

Phytoremediation for the management of metal flux in contaminated sites

Brett Robinson^{1*}, Rainer Schulin¹, Bernd Nowack¹, Stéphanie Roulier¹, Manoj Menon¹, Brent Clothier², Steve Green² and Tessa Mills²

¹ Institute of Terrestrial Ecology, Swiss Federal Institute of Technology (ETH), Universitätstrasse 16, CH-8092 Zürich, Switzerland. brett.robinson@env.ethz.ch, schulin@env.ethz.ch, nowack@env.ethz.ch, Stephanie.roulier@env.ethz.ch, menoneth@gmail.com

² HortResearch, Private Bag 11030, Palmerston North, New Zealand. bclothier@hortresearch.co.nz, sgreen@hortresearch.co.nz, tmills@hortresearch.co.nz

* Corresponding author

Abstract

Phytoremediation improves metal-contaminated sites by the extraction of contaminating metals (phytoextraction), or their immobilisation (phytostabilisation). Phytoextraction removes metals from the soil by repeated crops of plants that accumulate large amounts of one or more target metals in their above-ground biomass. The harvested plant material is removed from the site. Despite more than ten years of research, there are few examples of successful phytoextraction. This technology is limited by the long period required for cleanup, the restricted number of target metals that can be extracted, the limited depth that can be accessed by roots, and the difficulty of producing a high-biomass crop of the desired species. There is also concern about metal-accumulating plants providing an exposure pathway for toxic elements to enter the food chain. The addition of chelants to enhance plant-metal uptake, invariably increases the risk of metal leaching. Phytostabilisation exploits transpiration and root-growth to immobilise contaminants by reducing leaching, controlling erosion, creating an aerobic environment in the root-zone, and adding organic matter to the substrate that binds metals. Soil amendments can promote plant growth and enhance metal immobilisation. Phytostabilisation requires the establishment of tailored vegetation on the site that is left there in perpetuity. A succession of plant species may be used to establish the desired climax vegetation. Unlike phytoextraction, there are numerous examples of successful phytostabilisation on metal-contaminated sites.

Phytoremediation technology is site specific due to the plethora of environmental variables that affect plant growth and metal mobility. Most contaminated sites contain a heterogeneous mixture of several elemental and organic contaminants. Plant-growth may be limited by other environmental variables, such as low pH, low nutrient availability, salinity, insufficient aeration or low water availability. The commercial success of phytoremediation is thus dependent on convincing decision makers that phytoremediation can satisfy environmental regulations. Obviously, field demonstrations at each site are not practical; therefore validated mechanistic models are required to calculate the effect of phytoremediation on metal fluxes. Central to such models is an understanding of root-metal interactions in these typically heterogeneous media.

Keywords: hydraulic control, phytostabilisation, phytoextraction, bioenergy

1 Introduction

Phytoremediation is the use of plants to improve degraded environments. Plants affect metal fluxes via the extraction of contaminating metals into the above-ground biomass, or changing their mobility in the soil profile. Thus, there are two ways of achieving metal phytoremediation.

In phytoextraction, vegetation is engineered so that the site is eventually cleansed via metal removal, whereas in phytostabilisation metal mobility and metal toxicity are decreased, thus lowering the environmental risk. In both of these roles, plants function as bio-pumps (ROBINSON *et al.* 2003a) that use the sun's energy to pump water and solutes from the soil to the above-ground portions, whereupon water returns to the atmosphere via transpiration. Plants also pump organic matter into the rhizosphere via root exudates and decaying tissue. This organic matter may reduce or promote metal flux.

Water is the main vehicle for transport of metals through soil. Metal fluxes in soil are dependent on spatial concentration gradients driving diffusion and dispersion, and the mass flow of water (VOGELER *et al.* 2001). CLOTHIER and GREEN (1997) described roots as "the big movers of water and chemicals in soil. Of the global average rainfall of 720 mm that falls on soil each year (SELLERS 1965), some 410 mm is returned back to the atmosphere, either directly from the soil or, more often, by evapo-transpiration from vegetation growing therein (CLOTHIER and GREEN 1997). This represents a 57% reduction in the average water flux through soil, and a significant reduction in the volume of soil solution that exits the root-zone and enters receiving waters. In arid regions, evapotranspiration can eliminate drainage and hence render trace elements immobile.

Phytoremediation can also affect metal fluxes via plant-induced physico-chemical changes in the soil. Vegetation affects the fate of trace elements in soil in the following ways:

- Changing the water flux
- Adding organic matter to the soil
- Changing soil pH
- Changing the metal speciation
- Promoting the growth of soil-borne organisms
- Changing the physical characteristics of the soil
- Bioaccumulation

Here we investigate these plant processes as they affect metal phytoremediation, the potential applications of metal phytoremediation and the actions required for the successful implementation of this technology. We divide metal phytoremediation into phytoextraction, which only has limited potential for the remediation of contaminated land, and phytostabilisation, which has a greater potential, but is constrained by the lacuna of knowledge on soil-root interactions.

2 Phytoextraction: not ready for action

Phytoextraction describes the use of plants to remove metals and other contaminants from soils. Theoretically, metal-contaminated sites could be cleansed by the repeated cropping of plants, provided that harvested amounts of metals exceeds further inputs, until the soils' metal concentrations have reached acceptable levels. Phytoextraction relies on plants that translocate large amounts of one or more target metals into the above ground biomass.

After each cropping, the metal-rich biomass would be removed from the area and may be burned to reduce its volume, whereupon it could be stored in an appropriate area, such as a contained landfill, that does not pose a risk to the environment.

Successful phytoextraction requires that the soil be cleansed to a level that complies with environmental regulations, and from an economic viewpoint, this should be achieved at a lower cost than an alternate technology or the cost of inaction (ROBINSON *et al.* 2003a). Field trials or commercial operations that demonstrate successful phytoextraction are conspicuously absent. There is considerable scope to improve this technology by developing crops that remove greater amounts of metal, or combining phytoextraction with a profit-making operation. Most phytoextraction studies focus on enhanced plant metal uptake, by discovering or engineering new plants, and by soil amendments to enhance metal uptake. However, even with these improvements, basic plant physiology renders phytoextraction ineffective for most contaminated sites. Here we discuss plant metal uptake as it relates to phytoextraction and explore the potential application of this technology.

