Vegetative Remediation at Superfund Sites

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1 Introduction

Non-ferrous metal mining activities across the world have produced a variety of environmental problems. Three types of contamination created by large-scale metal extraction have been identified.[1] Waste-rock, tailings, and slag are primary contaminants. Secondary contamination occurs in groundwater beneath open pits and ponds, sediments in river channels and reservoirs, floodplain soils impacted by contaminated sediment, and soil affected by smelter emissions. River sediments reworked from floodplains and groundwater from contaminated reservoir sediments were identified as tertiary contaminants. In the United States, many of these contaminated sites have been classified as Superfund sites, which dictates that some remedial action be taken in the future.

The metals or metalloids most commonly found at Superfund sites are arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), and zinc (Zn).[2] Most of the discussion will focus on As, Cd, Pb, and Zn as elements of concern for two Superfund sites: the Whitewood Creek in the Black Hills of western South Dakota and the Galena site located in southeastern Kansas. Contamination of surface water and groundwater with As and Cd from over one hundred years of gold mining activity is the principal concern at the Whitewood Creek site. The Galena site is located in the Tri-State mining region (southeast Kansas, southwest Missouri, and northeast Oklahoma), where Pb and Zn sulfide ores were mined and smelted extensively from the mid-1800s to approximately the 1950s. Pb and Zn contaminated mine spoils, soils, groundwater, and surface water are extensive problems in the Tri-State Region.

There are two primary reasons for concern over elevated concentrations of trace elements in waters, soils, or mine spoils. First, elevated human and animal exposure to the metals can occur through food chain transfer, ingestion of wind-blown dusts, or direct ingestion of soil. Persons living downwind of an old smelter site in the Tri-State region could consume at least 50% more Pb and Cd by eating some of their home-produced food items than by eating comparable

[1] J. N. Moore and S. N. Luoma, *Environ. Sci. Technol.*, 1990, **24**, 1278–1285.
[2] J. E. McLean and B. E. Bledsoe, 'Behavior of Metals in Soils', EPA Ground Water Issue, EPA/540/S-92/018, US Environmental Protection Agency, Washington, DC, 1992.

Table 1 Remediation options for metal-contaminated sites

Method	*Comments*
Excavation followed by:	
Solidification	Addition of cementing agent to produce a hardened, non-porous, non-leachable material.
Vitrification	Heating to produce a glass-like, non-porous, non-leachable material.
Washing	Chelate or acid extraction.
Leaching	Pile or batch leaching with chelates or acids.
Particle size segregation	Selective removal of finer particle sizes (*e.g.* clay) that have the highest metal concentrations.
In situ	
Solidification	As described above.
Vitrification	As described above.
Encapsulation	Cover site with impermeable layer.
Attenuation	Dilution with uncontaminated material.
Volatilization	Promote formation of volatile methylated species (Se, As, Hg).
Vegetative	Promote vegetative growth by providing proper fertility and water availability, reducing metal bioavailability, and/or using metal-tolerant plant species.

items purchased in a control area.[3] Epidemiological studies have shown a significantly higher prevalence of chronic kidney disease, heart disease, skin cancer, and anemia in persons living for more than 5 years in Galena, KS, than in the populations of two nearby control towns.[4] Inhalation of As has been associated with lung cancer, and ingestion of As is judged to cause skin cancer.[5] The second reason for concern relates to the phytotoxic potential of the metals, which can limit biomass production.[6,7] This inhibition of plant growth can have direct negative effects, such as a limitation of crop yields. The effects also can be indirect. For example, the lack of vegetative cover probably will result in enhanced wind and water erosion, which further disperses the contaminants and increases the likelihood of human exposure via wind-blown dusts.

Numerous remediation options exist for metal-contaminated sites, as shown in Table 1. An excellent description of some experimental methods has been published.[8] The methods requiring excavation have a significant drawback given that the volume of material to be treated can be quite large. For example,

[3] J. V. Lagerwerff and D. L. Brower, in 'Trace Substances in Environmental Health, Vol. 8, ed. D. D. Hemphill, University of Missouri, Columbia, MO, 1974.

[4] J.S. Neuberger, M. Mulhall, M.C. Pomatto, J. Sheverbush, and R.S. Hassanein, *Sci. Total Environ.*, 1990, **94**, 261–272.

[5] D.W. North, *Environ. Geochem. Health*, 1992, **14**, 59–62.

[6] S.B. Bradley and J.J. Cox, *Sci. Total Environ.*, 1986, **50**, 103–128.

[7] G.M. Pierzynski and A.P. Schwab, *J. Environ. Qual.*, 1993, **22**, 247–254.

[8] United States Environmental Protection Agency, 'The Superfund Innovative Technology Evaluation Program: Technology Profiles', (ed. 5) EPA/S40/R-92/077. US Government Printing Office, Washington, DC, 1992.

Cherokee County, KS (which contains the Galena Superfund site) has numerous abandoned Pb and Zn mining and smelter sites. The soil survey for the county reports 1316 hectares of mine dump sites,[9] which have high Pb and Zn concentrations and would benefit from remediation. If only the top 300 mm of these areas were treated, this would involve approximately 4.8×10^6 Mg of material (1 Mg ≡ 1 tonne). This is a conservative estimate, because most areas would require more than the top 300 mm be treated, and some areas that need remediation are not shown in the soil survey.

The beneficial effects of plants in remediation of soil and groundwater contaminated with hazardous organic compounds have been presented.[10] The vegetative remediation methods for metal contaminated sites, which are the focus of this paper, can utilize amendments that reduce metal bioavailability as well as metal-tolerant plant species with the goal of establishing a vegetative cover sufficiently dense to prevent wind and water erosion and that will remain viable for extended periods. The vegetation can be native or introduced grasses, forbs, or trees. The advantages of vegetative remediation include the minimization of wind and water erosion, lower cost as compared with other remediation options, improvement of aesthetics, no production of waste products, increases in soil organic C concentrations (binds metals, improves soil tilth, *etc.*), and the potential to serve as a temporary remediation until more suitable methods are funded or developed. In addition, modeling efforts suggest that vegetation, particularly trees, probably would reduce net percolation through the soil or mine spoil material and reduce the leaching potential of the metals. Disadvantages include the lack of data on the long-term viability of the vegetation, the possibility of producing metal-rich plants that could be consumed by wildlife or other animals, the lack of transpiration by the plants during certain periods of the year, and the possibility of transport of radionuclides or metals in mixed wastes due to excretion of soluble exudates by plant roots.

The goals of this article are to briefly describe the chemical and microbiological environment in mine spoils and contaminated soils, to describe several case studies where vegetation has been used in remediation of Superfund mine sites, and to present a generalized model that can aid in predicting the effects of vegetation on a contaminated site.

2 Chemical Aspects of Metal-contaminated Soils and Mine Spoils

Chemical characteristics such as total metal concentrations, pH, cation exchange capacity, plant nutrient concentrations, and organic C content in contaminated soils and mine spoils can vary considerably. English soils having less than 50% vegetative cover contained 1660 mg kg^{-1} Pb and 4230 mg kg^{-1} Zn in the surface 50 mm.[11] Soils with vegetation exhibiting heavy metal chlorosis had 323 mg kg^{-1} Pb and 676 mg kg^{-1} Zn in the top 50 mm.[6] Zn and Pb concentrations as high as

[9] Soil Survey Staff, 'Soil Survey of Cherokee County, Kansas', USDA Soil Conservation Service, US Government Printing Office, Washington, DC, 1985.

