups typically present in organic matter have a high affinity to attract metal cations (Zaccone *et al.*, 2009). Organic matter also plays a vital role in the reduction of metal(loid)s such as Cr^{6+}, thereby reducing their toxicity and bioavailability (Bolan *et al.*, 2003b). Another indirect effect of soil components including organic matter is their role on limiting contaminant mass transfer. The rate of mass transfer of a contaminant from soil particles to the surrounding pore water is inversely proportional to the contaminant's soil pore water distribution coefficient (Clothier *et al.*, 2008; Menzie *et al.*, 2000). Therefore, with increasing organic matter content, retention of some metal(loid)s increases and rates of release decrease, thereby decreasing their overall bioavailability (Stokes *et al.*, 2005).

As discussed above, pH influences sorption through its effect on surface charge as quantified by cation and AECs of soils. In variable charge soils, while the AEC, a measure of available positively charged surface sites, decreases with increasing soil pH, the cation exchange capacity (CEC), a measure of negatively charged sites, increases with pH. Both AEC and CEC vary with the clay mineral content and type, organic matter, and soil pH (Bohn *et al.*, 1985). Soils with high clay content will have a high affinity to sorb cationic metal(loid) species due to high CEC, thus making contaminants less bioavailable relative to sandy soils. The AEC of most soils is small. Therefore, it is not generally considered an important parameter in assessing contaminant availability at most sites in the temperate regions. However, soils in the tropics and in volcanic and less-weathered soils such as Andepts can have a significant AEC.

In addition to soil pH, many other environmental variables influence the ion exchange characteristics of soils. These include the presence of inorganic and organic ligands that bind specifically to soil colloid surface. While the specific sorption of anions onto variable charge components has often been shown to increase the net surface charge (i.e., CEC) of soils and consequently increase the capacity of soils to bind cationic metals, sorption of cations increases the net positive charge, resulting in increased retention of anions (Bolan *et al.*, 1999). This process has been described by a number of researchers as anion-induced cation sorption (Bolan *et al.*, 1999, 1977; Wann and Uehara, 1978) and cation-induced anion retention (Bolan *et al.*, 1994; Cichota *et al.*, 2007). Metall(oid)s can also form complexes and precipitates with inorganic soil constituents, such as carbonate and phosphate minerals under certain soil conditions (Bolan *et al.*, 2003a). Carbonate– and phosphate–metal complexes have varying degrees of solubility and reactivity depending on the metal, its oxidation state, the ligand to which it is bound, and pH. Environmental managers often use changes in surface chemical properties of soils as influenced by pH and ligand ions such as P to reduce metal bioavailability in soils (Basta *et al.*, 2001; Bolan *et al.*, 2003a; Kumpiene *et al.*, 2007). Raising the soil pH using lime amendments reduces plant uptake of heavy metal such as Cd due to enhanced binding and hence reduced bioavailability of the metal (Bolan *et al.*, 2003c).

The nature of soil types varies considerably depending on the geographical location. Alfisols, Entisols, Inceptisols, Ultisols, Vertisols, and Oxisols are all commonly found in tropical and subtropical regions receiving more than 500 mm mean annual rainfall. Landscapes throughout the tropics and subtropics are, however, dominated by Oxisols and Ultisols occupying extensive areas of potentially highly productive soils. Given the widely different surface charge and chemical properties of the soils, their ability to adsorb contaminants varies considerably. Consequently, contaminant bioavailability varies significantly with soil type due to differences in soil properties. For instance, Naidu *et al.* (2008b) examined the effect of soil types on sorption of Cd and demonstrated that soils from the temperate region consisting of 2:1 layer silicate minerals generally sorbed the highest amount of Cd while the least was recorded for an Oxisol with a pH of 5.

5.2. Plant factors

Plants are central to phytostabilization because plant characteristics regulate both the transformation of metal(loid)s and binding of soil particles. Nyer and Gatliff (1996) predict that phytoremediation will be the next hot technology for the environmental remediation field, yet they caution "... that this technology is not simply the buying of plants from the local K-mart and placing them in the soil near a contaminated site!." Subsequently, phytostabilization has been slowly adopted to remediate some contaminated sites, while the technical and commercial success of phytoextraction is conspicuously absent (Robinson *et al.*, 2009). Plants with desirable phenotypic and genotypic characteristics are selected for the sustainable management of soil remediation (Tables 5 and 6). The density, morphology, and depth to which plant roots penetrate the soil are critical to potential application of this technology. Enhancement of root biomass and morphology is therefore desirable in any phytostabilization operation. Plants with dense and deep roots that can exploit larger volumes of contaminated soils have much larger surface area, thus facilitating the stabilization of soils and enhancing the microbial volatilization of metal(loid)s in the rhizosphere. Fibrous roots offer a large surface area for contaminant absorption (facilitating phytoextraction) and plant–microbe interactions (facilitating phytovolatilization). In addition, deep-rooted plants with high transpiration rates, such as hybrid poplar, can access deeper soil depths of as much as 6 m deep (Unterbrunner *et al.*, 2007). Deep-rooted willow species have been identified to accumulate substantial amounts of Cd and Zn (Utmazian *et al.*, 2007) and hold promise for their use in phytoextraction. Granel *et al.* (2002) observed a large variation in both leaf concentration of Cd and its bioaccumulation coefficient (plant:soil concentration ratio) among 15 clones of Tangoio willow (*Salix matsudana*) which they attributed to the difference in genetically controlled, plant-mediated changes in Cd bioavailability.