2.1 Plant metal uptake

The factor determining the duration of phytoextraction is the mass of metal removed by the crop per unit of time (years) compared to the mass of metal in the soil. Theoretically, the number of years required to lower the soil's metal concentration to acceptable levels can be calculated by:

$$t = \frac{M_i - M_f}{P(M)B(M)} \quad [1]$$

where t is the time (years), M_i is the initial soil metal burden (g/ha), M_f is the target soil metal burden (g/ha), P is the crop metal concentration (g/t), and B is the crop biomass production (t/ha/yr). In the field situation, Eq. 1 gives the shortest possible time for phytoextraction, because it does not incorporate spatial or temporal heterogeneity. However, it is useful to determine which scenarios are not suitable for phytoextraction.

The efficacy of phytoextraction is thus dependent on using plants with a high biomass and a high metal concentration in the above-ground portions. Some plants, known as hyperaccumulators (BROOKS *et al.* 1977) extract large amounts of trace elements from soil as part of their normal metabolic processes. BROOKS *et al.* (1977) used hyperaccumulation to describe plants that take up Ni to concentrations greater than 1000 mg/kg on a dry matter basis on Ni-rich ultramafic (serpentine) soil. This concentration is at least an order of magnitude greater than concentrations found in other plants growing in the same environment. At present, there are in total over 400 species of known hyperaccumulators for As, Cd, Mn, Na, Ni, Tl and Zn (BROOKS 1998). While hyperaccumulator plants can achieve a high metal concentration in their shoots, their biomass production is usually inferior to non-hyperaccumulator plants. Notable exceptions are Ni hyperaccumulators of the genera *Alyssum* (ROBINSON *et al.* 1997a) and *Berkheya* (ROBINSON *et al.* 1997b). These plants can achieve shoot Ni concentrations of >10000 mg/kg (1 %) on a dry matter basis, while producing more than fifteen tonnes of dry matter per hectare per year.

2.2 Induced hyperaccumulation

For some common metals, such as Pb, there are no reliable reports of any hyperaccumulator species. Induced hyperaccumulation is a possible solution. Induced hyperaccumulation requires that high concentrations of the target metal(s) be brought into soil solution and the disruption of the root-endodermis, allowing the metal in soil solution to pass directly into the root xylem via the apoplastic pathway. Chelating agents, such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) are effective in enhancing the solubility of Pb, Cd, Cu, Zn and other trace element cations (HUANG and CUNNINGHAM 1996; BLAYLOCK *et al.* 1997; ROBINSON *et al.* 1999; THAYALAKUMARAN *et al.* 2003; TANDY *et al.* 2004). Addition of thiosulphate and thiocyanate salts to mine spoil induced plants to accumulate Hg (MORENO *et al.* 2005) and, auspiciously, Au (ANDERSON *et al.* 1998). Chloride anions increased the Cd solubility in soils due to the formation of relatively stable chloride ion complexes [CdCl⁺ and CdCl₂] (WEGGLER *et al.* 2004). Similarly, MCLAUGHLIN *et al.* (1994) demonstrated that the addition of chloride to soils enhanced plant Cd-uptake.

Solubilisation, however, does not necessarily induce bioaccumulation. For example, plants do not take up Cu that is solubilised by dissolved organic matter because the complex cannot penetrate the root endodermis and enter the xylem (BOLAN and DURAISAMY 2003). Chelant addition to the Ni hyperaccumulator *Berkheya coddii* caused a decrease in Ni uptake, despite enhancing the Ni solubility in the soil (ROBINSON *et al.* 1999). TANDY *et al.* (2005) demonstrated that chelants increased Pb uptake into the shoots but reduced Cu and Zn uptake from solution. Uptake of essential metals that are normally taken up via the symplastic pathway, is reduced by the addition of chelates by rendering the metal unavailable to the plant's metal transporters into the symplast. Nevertheless, high concentrations of chelants and soluble metal in the substrate can induce plant uptake. Uptake of metals in the presence of chelates requires that the metal pass directly into the root xylem via the apoplastic pathway, in part helped by the disruption of the root endodermis caused by high concentrations of chelants in solution. A proposed strategy for chelate-enhanced phytoremediation is application of chelate to a mature crop growing on a contaminated soil. The application of selected pesticides can disrupt root-membranes allowing the complexed metal to pass directly into the root xylem via the apoplastic pathway (BLAYLOCK 2000).

There are environmental concerns about the use of induced bioaccumulation due to metal leaching through the soil profile, possibly entering groundwater (LOMBI *et al.* 2001). Processes such as preferential flow may exacerbate metal leaching (BUNDT *et al.* 2000). While EDTA is the most often studied compound for chelant-enhanced phytoextraction, its use in this role is unacceptable due to the severe risk of leaching high concentrations of mobile metal-complexes to groundwater (NOWACK 2002). EDTA is not readily degraded under natural conditions and thus persistent in the environment. Thayalakumaran *et al.* (2003) demonstrated that, in an undisturbed soil profile containing 300 mg/kg Cu, plants removed just 5% of the Cu solubilised by EDTA. The remaining 95% leached below the root zone.

To achieve adequate solubility, chelants are usually added as Na salts. The resultant Na concentrations in the soil can reduce plant growth. Sodium also causes the dispersion of clay minerals, possibly resulting in increased preferential flow. Most chelating agents also solubilise metals other than the target metals and these then may be phytotoxic. Examples include Al and Mn. Chelators can act as chemical ploughs, redistributing surface contamination down the soil profile. There is a reduction in the concentration near the soil surface, thereby reducing exposure pathways, but there is little effect on the total amount of contaminant within the profile.

Chelant-induced phytoextraction may therefore be limited to applications where the connection to receiving waters has been broken, or where leaching is unimportant. In the former case, phytoextraction could be conducted *ex situ*. Here, the contaminated material would be placed on a liner whereby any leachate could be collected and recycled (KOS and LESTAN 2003). Such systems are already used for soil washing and the recovery of Au from low-grade ore bodies. Plants would aid in metal recovery by concentrating the metal in their biomass. The economic feasibility of lixiviant-induced Au phytoextraction has been demonstrated (ANDERSON *et al.* 2005), although the focus here is on Au recovery, rather than the cleansing of contaminated soil.

