REMEDIATION OF SMELTER-CONTAMINATED SOILS BY CHEMICAL IMMOBILIZATION

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ABSTRACT

Chemical immobilization, an in-situ remediation method where inexpensive chemicals are used to reduce contaminant solubility in contaminated soil, has gained attention in the last decade. The results from two immobilization studies are presented. In the first study, three Pb-,Zn-, and Cd-contaminated smelter soils were treated with four chemical immobilization amendments: a lime stabilized municipal biosolid (LSB), a municipal biosolid-alkaline admixture blend marketed as N-Viro Soil (NV), North Carolina rock phosphate (RP), and an anaerobically digested municipal biosolid (AB). The effect of soil treatment on metal extractability was evaluated by sequential extraction, on phytoavailability by a lettuce bioassay (Lactuca sativa L.), on human gastrointestinal (GI) bioavailability of Pb from incidental ingestion by the Physiologically Based Extraction Test. In the second study, the effectiveness of diammonium phosphate, as a chemical immobilization treatment to reduce heavy metal solubility and transport in a smelter contaminated soil is reported. Diammonium phosphate treatments were evaluated using solute transport experiments with repacked soil columns. DAP was added to the soil at 460, 920, and 2300 mg P/kg.

Alkaline organic treatments reduced metal extractability and phytoavailability but not GI availability because their immobilization products were unstable under acidic conditions. Rock phosphate treatment reduced metal extractability and GI availability but not phytoavailability. However, acidification of treated soils showed RP provided a larger degree of "permanence" than the other remediation treatments. Alkaline organic treatments decreased Cd and Zn exposure through the food chain pathway, whereas rock phosphate decreased exposure to Pb via the incidental ingestion pathway. Chemical immobilization of heavy metals using DAP is an effective method of reducing metal solubility and mobility. DAP is inexpensive and commercially available in large quantities as a fertilizer. In-situ treatment with DAP at the 2300 mg P/kg treatment corresponds to estimated material costs of only US \$2.5 m-2 to 60 cm depth (assuming bulk density of 1.4 g cm-3) compared with US \$730 m-2 to 60 cm depth for excavation and landfilling.

KEYWORDS

in-situ immobilization, contaminated soil, phosphate, biosolids, incidental ingestion, contaminant transport

INTRODUCTION

Adverse environmental impacts from exposure to Cd, Pb, and Zn from contaminated smelter sites include risk to human health, phytotoxicity, contamination of water and soil, soil erosion, and ecotoxicity. Commonly used cleanup methods involve excavation and landfilling of smelter-contaminated soil. Chemical immobilization is an inexpensive in-situ remediation method where inexpensive chemicals (i.e., fertilizer, waste materials) are added to contaminated soil to reduce the solubility or immobilize the heavy metal contaminants. Many studies using chemical amendments (including organic matter, alkaline material, and phosphate fertilizer for chemical remediation of Pb, Cd, and/or Zn in contaminated soil) have been conducted in the last decade. Treatments to immobilize Pb, Cd, and Zn in contaminated soil include biosolids, composts, manures, alkaline materials (Brown et al., 1996; Pierzynski and Schwab, 1993) and phosphate-based amendments (Ma et al., 1995; Hettiarachchi et al., 1998; Lambert et al., 1997; Laperche et al., 1997; McGowen, 2000). The success of chemical immobilization can be evaluated by its ability to reduce contaminant bioavailability and human exposure to heavy-metal contaminants in treated contaminated soil. Two important human exposure pathways are exposure to Cd and Zn through the food chain via plant uptake, and exposure to Pb through incidental ingestion of contaminated soil.

To be a successful remediation method, reductions in contaminant solubility and bioavailability realized by chemical immobilization must be long-term or *permanent*. Chemical immobilization of Pb in contaminated soil using phosphate treatments to produce Pb pyromorphite, a geochemically stable form of Pb in soil, may meet the "permanence" or long-term stability requirement for site remediation. However, it is not possible to identify or quantify many amorphous chemical immobilization products by spectroscopic analysis or other methods. An alternate approach to evaluate the "stability" of chemical immobilization products may be to determine the ability of heavy metals to remain insoluble (not extractable) upon acidification. Soil pH is one of the most important soil chemical property affecting solubility of Cd, Zn, and Pb. Soil weathering often involves soil acidification, and most chemical immobilization reactions are pH dependent.