Strategies to increase root biomass and to enhance root/rhizosphere associations, including mycorrhizae, have been reviewed by several authors (Cunningham *et al.*, 1997; Entry *et al.*, 1996; Morgan *et al.*, 2005; Stomp

Table 6 Some tree and shrub species used for revegetating mined land (Flege, 2000)

Latin name	Common name	Mined land
Acer pseudoplatanus	Sycamore maple	W-Europe, E-Europe
Alnus glutinosa[a,b]	European/black alder	UK, W-Europe, E-Europe, US/Canada
Alnus incana'[a,b]	White/gray alder	UK, E-Europe
Caragana arborescens[a,c]	Siberian peashrub	W-Europe, US/Canada
Eleagnus umbellata[d]	Autumn olive	W-Europe, US/Canada
Fraxinus Americana	White ash	UK, E-Europe
Fraxinus excersior	European ash	UK, W-Europe, US/Canada
Hippophae rhamnoides	Sea buckthorn	UK, W-Europe, E-Europe, Russia
Larux decudya	European larch	UK, E-Europe
Melia azedarach	Pride-of-India; mahogany tree	India, Australia
Pinus contorta	Lodgepole pine	UK, W-Europe, US/Canada
Pinus nigra	Austrian/Corsican pine	UK, US/Canada
Pinus sylvestris	Scots pine	UK, US/Canada
Populus tremiula	Aspen	UK, W-Europe, E-Europe, Russia, Ukraine, India, Australia, NZ, US/Canada
Prunus serotina	Black cherry	W-Europe, US/Canada
Quercus petraea	Durmast oak	W-Europe, E-Europe, US/Canada
Quercus robur	English/truffle/summer oak	UK, W-Europe, E-Europe
Rhus tribolata	Skunkbush sumac	W-Europe, US/Canada
Robinia pseudoacacia1	Black locust	UK, E-Europe, Ukraine, Australia, US/Canada
Rosa multiflora	Multiflora rose	W-Europe, US/Canada
Salix alba	White willow	UK, US/Canada
Sorbus aucuparia	Rowan mountain ash	UK, E-Europe

[a] Nitrogen-fixing species.
[b] Acid sensitive.
[c] Acid tolerant.
[d] Salt tolerant.

et al., 1993). Genetic engineering may provide a tool to modify root morphology and/or to identify and clone relevant enzyme-controlling genes into more deep-rooted plants. However, as demonstrated by the recent discovery of As-accumulating fern species (Francesconi *et al.*, 2002; Ma *et al.*, 2001), additional screening combined with traditional breeding also offers a promising resource for enhancing phytoextraction and associated rhizosphere capabilities (Baker and Whiting, 2002; Fitz *et al.*, 2003). However, it is unlikely that genetically modified plants that extract contaminants will find widespread use. First, the technology of phytoextraction, for which these plants would be used, is unsuitable for most contaminated sites (Robinson *et al.*, 2009), and second, environmentalists could reasonably claim that such plants represent an environmental and human health risk by facilitating the passage of toxic elements into the food chain. Modification of root morphology could change microbial associations in the rhizosphere qualitatively and quantitatively (Cunningham *et al.*, 1997). For example, a mature scotch pine has been estimated to have 50,000 m of roots with 5 million root tips. These root tips could support the growth of about 5 kg of bacteria. *Agrobacterium rhizogenes* transformation could increase the number of root tips two- to fourfold and result in enhanced microbially mediated remediation (Stomp *et al.*, 1993). This is complemented by findings that uptake of Cd from sewage sludge by *A. rhizogenes* transformed *Calystegia pepium* plants was higher than in non-transformed specimen (Tepfer *et al.*, 1989).

Among the most extreme examples of metal(loid)-tolerant plant are the so-called hyperaccumulators, which can accumulate elements such as Zn, Mn, Ni, Co, Cd, or Se at high concentrations in their above-ground biomass (Yang *et al.*, 2005). Hyperaccumulators are defined as the plant species that are capable of accumulating metal(loid)s above the threshold concentrations of 10,000 mg kg^{-1} dry weight of shoots for Zn and Mn, 1000 mg kg^{-1} for Co, Cu, Ni, As, and Se, and 100 mg kg^{-1} for Cd (Baker and Brooks, 1989; Brown *et al.*, 1994). Instead of these rather arbitrary values, the bioconcentration factor (the shoot:root ratio of metal(loid) concentration) greater than 1, which is indicating efficient root-to-shoot transportation, is now used to define hyperaccumulators (McGrath and Zhao, 2003). The major processes of metal(loid) hyperaccumulation by the plants include: (a) bioactivation of metal(loid)s in the rhizosphere through root–microbe interaction; (b) enhanced uptake by metal(loid) transporters in the plasma membranes; (c) detoxification of metal(loid)s by distributing to the apoplasts like binding to cell walls and chelation of metal(loid)s in the cytoplasm with various ligands (e.g., phytochelatins, metallothioneins, metal(loid)-binding proteins); (d) sequestration of metal(loid)s into the vacuole by tonoplast-located transporters (Yang *et al.*, 2005).

The first recognized hyperaccumulators were members of the *Brassicaceae* and *Fabaceae* families, and to date, more than 400 plant species of metal (loid) hyperaccumulator plants have been reported in the literature (Salt *et al.*, 1998). An alternative to hyperaccumulators is the use of high biomass producing nonaccumulator plants or excluder plants, which actively restrict metal(loid) uptake into the shoots. These kinds of plants can be employed for revegetation of heavy metal(loid)-contaminated sites coupled with manipulation of soil conditions to increase the metal(loid) stabilization and improve plant growth (Pulford and Watson, 2003). Revegetation of heavy metal(loid)-contaminated sites can achieve the objectives of stabilization, pollution control, visual improvement, and removal of threats to human beings (Freitas *et al.*, 2004).

The role of hyperaccumulators in phytostabilization is unclear. Generally, hyperaccumulators have a low biomass production, are exotic to most environments, and potentially facilitate the entry of metals into the food chain. Nevertheless, the hyperaccumulator *Alyssum bertolonii* has been used successfully as a colonizing plant in mine spoil (Robinson *et al.*, 2009). Here, the desirable property of the hyperaccumulator was its ability to tolerate nutrient imbalances and high Ni concentrations in the mine spoil, while adding organic matter to the spoil, thus allowing the spontaneous colonization of other species.

The selection of plants suitable for the restoration is one of the key factors to accomplish revegetation of heavy metal(loid)-contaminated sites. Plant community tolerant to the metal(loid)s plays a major role in restoration of heavy metal(loid)-contaminated sites (Banuelos and Ajwa, 1999). Plants suitable for restoration should develop an extensive root system and a large amount of biomass while keeping the translocation of metal(loid)s from roots to shoots as low as possible in soils with high metal(loid) concentrations (Rizzi *et al.*, 2004). In addition, they must adapt to diverse site conditions, establish readily, and require little money and effort to maintain. Further, they must be able to survive and reproduce in contaminated soil (Flege, 2000).