2.3 Phytovolatilisation

Phytovolatilisation is a form of phytoextraction where plants transform soil contaminants into volatile compounds that disperse in the atmosphere. Plant-microbial systems have been discovered that volatilise Hg, As and Se (BROOKS 1998). One obvious drawback of phytovolatilisation is that there is no control on the destination of the volatilised elements. For essential trace elements such as Se, however, phytovolatilisation offers the possibility of redistributing this element from areas where Se toxicity exists to downwind areas where there is Se deficiency (ZAYED *et al.* 2000). Selenium volatilisation using genetically engineered *Brassica juncea* is one of the few examples of the successful field application of phytoextraction (BAÑUELOS *et al.* 2005; BAÑUELOS 2006).

2.4 Plant-metal uptake in the field: metal heterogeneity

Most studies on plant-metal used homogeneous growth media in green-house environments. In the metal-contaminated sites where phytoextraction would be applied, the distribution of metals is typically highly heterogeneous both spatially and temporally. Eq. 1 does not account for such heterogeneity. Unlike pot trials, roots in the field may not be in intimate contact with the contaminated material, thus resulting in lower-than-expected metal uptake. Similarly, after successive croppings, the pool of metal that is available for plant uptake decreases – again reducing metal uptake. Areas of high metal contamination, so-called “hot spots”, may inhibit plant growth, rendering phytoextraction ineffective in these zones. Rewriting Eq 1 to incorporate site heterogeneity we get:

$$t = \frac{M_i(x)_{\max} - M_f}{P(E)B(E)} \quad [2]$$

where t is the time in years, x is the spatial position (latitude, longitude) $M_i(x)_{\max}$ is the maximum initial metal burden (g/ha), M_f is the target metal soil burden (g/ha), P is the crop metal concentration (g/t), and B is the biomass production (t/ha/yr), both of which are a function of the root exposure to bio-available metal E (g/t). E can be calculated thus:

$$E = \int_0^z \int_0^t R(t', z) C(M(t', z)) dt' dz \quad [3]$$

where z is depth (m), R is the root fraction (dimensionless) that is in contact with the bioavailable metal, C (g/t), which is a function of M .

Eq. 3 requires a numerical solution because it is non-linear. The times calculated using Eq. 2 will always be longer than those using Eq. 1 because the maximum metal burden $M_1(z)_{\max}$ is greater than the average metal burden, and because heterogeneity reduces plant uptake due to the above-mentioned reasons. Eq. 2 is applicable over a wide range of scales. Clearly, the degree of heterogeneity, and therefore cleanup time, will increase as the scale decreases. Setting the scale of heterogeneity is the domain of regulators. This presents difficulties, since it is an “unknown unknown” (RUMSFELD 2002).

An important parameter influencing the uptake of a metal is its bioavailability, C . Of the total metal concentration, only some fraction is available for plant uptake. Therefore, phytoextraction would be limited to this pool if there were no re-supply from less available pools. Such re-supply processes are, by definition, kinetically limited and may be very slow. HAMON and MCLAUGHLIN (1999) introduced the concept of “bioavailable contaminant stripping” for a phytoextraction procedure that aims to keep the bioavailable fraction of soil metals low enough to be harmless.

Ploughing may decrease metal heterogeneity. It may also bring metal-contaminated soil at depth to the surface, thus increasing the volume of material that can be treated using phytoextraction. However, ploughing may increase metal mobility by creating dust and enhancing metal solubility due to an increase in organic ligands caused by oxidation of the soil’s organic matter.

2.5 Other challenges facing successful phytoextraction

Eq. 2 calculates the time to cleanse a site of only one metal. However, most contaminated sites contain more than one pollutant. Few plant species can extract high concentrations of more than one element. Consequently, specific crops may have to be grown sequentially to remove several contaminants. Additional contaminants may further reduce plant growth. Therefore, the time to cleanse sites with a suite of contaminants will be longer than that required for the removal of a single metal.

The practical implementation of phytoextraction in the field presents additional challenges. At present, there are no commercial providers of seeds or seedlings of hyperaccumulator species. The growth of these crops may be reduced when they are cultivated outside their normal range. Plant-metal uptake may provide an additional exposure pathway into food chains if local herbivores consume these plants.

Phytoextraction requires ongoing site management and the processing and storage of the metal-rich biomass. Burning may reduce the volume of the biomass, however, specialised incineration facilities may be required to prevent metal-loss in the smoke (KELLER *et al.* 2005).

Environmental regulator’s limited acceptance of phytoextraction as an effective land treatment option hinders its commercial application. Regulators may be more willing to accept a long-term cleanup operation if it were demonstrated that the environmental risk is minimal during the phytoextraction because of the stabilising action of plants on soil. Therefore, use of chelators that significantly increases the risk of contaminant leaching will do little to enhance the ability of phytoextraction to meet the demands of current environmental legislation.

2.6 Outlook for metal phytoextraction

High biomass plants can be genetically altered to extract larger amounts of metal from soils (RUGH *et al.* 1998). Similarly, the potential biomass of smaller varieties of hyperaccumulator plants is being improved (OW *et al.* 1998). DHANKHER *et al.* (2002) engineered *Arabidopsis thaliana* to accumulate As by inserting two bacterial genes that imparted tolerance and the ability to translocate As to the aerial portions. The soil's microbiota plays a crucial role in plant – metal tolerance and uptake (WHITING *et al.* 2001). Engineering the rhizobiota could enhance plant uptake (NIE *et al.* 2002).

In its pure form, metal phytoextraction is only potentially applicable to a few sites because of the high costs associated with the length of time required for remediation, which may be several decades. This Achilles' heel may be circumvented if phytoextraction is combined with a profit making operation that is unaffected by any elevated plant-metal loadings. NICKS and CHAMBERS (1994) demonstrated that hyperaccumulator plants could generate revenue by extracting saleable heavy metals from otherwise sub-economic ore bodies, a technology termed phytomining. An American company, Viridian Environmental, subsequently patented the phytomining process. (US patent Nos 5711784 and 5944872). Other such revenue-generating operations may include forestry (PULFORD *et al.* 1995) and bioenergy production. Recent concern over global warming due to CO₂ emissions may provide economic incentives to produce plant-based fuels because such systems do not result in net CO₂ production. As bio-fuels are not consumed, elevated metal concentrations in such fuel-crops are of lower concern than they would be in food crops. Bio-fuels production may be an effective way for the land to be cleansed while providing a positive economic return, thus rendering the clean up time less important.