Many studies have reported on the ability of chemical immobilization treatments to reduce phytoavailability, solubility, or gastrointestinal availability of Cd, Zn, and/or Pb. An overview of the effectiveness of organic, alkaline, and phosphate chemical immobilization amendments to reduce contaminant bioavailability and evaluate the effect of soil acidification on the extractability of metal in treated contaminated smelter soils will be presented.

<u>METHODOLOGY</u>

The results from two immobilization studies are presented. In the first study, three Pb-,Zn-, and Cd-contaminated smelter soils were treated with four chemical immobilization amendments: a lime stabilized municipal biosolid (LSB), a municipal biosolid-alkaline admixture blend marketed as N-Viro Soil (NV), North Carolina rock phosphate (RP), and an anaerobically digested municipal biosolid (AB). Each amendment was thoroughly incorporated into soil (100 g/kg soil) in plastic tubs. Soil moisture was adjusted to field capacity (0.33 bar, ca. 25% water) and the soils were incubated at 27°C for 90 d.

The effect of soil treatments on contaminant extractability was evaluated by using the Potentially Bioavailable Assessment Sequential Extraction or PBASE method (Basta and Gradwohl, 2000). To examine the effect of soil treatment on phytotoxicity and contaminant phytoavailability, lettuce (Lactuca sativa var. Paris Island Cos) was grown in 15-cm pots containing 1-kg samples of soil over a 3-cm layer of vermiculite in a completely randomized design with three replicates. The human gastrointestinal bioavailability of Pb from incidental ingestion of treated soil was estimated using the Physiologically Based Extraction Test or PBET method (Ruby et al.,1996). The PBET method is a two-step sequential extraction of soil by a procedure that simulates GI biochemistry. The *permanence* of immobilization treatments was evaluated by acidification of treated soils to target pH levels of 6, 5.5, and 4. Acidified samples were extracted by the PBASE method to determine changes in Cd, Pb, and Zn extractability.

In the second study, the effectiveness of diammonium phosphate, as a chemical immobilization treatment to reduce heavy metal solubility and transport in a smelter contaminated soil is reported. Diammonium phosphate treatments were evaluated using solute transport experiments with repacked soil columns. DAP was added to the soil at 460, 920, and 2300 mg P/kg. These treatments correspond to approximate P/Mtotal ratios of 1/74, 1/37, and 1/15 respectively. Deionized water was passed through columns repacked with DAP-treated soil. Sample effluent pH and anion concentrations (F, Cl, Br, NO_3, PO_4, and SO_4) were immediately analyzed after collection by combination electrode and ion chromatography. Remaining effluent was acidified with trace metal grade HNO_3 (pH < 2) for metal analysis (Al, As, Ba, Ca, Cd, Cr, Cu, K, Fe, Mg, Mn, Na, Ni, Pb, Zn) by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP).

RESULTS

Results from the first study, that evaluated the effectiveness of biosolids, N-Viro Soil, and rock phosphate to reduce metal extractability, phytoavailability, gastrointestinal availability, are summarized in Table 1. The largest reductions in metal extractability and phytoavailability were realized using alkaline organic treatments (LSB and NV). However, the products of the LSB and NV treatments were not stable under acidic conditions of the acidic pH 1.8 gastric solution of the PBET procedure. The ability of LSB and NV soil treatments to reduce metal extractability was lost when soil was acidified to pH < 6. The chemical immobilization products formed in these treated soils would not be stable to soil acidification processes under natural or cultivated conditions. However, repeated applications of LSB or NV could be used to prevent strongly acidic soil conditions (pH < 5) and maintain reductions in metal extractability and phytoavailability.

Table 1. Summary of the effects of chemical immobilization treatments on Cd, Zn, and Pb phytoavailability, gastrointestinal availability, and changes in soil acidification to pH <5.†

Soil Treatment	Metal	Metal Phytoavailability‡	Gastrointestinal Pb Availability	Soil Acidification pH <5§
LSB	Cd	B4(-); BW(-)		
	Zn	B4(-); BW (-)		
	Pb	H12(-)		E1(+);E2(+);E3(+);E4(-)
NV	Cd	B4(-); BW (-)		
	Zn	B4(-); BW(-); H12(+)		
	Pb	H12(+)	Intestinal (-)	E1(+); E4(-)
AB	Cd			
	Zn	B4(+); H12(+)		
	Pb	H12(-)	Intestinal (-)	E1(+);E2(+);E3(+);E4(-)
RP	Cd			E1(-); E3(+); E4(+)
	Zn			E1(-); E3(+); E4(+)
	Pb	B4(+)	Gastric (-) Intestinal (-)	E1(-); E3(+)

†Effects are expressed as increased (+) or decreased (-) values compared to the control soil. Treatments that were not different than the control soil are not listed in the table.
‡B4 is the Bartlesville soil, BW is the Blackwell soil, and H12 is the Henryetta soil.
§Changes in metal extractability of treatment vs. control soil after soil acidification to pH<5.