[10] J. F. Shimp, J. C. Tracy, L. C. Davis, E. Lee, W. Huang, and L. E. Erickson, *Crit. Rev. Environ. Sci. Technol.*, 1993, **23**, 41–77.

[11] M. S. Johnson and J. W. Eaton, *J. Environ. Qual.*, 1980, **9**, 175–179.

43 750 and 4500 mg kg^{-1}, respectively, have been reported for mine spoil material.[12] Gold mine tailing in South Dakota contained 917 mg kg^{-1} As.[13] In the United States, the Toxicity Characteristic Leaching Potential (TCLP) is used to classify materials as hazardous or not.[14] The procedure involves a single extraction with 0.1 M acetic acid in an effort to simulate leaching conditions that a waste might experience. If the concentrations of certain metals exceed some standard values, the material is classified as hazardous.

The pH of the contaminated soils or mine spoil materials can range from values as low as 2.0 to as high as 8.0. The very acid conditions typically are associated with the weathering of sulfide-bearing minerals. The alkaline conditions can be caused by the presence of a calcareous matrix. In terms of cation exchange capacities, plant nutrient concentrations, and organic C concentrations, one can consider contaminated soils and mine spoils as diluted soils. That is, these parameters will range from extremely low values (highly diluted) to those typical for soils (not diluted). Indeed, low fertility because of low cation exchange capacities and plant nutrient concentrations and low water holding capacities because of low organic C concentrations are as limiting as metal phytotoxicities in establishment of vegetation in mine spoil materials.

The behavior of metals in soils has been reviewed.[2] Most metals interact with the inorganic and organic matter that is present in the root–soil environment; potential pools or forms of metals include those dissolved in the soil solution, adsorbed to the vegetation's root system, adsorbed to insoluble organic matter, bonded to exchange sites on inorganic soil constituents, precipitated or coprecipitated as solids, and within the soil biomass. Generally, the total metal concentration in soil is a poor indicator of metal availability to plants. The concept of metal bioavailability, in the context of soils and mine spoils, refers to some sub-fraction of the total amount of a metal that best correlates to plant response. That response is typically measured in terms of biomass production or metal concentrations in plant tissue. Any of the pools or forms of metals described above can contribute to the bioavailable fraction. In practice, metal bioavailability is often operationally defined as that extracted with a particular extractant.

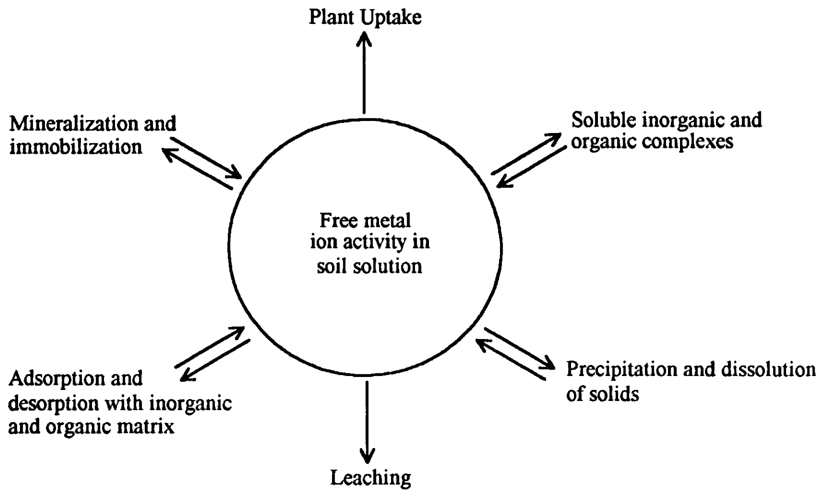
Metals present in the soil solution can be free metal ions, soluble complexes with organic or inorganic ligands, or associated with mobile colloidal materials. Soil solution studies generally show that plant response to metals is correlated with the free metal ion activity. Therefore, one aspect of metal bioavailability is related to which factor or factors contribute to the activity of the free metal ion in the soil solution. These interactions are summarized in Figure 1. Equilibrium models often are used to estimate free metal ion activities. The difficulty with the application of these models in the soil–root environment is associated with properly modeling all of the interactions identified above.

[12] G. M. Pierzynski and A. P. Schwab, in Proceedings of the Conference on Hazardous Waste Research, ed. L. E. Erickson, Manhattan, KS, 1990, pp. 511–520.

[13] D. F. Aoki, 'The Uptake of Arsenic and Cadmium in Mine Tailings by Poplar Trees', MS Thesis, University of Iowa, Iowa City, IA, 1992.

[14] US Environmental Protection Agency, 'Test Methods for Evaluating Solid Waste: Physical/Chemical Methods', SW-846. USEPA, Office of Solid Waste and Emergency Response, Washington, DC, 1986.

Figure 1 Processes influencing free metal ion activities in soil solutions



Metal fractionation or sequential extraction schemes sometimes are used to describe metal behavior in soils.[7] The schemes cannot be entirely specific for a given fraction within the soil, and an additional problem of re-adsorption of extracted metals to the soil constituents exists. Therefore, the value of the schemes in obtaining information on fundamental processes that influence metal behavior in soils is limited. However, the schemes can be useful in an empirical sense.

Remediation of a metal-contaminated site can include three possible changes in the chemical characteristics of the soil or mine spoil material. The total metal concentration can be reduced, as is the case with washing or leaching procedures. The TCLP concentration can be reduced without removing any of the metal, as is the case with solidification or vitrification processes. The metal bioavailability can also be reduced. *In situ* methods for reducing bioavailability include sorption, ion exchange, precipitation, and attenuation.[15] Increasing soil pH also has been evaluated for cationic metals.[7] Little information has been published with regard to the effectiveness of the soil treatments other than data on yield and metal concentrations in plant tissue.[16,17] In particular, detailed studies of the effects of soil amendments on free metal ion activities have not been reported. This is partly due to a lack of the necessary thermodynamic data.

3 Microbial Aspects of Metal-contaminated Soils and Mine Spoils

Plants may accumulate as much as 10 000 mg of Zn or 2500 mg of Pb per gram of shoot biomass.[18] Heavy metal tolerant plant species which concentrate and

[15] R. Sims, D. Sorensen, J. Sims, J. McLean, R. Mahmood, R. Dupont, J. Jurinak, and K. Wagner, 'Contaminated Surface Soils In-place Treatment Techniques', Noyes Publications, Park Ridge, NJ, 1986.
[16] M. S. Johnson, T. McNeilly, and P. D. Putwain, *Environ. Pollut.*, 1977, **12**, 261–277.
[17] W. E. Sopper, *Landscape Urban Planning*, 1989, **17**, 241–250.
[18] A. J. M. Baker, *J. Plant Nutr.*, 1981, **3**, 643–654.

detoxify metals in above ground plant parts are known as accumulator species. Detoxification mechanisms for these species may include binding of heavy metals to cell walls, pumping heavy metal ions into vacuoles, or complexing of heavy metals by organic acids. In contrast, excluder plants species may absorb heavy metals but restrict their transport into shoots. This type of heavy metal tolerance does not prevent uptake of heavy metals but restricts translocation, and detoxification of the metals takes place in the roots. Mechanisms proposed for excluder detoxification include immobilization of heavy metals on cell walls, exudation of chelate ligands, or formation of a redox or pH barrier at the plasma membrane.[19] Microbial immobilization of heavy metals in the root zone would also reduce availability to and uptake by plants.