The identification of plants which exclude heavy metal(loid)s in soils is important for phytostabilization. Metal(loid) excluders can not only survive in highly polluted soils but also take up low levels of heavy metal(loid)s even in the presence of high concentrations in soils (Baker, 1981; Wenzel *et al.*, 2003). In particular, weed species often possess stress-resistant properties compared with crops and can maintain growth under adverse water and fertilizer conditions (Wei *et al.*, 2005).

Plants possess various tolerance mechanisms to withstand metal(loid) stress. Extracellularly metal(loid) tolerance may include roles for mycorrhizae and for cell wall and extracellular exudates. Tolerance could also involve the plasma membrane, either by reducing the uptake of heavy metal(loid)s or by stimulating the efflux pumping of metal(loid)s that have entered the cytosol. A variety of potential mechanisms occur within the protoplast. The mechanisms involve the repair of stress-damaged proteins such as heat shock proteins and metallothioneins, and the chelation of metal(loid)s by organic acids, amino acids, or peptides, or their compartmentation away from metabolic processes by transport into the vacuole (Hall, 2002).

Plant tolerance of heavy metal(loid)s may also be achieved by causing chemical changes to specific metal(loid)s, thereby decreasing their bioavailability (Chaney *et al.*, 1997). Deep-rooted plants can reduce the highly toxic Cr^{6+} to Cr^{3+}, which is less soluble and therefore less bioavailable (Chaney *et al.*, 1997). For example, *Eichhornia crassipes* (water hyacinth) reduced Cr^{6+} to Cr^{3+} in the fine lateral roots and transported a portion of the detoxified Cr to leaf tissues (Lytle *et al.*, 1998). Similarly, Pulford *et al.* (2001) noticed that Cr was held in plant roots and poorly translocated from root to shoot whether supplied as Cr^{6+} or Cr^{3+}, which may demonstrate reduction and stabilization of Cr in the plant roots (Pulford and Watson, 2003). Lead also can be immobilized within plant roots by the formation of the lead phosphate mineral (Cotter-Howells *et al.*, 1994). However, the effect of plants on the bioavailability of other metal(loid)s is uncertain (Pulford and Watson, 2003). The effect of plant roots and their interaction with rhizosphere bacteria on the chemistry and bioavailability of heavy metal(loid)s in contaminated soils is an area that requires much more study for successful restoration.

5.3. Contaminant factors

The reactions of contaminants affect their bioavailability and mobility, thereby influencing phytostabilization. Metal(loid)s introduced to soils undergo a number of reactions that include adsorption, complexation, precipitation, and reduction, which control their leaching and runoff losses, and bioavailability. Chemical interactions that contribute to metal(loid) retention by soil colloids include sorption and complexation with inorganic and organic ligands. Charged ions are attracted to charged soil surfaces by electrostatic and/or stronger covalent bonds (Mott, 1981), which can be specific or nonspecific in nature (Bolan *et al.*, 1999). In nonspecific adsorption, the ion charge balances on the soil surface by electrostatic attraction, while in specific adsorption, chemical bonds form between the ions and the soil surface (Spark, 1986; Sposito, 1984).

Most metal(loid) cations are strongly retained as inner sphere complexes with variable charged surfaces by the formation of covalent bonds. Metal(loid)s can react with soil organic matter by ion exchange, complexation, and precipitation. Metal(loid)s are known to form organic complexes which affect their sorption onto soil particles (Adriano, 2001). For example, Bolan *et al.* (2003d) demonstrated that the addition of organic manures increased the complexation of Cu in soils. Additionally, they observed that while Cu^{2+} adsorption measured as the change in the total Cu in soil solution was not affected by biosolids addition, Cu complexation measured as the change in free Cu^{2+} concentration increased with increasing level of biosolids. The extent of metal (loid)s–organic complex formation, however, varies with a number of factors including temperature, steric factors, and concentration. All these interactions are controlled by solution pH and ionic strength, the nature of the metal(loid)s species, dominant cation, and inorganic and organic ligands present in the soil solution.

At high soil pH and in the presence of SO_4^{2-}, CO_3^{2-}, OH^-, and HPO_4^{2-}, precipitation appears to be the predominant process when metal(loid) cation concentrations are high (Naidu *et al.*, 1996). This occurs when the ionic product in the solution exceeds the solubility product of that phase. In normal soils, precipitation is relatively unimportant, but in heavy metal-contaminated soils, precipitation process can play a major role in remediation, especially under alkaline conditions. Increasingly, addition of phosphate is being used to precipitate excessive levels of metals such as Zn (He *et al.*, 2005) and Pb (Park *et al.*, 2011b), although phosphate may mobilize arsenic if this is present as a co-contaminant.

Both chemical and biological redox reactions affect the bioavailability of metal(loid)s such as As, Hg, and Se. Because of the great heterogeneity in the pore space of most soils, zones of reducing and oxidizing conditions are often in close proximity to one another allowing roots to access the available forms at different points in the soil. Volatilization occurs through microbial conversion of metal(loid)s to their respective metallic, hydride, or methylated forms. These forms have low boiling points and/or high vapor pressure and are therefore susceptible for volatilization. Methylation is considered to be the major process of volatilization of As, Hg, and Se in soils and sediments, resulting in the release of poisonous methyl gas (Adriano *et al.*, 2004). Although methylation of metal(loid)s occurs through both chemical (abiotic) and biological processes, biological methylation (biomethylation) is considered to be the dominant process in soils and aquatic environments. Microorganisms in soils and sediments act as biologically active methylators. Organic matter provides the source of methyl donor for both biomethylation and abiotic methylation in soils and sediments. Selenium biomethylation is of interest because it represents a potential mechanism for the removal of Se from contaminated environments, and it is believed that methylated compounds, such as dimethyl selenide, are less toxic than dissolved Se oxyanions (Meyer *et al.*, 2007).

Contaminants affect phytostabilization by changing plant growth and associated microbial communities. Phytostabilization of mine tailings is sometimes impractical, as tailings are characterized by elevated concentrations of metals such as As, Cd, Co, Mn, Pb, and Zn, and microbial community is extremely low (Mendez and Maier, 2008). In such cases, the establishment of vegetation requires soil amendments to reduce the bioavailability of phytotoxic metal(loid)s using soil amendments. For example, Ko *et al* (2008) noted that germination of Indian mustard seeds (*Brassica juncea)* was inhibited in the presence of high levels of As^{5+} in mine tailings and application of lime and iron oxide decreased bioavailable As concentration, thereby increasing germination.

