Section II

Biogeochemistry

6 Solubility, Mobility, and Bioaccumulation of Trace Elements: Abiotic Processes in the Rhizosphere

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CONTENTS

6.1 INTRODUCTION

Trace elements are elements that are present in small concentrations (<1000 mg/kg) in living organisms. This definition includes all the elements except H, C, N, O, Na, Mg, P, S, Cl, K, and Ca. Despite their presence as only traces, they nonetheless affect biological processes positively as well as deleteriously.

Trace elements in soils originate from natural and anthropogenic sources. Consequently, their concentrations can vary considerably. The trace element loading in soil is a function of the parent material plus subsequent atmospheric or water-borne deposition. Elevated levels of trace elements in soil can adversely affect the soil's fertility and may represent an ecological and human health risk if they enter the food chain or leach into receiving waters. However, the impact of trace metals on soil and the surrounding environment often cannot be predicted simply by measuring the total concentration. This is because only the soluble and mobile fraction has the potential to leach or to be taken up by plants and enter the food chain.

The mobility, solubility, and bioaccumulation of trace elements depend on a plethora of soil, microbial, and plant factors, as well as the properties of the trace element. Chemical solubility is a prerequisite for physical mobility and bioavailability. Bioaccumulation can result from trace element transport in the rhizosphere and absorption onto soil organisms or passage through plants' plasmalemma at the root: soil interface. These processes can be augmented or retarded through soil amendments or modification of the soil's vegetation. The goal of such engineering approaches may be to diminish trace element mobility so that it poses minimum risk to the surrounding environment, or to promote solubility so that trace elements are taken up by plants or leached out of the rhizosphere.

Enhancing trace element solubility may be a tool for the remediation of contaminated soils through the use of plants to remove the trace element, phytoremediation, or by leaching contaminants out of the root zone. Alternatively, plant and animal productivity may be improved by increasing the trace element solubility in a soil that is deficient in one or more essential elements.

This chapter discusses the physicochemical processes that affect the fate of trace elements in the rhizosphere with a view to the remediation of contaminated soils.

6.2 TRACE ELEMENT SOLUBILITY IN THE RHIZOSPHERE

The key abiotic mechanisms that control solubility will now be discussed and how these processes can be represented analytically will be outlined. For any trace element, only some fraction of the total concentration will be in soil solution, with the remainder bound to the soil matrix. Mass balance of this distribution gives

$$M = \theta C + \rho S \,, \tag{6.1}$$

where

M is the total concentration (mg/kg)
θ is the volumetric water content (m^3/m^3)
C is the trace element concentration in the soil solution (mg/L)
ρ is the bulk density of the soil (t/m^3)
S is the concentration bound to the soil matrix (mg/kg)

The solubility of a trace element in the rhizosphere is often described in a simple way by a distribution coefficient (K_d) where

$$K_d = \frac{S}{C} \,. \tag{6.2}$$

In some cases, however, as the total concentration of trace elements in a soil increases, unlike the representation of Equation 6.2, the soil's ability to adsorb these further loadings decreases, due to a saturation of the chemical-binding sites in the soil. The observations of sorption of most trace elements can be described using a Langmuir (Equation 6.3) or a Freundlich (Equation 6.4) isotherm, which accounts for this nonlinearity in sorption.

Langmuir: $$S = \frac{KQA_rC}{(1+KC)} \tag{6.3}$$

Freundlich: $$S = KC^n \,, \tag{6.4}$$

where

K is the adsorption constant
Q is number of sorption sites (mol/m^3)
A_r is the atomic mass of the trace element (g/mol)
n is the Freundlich exponent

If $n = 1$, then Equation 6.4 collapses to the linear model of Equation 6.1.

In the Langmuir case, when Q is finite, as in the case of soils and sediments, the value of S approaches QA_r as the concentration of trace element in soil solution increases. Figure 6.1 shows the adsorption of Cd by a silt loam at a range of Cd concentrations in soil solution. In this case, the isotherm is described by the Langmuir equation (Equation 6.3) with values of Q and K equal to 28.7 and 0.14, respectively.

The solubility of trace elements in the rhizosphere is a function of the soil's chemical and physical properties. Most trace element ions carry a positive charge and can therefore be retained by the negative binding sites of the soil's matrix. The soil's cation exchange capacity (CEC), which indicates the number of negative charges per unit mass, provides an indication as to the soil's potential to retain positively charged ions. The negatively charged binding sites for trace elements occur on organic matter, clays, and the oxides of Fe, Mn, and Al, which make up the soil's matrix.