In contaminated sites, heavy metal concentrations may be high enough to inhibit microbial activity. Soil micro-organisms may be critical to plant growth because they encourage development of a stable soil structure, release required nutrients in inorganic forms by mineralization, and produce growth-regulating substances. Also, soil micro-organisms may contribute to plant growth by immobilizing heavy metals in soil. The direct effects of Cd, Cu, Zn, and Pb on soil micro-organisms are generally understood.[20] Heavy metal contamination of soil decreases microbial activity, microbial numbers, and microbially mediated soil processes such as nitrification, denitrification, and decomposition of organic matter.[21–24] Higher numbers of resistance bacteria are found in heavy metal contaminated soil than in uncontaminated soil, and resistant communities isolated from long-term contaminated soils are more diverse than those found in recently contaminated soils.[25–28] However, at extremely high levels of contamination, fewer resistant bacteria have been isolated than from less polluted soils.[24]

Previous research has indicated that microbes can bind metals. Micro-organisms may accumulate metal ions by complexation with extracellular polymers,[29] or by ion exchange with polyanions of the bacterial cell wall.[30] Gram-positive bacteria have a greater ability to bind metals than Gram-negative bacteria due to cell wall structural differences,[31] although it has been suggested that the Gram-negative cell envelope acts to impede metal ion entry into the cell interior. Bacteria may be able to transform heavy metals by the production of

[19] G.T. Taylor, *J. Plant Nutr.*, 1987, **10**, 1213–1222.
[20] E. Baath, *Water Air Soil Pollut.*, 1989, **47**, 335–379.
[21] F.H. Chang and F.E. Broadbent, *Soil Sci.*, 1981, **132**, 416–421.
[22] A. Nordgren, E. Baath, and B. Soederstroem, *Soil Biol. Biochem.*, 1988, **20**, 949–954.
[23] J.M. Bollag and W. Barabasz, *J. Environ. Qual.*, 1984, **11**, 196–201.
[24] P. Doelman and L. Haanstra, *Soil Biol. Biochem.*, 1979, **11**, 487–491.
[25] B.H. Olsen and I. Thornton, *J. Soil Sci.*, 1982, **33**, 271–277.
[26] M. Kiroki, *Soil Sci. Plant Nutr.*, 1992, **38**, 141–147.
[27] K.G. Shetty, M.K. Banks, B.A. Hetrick, and A.P. Schwab, *Water Air Soil Pollut.*, 1993, accepted.
[28] T.J. Beveridge, in 'Metal Ions and Bacteria', ed. T.J. Beveridge and R.J. Doyle, John Wiley and Sons, Inc., New York, NY, 1989, 1–29.
[29] G. Bitton and V. Freihofer, *Microb. Ecol.*, 1978, **4**, 119–125.
[30] T. Rudd, R.M. Sterritt, and J.N. Lester, *Microb. Ecol.*, 1983, **9**, 261–272.
[31] T.J. Beveridge and S.F. Koval, *Appl. Environ. Microb.*, 1981, **42**, 315–335.

water-soluble organics which would increase metal solubility,[32] or release metals previously bound due to variations in metabolism or growth.[33]

The soil fungal population may similarly be affected by heavy metal contamination, with the diversity of micro- and macro-fungi decreasing in contaminated soils.[34] In the higher fungi, the production of sporophores is a sensitive measure of metal pollution.[20] One specific group of fungi, the mycorrhizal fungi, can directly contribute to plant tolerance of heavy metals. Mycorrhizal fungi are plant symbionts which proliferate inside and outside of host plant roots. The hyphal strands of the fungus exterior to the root absorb nutrients and translocate them into the plant. These fungi can bind metals to hyphae, restricting them from translocation to shoots.[35] To what extent mycorrhizal symbiosis affects heavy metal translocation patterns expressed by plants is not known.

The effect of vegetation on groundwater contamination by leachate from contaminated soils is uncertain.[36] The mobilization of biologically available metals may be slightly higher in vegetated soil[37] due to the release of complexing agents by the plant. The concentration of Zn in the leachate from contaminated mine tailings is higher in soils treated with 1.0 mM succinic acid than in the absence of organic acid (Table 2).[38] The adsorption of heavy metals to soil may also decrease in the presence of organic ligands found in the rhizosphere.[39] Plant roots may also influence water transport and metal movement by providing flow channels in the soil. Other research indicates that heavy metal leachate may be affected by the type of soil microflora associated with the plant (Table 3). Revegetation of heavy metal contaminated soil may increase heavy metal leaching, especially if soil microflora have not been fully restored.[40]

4 Vegetative Remediation at Mine Sites: Case Studies

Whitewood Creek

Revegetating mine sites and metal wastes offers several advantages that have been under-appreciated in the literature. Fast growing hybrid poplar trees have been used in a variety of climate zones in riparian area applications to stabilize soils, decrease wind-blown dust, and decrease vertical migration of pollutants. Most risk assessments at mine tailings sites indicate that the largest cancer risk for elements like As and the largest chronic health risk to humans from elements such as Cd are due to inhalation of wind-blown dust or ingestion of aeolian-deposited soil by children. Vegetation can decrease these exposure pathways

[32] A. J. Francis, S. Dobbs, and B. J. Nine, *Appl. Environ. Microb.*, 1980, **40**, 108–113.
[33] C. A. Flemming, F. G. Ferris, T. J. Beveridge, and G. W. Bailey, *Appl. Environ. Microb.*, 1990, **56**, 3191–4203.
[34] H. Yamamoto, K. Tatsuyana, and T. Uchiwa, *Soil Biol. Biochem.*, 1985, **17**, 785–790.
[35] R. Bradley, A. J. Burt, and D. J. Read, *New Phytol.*, 1981, **91**, 197–209.
[36] F. L. Domergue and J. C. Vedy, *Int. J. Environ. Anal. Chem.*, 1992, **46**, 13–23.
[37] J. M. Besser and C. F. Rabeni, *Environ. Toxicol. Chem.*, 1987, **6**, 879–890.
[38] M. K. Banks, C. Y. Waters, and A. P. Schwab, *J. Environ. Sci. Health*, 1993, accepted.
[39] P. Chairidchai and G. S. P. Ritchie, *Soil Sci. Soc. Am. J.*, 1990, **54**, 1242–1248.
[40] M. K. Banks, G. R. Fleming, A. P. Schwab, and B. A. Hetrick, *Chemosphere*, 1993, accepted.

Table 2 Average zinc concentration in the leachate of organic acid amended mine tailings[38]

Type of Acid	*Average Zinc Concentration in Leachate*/$\mu g\,l^{-1}$ *Acid Concentration*/μm 0	50	250	1000
Formic	361	423	352	332
Succinic	362	308	492	506

Table 3 Average concentration of zinc leached from heavy metal contaminated soil by varying plant and microbial treatment[40]

Treatment	*Zinc*/$mg\,l^{-1}$
With plants	
Unamended	371
Microbes	228
Mycorrhizae	360
Microbes and Mycorrhizae	271
No plants	
Unamended	263
Microbes and Mycorrhizae	189

dramatically. Revegetation can be considered as a remediation method or used in tandem with other techniques for stabilizing soils and closing sites at low cost.

If contamination is in the upper 2–3 m of soil, deep-rooted poplar trees can significantly decrease the downward migration of leachate via evapotranspiration.[41] The trees start from 2 m 'whips', cuttings that have preformed root initials. When planted at a depth of 2 m, they form a dense root mass that will take up large quantities of moisture, increase soil suction, and decrease downward migration of pollutants. In the dormant season, some leakage of water can occur through the system but, precipitation is not great during this period. The trees grow 2 m in the first growing season and reach a height of 6–8 m after three years when planted at a density of 10 000 trees per hectare. Carbon fixation is approximately 2.5 $kg\,m^{-2}\,yr^{-1}$. Various management schemes can be adopted, and the trees can remain with very little attention for twenty years or more after the second season.