Mine spoils are the most common environments where high metal(loid) concentrations limit plant establishment. An example is the 1.5 ha Tui Mines, Te Aroha, which has had the worst environmental effects of any New Zealand mine (Morrell *et al*., 1996). The tailings contain 0.5% Pb and 8 mg kg^{-1} Hg. Oxidation of sulfide minerals has resulted in a pH of <3, and consequently, high concentrations of the aforementioned metals are leaching into nearby waterways (Sabti *et al*., 2000). Vegetation has failed to establish on the tailings and there is considerable wind and water erosion, which spreads contaminated materials onto surrounding areas. Robinson and Anderson (2007) report the results of a phytostabilization field trial on these tailings. The trial involved raising the pH of the tailings with repeated lime applications, the incorporation of organic matter (mushroom compost) into the top 15 cm of the tailings, and indigenous metal-tolerant species planted. Vegetation was successfully established on the 10×10 m plot (Plate 1). This has persisted and prevented further oxidation of the sulfides beneath the plot. The roles of the plants in this phytostabilization operation are to eliminate erosion and reduce the water flux through the site and hence reduce Pb and Hg leaching.

5.4. Environmental factors

Rainfall and temperature affect phytostabilization through their effects on plant growth, contaminant reactions, and soil erosion. As most contaminated sites may not have ready access to regular water supply for irrigation, rainfall plays a vital role in the establishment of vegetation. Rainfall also controls the leaching of contaminants and erosion of soil and sediments. Temperature affects both the plant growth and soil surface characteristics such as cracking and crust formation. While cracking increases the leaching of contaminants, loose, dry, and bare soil is susceptible to wind erosion by dispersion.

Phytostabilization requires that the plants tolerate trace elements in the substrate. The species or varieties should also tolerate any nutrient imbalances in the substrate. Use of exotic species in this role is fraught, as they may establish themselves as weeds. However, exotic species are less likely to suffer from native herbivores, thus increasing growth and reducing the amount of contaminant that enters into the food chain. Competition from weeds is often more problematic than soil contaminants in phytostabilization (Dickinson *et al*., 2009).

Each contaminated site has a unique environment. Therefore, choosing the most suitable species requires a short planting trial that tests several varieties on a small area of the site, particularly for nonsoil media such as mine spoil or biosolids.

6. Advantages and Disadvantages of Phytostabilization

Phytostabilization is considerably less expensive than other remediation technologies such as capping and soil removal (Miller and Miller, 2007). Nevertheless, phytostabilization has significant setup and ongoing costs. Phytostabilization requires that the site be assessed and the most suitable soil amendments and plant species are chosen. Thus, science costs are part of phytostabilization. Whole system models, such as the Phyto-DSS (Robinson *et al.*, 2003), can be used to calculate the impact of vegetation on the site and thus determine whether phytostabilization will meet environmental regulations. There are usually ongoing monitoring costs for phytostabilization. Phytostabilization will only be used if it satisfies environmental regulations, costs less than competing technologies, and costs less than inaction (Robinson *et al.*, 2009).

There is potential to generate income from the vegetation used in phytostabilization. Phytostabilized sites can be managed so that they produce valuable products from the biomass of the vegetation. These may be nonedible products such as timber, bioenergy, biochar, or the production of essential oils or phytochemicals. Revenue may also be obtained from carbon fixation schemes because the plants, left on the site in perpetuity, represent a small carbon sink.

Phytostabilization can be used to create an ecosystem of indigenous flora and fauna, thus adding to the ecological value of the site (Plate 3). In cases such

Plate 3 Phytostabilization of Bunker Hill, Idaho, Superfund site (courtesy Dr. Sally Brown).

as the Guadiamar river phytomanagement scheme, the vegetation used to phytostabilize the site provides a "green corridor" for migrating animals between two national parks (Dominguez *et al.*, 2010). As the site is necessarily left vegetated, it is thus more esthetically appealing than sites capped with concrete, or pits resulting from soil removal. Establishing vegetation with more than 250,000 trees, shrubs, and saltbush around a lead smelter site in Port Pirie, South Australia has been crucial in reducing Pb dust movement. Red gum trees have been planted on site and *Arundo donax* formed thick stable clumps which have ability to act as a windbreak (http://www.tenby10.com/Index).

One of the major issues with phytostabilization technology is a successful operation that entails the contaminants remain on site. Therefore, site will always be contaminated and unsuitable for other land uses. The land is no longer able to be used for food production. In contrast, some engineering technologies, such as soil replacement, can return the site to its former land use. Phytostabilization suffers from a risk of future adverse advents and thus requires ongoing monitoring. Some soil processes, such as the oxidation of carbonates, can result in a rapid drop in pH and remobilization of metal (loid)s. Extreme weather events, such as high rainfall and flooding, can result in mass migration of contaminants.

The vegetation may provide an exposure pathway for contaminants to enter food chains. Dominguez *et al.* (2010) showed that the use of *Populus alba* in the Guadiamar phytostabilization program exposes herbivores to high Cd concentrations through accumulation into the leaves.

7. Enhancement of Phytostabilization

Phytostabilization can be enhanced by increasing plant growth and altering bioavailability of metal(loid)s using both organic and inorganic amendments. Although fertilizer application increases plant growth thereby enhancing phytostabilization, this approach can lead to environmental degradation resulting from the loss of nutrients through leaching and gaseous emission. Therefore, organic amendments such as biosolids and manures and biological inoculants such as plant growth-promoting bacteria (PGPB) are used to enhance plant growth. Similarly, a number of organic and inorganic amendments are used to alter the bioavailability of metal(loid)s. This section examines the values of some of these amendments in enhancing phytostabilization technology.

7.1. Plant growth-promoting bacteria

Bacteria associated with plants may have profound effects on the plant growth and nutrition through a number of mechanisms such as increasing nutrient availability and altering root morphology and surface area.

Improvement of the interactions between plants and beneficial rhizosphere microorganisms can enhance biomass production and tolerance of the plants to heavy metal(loid)s, thereby leading to successful phytostablization (Belimov *et al.*, 2005). Although these strains are helpful and persistent in pot trial for the phytostabilization (de-Bashan *et al.*, 2010), microorganisms under field conditions might face competition problems with existing microbial communities (Sessitsch and Puschenreiter, 2008).