3 Phytoremediation to limit metal fluxes

Immobile metals in soil pose little risk to humans unless they are consumed directly via soil ingestion. Soil organisms such as earthworms notwithstanding, immobile metals have limited negative effects on ecosystems. Regulators are now recognising the influence of metal solubility and mobility on environmental risk. Consequently, there is an increasing adoption of a risk-based approach when assessing soil quality (SWARTJES 1999; FERNÁNDEZ *et al.* 2005). Such risk-based regulatory systems are based on the effect of the contaminant, rather than on its total concentration in the soil. Here we discuss how phytostabilisation aims to limit metal fluxes and thus may result in site remediation under risk-based regulatory regimes.

In phytostabilisation transpiration and root growth immobilise 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. Phytostabilisation involves the establishment of vegetation on the contaminated site that is left in perpetuity. Substrate amendments and a succession of plant species may be required to establish the desired climax vegetation. Establishing a healthy substrate microflora, especially mycorrhizal symbiots can greatly enhance phytostabilisation (VOSÁTKA 2001).

VANGRONSVELD *et al.* (1996) detailed how phytostabilisation could control erosion and leaching on metalliferous mine tailings. Establishing vegetation directly on the tailings reduces dust and leaching, enhances public appeal, and is often more cost effective than capping, which could require re-engineering of any tailings dam as well as a large earth-moving operation. DIX *et al.* (1997) described how phytostabilisation could prevent contaminants leaching to groundwater or local waterways, thus mitigating some of the negative environ-

mental effects associated with tip-sites, land effluent disposal and intensive farming. Phreatophytic trees such as poplars and willows are particularly suited to this role (FERRO *et al.* 1997). Deep-rooting, high water-use, evergreen trees can be used to lower a saline water table thus reducing salt toxicity to crops, a technology that has been demonstrated to be effective on some Australian soils (BELL 1999).

3.1 Metal phytostabilisation by hydraulic control

Plants require water for growth. Transpiration cools the plant and translocates essential, and nonessential, elements to the aboveground portions. Solar radiation drives plant growth and water use, and the climate sets an upper limit on evapo-transpiration (ET), defined as the volume of water transpired plus rainfall that re-evaporates from the plant's surface. Biological and soil variables determine the actual evapotranspiration of various vegetation types, which may be much less than the theoretical upper limit. In many climates, annual evapotranspiration is greater from fast-growing deep-rooted trees than from shallow rooted herbs or grasses (VOGELER *et al.* 2001). During periods of drought, deep-rooted species have greater access to water and continue to transpire after drought renders shallow-rooted species dormant. Tree canopies act as umbrellas. In addition to intercepting precipitation, canopies also reduce evaporation from below and thus keep the forest floor moist. Depending on climatic conditions, more than 15 % of rainfall may evaporate before it reaches the ground (MCNAUGHTON and JARVIS, 1983).

3.2 Plant borne organic matter affecting metal flux

Vegetation provides a continual source of organic matter in soil via plant exudates and the decomposition of litter. Metal mobility is affected by interactions between metals, mineral surfaces and ligands in solution. The effect of organic ligands on metal adsorption is dependent on the properties of both the ligand and the soil (BENJAMIN and LECKIE 1981). On one hand, organic ligands in solution compete with the surface functional groups for metal complexation and thus decrease the amount of metal adsorbed on surfaces. Dissolved Organic Carbon (DOC) is a main factor in mobilising metals, such as Cd, Cu, Pb and Zn in soils (TIPPING 2002). On the other hand, enhanced metal adsorption can occur in the presence of organic ligands by the formation of ternary surface complexes (surface-ligand-metal or surface-metal-ligand). Adding insoluble organic matter into soil can immobilise metals by increasing the amount of available binding sites.

Only few studies have investigated the influence of plants on metal leaching from contaminated soils under controlled conditions. BANKS *et al.* (1994) found that the Zn leaching from a mine-tailing contaminated soil increased in the order no plants < plants with microbes < plants without microbes. In a further study using contaminated mine tailings and clean subsoil and topsoil covering, the presence of plants increased Cu and Cd leaching in all columns, while Pb was unaffected (ZHU *et al.* 1999). TURPEINEN *et al.* (2000) demonstrated that pine seedlings reduced Pb solubility by up to 93 %. RÖMKENS *et al.* (1999) compared Cu speciation in soils with and without plants. Cu solubility was higher in planted pots, but the calculated free Cu²⁺ ion concentration was orders of magnitude lower than in soils without plants.

3.3 Rhizosphere acidification

Plant roots excrete H^+ ions that exchange with nutrient base cations. In addition, many plants exude organic acids that mobilise iron and perhaps other essential metals of low availability. These organic acids solubilise metals by competing for cation binding sites. Root exudations may acidify the rhizosphere by up to 2 pH units (SALISBURY and ROSS 1978). Such acidification invariably increases the solubility of non-essential metal cations such as Cd^{2+} (NAIDU *et al.* 1994).

3.4 Vegetation promoting the growth of soil organisms

The exudation of organic substances by plant roots into the rhizosphere generally promotes the growth of bacteria, fungi and soil-borne animals. Root exudates provide a substrate for growth and roots improve soil aeration by extracting soil moisture and forming continuous channels for drainage and air exchange. However, increased metabolic activity can result in anaerobic conditions if more oxygen is consumed than can be re-supplied. The stimulation of soil biological activity thus affects the speciation, and therefore mobility, of trace elements (PEDERSEN and ALBINSSON 1992). The influence of redox processes on toxic trace metal speciation in soil is particularly striking in the case of chromium. Some soil bacteria reduce Cr(IV) to Cr(III) (PAL and PAUL 2004). When present in the +6 oxidation state, Cr is more mobile, more readily bioaccumulated, and 100 to 1000 times more toxic than when present in the +3 oxidation state (KERNDORFF and SCHNITZER 1980). Motile soil animals such as worms and rotifers that feed on decaying plant matter can also affect the transport and distribution of trace elements in soils.