Advantages and disadvantages of vegetative remediation were discussed previously. Additional concerns specifically for trees include leaf litter and whether associated toxic residues might be blown off site. This concern may be tested in the laboratory or field to determine whether uptake and translocation of the metals into the leaves of trees or grasses exceed standards. In general, Cd and As (arsenate) are the most problematic because of their chemical similarity to nutrients (Ca, Zn, and P). Pb, Cr, Hg, and other metals are of lesser concern because of smaller rates of uptake. Following is a case study that illustrates an investigation of this potential problem at a Superfund site.

[41] L. Licht, 'Poplar Tree Buffer Strips Grown in Riparian Zones for Biomass Production and Non-point Source Pollution Control', PhD Dissertation, Civil and Environmental Engineering, The University of Iowa, Iowa City, IA, August, 1990.

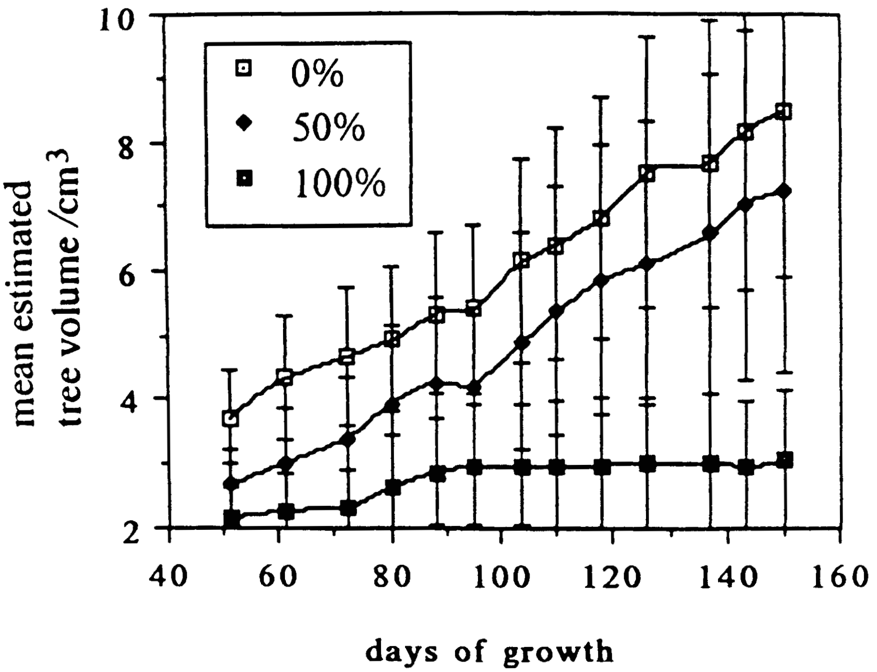


Figure 2 Cumulative growth curves for poplar trees in three fertilized laboratory treatments of 0, 50, or 100% mine tailings[13]

An eighteen mile stretch of Whitewood Creek is a US Superfund site because of contamination of surface water and groundwater with As and Cd (arsenopyrite is the major mineral in the tailings) from 130 years of gold mining activity. It is located in the Black Hills of extreme western South Dakota below the town of Whitewood. Chemical characterization indicated that the tailings contained an average of 1250 mg kg^{-1} total As and 9.4 mg kg^{-1} total Cd with pH ranging from 3.9 to 5.4. Plant-available P and K levels were quite low. An experimental plot was planted with 3100 hybrid poplar trees to a depth of 1.6 m in April of 1991. A commercial NPK fertilizer was used at recommended rates to ensure vigorous early growth of the cuttings. Roots formed along the entire length of the cutting in the soil, so a dense root mass was established that takes up infiltration and intercepts interflow moving towards the creek.

Genetically identical cuttings also were established in a plant incubator in the laboratory.[13] Figure 2 shows that the cuttings established in 100% mine tailings, the worst case from the site, grew more slowly than the other trees under optimal conditions in the laboratory. All trees were fed Hoagland R growth medium containing major nutrients. Other treatments were grown in a mixture of mine tailings and peat : vermiculite (50 : 50 by mass mixture). The treatment with 0% mine tailings was composed of a peat : vermiculite mixture, ideal for plant growth.

At the end of the first growing season, the trees had grown to 12 m at the field site. Leaves, stems, and roots were collected from the field as well as the laboratory trees to compare As and Cd uptake and translocation. Poplar leaves in the field did not accumulate significant amounts of As or Cd (Figures 3 and 4). These concentrations are below most levels established for field application of municipal sewage sludge or compost. Furthermore, they are well below the

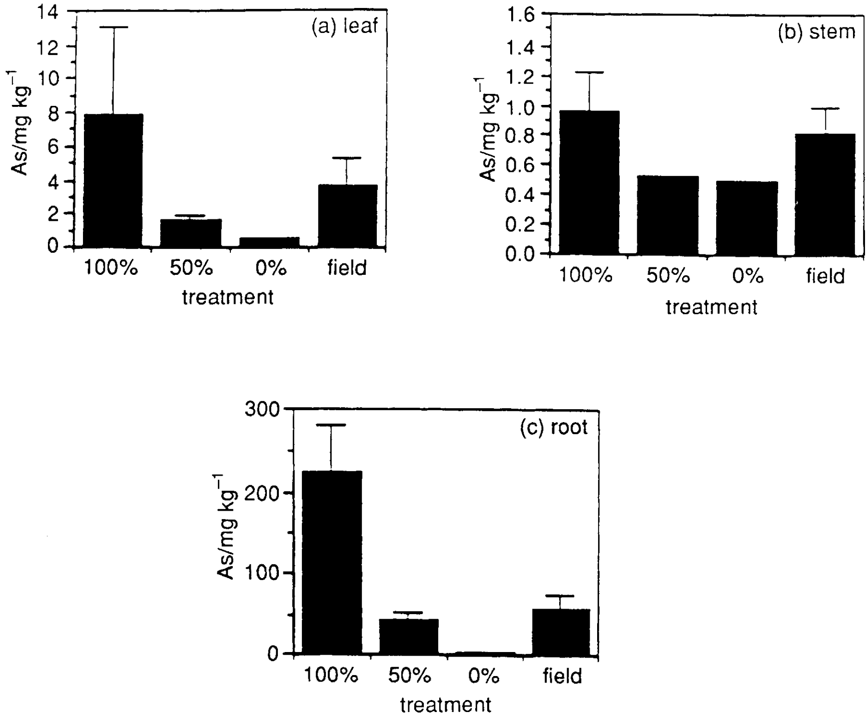


Figure 3 Total acid-digestable As in leaves, stems, and roots in fertilized laboratory (0, 50, or 100% mine tailings) and field poplars[13]