Treatment of contaminated soil with non-alkaline biosolids, AB, increased phytoavailable Zn and did not reduce plant uptake of Cd or Pb. Similar to LSB and NV, immobilization products were not stable under acidification (pH < 5) and did not decrease gastrointestinal Pb in the gastric phase. Rock phosphate decreased metal extractability but not metal phytoavailability in the contaminated soils. The reductions in metal extractability obtained with RP were much smaller than the alkaline treatments and did not result in reductions in plant uptake obtained with LSB and NV. However, the RP immobilization products were stable under acidification (pH < 5) and, unlike other treatments, reductions in gastrointestinal availability and metal extractability were realized under acidic (pH < 5) soil conditions. Treatment with rock phosphate would reduce Pb bioavailability associated with incidental ingestion of contaminated soils by humans. Some of the RP treatment products should be stable under conditions that favor soil acidification, and repeat applications of RP would not be necessary upon soil acidification.

Results from the second study showed DAP decreased transport of Cd, Pb, and Zn from contaminated soil (Table 2).

Table 2. Cumulative mass† of Cd, Pb, and Zn and percent of metal eluted from the untreated column (in parentheses) through 60 pore volumes of elution.

DAP Treatment	Cd	Pb	Zn
mg P kg^{-1}	mg kg^{-1}	μg kg^{-1}	mg kg^{-1}
0	14.9 (100)	460 (100)	108 (100)
460	7.1 (47.7)	237 (51.4)	5.7 (5.3)
920	4.1 (27.5)	9.5 (2.1)	6.0 (5.6)
2300	0.8 (5.4)	5.2 (1.1)	4.5 (4.2)

The 2300 mg P/kg application was the most effective for immobilizing Cd, Pb, and Zn eluted from the contaminated soil when compared with the untreated check. This treatment corresponds to a P/Mtotal ratio of 1/15, where Mtotal = Σ total Cd, Pb, and Zn determined by XRF. Model fitted metal elution curves showed increased retardation factors (R) and distribution coefficients (Kd) with increased DAP application. Modeled elution curves showed DAP treatment increased retardation (R) of 2-fold for Cd, 6-fold for Zn, and 3.5-for Pb. Distribution coefficients (Kd) increased with P application from 4.0 to 9.0 L/kg for Cd, from 2.9 to 10.8 L/kg for Pb, and from 2.5 to 17.1 L/kg for Zn.

CONCLUSIONS

None of the soil treatments met all the criteria used to determine successful remediation of Cd-, Pb-, and Zn- contaminated soil. Alkaline organic treatments reduce metal extractability and phytoavailability but not GI availability. Rock phosphate treatment reduces metal extractability and GI availability but not phytoavailability. Transmission of Cd and Zn through the food chain via plant uptake and exposure to Pb through incidental ingestion of contaminated soil are important human exposure pathways. Use of alkaline organic treatments (LSB, NV) are well-suited to decrease Cd and Zn transmission through the food chain pathway. Whereas, rock phosphate is well-suited to decrease exposure to Pb via the incidental ingestion pathway. Remediation of these soils using RP would offer a larger degree of permanence than the other treatments.

Chemical immobilization of heavy metals using DAP is an effective method of reducing metal solubility and mobility. DAP is inexpensive and commercially available in large quantities as a fertilizer. In-situ treatment with DAP at the 2300 mg P/kg treatment corresponds to estimated material costs of only US $2.5 m-2 to 60 cm depth (assuming bulk density of 1.4 g cm-3) compared with US $730 m-2 to 60 cm depth for excavation and landfilling. The optimum P/Mtotal ratio of 1/15 observed for this study soil may differ with varying concentrations of reactive metals in other contaminated soils and wastes.

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