Trace elements that carry a negative charge, such as F^-, Br^-, and the oxyanions AsO_2^- and CrO_4^{2-}, can bind electrostatically to positively charged sites in the soil matrix, as occurs in variably charged soils. This is measured by the soil's anion exchange capacity (AEC). In many temperate soils, the AEC is so small as to be insignificant. Therefore, many negatively charged ions, such as Br^-, can move freely with soil moisture unaffected by exchange. They can be used as chemical "tracers" of water movement through soil.

However, some highly weathered soils, and those that contain significant quantities of such volcanic minerals as allophane and imogolite can have a significant AEC. The AEC depends on pH. Some trace element anions, such as arsenate and selenate, also form specific chemical bonds with soil components. This results in their adsorption exceeding the AEC of the soil. The strength of the

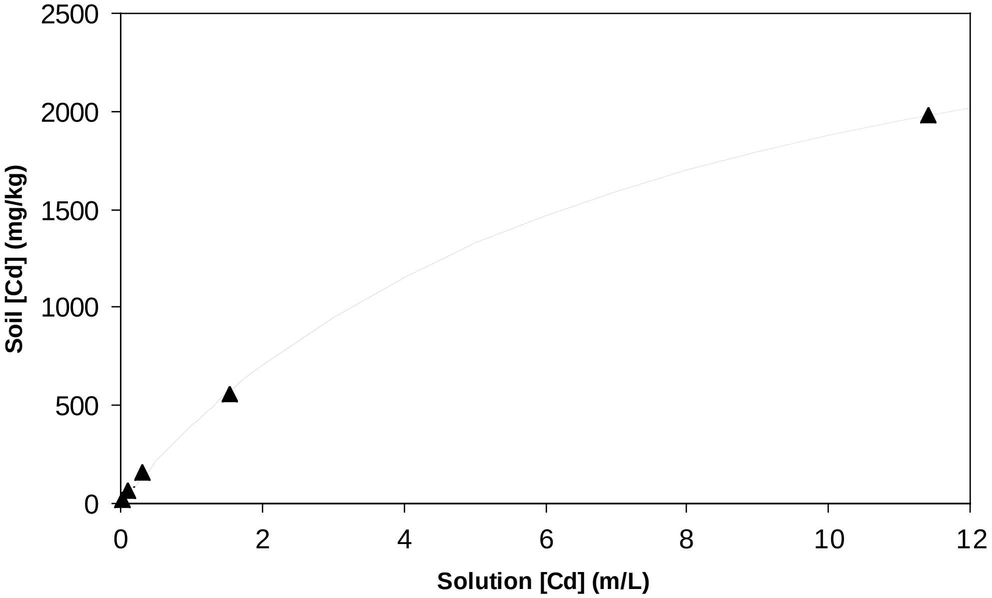


FIGURE 6.1 The effect of Cd^{2+} concentration on soil adsorption. The soil used was a silt loam pH 5.7, an organic matter content of 6.3%.

bond between the binding site of the soil and the trace element is a function of the size and charge on the trace element ion or complex. Smaller ions, with a higher charge, form the strongest bonds.

Although a small percentage of a soil's clay fraction carries a permanent negative charge, the charge carried by organic matter and, as mentioned some variable-charge clay minerals is pH dependent. Therefore, pH also profoundly affects the binding of trace elements in the rhizosphere. For positively charged ions such as Cd^{2+}, soil acidification invariably results in increased trace element solubility due to increased competition from H^+ ions at the negatively charged binding sites [1] (Figure 6.2). Conversely, soil adsorption of some trace elements such as Zn^{2+} can lower soil pH by releasing H^+ ions from bound surfaces [2]. Negatively charged trace elements, or trace element complexes, tend to be more soluble at a higher pH. The adsorption of trace elements onto variable charge minerals such as Fe, Al, and Mn oxides is also pH dependent. As these materials assume more negative charge under alkaline conditions, their capacity to absorb trace elements, which is generally positively charged, increases [3].

Trace elements may be displaced from exchange sites by other ions attracted from the soil solution. The extent of this competition for binding sites depends on the type and concentration of the trace element as well as that of the competing ion. As a general rule, trace elements such as Cd^{2+}, which has an atomic radius (r) of 0.97Å, can be displaced by other ions of a similar size and charge in soil solution, such as Ca^{2+} ($r = 0.99$Å). Therefore, soil amendments such as phosphates that are designed to immobilize heavy metals may actually promote the solubility of some co-contaminants such as As.