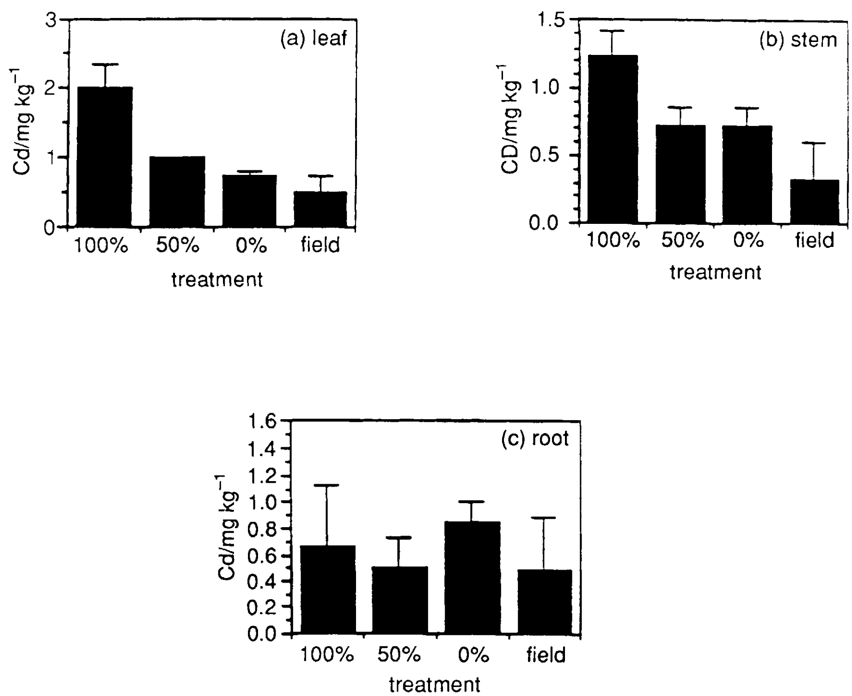


Figure 4 Total acid-digestable Cd in leaves, stems, and roots in fertilized laboratory (0, 50, or 100% mine tailings) and field poplars[13]

reference concentrations accumulated by leaves in the laboratory treatments of 100% mine tailings, indicating that the laboratory study overestimated the amount that would be accumulated in the field, possibly because of ideal growth conditions in the laboratory. It is interesting to note that the commercial peat : vermiculite mixture allowed a greater uptake of Cd by leaves than did the field situation (Figure 4a). Small amounts of Cd are always present in most commercial nursery mulches and soil amendments.

Concentrations of Cd and As in native vegetation at the site were generally of the same order of magnitude as those in poplar trees. But the leaves of lambsquarter were particularly high in As (14 $mg\,kg^{-1}$), and the leaves of the native cottonwoods (a cousin of the hybrid poplar trees) have a somewhat higher concentration (1.6 $mg\,kg^{-1}$) than leaves of the poplars planted for vegetative remediation. Results indicate that the poplars are not a serious concern in terms of their bioconcentration potential as compared with native vegetation at the site.

Laboratory and field investigations have shown that hybrid poplar trees can be established in mine tailings at a Superfund site without objectionable uptake of As and Cd into leaves. The laboratory study showed that estimates can be made easily and quickly regarding uptake and toxicity of metals. Field results demonstrated that the technology can be used at shallow contaminated sites for soil stabilization or in conjunction with other methods for closing a site.

Tri-State Mining Region

A number of studies have been made relating directly to vegetative remediation or to factors involved in establishing vegetation on contaminated soils or mine spoils in the Tri-State Mining Region. Several studies have dealt with a mine waste material known as chat, and one study examined a contaminated alluvial soil. Chat is a rock waste material generated from the initial processing of the metalliferous ore and consists primarily of rock fragments ranging in size from approximately 4 mm to clay sized ($<2\,\mu m$) and having Zn, Pb, and Cd concentrations as high as 43 750, 4500, and 160 $mg\,kg^{-1}$, respectively.[12] Chat piles are scattered throughout the area. The finer sized particles are selectively eroded away from the piles by wind and water and contribute to metal-enriched sediments and wind-blown dusts.

The Galena Superfund site consists of a large area that is nearly void of vegetation and contains numerous piles of chat and other waste materials. The remediation plan calls for using the piles of material to fill in mine shafts and other voids, recontouring to control run-off, and establishing vegetation to further control erosion and run-off.

An unbalanced factorial arrangement of organic waste amendments (composted yard waste, composted cattle manure, spent mushroom compost, and turkey litter); organic waste application rate (0, 22.4, 44.8, and 89.6 $Mg\,ha^{-1}$); and inorganic fertilizer rate (zero, a rate recommended for native grass establishment, and a rate recommended for establishment for a grass–legume mixture) was used to evaluate vegetative responses in a chat material seeded with a mixture of native

Table 4 The effect of organic waste source and rate and of fertilizer rate on plant density, species richness, and total cover after amendment of a zinc–lead chat tailing[42]

Main effect	*Plant density*/ plants m^{-2}	*Species richness (number of species)*	*Total cover*/%
Organic waste source[a]			
TL	15.6a[b]	6a	35a
CM	86.3b	26b	44b
MC	57.9c	16c	36ab
YW	61.5c	21bc	41ab
C	33.0d	9a	10c
Organic waste rate ($mg\,ha^{-1}$)			
0	32.9a	9a	10a
22.4	53.7b	21bc	32b
44.8	54.4b	18b	40c
84.6	57.9b	25c	45c
Fertilizer rate[c]			
none	57.5a	22a	40a
NG	55.4a	20a	35a
GL	47.9a	20a	35a

[a]TL = turkey litter, CM = composted cattle manure, MC = spent mushroom compost, YW = composted yard waste, C = control
[b]Means within the same column and main effect followed by the same letter are not significantly different at the 0.05 level
[c]NG = rate recommended for establishment of native grasses, GL = rate recommended for establishment of a grass–legume mixture

and tame grasses and leguminous forbs.[42] Table 4 shows the effects of organic waste source, organic waste rate, and fertilizer rate on total plant density, species richness, and total cover after the initial growing season. All three response variables were increased significantly by the organic waste sources as compared with the control, with composted cattle manure generally providing the greatest increase and turkey litter giving the least increase. The poor performance of turkey litter as compared with the other organic waste sources was due to acidification caused by nitrification of ammoniacal nitrogen forms in the material. Significant increases were also evident with increasing rates of organic waste. The addition of fertilizer had little beneficial effect, however. The combined results suggested that merely supplying the primary plant nutrients (N, P, and K) is not sufficient for acceptable establishment of vegetation in this material. Although the organic waste materials increased plant-available N, P, and K as well, they also increased organic C levels, cation exchange capacities, and the concentrations of other secondary and micronutrients (data not shown). Any potential benefits with regard to alleviating Zn phytotoxicity are unknown. This work has been applied directly to the remediation efforts at the Galena Superfund site.

[42] M. R. Norland, Proceedings of the Association of Abandoned Mine Land Programs, Dept. of Natural Resources, Div. Environ. Qual., Jefferson City, MO, 1991, pp. 251–264.

Table 5 The influence of organic and inorganic fertilizers and mycorrhizal fungi on biomass production and in uptake by *Andropogon geradii* and *Festuca arundinacea* grown in chat[43]

	Fertilizer amendment					
Mycorrhizal treatment	*none*	NH_4	*manure*	KH_2PO_4	NH_4 *and manure*	*Manure and* KH_2PO_4
Biomass/g						
A. geradii[a]						
mycorrhizae	0.07bc	0.03c	0.08b	0.08b	0.41a	0.51a
no mycorrhizae	0.07bc	0.05bc	0.05bc	0.07bc	0.06bc	0.05bc
F. arundinacea						
mycorrhizae	0.07b	0.04b	1.04a	0.07b	1.43a	1.47a
no mycorrhizae	0.08b	0.07b	0.03b	0.07b	0.03b	0.06b
Zn uptake/mg plant^{-1}						
A. geradii[b]						
mycorrhizae	66c	nd	168bc	127bc	330ab	520a
no mycorrhizae	88c	78.8c	nd	75c	nd	95c
F. arundinacea						
mycorrhizae	159c	120c	905b	167c	1827a	984b
no mycorrhizae	241c	119c	84c	186c	294c	133c

[a]Means for each plant species followed by the same letter are not significantly different ($P = 0.05$)
[b]nd = not determined because of insufficient root biomass

The role of mycorrhizal fungi in establishing vegetation in the chat material also has been studied.[43] Table 5 shows the effect of various amendments and mycorrhizal fungi on biomass production and Zn uptake by big bluestem [*Andropogon geradii* Vit.] and tall fescue [*Festuca arundinacea* Schreb.]. Big bluestem is an obligate mycotroph that requires mycorrhizae to grow in soils with low fertility, whereas tall fescue is a facultative mycotroph that grows well in low fertility environments in the absence of mycorrhizae. In this situation, additional biomass production occurred only when mycorrhizae were present with adequate nutrients, illustrating the importance of fungi in alleviating Zn toxicity to the plants. The exact mechanism for this is not known. It may be related to the binding of the metals in the rhizosphere by the fungi or a change in the metal binding capacity of the cell walls, both of which could act to increase plant resistance to Zn.