7.1.1. Increase in nutrients availability

Nitrogen availability is the main yield-limiting factor in plant growth, especially in contaminated sites (Mantelin and Touraine, 2004). Many of the PGPB can provide nitrogen fixed to the host plant (Mantelin and Touraine, 2004). Nitrogen deficiencies can be corrected initially by applying fertilizer, but their effects are not permanent. However, PGPB can support long-term nitrogen cycling by providing a continuous supply of nitrogen (Flege, 2000).

Sajjad *et al.* (2004) have demonstrated that nitrogen fixing and phytohormone producing bacteria *Enterobacter* sp. isolated from sugarcane have beneficial effects on the growth of micropropagated sugarcane plantlets. By using ^{15}N isotope dilution technique, maximum nitrogen fixation contribution (28% of total plant nitrogen) was detected in plantlets inoculated with bacteria (Sajjad *et al.*, 2004). Similarly Bashan *et al.* (1998) showed that diazotrophic filamentous cyanobacterium *Microcoleus chthonoplastes* inoculated onto young mangrove seedlings significantly increased the levels of total N and ^{15}N isotope in the inoculated leaves over the noninoculated plants. *Azospirillium brasilense* has been shown to stimulate N accumulation by the roots and N concentration in the tissues, thereby increasing plant growth (María *et al.*, 2002).

Application of phosphorus solubilizing bacteria, *Bacillus megatherium* var. *Phosphaticum* to soil planted with sugarcane has been shown to increase the plant available P status in the soil, thereby increasing cane yield (Sundara *et al.*, 2002). Similarly, Harris *et al.* (2006) noticed an increase in the solubilization of dicalcium phosphate with phosphate-solubilizing bacteria, which resulted in an increase in wheat grain yield. Villegas and Fortin (2002) reported that the interactions between arbuscular mycorrhizal fungi with phosphate-solubilizing bacteria such as *Pseudomonas aeruginosa* and *Pseudomonas putida* significantly increased the levels of soluble P in soil.

In addition to N and P, other micro- and macronutrients uptake can be stimulated by bacteria. Inoculation with associative rhizobacteria slightly stimulated root length and biomass of hydroponically grown Cd-treated barley seedlings. The bacteria significantly increased the total amount of nutrients such as P, Mg, Ca, Fe, Mn, and Na in roots and shoots of the Cd-treated plants. The results showed that associative bacteria were capable of decreasing partially the toxicity of Cd for the barley plants through the improvement in uptake of nutrient elements (Belimov and Dietz, 2000).

Siderophores are low-molecular-weight Fe^{3+} coordination compounds that bacteria excrete under Fe-deficient conditions (Gadd, 1992). The elevated level of heavy metal(loid)s in soil interfere with uptake of nutrients such as Fe and P, but siderophores producing bacteria can promote plant growth by increasing nutrient uptake (Zayed and Terry, 2003). Siderophore-producing and phosphate-solubilizing isolates, *Pseudomonas* sp. and *Bacillus* sp., protected the plants against the inhibitory effects of Cr and these effects might be the results of enhanced uptake of soil minerals such as Fe and P by the plants (Rajkumar *et al*., 2006). Sharma and Johri (2003) used *Pseudomonas fluorescens* sp., which produced siderophores for maize growth promotion experiments. Inoculation of seeds with the bacteria showed significant increase in germination percentage and plant growth. Maximum shoot and root length and dry weight were observed with 10 μM Fe^{3+} along with bacterial inoculants suggesting the value of siderophores producing PGPB in enhancing crop productivity in calcareous soil system which is deficient in Fe (Sharma and Johri, 2003).

Burd *et al*. (2000) inoculated *Kluyvera ascorbata* and a siderophore overproducing mutant of this bacterium into tomato, canola, and Indian mustard seeds in Ni, Zn, and Pb-contaminated soils. In most cases, the siderophore overproducing mutant *K. ascorbata* exerted a more pronounced effect on plant growth than the wild-type bacterium. The data indicate that the ability of these bacteria to protect plants against the inhibitory effects of high concentrations of Ni, Pb, and Zn is related to the bacteria providing the plants with sufficient Fe by siderophore production (Burd *et al*., 2000).

Similar to other PGPB, siderophore-producing PGPB also can protect host plants from phytopathogenic diseases. PGPB control the damage to plants from phytopathogens by secretion of siderophores to prevent pathogens in the immediate vicinity from proliferating (Glick and Bashan, 1997). *Serratia plymuthica* isolated from soil around melon roots produced the antibiotic pyrrolnitrin, siderophores, and Indole-3-acetic acid (IAA), thereby suppressing a wide range of phytopathogenic fungi *in vitro*. Foliar application of the bacteria protected cucumber against *Botrytis cinerea* gray mold and *Sclerotinia sclerotiorum* white mold diseases of leaves under greenhouse conditions (Kamensky *et al*., 2003).

7.1.2. Alteration of root morphology

An increase in the root surface area and the volume of soil explored by the root, which leads to increased nutrient uptake, is the most commonly proposed explanation for the beneficial effects of PGPB on plant growth. The improvement in mineral nutrition promotes shoot growth and this rationale is consistent with the observation that plants inoculated with *Azopsirillum* take up N, P, K, and microelements more efficiently from the soil (Okon and Vanderleyden, 1997). In the nutrient deficient conditions, PGPB increase the elongation rate of lateral roots resulting in a more branched root system and an increase in root surface area. This results in increased mineral uptake which, in turn, enhances shoot biomass accumulation (Lifshitz *et al.*, 1987; Mantelin and Touraine, 2004).

Soil physical parameters are critical for plant growth. Many metal(loid)-contaminated mine sites have poor soil structure, resulting in poor water infiltration or retention. Alami *et al.* (2000) demonstrated that *Rhizobium* sp. isolated from the rhizosphere of sunflower caused a significant increase in root-adhering soil per root dry mass and in soil macropore volume even in dry conditions. Further, inoculated sunflower increased nitrogen uptake, thereby promoting plant growth. Isolated strain was also able to relieve the effect of water stress on sunflower growth (Alami *et al.*, 2000).