Trace element adsorption onto charged exchange sites is not the only mechanism governing trace element solubility in the rhizosphere. The extent, soluble–insoluble partitioning, and mobility of soil organic matter play an important role in the solubility and environmental fate of trace elements. Metal complexation by organic matter can promote or reduce metal solubility, depending on the solubility of the organic ligand.

Although the exact composition of dissolved organic matter is variable and complex, a large portion of this mobile material is composed of fulvic and humic acids. Minor components can also include macromolecular hydrophilic acids, carbohydrates, and carboxylic and amino acids [4]. Dissolved organic matter has been demonstrated to promote heavy-metal solubility [5] and mobility,

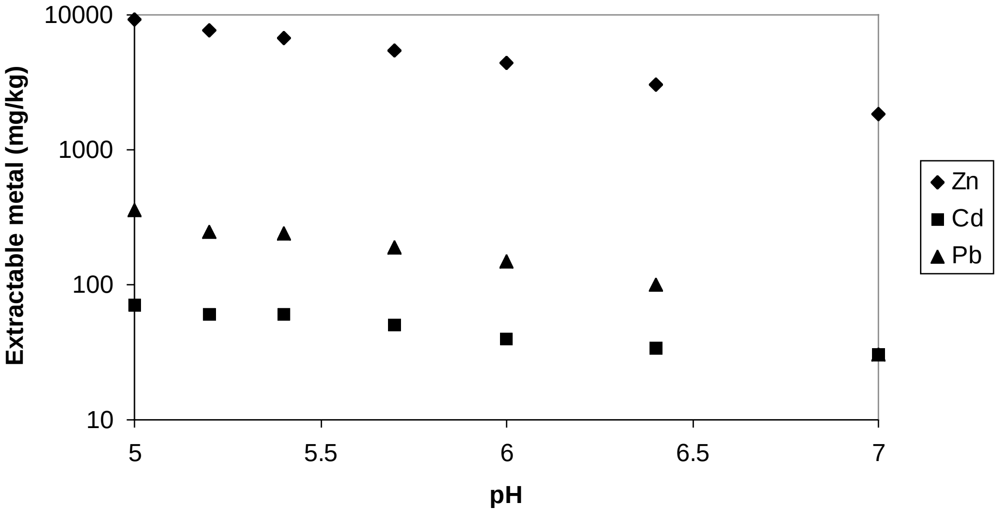


FIGURE 6.2 Metal extracted using 1 M ammonium acetate buffered at various pHs. Note the log scale on the y-axis. The total concentrations of Zn, Cd, and Pb in the soil were 40,416, 360, and 6209 mg/kg, respectively.

as will be discussed. In particular, Cu^{2+}, Hg^{2+}, and Pb^{2+} are strongly bound by humic acid [6], so their solubility and transport is thus promoted by increasing concentrations of dissolved organic matter. Wu et al. [7] demonstrated that, in a kaolinite soil, the Cu–humate complexes are mobile in acid and alkaline conditions, but not in neutral conditions, where they are sorbed. Almås et al. [8] found that the application of organic matter to soil enhanced the solubility of Zn and Cd due to the formation of complexes with dissolved organic acids.

A continual source of soluble organic matter in the rhizosphere is provided by plant exudates. These include metabolic products of fungi and microorganisms, the degradation of leaf litter and insoluble organic matter. The addition of organic fertilizers, effluents, and sludges can also provide sources. Fischer [4] demonstrated that amino acids derived from these solubilized heavy metals that have been bound to typical soil components.

The solubility of trace elements in the rhizosphere can also change over time. The soil's organic matter content is naturally dynamic. Furthermore, it may be augmented through the establishment of vegetation or the addition of composts or sewage sludge. Conversely, continual oxidation of organic matter occurs, particularly in tropical soils. Compost or sewage sludge amendment can offset this decline. The solubility trace elements that are strongly adsorbed by humic and fulvic acids will be affected by a change in the soil's organic matter content.

Over time, the solubilized trace elements can migrate and diffuse into the less accessible and immobile soil–water regions. There, they may become bound to the soil's solid phase. Consequently, the time needed for a contaminant to be redissolved or again be transferred from the stagnant- to the mobile-water phase may increase with aging of the compound in soil [9].