Figure 5 shows the effects of various soil amendments on changing Zn bioavailability and the resulting changes in soybean [*Glycine max* (L.) Merr.] tissue composition and yields in a metal-contaminated alluvial soil. This soil was collected approximately 125 m from the Spring River in the Tri-State mining region and was in a field under crop production. Soybeans growing on site were severely chlorotic, and Zn phytotoxicity was the suspected cause because of high Zn concentrations (1090 mg kg^{-1}) in soybean tissue samples collected there. No mining activity had occurred adjacent to the field and the source of the Zn was

[43] B. A. D. Hetrick, G. W. T. Wilson, and D. A. H. Figge, *Environ. Pollut.*, 1993, accepted.

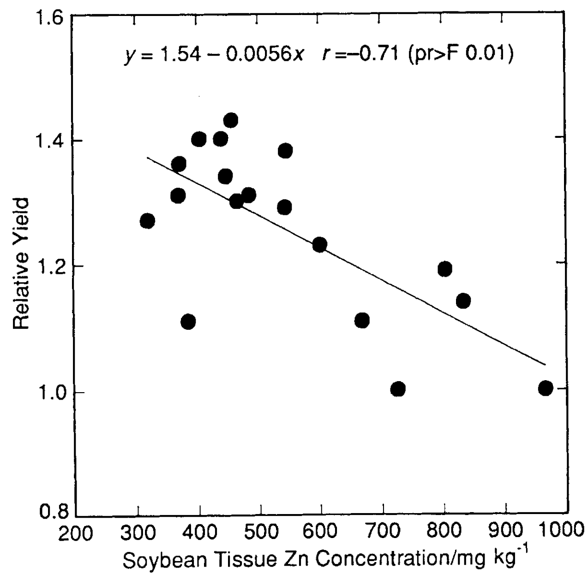


Figure 5 Relationship between soybean tissue Zn concentrations and relative yield in a metal contaminated alluvial soil. The variation in tissue Zn concentrations was a result of changes in soil bioavailable Zn levels induced by various soil amendments without changing the total Zn concentration[7]

metal-contaminated sediments deposited during periodic flooding events. The amendments were lime, P, cattle manure, sewage sludge, poultry litter, or various combinations of lime and cattle manure. The amendments produced KNO_3-extractable Zn concentrations from 3.7 to 63.3 mg kg^{-1} with a corresponding range of soybean tissue Zn concentrations of 318 to 1153 mg kg^{-1}. Soybean yields were influenced by the changes in tissue Zn concentrations with a range of 1.0 to 1.4 (Figure 5). The manipulation of bioavailable Zn levels was done without changing the total Zn concentration of the soil. Although the overall thrust of this project was not vegetative remediation, it is one of the few studies that provides data on soil chemical changes induced by soil amendments designed to reduce metal bioavailability.

Studies have shown that various amendments and mycorrhizal fungi aid in enhancing plant growth in contaminated soils and mine spoils from the Tri-State Mining Region. As a result, a vegetative remediation strategy is being used at the Galena Superfund site as part of the overall clean-up effort. Additional information has been obtained regarding the importance of mycorrhizae for plant growth under Zn toxic conditions and on the usefulness of soil chemical fractionation schemes in assessing soil chemical changes induced by amendments.

5 Modeling of the Fate of Heavy Metals in Vegetated Soils

The root–soil water transfer process is a major part of the sub-surface hydrologic system. The development of quantitative models that describe water movement in the root–soil environment has been reviewed.[10] The Leaching Estimation and

Chemistry Model, LEACHM, has been used to simulate the movement of water and solutes through both layered and non-layered soil profiles.[44] A coupled root–soil water flow model that includes the vertical movement of water through the root system has been developed.[45,46] Soil water movement in the vertical and horizontal directions of a non-homogeneous variably saturated soil can be simulated with this model.

Some of the processes that occur in the soil–root environment are limited by the rate of diffusion or reaction and kinetic models should be used rather than the equilibrium models described earlier. Diffusion within solids is slow; it is often an important consideration when modeling the leaching of metals in soil.

Two important considerations in modeling the fate of metals in the root–soil environment are the uptake into the plant and the impact of root exudates on pH and leaching. Because micro-organisms degrade root exudates, any modeling of the impact of the organic ligands on metal leaching should include a root exudate and a microbial population balance.[47]

When the behavior of the solute is modeled with an equilibrium model, two distinct cases can be considered. Below the solubility limit, the metal will not precipitate, and a precipitated solid phase will not be present. On the other hand, when a precipitated solid phase is present, the solute concentration will be at the solubility limit and will remain at that value until all of the solid phase is dissolved. In this case, a model for the solid phase is needed to simulate the dissolution process and follow the transient behavior of the mass of precipitated metal. In the model that follows, the first case is considered.

As discussed previously, a variety of factors govern the fate of heavy metals in a vegetated soil; however, providing detailed mathematical expressions describing all of these processes would produce a nearly intractable problem. Thus, a somewhat simplified approach will be employed for developing a method to predict the fate of heavy metals in a rooted soil. Figure 6 depicts the conceptual approach used in development of the fate and transport model. It is assumed that the primary mechanism for metal transport through a soil is water movement, with losses or additions of metals to the soil–water occurring from four sources: (1) uptake into the vegetation's root system by plant transpiration; (2) adsorption onto the vegetation's root system; (3) bonding to exchange sites on inorganic soil constituents; and (4) adsorption to insoluble soil organic matter.

A model that has been shown to provide an accurate depiction of the movement of water in the presence of a transpiring crop's root system can be described as:[45,46]

$$\frac{\partial}{\partial z}\left[K_s \frac{\partial(\psi_s + z)}{\partial z}\right] - q = \left[\beta S_s + S_y \frac{dS_e}{d\psi_s}\right]\frac{\partial \psi_s}{\partial t} \tag{1}$$