3.5 Root effects

The formation of root channels not only affects water flux via enhanced soil drainage and aeration, but also provides pathways for the rapid transport of solutes and suspended particles and colloids (LESTURGEZ *et al.* 2004). These transport pathways can exacerbate the risk of groundwater contamination by reducing the contact time of the soil solution with the soil matrix and soil organisms that could otherwise retard the movement by sorption and transformation processes (BUNDT *et al.* 2000).

The roots of some tree species avoid metal-contaminated hotspots (DICKINSON *et al.* 1991; BRECKLE and KAHLE 1992). Conversely, roots of the zinc hyperaccumulator plant *Thlaspi caerulescens* actively forage zinc-rich hotspots in soils (SCHWARTZ *et al.* 1999; WHITING *et al.* 2000). Both types of growth response may profoundly affect metal uptake as well as leaching. However, there is a lacuna of knowledge on the underlying principles of how heterogeneously distributed trace elements influence root growth.

3.6 Implementing phytostabilisation

As discussed above, biological parameters are of prime importance for metal phytostabilisation. Species should necessarily tolerate local climatic and edaphic conditions. Shallow-rooted turf species control surface erosion and dust; however, most turf species do not remove water from deep within the soil profile. The shallow-rooted nature of many turf species results in greater contaminant leaching than would be the case if trees were planted

(VOGELER *et al.* 2001). *Populus* spp. and *Salix* spp. are commonly-used tree species. They are effective because of their rapid establishment, high water-use, tolerance to a wide range of environmental conditions, ease of propagation, and their ability to take up high levels of some contaminants (QUIN *et al.* 2001).

Phytoremediation systems that use several species or varieties overcome the risk that a new pest or climatic event destroys all the plants. Phytostabilisation may require plant trials to determine the optimal suite of species, particularly for non-soil media such as sewage sludge or mine tailings. Low-growing species may be combined with deciduous tree species to provide a transpiring green surface during the winter months. Legumes enhance fertility in nitrogen-deficient substrates.

Before planting, capping contaminated sites with fertile soil provides a better substrate for plant growth and a buffer zone that stores water from heavy rainfall events. Although more expensive, such capping systems reduce leaching by providing a deeper root zone, thus providing more time for the vegetation to extract and transpire the infiltrated rain water. The cost of earthmoving and reengineering the site offsets the advantages of a soil cap.

Vegetative caps are porous and leaching will occur in humid climates. Similarly, surface runoff is likely after a bout of high intensity rainfall. Trapping any leachate and circulating it back onto the vegetation will further reduce the metal flux (NIXON *et al.* 2001). Leachate recirculation can occur ad infinitum: each pass through the root zone further modifies the leachate. An increase in the level of solutes, especially Na^+ and Cl^- , may be of concern during leachate reapplication. However, depending on the composition of the leachate, reapplication may have beneficial effects on plant growth compared to un-irrigated vegetation (NIXON *et al.*, 2001). Leachate irrigation via overhead sprinklers increases total evaporation, but may negatively affect plant growth if the leachate contains high contaminant concentrations. Surface irrigation may avoid this problem. Drainage is inevitable when rainfall is greater than evapotranspiration. However, vegetative caps may eliminate drainage during low-rainfall periods. Depending on the metal, the high flow rates of receiving waters may dilute any leachate to the point that they do not pose an environmental risk.

3.7 Limitations of phytostabilisation

Like any remediation technology, phytostabilisation is not suitable for all metal-contaminated sites. Metal toxicity or adverse environmental conditions may prevent plant development. In high-rainfall regions, plant transpiration may not sufficiently reduce drainage from the site. The time required to implement phytostabilisation is dependent on the plant species. In general, it will take 2–4 years with perennial tree species. Most importantly, phytostabilisation requires that the site be permanently vegetated, thus limiting future land use options. Phytostabilisation is therefore more suitable for low value sites, where the land value is small compared to the cost of soil excavation and land-filling. As with phytoextraction, phytostabilisation requires that regulators be convinced of its efficacy. Unlike phytoextraction, providers of phytostabilisation technology can point to numerous examples of its successful application on areas as diverse as acidic mine tailings (BROWN *et al.* 2005), wood-waste piles (ROBINSON *et al.* 2003b) and disused sheep-dipping sites (ROBINSON and ANDERSON 2006).

4 Conclusions

Unlike other remediation systems such as capping and soil removal, phytoremediation systems are site dependent. It is impractical to conduct long-term field trials to optimise the phytoremediation system for every site. Therefore, whole system models that calculate metal flux are an essential component of phytoremediation. Such models can eliminate unnecessary field trials by revealing where phytoremediation will not meet regulations under a risk-based regime. Conversely, validated models could be used to gain regulatory approval for phytoremediation without the need for lengthy demonstration trials. Site management can also be optimised via modelling.

Although various aspects of vegetation-trace element interactions have been investigated in detail, there is, as yet, no quantitative model that integrates the aforementioned interactions thus calculating the environmental “fate” of trace elements in plant soil systems. This is illustrated by the current body of literature on the role of vegetation for the immobilisation of trace elements on contaminated sites. A wealth of information exists on plant metal-tolerance and plant metal-accumulation, whereas the effects of phytostabilisation on the mobility of the trace elements have received only minor attention.

Existing “whole system” models such as Soil Plant Atmosphere System Model (SPASMO), Leaching Estimation and Chemistry Model (LEACHM), HYDRUS – 1D, Water and Agrochemicals in soil, crop and Vadose Environment (WAVE) are designed to calculate leaching of agrichemicals (SHARMAH *et al.* 2005). These models use the Penman-Monteith equation for evapotranspiration (ALLEN *et al.* 1998), Richards’ and the Convection – Dispersion Equations for water and solute transport, as well as simplified “tipping bucket” algorithms (GREEN *et al.* 1999). While such simulation models can be adapted to calculate trace element movement, they do not incorporate specific root-trace element interactions, nor do they calculate the long-term changes in soil induced by vegetation that affect trace element mobility. However, these models provide a frame work of water and solute-transport equations into which chemical and biological interactions could be incorporated.