6.3 TRACE ELEMENT SPECIATION IN THE RHIZOSPHERE

The chemical speciation of trace elements in the rhizosphere profoundly affects their solubility, mobility, and toxicity. In soils, Cr that is present in the +6 oxidation state [Cr(VI)] is more mobile, more readily bioaccumulated, and 100 to 1000 times more toxic when present in the +3 oxidation stare [Cr(III)] [6].

In the rhizosphere, the various phases of trace elements are in dynamic equilibrium. Therefore, as trace elements are removed from soil solution by leaching or plant uptake, more will be desorbed from soil particles into solution. The rate at which this occurs depends on the distribution (see earlier equations) as well as the speciation of the trace element in the soil matrix.

Trace elements in soil solution and those weakly bound to exchange sites on the surface of the soil matrix are the most mobile and biologically active. Carbonate or sulphide precipitates, which may be occluded in Fe, Mn, or Al oxides, are immobile and biologically inactive. However, they may readily become mobilized by a shift in equilibrium caused by a change in soil pH and/or the redox conditions. The trace elements of the crystalline lattices of clays are generally inert. Other trace elements may be bound by more than one soil component. Alcacio et al. [10] demonstrated three possible binding configurations of Cu^{2+} on complexes of oxide minerals and organic matter. These are the Cu^{2+} bound to mineral surfaces and the Cu^{2+} bound to the organic matter that is absorbed onto oxides, along with Cu^{2+} bridges between oxides and organic matter.

The speciation of trace elements in the rhizosphere may be measured directly using analytical techniques, or it can be calculated using other parameters. The analytical procedures used to determine the speciation of trace elements in soils are usually specific for the solid phase or the solution phase. For example, sequential extraction procedures can be used to determine the distribution of trace elements in various soil fractions: soluble; exchangeable; sulfide/carbonate bound; organically bound; oxide bound; and residual or lattice mineral bound. Given the limitations and costs of analytical procedures, rather than measuring speciation and distribution of trace elements in soils, it is often calculated using speciation models such as GEOCHEM [11] and MINTEQ2 [12]. These are based on theoretical thermodynamics. Despite the fundamental principles that drive these models, their simplicity makes it problematic to model accurately trace element speciation and distribution in soils that contain a plethora of organic and inorganic matrices.

6.4 TRACE ELEMENT MOBILITY

Water is the vehicle for transport of solutes, including trace elements, through soil. Although solubility is a prerequisite of mobility, various rate-limited or kinetic geochemical and hydrological processes in the rhizosphere affect the transport of trace elements. The transport of dissolved trace elements in soils depends primarily on their concentration gradient spatially, and the mass flow of water. The latter is a function of the soil's matric water potential, its porosity, and long-distance preferential processes of transport through macropores. Nonequilibrium chemical or physical reactions may also occur. Physical nonequilibrium can result from nonuniform water flows and preferential transport.

The long-distance transport of trace elements in soils can be described using the convection dispersion equation (CDE), which describes the movement of solutes during transient flow [13]: In one-dimensional form, this is

$$\frac{\partial M}{\partial t} = \frac{\partial}{\partial z}\left[\left(\theta D_s\right)\frac{\partial C}{\partial z}\right] - \partial \frac{(q_w C)}{\partial z} - S_m(z)\ , \tag{6.5}$$

- where
- M is the total trace element concentration (mg/kg)
- t is time (s)
- z is depth (m)
- θ is the volumetric water content (m^3/m^3)
- C is the local trace element concentration in the soil solution (mg/L)
- D_s is the solution diffusion coefficient (m^2/s)
- q_w is the soil water flux (m/s)
- $S_m(z)$ is the solute uptake, or release, by plant roots as a function of depth

Here, M is the total concentration, which is partitioned according to Equation 6.1.

Dissolved trace elements will be more mobile in sandy soils because the diffusive and connective water fluxes tend to be higher than in loams or clays. Mobility is reduced by plant uptake or sorption onto plant roots that are a sink for water and solutes. Mobility will be enhanced by plant release or desorption.

6.5 BIOACCUMULATION OF TRACE ELEMENTS

Some soil microorganisms accumulate trace elements, so-called bioaccumulation, from substrates that have a low total concentration. Bacteria and fungi can bioaccumulate trace elements. This uptake is via two processes: (1) sorption of metals by microbial biomass and its byproducts; and (2) the physiological uptake of trace elements by microorganisms through metabolically active and passive processes.