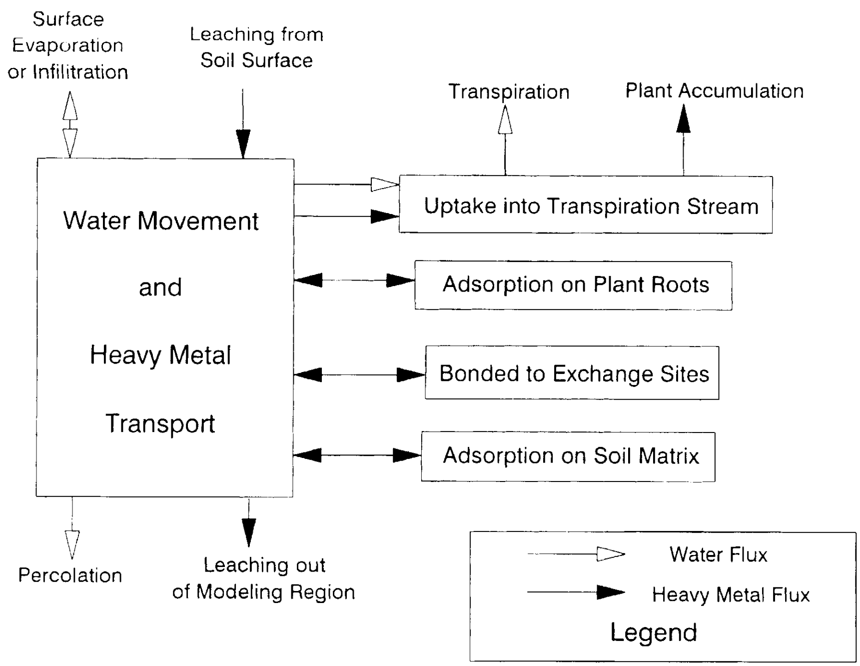
[44] R.J. Wagenet and J.L. Hutson, 'Leaching Estimation and Chemistry Model, Version 2.0, A Process Based Model of Water and Solute Movement, Transformations, Plant Uptake, and Chemical Reactions in the Unsaturated Zone', *Continuum*, Vol. 2, Water Resources Institute, Cornell University, Ithaca, NY, 1989.

[45] M.A. Marino and J.C. Tracy, *J. Irrig. Drain. Eng.*, ASCE, 1988, **114**, 588–604.

[46] J.C. Tracy and M.A. Marino, *J. Irrig. Drain. Eng.*, ASCE, 1989a, **115**, 608–625.

[47] L.C. Davis, L.E. Erickson, E. Lee, J.F. Shimp, and J.C. Tracy, *Environ. Prog.*, 1993, **12**, 67.

Figure 6 Schematic representation of the modeling approach



$$\frac{\partial}{\partial z}\left[K_r\frac{\partial(\psi_r + z)}{\partial z}\right] + q = R_d\frac{\partial WC_r}{\partial t} + WC_r\frac{\partial R_d}{\partial t} \qquad (2)$$

in which z is the vertical direction in the soil; K_s is the hydraulic conductivity of the soil in the vertical direction; K_r is the hydraulic conductivity of the root in the vertical direction; ψ_s is the soil–water pressure head; ψ_r is the root–water pressure head; S_y is the specific yield of the soil; S_s is the specific storage of the soil; $\beta = 0$ if $\psi_s < 0$ and $\beta = 1$ elsewhere; WC_r is the root–water content, a function of the root–water pressure head; R_d is the root density in the soil; t equals time; $S_e = \theta/n$ which is the effective saturation of the soil, where θ is the soil–water content and n is the soil porosity; and q equals the rate at which soil–water is extracted by the plant's root system per unit volume of soil, defined as:

$$q = S_e R_d \Gamma(\psi_s - \psi_r) \qquad (3)$$

where Γ is a lumped parameter representing the permeability of a plant's root system.

Equations (1) through (3) represent a coupled set of partial differential equations that can be solved numerically, given that the root parameters, the soil characteristics, the initial conditions, and boundary conditions are known.

The solutions of equations (1) through (3) describe the distributions of the water flux throughout the soil profile. Thus, Darcy's law is employed to calculate the water flux, V, distribution based on the soil–water pressure heads, such that:

$$V = -K_s\frac{\partial(\psi_s + z)}{\partial z} \qquad (4)$$

The transport of heavy metals through the soil profile can then be described using the water flux distribution and the advection–dispersion equation, as:

$$\frac{\partial}{\partial z}\left[\theta D \frac{\partial C}{\partial z} - VC\right] - q_{\mathrm{m}} + S = \frac{\partial}{\partial t}[C(\theta + K)] \tag{5}$$

in which C is the concentration of heavy metals in the soil–water; D is the macrodispersion coefficient for heavy metals in the soil; q_{m} is the uptake of heavy metals by roots into the plant transpiration stream; S is the sink/source of contaminants across modeling boundaries; and K equals a lumped parameter accounting for the adsorption onto root and soil surfaces and ion exchange.

Several heavy metals are necessary as plant nutrients (*e.g.* Cu and Zn)[48] and a significant fraction of these metals can be taken up by the roots during plant transpiration. However, other metals are toxic to some plant species and a larger fraction of these metals are excluded during the root uptake process. Thus, development of the uptake term, q_{m}, in equation (5) will have to be based on the specific plant type and metal being studied, and very few generalizations can currently be made about this process. Nonetheless, a general model that may be useful for developing a mathematical simulation model of this process is similar to a proposed model[49] for the uptake of organic chemicals into a plant's transpiration stream, simulated as a linear function of root water uptake, so that:

$$q_{\mathrm{m}} = f_{\mathrm{u}} q \tag{6}$$

where f_{u} equals the ratio of the concentration of the chemical in the root water to the concentration in the soil water. Use of this expression for metals in conjunction with equation (3) would allow the uptake to be calculated as:

$$q_{\mathrm{m}} = f_{\mathrm{u}} R_{\mathrm{d}} S_{\mathrm{e}} \Gamma(\psi_{\mathrm{s}} - \psi_{\mathrm{r}}) \tag{7}$$

where f_{u} would have to be calibrated as a site-specific parameter.

The lumped parameter, K, in equation (5) actually accounts for three processes: (1) adsorption to the root mass; (2) adsorption to the soil matrix; and (3) ion exchange. Very little information is available to quantify these relationships based on the general characteristics of a site. However, it is felt that a reasonable approximation would be to assume that the heavy metals partition into each phase (water, root, soil, and biomass) in a linear fashion and that the time frame of the simulations is of long enough duration to assume equilibrium conditions. In this fashion, the lumped adsorption parameter, K, can be described as:

$$K = \rho k + R_{\mathrm{d}} k_{\mathrm{r}} + k_{\mathrm{e}} E \tag{8}$$

in which ρ is the soil density; k equals the linear partition coefficient between the soil–water and soil matrix; k_{r} is the linear partition coefficient between the soil–water and the root mass; k_{e} is the linear partition coefficient between the soil–water and the ion exchange sites on the solid phase; and E is the cation exchange capacity of the soil.

The concentration C includes all forms of the metal dissolved and suspended in the soil–water, and can be written in terms of its components: C_1, the

[48] A. J. Friedland, in 'Heavy Metal Tolerance in Plants: Evolutionary Aspects', ed. A. J. Shaw, CRC Press, Boca Raton, FL, 1989, pp. 7–20.

[49] G. G. Briggs, R. H. Bromilow, and A. A. Evans, *Pestic. Sci.*, 1982, **13**, 495–504.

concentration of the charged species; C_2, the concentration of metal complexed with an inorganic species, A_2; and C_3, the concentration of metal complexed with organic species, A_3.

The total concentration, C, can then be expressed in terms of C_1 as:

$$C = C_1 + K_2A_2C_1 + K_3A_3C_1 \tag{9}$$

where K_2 and K_3 are the partition coefficients associated with the metal complexed with the inorganic and organic species, respectively.

If the ion exchange process involves only the charged species C_1, then equation (5) may be written in the form:

$$\frac{\partial}{\partial z}\left[\theta D\frac{\partial[C_1(1 + K_2A_2 + K_3A_3)]}{\partial z} - VC_1(1 + K_2A_2 + K_3A_3)\right] - f_uR_dS_e\Gamma(\psi_s - \psi_r) + S$$
$$= \frac{\partial}{\partial t}[C_1(1 + K_2A_2 + K_3A_3)(\theta + \rho k + R_dk_r) + C_1k_e'E] \tag{10}$$

It is likely that the root exudate concentration, rhizosphere biomass density, and root density probably will be variable over time. Thus, some mechanism of predicting these densities as they vary in relation to the time of year, climatic conditions, and general site conditions must be employed. However, such models will not be included here due to the limited scope of this paper.