5 References

- ALLEN, R.G.; PERERIRA, L.S.; RAES, D.; SMITH, M., 1998: Crop Evapotranspiration. Guidelines for Computing Crop Water Requirements. In: FAO Irrigation and Drainage Paper No. 56; FAO, Rome.
- ANDERSON, C.W.N.; BROOKS, R.R.; STEWART, R.B.; SIMCOCK, R., 1998: Induced hyperaccumulation of gold in plants. *Nature* 395: 553–554.
- ANDERSON, C.; MORENO, F.; MEECH, J., 2005: A field demonstration of gold phytoextraction technology. *Miner. Eng.* 18: 385–392.
- BANKS, M.K.; SCHWAB, A.P.; FLEMING, G.R.; HETRICK, B.A., 1994: Effects of plants and soil microflora on leaching of zinc from mine tailings. *Chemosphere* 29, 8: 1691–1699.
- BAÑUELOS, G., 2006: Multi-faceted considerations for sustainable phytoremediation under field conditions. *For. Snow Landsc. Res.* 80, 2: ???–???
- BAÑUELOS, G.; TERRY, N.; LEDUC, D.L.; PILON-SMITS, E.A.H; MACKEY, B., 2005: Field trial of transgenic Indian mustard plants shows enhanced phytoremediation of selenium-contaminated sediment. *Environ. Sci. Technol.* 39, 6: 1771–1777.
- BELL, D.T., 1999: Australian trees for the rehabilitation of waterlogged and salinity damaged soils. *Aust. J. Bot.* 47, 5: 697–716.
- BENJAMIN, M.M.; LECKIE, J.O., 1981: Conceptual model for metal-ligand-surface interactions during adsorption. *Environ. Sci. Technol.* 15, 9: 1050–1057.

- BLAYLOCK, M.J., 2000: Field demonstrations of phytoremediation of Pb contaminated soils. In: TERRY, N.; BAÑUELOS, G. (eds) Phytoremediation of contaminated soil and water. Boca Raton, FL. Lewis Publishers, 1–12.
- BLAYLOCK, M.J.; SALT, D.E.; DUSHENKOV, S.; ZAKHAROVA, O.; GUSSMAN, C.; KAPULNIK, Y.; ENSLEY, B.D.; RASKIN, I., 1997: Enhanced accumulation of Pb in Indian Mustard by soil-applied chelating agents. *Environ. Sci. Technol.* 31, 860–865.
- BOLAN, N.S.; DURAISAMY, V.P., 2003: Role of inorganic and organic soil amendments on immobilisation and phytoavailability of heavy metals: a review involving specific case studies. *Aust. J. Soil Res.* 41: 533.
- BRECKLE, S.W.; KAHLE, H., 1992: Effects of toxic heavy-metals (Cd,Pb) on growth and mineral nutrition of beech (*Fagus sylvatica* L.) *Vegetatio* 101: 43–53.
- BROOKS, R.R., 1998: Phytoremediation by volatilisation. In: BROOKS, R.R. (ed) Plants that hyperaccumulate heavy metals: their role in phytoremediation, microbiology, archaeology, mineral exploration and phytomining. Wallingford, UK. CAB International. 289–312.
- BROOKS, R.R.; LEE, J.; REEVES, R.D.; JAFFRÉ, T., 1977: Detection of nickeliferous rocks by analysis of herbarium specimens of indicator plants. *J. Geochem. Explor.* 7: 49–77.
- BROWN, S.; SPRENGER, M.; MAXEMCHUK, A.; COMPTON, H., 2005: Ecosystem function in alluvial tailings after biosolids and lime addition. *J. Environ. Qual.* 34, 1: 139–148.
- BUNDT, M.; ALBRECHT, A.; FROIDEVAUX, P.; BLASER, P.; FLUHLER, H., 2000: Impact of Preferential Flow on Radionuclide Distribution in Soil. *Environ. Sci. Technol.* 34: 3895–3899.
- CLOTHIER, B.E.; GREEN, S.R., 1997: Roots: The big movers of water and chemical in soil. *Soil Sci.* 162, 8: 534–543.
- DHANKHER, O.P.; LI, Y.; ROSEN, B.P.; SHI, J.; SALT, D.; SENECOFF, J.F.; SASHTI, N.A.; MEAGHER, R.B., 2002: Engineering tolerance and hyperaccumulation of arsenic in plants by combining arsenate reductase and γ -glutamylcysteine synthetase expression. *Nat. Biotechnol.* 20: 1140–1145.
- DICKINSON, N.M.M TURNER, A.P.; LEPP, N.W., 1991: Survival of trees in a metal-contaminated environment. *Water Air Soil Pollut.* 92: 253–256.
- DIX, M.E.; KLOPFENSTEIN, N.B.; ZHANG, J.W.; WORKMAN, S.W.; KIM, M.S., 1997: Potential use of *Populus* for phytoremediation of environmental pollution in riparian zones. USDA For. Serv. Gen. Tech. Rep. RM-GTR-297.
- FERNÁNDEZ, M.D.; CAGIGAL, E.; VEGA, M.M.; URZELAI, A.; BABÍN, M.; PRO, J.; TARAZONA, J.V., 2005: Ecological risk assessment of contaminated soils through direct toxicity assessment. *Ecotoxicol. Environ. Saf.* 62: 174–184.
- FERRO, A.M.; RIEDER, J.P.; KENNEDY, J.; KJELGREN, R., 1997: Phytoremediation of groundwater using poplar trees. In: THIBEAULT, C.A.; SAVAGE, L.M. (eds) Phytoremediation. International business communications inc. Southborough. 201–212.
- GREEN, S.R.; CLOTHIER, B.E.; MILLS, T.M.; MILLAR, A., 1999: Risk assessment of irrigation requirements of field crops in a maritime climate. *J. Crop Prod.* 2, 2: 353–377.
- HAMON, R.E.; MCLAUGHLIN, M.J., 1999: Use of the hyperaccumulator *Thlaspi cearulescens* for bioavailable contaminant stripping. In: WENZEL, W.W.; ADRIANO, D.C.; ALLOWAY, B.; DONER, H.; KELLER, C.; LEPP, N.W.; MENCH, M.; NAIDU, R.; PIERZYNSKI, G.M. (eds) Proc. 5th International Conference on the Biogeochemistry of Trace Elements. Vienna. 908–909.
- HUANG, J.W.; CUNNINGHAM, S.D., 1996: Lead phytoextraction: species variation in lead uptake and translocation. *New Phytol.* 134: 75–84.
- KELLER, C.; LUDWIG, C.; DAVOLI, F.; WOCHLE, J., 2005: Thermal Treatment of Metal-Enriched Biomass Produced from Heavy Metal Phytoextraction. *Environ. Sci. Technol.* 39, 9: 3359–3367.
- KERNDORFF, H.; SCHNITZER, M., 1980: Sorption of metals on humic acids. *Geochim. Cosmochim. Acta.* 44: 1701.
- KOS, B.; LESTAN, D., 2003: Induced phytoextraction/soil washing of lead using biodegradable chelate and permeable barriers. *Environ. Sci. Technol.* 37: 624–629.
- LESTURGEZ, G.; POSS, R.; HARTMANN, C.; BOURDON, E.; NOBLE, A.; RATANA-ANUPAP, S., 2004: Roots of *Stylosanthes hamata* create macropores in the compact layer of a sandy soil. *Plant Soil* 260, 1–2: 101–109.