The uptake of trace elements by organisms is a function of biological species as well as the trace element's solubility and mobility. Soil fauna and microorganisms behave similarly to soil organic matter in that they possess binding sites for some trace elements. Robinson et al. [14] found that rhizobacteria such as *Pseudomonas fluorescens* from New Zealand pasturelands accumulated Cd to levels about 100 times that of the ambient solution in which they were grown. As with soil organic matter, the adsorption of Cd by these microorganisms decreased at lower solution pHs.

Motile soil animals such as worms and rotifers affect the transport and distribution of trace elements in soils. However, these biotic factors are beyond the scope of this chapter.

Plant roots differ from soil fauna and microorganisms in that they are a sink for soil water and by absorption they have the capacity to remove some trace elements from the rhizosphere. Soil solution is drawn from the root zone into the plants' roots and then via the stems to the leaves; it is lost to the atmosphere via transpiration. Any trace element taken up in the soil solution and entering the roots will accumulate in the roots or the shoots of the plant. High trace-element concentrations in the roots can result from water uptake inducing migration of the trace elements, via mass flow, to the root surface where they are precipitated [15]. In the aboveground portions, the highest concentrations are often found in the leaves because they are the major water sink prior to evaporation of the water. Metal translocation from the roots to the shoots is driven by water uptake [16,17].

The total amount of metal that accumulates in the plant does not necessarily equal the cumulative product of the soil-solution metal concentration times the volume of water transpired by the plant, as might be predicted for passive uptake. For a metal to be translocated to the aerial parts of a plant, it must enter the root via the symplastic or apoplastic [18] pathways, where some active or passive filtering may occur.

The fraction of dissolved trace elements that passes into the root xylem may be described by a root absorption factor (ϕ), a dimensionless lumped parameter that represents the root xylem/soil solution metal concentration quotient [19].

$$\phi = \frac{[C]_r}{[C]}\ , \tag{6.6}$$

where $[C]_r$ is the soluble metal concentration (mg/L) in the root xylem and $[C]$ is the soluble metal concentration (mg/L) in the soil solution.

The quotient ϕ is a lumped parameter incorporating many complex and often poorly understood biogeochemical factors that influence the passage of metals from soil into roots. Rhizobiological activity, root exudates, temperature, moisture, pH, and the concentration of competing ions will all affect ϕ. Also, ϕ will change depending on the trace element concentration in the soil solution. This would be particularly pronounced for essential elements that are subject to active uptake or root exclusion [20].

The speciation of the trace element in the rhizosphere is important in determining ϕ. Trace elements complexed with large organic molecules cannot easily pass through the roots' plasmalemma. This has implications for engineering plant uptake, which is discussed later. Free trace element ions are the most readily adsorbed. However, there is increasing evidence that some complexes, such as chloro–complexes can also be taken up by plant roots, although at lower efficiency [21].

6.6 BIOACCUMULATION AS AFFECTED BY Φ

Baker [22] divided plant species into three groups according to their above-ground metal concentrations in relation to the metal concentration in the soil. These three groups may be delineated using ϕ:

- For nonessential elements such as cadmium, nickel, and arsenic, plants with a very low ϕ are termed "excluders." Most plants that occur naturally on metalliferous soils are recognized as excluders.
- Plants that have a relatively constant ϕ over a wide range of metal solution concentrations are known as "indicators." In this case, the concentration in the plant has a near-linear relationship to the soluble metal concentration in soil solution. Plants that do not occur

naturally on metalliferous soils usually behave as "indicators" when grown in the presence of nonessential elements.

- The third category of plants are those that tolerate very high concentrations of metal in their aerial parts or have an active uptake mechanism even for nonessential metals (high ϕ). These plants are known as "hyperaccumulators" [23].

For excluders and hyperaccumulators, ϕ might be constant over just a narrow concentration range. There can be a sudden increase in plant metal concentration at high soil–solution concentrations. At this point, control mechanisms break down, and metal "floods" into the plant. This may be an overload of the regulatory mechanism or a break down of the plasma membrane at the apoplast/symplast interface. When this occurs, the plants show toxicity symptoms and biomass production is reduced.

The bioaccumulation of trace elements plays a major role in determining their environmental fate. This determines whether the element remains in the rhizosphere, leaches, or is removed by plants. Adjusting trace element mobility or bioaccumulation can be used as a tool to remediate contaminated soils or improve the fertility of soils that have low bioavailability of essential nutrients.