The estimation of the soil matrix partition coefficient, k, in equation (8) also must be done on a site-specific basis and will depend on factors such as the soil's organic content and pH. With the introduction of vegetation at a site, both the organic content and the pH of the soil could change significantly and, thus, the partition coefficient must be described as a function of both, such that:

$$k = f(\text{pH}, \%Oc) \tag{11}$$

where $\%Oc$ is the percent organic matter in the soil matrix. In most cases it should be possible to develop this relationship on a site specific basis. However, a method also would have to be developed to predict the pH and organic content of a soil once vegetation has been introduced, which could prove difficult.

The model governing the fate and transport of a heavy metal can be solved numerically. The model solutions could then proceed by solving equations (1) through (3) to determine the water pressure distribution in the soil profile, then solving equation (4) to calculate the soil–water flux distribution. Finally, equation (10) could be solved using the soil–water flux and root water extraction calculations to determine the heavy metal concentration of the soil–water in the soil profile for each time increment during the simulation period. Equation (10) also could be solved simultaneously with the balances for root exudates and microbial biomass, if transient changes in root exudate concentration, A_3, are to be included in the model.

One of the challenges of using mathematical models to simulate the fate of heavy metals in soils is to collect sufficient equilibrium and soil characterization data. Although some data for root exudates has been collected,[50] more research

[50] A. P. Schwab and M. K. Banks, Proceedings of the 86th Annual Meeting and Exhibition of the Air and Waste Management Association, Denver, CO, June 14–18, 1993, Paper 93-WA-8906.

is needed before the model could be utilized to design a vegetative remediation scheme. However, the proposed model can be used to demonstrate the qualitative effects that the introduction of vegetation would have on soils contaminated with heavy metals.

Equations (1) and (2) simply describe the water flow regime in a variably saturated soil, with equation (4) providing a calculation of the water flux and equation (3) representing the amount of water extracted by a plant's root system. Any transpiration by vegetation introduced into a barren soil would result in the extraction of soil–water by plant roots. This would have two significant effects on the transport of heavy metals through a soil. First, the water sink provided by the plant roots generally would be strongest in areas with the largest root densities, typically near the soil surface. This would decrease the downward rate of water flow through the soil, thereby decreasing the mass of heavy metals leached below the root zone. Second, the water sink provided by the root system also would reduce the overall soil–water potential, ψ_s, which in turn would lower the soil–water content. Then, because the hydraulic conductivity of a soil decreases with decreasing soil–water content, the presence of the plant's root system also would decrease soil permeability, further restricting the movement of water and metals. Thus, equations (1) through (4) tell us that the introduction of a vegetative system to a heavy metal-contaminated soil would result in a type of hydraulic containment system.

Equation (5) describes the fate and transport of heavy metals through the soil profile. The advective and dispersive terms, V and D, are related to the movement of water. Equations (6) and (7) describe the uptake of heavy metals by a plant's root system. Because of their formulation, some metals probably would be taken up during the root–water uptake process described in equation (3), thereby reducing the mass of heavy metals in the soil profile. Thus, the introduction of vegetation would result in a reduction in the mass of heavy metals in a soil. However, the heavy metals that are taken up would accumulate in the plant biomass, typically in plant leaves. If the vegetative system were left unmanaged, plant dormancy at the end of a growing period would result in the decomposition of parts of the plant and the introduction of the heavy metals back into the soil at the soil surface where the leaves and other matter would fall, thus producing a source of metals, defined by the term S in equation (5). For the uptake to provide a true sink of heavy metals in the soil system, the vegetation would have to be managed in some way, such as harvesting, to prevent the reintroduction of the metals into the soil profile.

Equations (8) through (11) describe the adsorption of heavy metals to the organic and inorganic matter in the soil matrix. In general, heavy metals tend to adsorb readily to organic matter. The introduction of vegetation at a site would produce an increase in organic matter from the soil matrix to the plant's root system and the microbial mass associated with the plant's rhizosphere. Equation (8) thus indicates that the introduction of vegetation in a soil would decrease the mobility of the heavy metals, thereby providing a better containment system. However, most plant roots produce root exudates, so that a healthy environment is maintained in the rhizosphere for microbial and root growth. This property tends to alter the pH of a soil, so that root growth can be maintained at optimal levels, with pH values in the range of 6 to 8 favoring most plants.[51] If the natural pH of the contaminated soil is above these levels, the introduction of vegetation could result in a substantial lowering of the pH. This could reduce the partition coefficients in equation (9) and result in the metal becoming more mobile in the soil. In situations where the soil pH is below 8, soil amendments could be utilized to maintain a relatively constant pH, thus preventing an increase in the heavy metal mobility once the vegetative containment system is fully developed.

The modeling results that could be expected for the development of a vegetative remediation system would be extremely site dependent. However, the overall analysis of the model presented above suggests that, for many heavy metal contaminated soils, vegetation should provide a positive influence for enhancing the on-site containment of the metals and the possible removal of a portion of the metals through the harvesting of the vegetation.

6 Conclusions

Numerous remediation options exist for metal-contaminated sites. These range from complete excavation of contaminated material accompanied by some treatment to *in situ* encapsulation and to vegetative remediation. Vegetative remediation is aesthetically pleasing and it offers several advantages, including the minimization of erosion, low cost as compared with other remediation options, and the potential to reduce net percolation through contaminated sites. Amendments to contaminated soil or mine spoil materials may reduce metal uptake by plants by reducing metal bioavailability. Theoretically, such amendments likely reduce free metal ion activities in the soil solution although it is difficult to estimate or measure the actual treatment effects. On a more practical basis, chemical fractionation schemes are useful for quantifying treatment efficacy. Mycorrhizal fungi play an important role in establishing vegetation by allowing plants to utilize plant nutrients more efficiently and by decreasing plant sensitivity to phytotoxic metal concentrations. Thus, more contaminated areas may be suitable for vegetative remediation than was previously believed.

The use of trees holds particular promise for vegetative remediation. In addition to providing erosion protection, they have the potential to transpire considerable amounts of water compared to non-woody plant species. This may help in reducing the downward migration of contaminants. Trees can also produce biomass for chemical and/or energy use. Initial results suggest that food-chain transfer of contaminants due to uptake into leaves and stems is not a concern.

A model has been presented that can estimate the effects of vegetation on the fate of metals in contaminated soils and mine spoils provided the appropriate parameters can be obtained. The model takes into account root and soil characteristics, water balance, and the influence of vegetation on certain soil chemical properties with time. Use of the model would allow a more thorough appreciation and understanding of vegetative remediation.

[51] G. B. Tucker, W. A. Berg, and D. H. Gentz, in 'Reclaiming Mine Soils and Overburden in the Western United States: Analytical Parameters and Procedures', ed. R. D. Williams and G. E. Schuman, Soil Conservation Society of America, Ankeny, IA, 50021, pp. 3–26.

Acknowledgements

The work presented here was partially supported by the US EPA under assistance agreements R-815709 and R-919653 for the Great Plains–Rocky Mountain Hazardous Substance Research Center for regions 7 and 8. It has not been submitted to the EPA for peer review and therefore may not reflect the views of the agency and no official endorsement should be inferred. The US Department of Energy, Office of Environmental Restoration and Waste Management, Office of Technology Development, the Kansas Agricultural Experiment Station, and the Center for Hazardous Substance Research also provided partial funding.