- LOMBI, E.; ZHAO, F.J.; DUNHAM, S.J.; MCGRATH, S.P., 2001: Phytoremediation of heavy-metal contaminated soils: Natural hyperaccumulation versus chemically enhanced phytoextraction. *J. Environ. Qual.* 30: 1919.
- MCLAUGHLIN, M.J.; PALMER, L.T.; TILLER, K.G.; BEECH, T.A.; SMART, M.K., 1994: Increased soil salinity causes elevated cadmium concentrations in field grown potato tubers. *J. Environ. Qual.* 23: 1013.
- MCNAUGHTON, K.G.; JARVIS, P.G., 1983: Effects of Vegetation on Transpiration and Evaporation. In: KOZLOWSKI, T.T. (ed) *Water Deficits and Plant Growth, Vol. VII, Additional Woody Crop Plants*. New York, Academic Press. 1–47.
- MORENO, F.N.; ANDERSON, C.W.N.; STEWART, R.B.; ROBINSON, B.H.; GHOMSHEI, M.; MEECH, J.A., 2005: Induced plant uptake and transport of mercury in the presence of sulphur-containing ligands and humic acid. *New Phytol.* 166, 2: 445–454.
- NAIDU, R.; BOLAN, N.S.; KOOKANA, R.S.; TILLER, K.G., 1994: Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. *Eur. J. Soil Sci.* 45: 419.
- NICKS, L.; CHAMBERS, M.F., 1994: Nickel farm. *Discover* September, 19.
- NIE, L.; SHAH, S.; RASHID, A.; BURD, G.I.; DIXON, G.D.; GLICK, B.R., 2002: Phytoremediation of arsenate contaminated soil by transgenic canola and the plant growth-promoting bacterium *Enterobacter cloacae* CAL2. *Plant Physiol. Biochem.* 40: 355–361.
- NIXON, D.J.; STEVENS, W.; TYRREL, S.F.; BRIERLEY, E.D.R., 2001: The potential for short rotation forestry on restored landfill caps. *Bioresour. Technol.* 77: 237–245.
- NOWACK, B., 2002: Environmental chemistry of aminopolycarboxylate chelating agents. *Environ. Sci. Technol.* 36: 4009–4016.
- OW, D.W.; SHEWRY, P.R.; NAPIER, J.A.; DAVIS, P.J., 1998: Prospects of engineering heavy metal detoxification genes in plants. In: *Engineering crop plants for industrial end uses. Proceedings of the Symposium of the Industrial Biochemistry and Biotechnology Group of the Biochemical Society, IACR-Long Ashton Research Station, Long Ashton, Bristol, UK, September.* 111–124.
- PAL, A.; PAUL, A.K., 2004: Aerobic chromate reduction by chromium-resistant bacteria isolated from serpentine soil. *Microbiol. Res.* 159, 4: 347–354.
- PEDERSEN, K.; ALBINSSON, Y., 1992: Possible effects of bacteria on trace element migration in crystalline rock beds. *Radiochim. Acta* 58–9: 365–369.
- PULFORD, I.D.; MCGREGOR, S.D.; DUNCAN, H.J.; WHEELER, C.T., 1995: Uptake of Heavy Metals From Contaminated Soil by Trees. Fourteenth Annual Symposium. *Current Topics in Plant Biochemistry, Physiology and Molecular Biology. Will Plants have a role in Bioremediation?* April 19–22, 1995, Columbia, MO. Interdisciplinary Plant Group, University of Missouri, Columbia, MO. 49–50.
- QUINN, J.J.; NEGRI, C.M.; HINCHMAN, R.R.; MOOS, L.P.; WOZNIAK, J.B.; GATLIFF, E., 2001: Predicting the effect of deep-rooted hybrid poplars on the groundwater flow system at a large scale phytoremediation site. *Int. J. Phytoremediat.* 3, 1: 41–60.
- ROBINSON, B.H.; ANDERSON, C.W.N., 2006: Phytoremediation in New Zealand/Australia. In: WILLEY, N. (ed) *Phytoremediation Methods and Reviews*. Totowa, NJ Humana Press. 453–466.
- ROBINSON, B.H.; BROOKS, R.R.; HOWES, A.W.; KIRKMAN, J.H.; GREGG, P.E.H., 1997a: The potential of the high-biomass Ni hyperaccumulator *Berkheya coddii* for phytoremediation and phytomining. *J. Geochem. Explor.* 60: 115–126.
- ROBINSON, B.H.; BROOKS, R.R.; CLOTHIER, B.E., 1999: Soil Amendments Affecting Nickel and Cobalt Uptake by *Berkheya coddii*: Potential Use for Phytomining and Phytoremediation. *Ann. Bot.-London* 84: 689–694.
- ROBINSON, B.H.; CHIARUCCI, A.; BROOKS, R.R.; PETIT, D.; KIRKMAN, J.H.; GREGG, P.E.H.; DE DOMINICIS, V., 1997b: The nickel hyperaccumulator plant *Alyssum bertolonii* as a potential agent for phytoremediation and the phytomining of nickel. *J. Geochem. Explor.* 59: 75–86
- ROBINSON, B.H.; FERNÁNDEZ, J.E.; MADEJÓN, P.; MARAÑÓN, T.; MURILLO, J.M.; GREEN, S.R.; CLOTHIER, B.E., 2003a: Phytoextraction: an assessment of biogeochemical and economic viability. *Plant Soil* 249, 1: 117–125.