6.7 ENGINEERING TRACE ELEMENT SOLUBILITY, MOBILITY, AND BIOACCUMULATION FOR IMPROVED FERTILITY OR ENVIRONMENTAL PROTECTION

Soil amendments can be used to promote or reduce trace element solubility and bioaccumulation in contaminated soils. Amendments that induce solubility can be used to cleanse polluted sites via leaching the contaminating trace elements or by facilitating their uptake by plants. Subsequent removal of the plants would also remove the contaminant from the site. Alternatively, soil amendments that immobilize trace elements can lessen their impact on soil-borne organisms and reduce exposure pathways.

Amendments may also serve to enhance the fertility of a soil in which the bioavailability of one or more trace elements is limiting agricultural production. Essential trace elements such as Fe, Co, and Se may be present in soils at relatively high total concentrations, yet be unavailable to organisms due to physicochemical conditions in the soil.

6.8 TRACE ELEMENT SOLUBILIZATION

Solubilizing trace elements for the purposes of *ex situ* soil washing has been used widely for the remediation of contaminated soils in Europe [24]. Tokunaga and Hakuta [25] evaluated an acid-washing process to extract the As(V) from a soil contaminated at 2830 mg/kg by As. Phosphoric acid proved to be a promising extractant, attaining 99.9% As extraction at 9.4% acid concentration. The success of soil washing largely depends on the speciation of the trace elements because it is based on the desorption or dissolution of trace elements from the soil inorganic and organic matrix during washing with acids or chelating agents. Although soil washing is suitable for off-site treatment, it can also be used for on-site remediation using mobile equipment.

6.9 INDUCED BIOACCUMULATION

Plants can be induced to take up trace elements by the use of amendments. Chelating agents, such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and nitrilotriacetic acid (NTA), and organic acids such as citric and oxalic acids are commonly proposed. These agents have been proven effective in enhancing the solubility of Pb, Cd, Cu, Zn, and other trace element cations [26–29].

Addition of thiosulphate and thiocynate salts to mine spoil induced plants to accumulate Hg [30] and, auspiciously, Au [31]. Chloride anions increased the Cd solubility in soils due to the formation of relatively stable chloride ion complexes ($CdCl^+$ and $CdCl_2$) [32]. Similarly, the addition of chloride to soils has also been demonstrated to enhance the uptake of Cd by plants [33].

Solubilization, however, does not necessarily induce bioaccumulation. For example, Cu^{2+} is solubilized by dissolved organic matter, but the resulting complex is not taken up by plants due to its inability to pass through the plasmalemma [34]. Experiments using the nickel hyperaccumulator *Berkheya coddii* have shown that the chelating agents cause a decrease in nickel uptake, despite enhancing the nickel solubility in the soil (Figure 6.3A). However, increasing the concentration of EDTA and soluble metal in the substrate can induce plant uptake. Figure 6.3B shows that when 4 g of EDTA per kg of soil is added, *Arrhenatherum elatius* can be induced to take up nearly 1000 mg/kg Ni on a dry matter basis. Depending on the metal species, induced uptake can cause plant death. Disruption of the plasmalemma possibly allows the Ni–EDTA complex to enter the xylem.

The strategy used for chelate-enhanced phytoremediation is to apply chelate to a mature crop growing on a contaminated soil. As well, a pesticide can be used to disrupt root membranes allowing the complexed metal to pass directly into the root xylem [35].