Plants produce ethylene in response to stress (Deikman, 1997). However, high levels of ethylene lead to the inhibition of root elongation. PGPRs contain an enzyme, 1-aminocyclopropane-1-carboxylate (ACC) deaminase, that catalyzes the cleavage of ACC, which is the precursor of ethylene, and as a result, the endogenous ethylene concentration in plants is reduced (Glick *et al.*, 1998). These processes can promote plant growth by decreasing plant's ethylene level. When canola seeds were imbibed in several ACC deaminase containing strains of bacteria, the ACC levels in these roots were lowered and the growth of canola seedling roots was increased (Penrose *et al.*, 2001). Hall *et al.* (1996) demonstrated that PGPB promote root elongation in a variety of plants. Seeds of canola, lettuce, tomato, and wheat when inoculated with PGPB (*P. putida*) increased the root lengths. These observations are consistent with a model in which promotion of root growth by *P. putida* is a consequence of inhibition of ethylene production within the developing seedling (Hall *et al.*, 1996).

ACC deaminase activity can not only improve root growth but also protect plant from pathogenic disease. Transformed *Pseudomonas fluorescens* strains with ACC deaminase activity improved its ability to protect cucumber against Pythium damping-off, and potato tubers against Erwinia soft rot in small completely sealed containers (Wang *et al.*, 2000).

Production of the phytohormone IAA is widespread among bacteria that inhabit the rhizosphere of plants (Patten and Glick, 1996). An Ni tolerant *Bacillus subtilis* produced substantial amount of IAA during stationary phase of growth in the medium and showed time-dependent increase in IAA production. Enhanced production of IAA (55 $\mu g\ mL^{-1}$) was noticed in the presence of tryptophan (500 $\mu g\ mL^{-1}$). The phytohormone IAA production offers great promise for sustaining the increased crop productivity (Zaidi *et al.*, 2006). In addition, Cd-tolerant bacterial strains, *Variovorax paradoxus* and *Rhodococcus* sp., isolated from the rhizosphere of Indian mustard seedlings grown in highly Cd-contaminated sites produced IAA. The bacteria also showed increased tolerance to other metal(loid)s including

Zn, Cu, Ni, and Co. These strains were capable of stimulating root elongation of *B. juncea* seedlings either in the presence or absence of toxic Cd concentrations (Belimov *et al*., 2005), and *Pseudomonas* sp. and *Bacillus* sp. facilitated rape growth (Sheng and Xia, 2006).

The primary roots of canola seedlings from seeds treated with wild-type *P. putida* were on average 35–50% longer than the roots from seeds treated with the IAA-deficient mutant and the roots from uninoculated seeds, and these results suggest that bacterial IAA plays a major role in the development of the host plant root system (Patten and Glick, 2002). Rajkumar *et al.* (2006) isolate Cr^{6+} resistant PGPB, *Pseudomonas* sp. from heavy metal(loid) contaminated soils. They noticed that the inoculation of bacteria protected the plants against the inhibitory effects of Cr and promoted the growth of Indian mustard and this effect was higher in IAA producing bacteria than IAA nonproducing bacteria.

Gibberellins are phytohormones that control a number of developmental and physiological processes in plants (Crozier *et al*., 2000) and affect root elongation (Tanimoto, 1987), promotion of root growth, and root hair abundance (Bottini *et al*., 2004). Bacteria and fungi also produce Gibberellins. *Bacillus pumilus* and *Bacillus licheniformis,* isolated from the rhizosphere of alder, had a strong growth-promoting activity. Gibberellins (GA_1, GA_3, GA_4, and GA_{20}) in extracts of bacterial media were detected by full-scan gas chromatography–mass spectrometry analyses.

7.2. Inorganic amendments

A number of inorganic amendments such as liming materials, phosphate compounds, and clay materials are used for immobilizing heavy metal(loid)s and improving soil conditions to facilitate revegetation of contaminated soils (Kumpiene *et al*., 2007). For example, the addition of liming materials is a common practice to overcome plant growth constrains relating to soil acidification. Normally, as the pH decreases, the mobility of some metal(loid)s is elevated. The solubility of Zn and Ni in dredged sediment increased when the pH was less than 6, pH 4 for Cd, pH 6 for Co, and pH 2 for Cu and Pb (Tack *et al*., 1996). The addition of lime as ground limestone not only raises pH but also renders metal(loid)s insoluble, thus reducing their bioavailability to plants (Down, 1975).

Lime is effective in reducing the phytoavailability of Cd and Cr^{3+} (Bolan and Duraisamy, 2003). Sugar beet lime, a residual material from the sugar manufacturing process with 70–80% (dry basis) of $CaCO_3$ and biosolids compost, reduced $CaCl_2$-extractable Cd, Cu, and Zn concentrations. This behavior seems to be related to the pH increase as it is well known that increasing the pH of the soil leads to a decrease in metal(loid) mobility. Soluble Cd, Cu, and Zn concentrations in soils are often found to be negatively correlated with pH values (Burgos *et al*., 2006).

Gray *et al.* (2006) evaluated the effectiveness of lime to reduce Pb availability, and the treatment reduced Pb concentration of pore water and NH_4NO_3-extractable Pb concentration of the amended soil. Three soil amendments (red mud, beringite, and lime) were applied to metal(loid)-contaminated soil. Treatment of lime and red mud reduced Pb concentrations in plants. Treatment applications shifted the distribution of Pb from the exchangeable fraction to the carbonate and oxide fraction and decreased acid extractability of Pb. Lead solubility is generally very low in nonacidic soils, and the amendments used can only slightly reduce its mobility (McGrath *et al.*, 2002).

Inorganic amendments such as quarry waste, pulverized refuse, and pulverized fuel ash have also been used to improve substrate characteristics (Wong, 2003). For instance, expanded clay and N and P fertilizer increased the plant biomass of *Andropogon gerardii* in mine tailings (Hetrick *et al.*, 1994). Lead immobilization efficiency in artificially polluted soil with modified clay was 93% for Mn-montmorillonite, 86% for Mn-diatomite, 81% for Fe-montmorillonite, and 80% for Fe-diatomite. The results of sequential extraction of Pb from soil after immobilization with modified clays indicated that mobile fraction (i.e., exchangeable and carbonate fraction) decreased as contact time increased, while less mobile (i.e., reducible) fraction increased from 27% to 60% of the total amount extracted (Park and Shin, 2006). Bolan and Duraisamy (2003) demonstrated that P compounds immobilized Cd through phosphate-induced metal(loid) adsorption and the formation of cadmium–phosphate complex. Similarly, Park *et al.* (2011b) have demonstrated the potential value of both soluble and insoluble P compounds in the immobilization of Pb, thereby reducing its bioavailability and toxicity.