- ROBINSON, B.H.; GREEN, S.R.; MILLS, T.M.; CLOTHIER, B.E.; VAN DER VELDE, M.; LAPLANE, R.; FUNG, L.; DEURER, M.; HURST, S.; THAYALAKUMARAN, T.; VAN DEN DIJSSSEL, C., 2003b: Phytoremediation: using plants as biopumps to improve degraded environments. *Aust. J. Soil Res.* 41, 3: 599–611.
- RÖMKENS, P.F.A.M.; BOUWMAN, L.A.; BOON, G.T., 1999: Effect of plant growth on copper solubility and speciation in soil solution samples. *Environ. Pollut.* 106: 315.
- RUGH, C.L.; SENECOFF, J.F.; MEAGHER, R.B.; MERKLE, S.A., 1998: Development of transgenic yellow poplar for mercury phytoremediation. *Nat. Biotechnol.* 16, 10: 925–928.
- RUMSFELD, D.H., 2002: DoD News Briefing – Secretary Rumsfeld and General Myers. United States Department of Defence. http://www.defenselink.mil/transcripts/2002/t02122002_t212sdv2.html. (Accessed December, 2005).
- SALISBURY, F.B.; ROSS, C.W., 1978: The Photosynthesis–Transpiration Compromise. In *Plant Physiology*, 2nd Ed.; Belmont, CA: Wadsworth Publishing Company Inc. 1978.
- SCHWARTZ, C.; MOREL, J.L.; SAUMIER, S.; WHITING, S.N.; BAKER, A.J.M., 1999: Root development of the zinc-hyperaccumulator plant *Thlaspi caerulescens* as affected by metal origin, content and localization in the soil. *Plant Soil* 208: 103–115.
- SELLERS, W.D., 1965: *Physical Climatology*. Chicago: University of Chicago Press. 272 pp.
- SHARMAH, A.J.; CLOSE, M.E.; PANG, L.; LEE, R.; GREEN, S.R., 2005: Field study of leaching in a Himatangi sand (Manawatu) and a Kiripaka bouldery clay loam (Northland) 2: Simulation using LEACHM, HYDRUS-1D, Gleams and SPASMO models. *Aust. J. Soil Res.* 43, 4: 471–489.
- SWARTJES, F.A., 1999: Risk-based assessment of soil and groundwater quality in the Netherlands: standards and remediation urgency. *Risk Anal.* 19: 1235–1249.
- TANDY, S.; BOSSART, K.; MUELLER, R.; RITSCHEL, J.; HAUSER, L.; SCHULIN, R.; NOWACK, B., 2004: Extraction of heavy metals from soils using biodegradable chelating agents. *Environ. Sci. Technol.* 40: 2753–2758.
- TANDY, S.; SCHULIN, R.; NOWACK, B., 2005: Uptake of metals during chelant-assisted phytoextraction related to the solubilized metal concentration. *Environ. Sci. Technol.* 38: 937–944.
- THAYALAKUMARAN, T.; ROBINSON, B.H.; VOGELER, I.; SCOTTER, D.R.; CLOTHIER, B.E.; PERCIVAL, H.J., 2003: Plant uptake and leaching of copper during EDTA-enhanced phytoremediation of repacked and undisturbed soil. *Plant Soil* 254: 415–423.
- TIPPING, E., 2002: *Cation binding by humic substances*. Cambridge, UK: Cambridge University Press.
- TURPEINEN, R.; SALMINEN, J.; KAIRESAALO, T., 2000: Mobility and bioavailability of lead in contaminated boreal forest soil. *Environ. Sci. Technol.* 34: 5152.
- VANGRONSVELD, J.; COLPAERT, J.V.; VAN TICHELEN, K.K., 1996: Reclamation of a bare industrial area contaminated by non-ferrous metals: physiochemical and biological evaluation of the durability of soil treatment and revegetation. *Environ. Pollut.* 94, 2: 131–140.
- VOGELER, I.; GREEN, S.R.; CLOTHIER, B.E.; KIRKHAM, M.B.; ROBINSON, B.H., 2001: Contaminant Transport in the Root Zone. In: ISKANDAR, I.K.; KIRKHAM, M.B. (eds) *Trace Elements in the Soil, Bioavailability, Flux and Transfer*. Boca Raton, FL: Lewis Publishers. 175–198.
- VOSÁTKA, M., 2001: A future role for the use of arbuscular mycorrhiza fungi in soil remediation: a chance for small-medium enterprises? *Minerva Biotechnol.* 13: 69–72.
- WEGGLER, K.; MCLAUGHLIN, M.J.; GRAHAM, R.D., 2004: Effect of chloride in soil solution on the plant availability of biosolid-borne cadmium. *J. Environ. Qual.* 33: 496.
- WHITING, S.N.; LEAKE, J.R.; MCGRATH, S.P.; BAKER, A.J.M., 2001: Rhizosphere bacteria mobilise Zn for hyperaccumulation by *Thlaspi caerulescens*. *Environ. Sci. Technol.* 35, 15: 3144–3150.
- WHITING, S.N.; LEAKE, J.R.; MCGRATH, S.P.; BAKER, A.J.M., 2000: Positive responses to Zn and Cd by the roots of the Zn and Cd hyperaccumulator *Thlaspi caerulescens*. *New Phytol.* 145: 199–210.
- ZAYED, A.; PILON-SMITS, E.; DESOUSA, M.; LIN, Z.Q.; TERRY, N., 2000: Remediation of selenium-polluted soils and waters by phytovolatilisation. In: TERRY, N.; BAÑUELOS, G. (eds) *Phytoremediation of contaminated soil and water*. Boca Raton, FL: Lewis Publishers 1–12.
- ZHU, D.; SCHWAB, A.P.; BANKS, M.K., 1999: Heavy metal leaching from mine tailings as affected by plants. *J. Environ. Qual.* 28: 1727–1732.