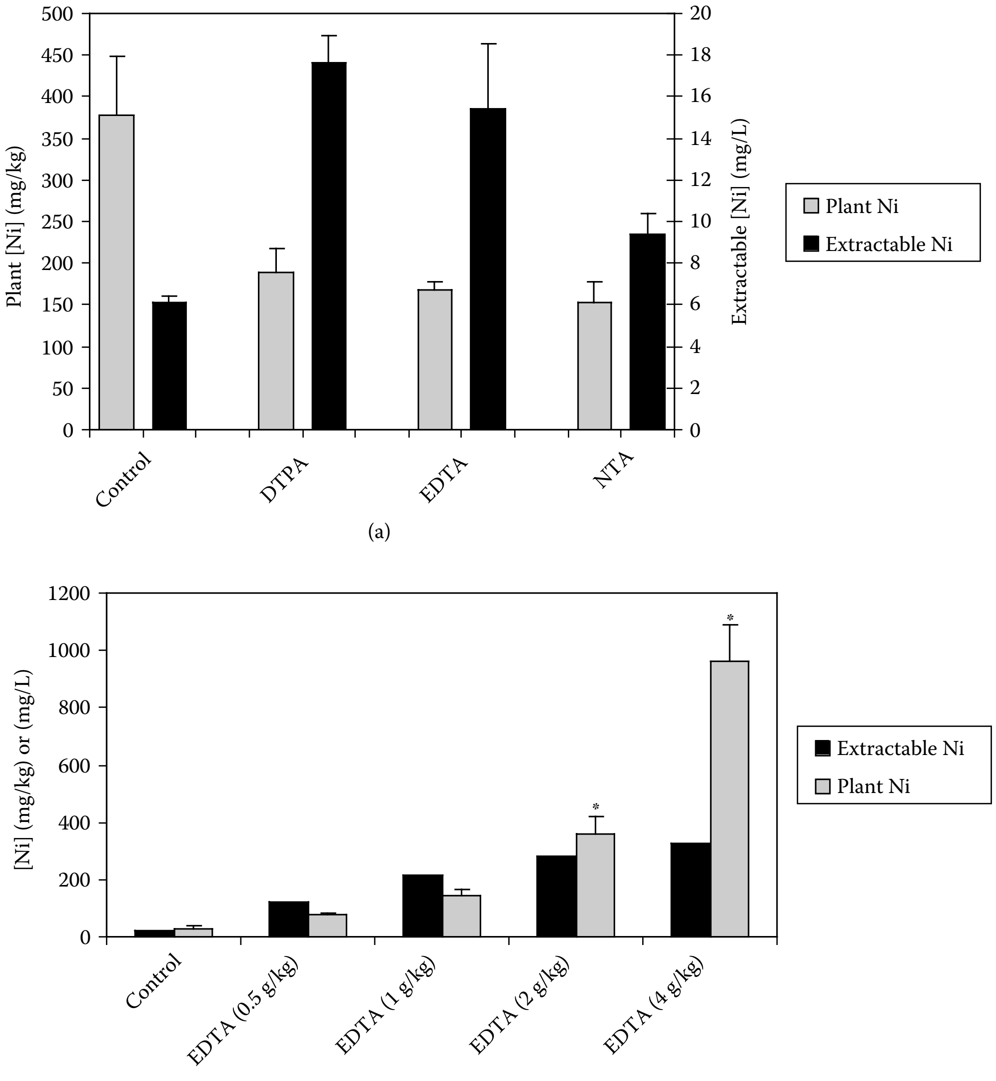
Blaylock [35] showed an impressive decrease in soil-lead concentration over 2 years at two sites in the U.S. using a combination of *Brassica juncea* and EDTA to induce accumulation. Unfortunately, the mass balance of lead was not shown. It is therefore uncertain just how much lead the plants removed and how much deleteriously leached through the soil profile to contaminated receiving environments.

Environmental concerns have been raised over the use of induced bioaccumulation due to the possibility that some of the metals might leach through the soil profile, possibly entering groundwater [36]. Processes such as preferential flow may exacerbate metal leaching [37]. Soil amendments may also persist in the environment, creating additional problems. The addition of chelating agents is likely to induce the solubilization of other than target metals — which may be phytotoxic — such as Al and Mn. Chelators such as EDTA can act as chemical plows, redistributing surface contamination down the soil profile. Concentration near the soil surface is reduced, thereby reducing exposure pathways, but the total amount of contaminant is not affected. Induced bioaccumulation should thus only be used on hydraulically isolated treatment sites where the connection to receiving waters has been "broken."

6.10 *IN SITU* IMMOBILIZATION

Reducing trace element solubility, mobility, and bioaccumulation in contaminated soils is an effective, low-cost means of remediation that does not require drastic disturbance of the site. Naturally occurring or artificial soil amendments such as liming material, phosphate, zeolite, bentonite, clay, Fe metal, Fe and Mn oxides, and organic matter, may be used to mitigate the toxic effects of trace elements [38]. These amendments reduce trace element mobility by promoting the formation of insoluble precipitates or by enhancing the soil's capacity to bind the trace element. The latter can be achieved directly through the addition of adsorbent material or indirectly by adjusting the soil's pH–Eh conditions to promote trace element absorption onto the soil's matrix.