Some minerals are known to have a metal(loid) immobilizing capacity. The application of synthetic zeolite pellets to Cd-contaminated soils has been shown to significantly reduce the concentrations of Cd in the roots and shoots of a range of crop plants (Gworek, 1992). The addition of beringite, a modified aluminosilicate, resulted in a complete disappearance of visual and metabolic symptoms of metal(loid) phytotoxicity by metal(loid) immobilization. The high metal(loid) immobilizing capacity of beringite is based on chemical precipitation, ion exchange, and crystal growth (Vangronsveld *et al.*, 1995b).

When combined with compost, inorganic metal(loid) immobilizing amendments resulted in better plant responses when compared to the addition of inorganic amendments alone. Compost, beringite, and steel shots treatment in metal(loid)-contaminated sandy soil reduced phytotoxicity and metal(loid) accumulation in grasses. This may be attributed to an increased efficiency of metal(loid) binding on Fe or Mn oxides due to the high pH and precipitation of Fe oxides on clay particles induced by the beringite (Ruttens *et al.*, 2006). Hydrous manganese oxides reduced Cd or

Pb transfer from soil to soil solution and their entry into the food chain via plant uptake. This material would be promising for restoration of Cd and Pb-contaminated soils (Mench *et al.*, 1994).

Castaldi *et al.* (2005) amended Pb-contaminated soils with zeolite, compost, and $Ca(OH)_2$. The amendments increased the residual fraction of heavy metal(loid)s in the soils and decreased the Pb uptake by white lupin (*Lupinus albus* L., cv. Multitalia). The concentration of Pb in the aerial part of plants grown in compost soil was 87% lower than in the control sample. All treatments with amendments had higher plant yield than control, especially, compost and $Ca(OH)_2$. Similarly, Ciccu *et al.* (2003) used red mud, bauxite ore processing waste, and/or fly ash produced by coal-fired power stations to immobilize the heavy metal(loid)s in severely contaminated soils. Eluted Pb concentration from red mud and fly ash amended soil was reduced by 59–97% compared to the control.

7.3. Organic amendments

Organic materials such as sewage sludge, domestic refuse, peat, and topsoil improve the physical nature of soils by increasing water holding capacity and also provide plant nutrients in a slow-release form (Park *et al.*, 2011b; Tordoff *et al.*, 2000; Wong, 2003). In particular, organic amendments have a high CEC and can form stable organic–heavy metal(loid) complexes, thereby lowering metal(loid) availability in contaminated soil (Hetrick *et al.*, 1994). Cerezo *et al.* (1999) have shown that the treatment of a clay quarry with sewage sludge increased the pH and organic matter content and decreased the available heavy metal(loid)s over time due to complexation and immobilization processes.

Rizzi *et al.* (2004) noticed that compost treatment in soils from an Italian mining area improved soil physical characteristics such as particle size distribution, cracking pattern, and porosity. The development of better soil structural characteristics may prevent the dispersion of metal(loid)-contaminated particles by formation of water-stable aggregates. Compost addition improved the growth of *Lolium italicum* and *Festuca arundinacea* and decreased Zn and Pb content in stems and leaves.

The addition of manure byproducts increases the complexation of metal(loid)s in soils, the extent of which is related to the amount of dissolved organic carbon (DOC; Hesterberg *et al.*, 1993). The mobility of metal(loid)s may be facilitated greatly in soils receiving DOC because of the increased concentration of soluble metal(loid)–organic complex in solution and decrease in metal(loid) sorption (Bolan *et al.*, 2011). Accordingly, in soils containing large amounts of organic matter, such as pasture soils, muck, peaty soils, and organic manure-amended soils, only a small proportion of soil solution metal(loid) remains as free metal(loid) ion and a large portion is complexed with DOC. For example, using cation-exchange column experiments as well as anodic stripping voltametry measurements, del Castilho *et al.* (1993) observed that 30–70% of the dissolved Cu and all Cd in soils treated with cattle manure slurry was bound in relatively fast dissociating organic–metal(loid) complexes.

Although a wide variety of organic compounds in DOC are involved in the formation of soluble complexes with metal(loid)s (Daum and Newland, 1982), Zhou, and Wong (2001) and del Castilho *et al.* (1993) observed that the low-molecular-weight fractions, such as hydrophilic bases in biosolids and manures, have strong affinity for forming soluble complexes with Cd, Cu, and Zn. Thus, the formation of soluble aqueous metal(loid)–organic and, to a lesser extent, metal(loid)–inorganic complexes is expected to dominate the solution chemistry of metal(loid)s in manure-amended soils (Hesterberg *et al.*, 1993).

A number of studies have shown that addition of organic matter-rich soil amendments enhances the reduction or transformation of certain metal(loid)s, such as Cr and Se (Alexander, 1999; Frankenberger and Losi, 1995). For example, Ajwa *et al.* (1998) noticed enhanced loss of Se in the presence of organic amendments such as manure, which they attributed to manure-facilitated volatilization due to the reduction of Se. Similarly, Losi *et al.* (1994) and Higgins *et al.* (1998) have noticed that the addition of cattle manure resulted in the reduction of Cr^{6+} to less-toxic and less-mobile Cr^{3+} (Fig. 5). Various reasons could be attributed to the enhanced reduction (i.e., lowering in valency) of Cr^{6+} in the presence of the organic manure

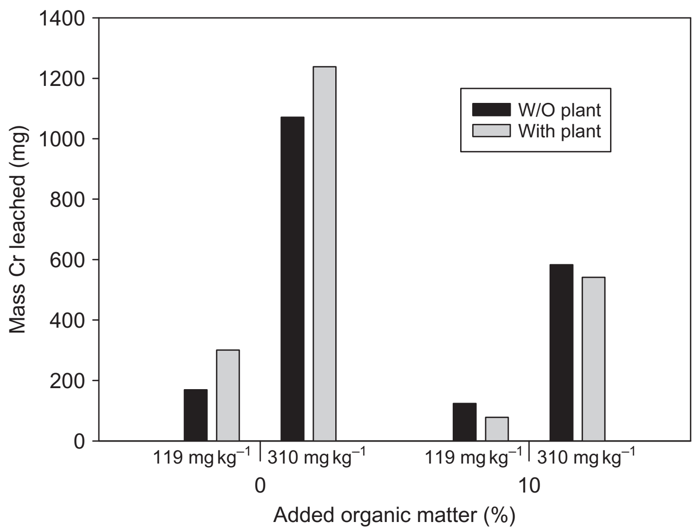

Figure 5 Effect of organic matter and plants on Cr leaching with low (119 mg kg^{-1}) Cr addition and high (310 mg kg^{-1}) Cr addition (Banks *et al.*, 2006).

compost, including the supply of carbon and protons and the stimulation of microorganisms that mediate and facilitate the reduction of Cr^{6+} to Cr^{3+} (Losi *et al.*, 1994).