Chemical immobilization using phosphate amendments, such as mineral apatite, synthetic hydroxyapatite, and phosphate salts, has proven effective in reducing heavy-metal solubility by the formation of metal–phosphate complexes [39] and by increasing the number of negatively charged exchange sites [40]. These additions reduce metal bioavailability not only to plants, but also for humans who may have ingested contaminated soil [41]. The solubility of lead in soil can be greatly reduced by the formation of chloropyromorphite [$Pb_5(PO_4)_3Cl$]. Several microcosm studies have shown that chloropyromorphite can be formed through the addition of hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] [42,43]. Brown et al. [44] demonstrated that phosphate fertilizers could poten-



(a)

(b)

FIGURE 6.3 (A) The effect of chelating agents added at 2 g/kg soil, on shoot Ni concentration (dry matter) by the hyperaccumulator *Berkheya coddii*. (B) The effect of increasing EDTA addition on the shoot Ni concentration (dry matter) of *Arrhenatherum elatius*. Extractable Ni was determined using a 1 *M* NH_4OAc extractant. * denotes plant death.

tially be used in combination with organic matter and Fe-rich material, as soil amendments to reduce plant availability of Cd, Zn, and Pb.

Phosphate amendments such as hydroxyapatite are effective in reducing the solubility of Pb, Cd, Zn, Al, Ba, Co, Mn, Ni, and U. However, phosphate has been shown to promote the solubility of As and Cr [45], possibly through reduced sorption of the oxyanions due to an increase in pH and competition from PO_4^{3-}.

A variety of inorganic and organic amendments have been used to reduce Cr(VI) to the less mobile, less toxic Cr(III) species. Fe(II)-bearing minerals form effective reductants. Surface-bound organic matter does this also. The latter is catalyzed by soil mineral surfaces, and Cr(III) binds tightly to surface species or is precipitated as $Cr(OH)_3$ [46]. Similarly, Bolan et al. [47] have shown that organic amendments, such as animal and poultry manures rich in dissolved organic carbon, are very effective in reducing Cr(VI) to Cr(III).

Lombi et al. [48] demonstrated that the 2% addition of bauxite residue, "red mud," to contaminated soils reduced the solubility of Cd, Pb, Ni, and Zn, but not Cu. The remedial action of this material was attributed to a rise in soil pH and adsorption of the metals onto oxides of Fe and Mn.

Liming has been demonstrated to be effective in reducing the mobility of trace element cations in variable-charge soils by increasing the negative charge on oxides, clays, and organic matter. The effectiveness of raising the pH on metal immobilization also depends on the liming agent. Bolan et al. [49] found that $Ca(OH)_2$ was less effective than KOH in immobilizing Cd^{2+} due to competition between Ca^{2+} and Cd^{2+} for adsorption sites.

Establishing vegetation on a contaminated site can reduce the solubility and mobility of trace elements. Plant growth reduces trace element mobility in the substrate through the addition of organic matter, creation of an aerobic environment, root uptake, and returning rainfall to the atmosphere by evapotranspiration [50]. Römkens et al. [51] showed that Cu solubility was lowered significantly in the root zone of *Agrostis capillaries* (var Parys Mountain). Turpeinen et al. [52] demonstrated that Pb solubility was reduced by up to 93% by pine seedlings. The use of vegetation for the remediation of contaminated sites, phytoremediation, has some advantage over other *in situ* immobilization techniques. Once established, the physicochemical change induced by vegetation is permanent (Figure 6.4).

FIGURE 6.4 Vegetation established on the Tui mine tailings, Te Aroha, New Zealand. The vegetation has reduced metal mobility by adding organic matter to the substrate and returning some rainfall to the atmosphere via evapotranspiration.

6.11 CONCLUSIONS

The effect of soil-borne trace elements on ecosystems and human health is a function of their solubility and mobility. These properties are often disproportionate to the trace element's total concentration. Rather, the speciation of the trace element and the physicochemical properties of the ambient soil are of overriding importance in determining bioavailability. Solubility is primarily a function of soil pH and organic matter content. Mobility depends on solubility and water transport processes.

Trace element bioaccumulation occurs via adsorption onto roots and soil microorganisms as well as absorption into roots and translocation to the aerial portions plants. The latter is affected by the permissivity of the roots' plasmalemma to the dissolved trace element species.

An innovative low-cost strategy for the remediation of trace element contaminated soils is *in situ* immobilization using chemical amendments, modified vegetation, or a combination of the two. Remediation technologies that rely on amendments that promote trace element solubility will be limited to sites where the risk of contaminant leaching to groundwater has been eliminated.

Future development of whole-system models that calculate the leaching and plant uptake of trace elements in the rhizosphere will facilitate the design and implementation of remediation technologies designed to isolate contaminated soils from the surrounding biota.

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