At the same level of total organic carbon addition, Bolan *et al.* (2003b) observed significant difference in the extent of Cr^{6+} reduction between various organic manure composts. The extent of Cr^{6+} reduction increased with increasing level of DOC added through manure addition, which has been identified to facilitate the reduction of Cr^{6+} to Cr^{3+} in soils (Jardine *et al.*, 1999). For example, the hydroquinone groups in organic matter have been identified as the major source of electron donor for the reduction of Cr^{6+} to Cr^{3+} in soils (Elovitz and Fish, 1995).

The increase in Cr^{6+} reduction in the presence of organic manure addition may also result from enhanced microbial activity. Although Cr^{6+} reduction can occur through both chemical and biological processes, the biological reduction is considered to be the dominant process in most arable soils which are low in Fe^{2+} ion. It has been shown that the addition of manure compost caused a larger increase in the biological reduction than chemical reduction of Cr^{6+}, indicating that the supply of microorganisms is more important than the supply of organic carbon in enhancing the reduction of Cr^{6+} when compost is added (Banks *et al.*, 2006; Chiu *et al.*, 2009; Losi *et al.*, 1994). Addition of manure compost has often been shown to increase the microbial activity of soil, as measured by increased respiration and enzymatic activities (Chang *et al.*, 2008; Kanazawa *et al.*, 1988; Saha *et al.*, 2008; Tejada, 2009). This arises from both increased supply of carbon and nutrients, such as nitrogen, phosphorus, and sulfur (Tejada *et al.*, 2006; Wardle, 1992).

7.4. Geotextile capping

Geosynthetics are thin polymeric materials that are widely used in geotechnical, environmental, and hydraulic applications (Bouazza *et al.*, 2006). A geotextile is a geosynthetic fabricated to be permeable and can be classified by the way they are manufactured as either woven or nonwoven (Koerner and Koerner, 2006). Nonwoven geotextiles are felt-like materials which are formed by a random placement of threads and do not have any visible thread pattern (Koerner and Koerner, 2006). They can also be used in canals and channels that are downstream from dredging operations, such as for the dewatering of sediments in geotubes (Moo-Young and Tucker, 2002) and other geotextile containers in one- (Kutay and Aydilek, 2004) and two-layer systems (Kutay and Aydilek, 2005). Geotextiles have been used along shorelines and landfill sites to reduce the introduction of suspended material through erosion (e.g., Bouazza and Vangpaisal, 2007; Brachman and Gudina, 2008).

Various reactive materials (e.g., activated carbon, apatite, organoclay, zeolite, zero-valent iron) used for the immobilization of contaminants may be applicable to *in situ* capping using geotextile mat. For example, geosynthetic clay liners (GCLs) consisting of a thin layer of bentonite supported by one or two layers of geosynthetics are now well recognized as an alternative to traditional compacted clay liners. A number of studies have established the use of clays for attenuating metallic contaminants. A reactive material mat will have several advantages over loose placement of reactive materials, including (Olsta *et al.*, 2006): (1) uniform and verifiable mass per area placement of reactive or adsorptive material; (2) ability to mix reactive or adsorptive materials in defined proportions; (3) easy separation of the reactive material from the contaminated sediment and cover material; (4) providing barrier to biointrusion, resistance to uplift and differential settlement, and stability on sloped areas. Geotextiles also help to separate micropollutants such as Cd, Zn, and Cu from the underlying soil in landfill sites, therefore preventing groundwater from becoming contaminated and are also effective in attenuating metals from mining leachates (Lange *et al.*, 2007).

8. Conclusions and Future Research Needs

Phytostabilization is primarily aimed at containing the mobility of contaminants through their immobilization within the root zone of plants and "holding" soil and sediments, thereby preventing off-site contamination through their migration via wind and water erosion and leaching, and soil dispersion. Phytostabilization also results in the removal of contaminants through plant uptake and volatilization and this technology can be enhanced by using soil amendments that are effective in the immobilization of metal(loid)s. This technique is readily suited to monitor natural attenuation of contaminated sites which is employed within the context of a carefully controlled site-specific cleanup strategy. For example, this technology (i.e., phytocapping) has been found to be very effective in mitigating leachate and greenhouse gas generation in the management of landfill sites. The main advantage of this technology is that it reduces the mobility, and therefore, the risk of contaminants without necessarily removing them from their source location. Further, this technology does not generate contaminated secondary waste that needs treatment and also provides ecosystem development to achieve biodiversity corridors. However, since the contaminants are left in place, the site requires regular monitoring in order to maintain the stabilizing conditions. If soil amendments are used to enhance immobilization, they may need to be periodically reapplied to maintain the effectiveness of the phytoimmobilization.

Given the current knowledge of phytostabilization technology, the following research areas could be pursued:

- Impact of plant roots and associated microorganisms on the nature and extent of immobilization, volatilization, and methylation of metal(loid)s (Hg, Pb, As, and Se).
- Effect of various carbon fractions (e.g., DOM) on sorption/desorption of metal(loid)s and their transport to soil strata, streams, and lakes.
- Impact of harvesting and natural death of plants on the solubility, mobility, and dispersion of contaminants.
- Nature and extent of soil mineral-OM-microbe interactions as influenced by environmental factors such as land use and acid rain, and edaphic factors such as soil type and clay mineralogy.
- Nature of microbial communities as affected by OM dynamics and their role on the degradation of OM.
- Effect of heterogeneity on the performance of the system. Both contaminants and plant nutrients are distributed heterogeneously in soil. Avoidance/foraging of hotspots may have a large effect on plant uptake and leaching.
- Modeling phytostabilization systems. Since plants on each contaminated site comprise a unique ecosystem, experiments are required to determine both the feasibility and costs of phytostabilization. Full-system models could reduce these costs.

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