# IN-SITU CHEMICAL TREATMENTS FOR REDUCING

# HEAVY METAL SOLUBILITY AND TRANSPORT

# IN SMELTER CONTAMINATED SOILS

By

STEVEN LYNN McGOWEN

Bachelor of Science
Oklahoma State University
Stillwater, Oklahoma
1994

Master of Science
Louisiana State University
Baton Rouge, Louisiana
1996

Submitted to the Faculty of the
Graduate College of the Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of DOCTOR OF PHILOSOPHY
May, 2000

# IN-SITU CHEMICAL TREATMENTS FOR REDUCING

# HEAVY METAL SOLUBILITY AND TRANSPORT

# IN SMELTER CONTAMINATED SOILS

Dissertation Approved:

_____
Dissertation Advisor

_____

_____

_____

_____
Dean of the Graduate College

# ACKNOWLEDGEMENTS

I would like to convey sincere gratitude to my major advisor, Dr. Nick Basta for his scientific and professional guidance throughout my studies, and for always keeping life in perspective with witty humor. I am especially appreciative of Dr. Bill Raun for his support and contributions to my research endeavors. I would also like to thank Dr. Brian Carter and Dr. Glenn Brown for their excellent input and support of my research.

Many thanks also to my fellow graduate students, Felicia Armstrong, Doug Cossey, Libby Dayton, Jon-Karl Fuhrman, Lori Gallimore, Randy Gradwohl, Eric Hanke, Steven Phillips, Robin Rodriguez, Jackie Schroder, D.C. Ward, Phil Ward, and Robert and Shawn Zupancic for their assistance in professional endeavors and the pleasure of their friendship. My sincere gratitude is due to Anne, Kate, and Christopher Raun for their cheerful visits that granted brief vacations from the toils of graduate school. I would also like to acknowledge Dr. Brad Lee for sparking my curiosity in soil science many years ago.

My parents, Butch and Pat McGowen, deserve thanks for my upbringing and its lasting impact on my life. Finally, I would like to thank my wife, Dia, for her love, support, and encouragement that continues to keep me inspired to accomplish my goals.

# TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

# FORWARD

Metal mining and smelting activities throughout the world have contaminated land with heavy metals in excess of natural soil conditions. Costs associated with excavation and landfilling of contaminated soil have proven to be expensive; therefore, research on alternative methods is needed. Recent research has investigated the use of in-situ chemical immobilization treatments to reduce metal solubility and bioavailability. The majority of these metal immobilization studies have focused on investigating the reduction of metal solubility and bioavailability associated with chemical treatments. In addition to soil contamination, many mining and smelting sites have significant groundwater contamination as a result of metal transport through contaminated soils. Research efforts to investigate the effectiveness of chemical immobilization treatments for reducing the mobility and transport of heavy metals from contaminated soils are needed. The work reported here seeks to address that need. This work couples the investigation of metal solubility and transport from contaminated soils amended with chemical immobilization treatments. This dissertation is presented in two chapters following the manuscript format for submission to the Journal of Environmental Quality or the Soil Science Society of America Journal.

# CHAPTER I

# REDUCING HEAVY METAL SOLUBILITY AND TRANSPORT IN SMELTER CONTAMINATED SOILS USING CHEMICAL IMMOBILIZATION

## ABSTRACT

Chemical immobilization treatments that adsorb/precipitate soil solution Cd, Pb, and Zn can prevent surface and groundwater contamination from the transport of heavy metals. The objective of this study was to evaluate agricultural limestone (AL), mineral rock phosphate (RP), and diammonium phosphate (DAP) chemical immobilization treatments to reduce heavy metal solubility and transport in a smelter contaminated soil. Chemical treatments were: check with no chemicals added, 10 g DAP $kg^{-1}$ (2300 mg P $kg^{-1}$), 90 g DAP $kg^{-1}$ (20700 mg P $kg^{-1}$), 60 g RP $kg^{-1}$, 180 g RP $kg^{-1}$, and 170 AL g $kg^{-1}$ mixed thoroughly with the soil. An additional treatment included layered 180 g RP $kg^{-1}$.

Mixed RP treatments were the least effective for reducing total Cd, Pb, and Zn elution from the contaminated soil. Limestone, although moderately effective for reducing Cd and Pb (45% and 54.8% reduction over the untreated check), was a poor performer for removing Zn from solution. Layered RP at 180

2

g kg$^{-1}$ was the most effective for reducing Pb transport with a 99.9% reduction over the untreated control; however, DAP treatments were superior for reducing Cd and Zn elution. Increasing DAP from 10 to 90 g kg$^{-1}$ released As via ligand exchange and elevated total As eluted from 0.13 to 29.5 mg kg$^{-1}$. Total P eluted through 60 pore volumes for the same DAP amendments was 2.31 mg and 335 mg, respectively. The 10 g DAP kg$^{-1}$ treatment was the most effective for immobilizing heavy metals transported from the contaminated soil, with only 5.4% of Cd, 1.1% of Pb, and 4.2 % of the Zn eluted compared with the untreated soil.

## INTRODUCTION

Historical and modern metal mining and smelting activities have contaminated soil and water resources with heavy metals. The action of natural geochemical weathering processes has transported and redistributed heavy metals from contaminated soils and industrial wastes to surrounding soils, streams, and groundwater (Fuge et al., 1993; Paulson, 1997). This redistribution of heavy metal contaminants through transport processes continues to endanger water supplies and threatens the health of surrounding ecosystems and human populations.

Cleanup of contaminated sites and disposal of metal-laden wastes are costly endeavors. Although highly effective at lowering risk, remediation technologies based on the excavation, transport, and landfilling of metal

3

contaminated soils and wastes are expensive. More cost-effective techniques treat contaminants in place; however, some methods may temporarily exacerbate environmental risks. Soil washing methods increase metal solubility and mobility to remove them from contaminated soil profiles. Increasing metal mobility for soil washing of contaminants may also increase the risk for transport and redistribution of contamination to underlying soil and groundwater (Vangronsveld and Cunningham, 1998). Other in-situ techniques, such as vitrification are not feasible due to the high costs of energy needed. In-situ chemical immobilization is a remediation technique that involves the addition of chemicals to contaminated soil to form less soluble and less mobile metal compounds. Products of chemical immobilization reactions should be less soluble and mobile to reduce heavy metal transport to surface and groundwater from contaminated soils. Additionally, chemical immobilization treatments may also be used as reactive barriers to prevent metal seepage from recovery pits and other processing areas on active and defunct smelter sites. Types of chemical treatment materials include organic, alkaline, or phosphate compounds that adsorb, chelate, or complex heavy metals in soil and reduce metal solubility. Compared with other remediation techniques, in-situ chemical immobilization is less expensive than other remediation techniques and may provide a long-term remediation solution through the formation of low solubility metal minerals and/or precipitates.

Alkaline materials used as chemical immobilization treatments include calcium oxides, calcium and magnesium carbonates (limestone), and industrial

4

by-products such as cement kiln dust and alkaline fly ash. Alkaline amendments can reduce heavy metal solubility in soil by increasing soil pH and metal sorption to soil particles (Filius et al., 1998; McBride et al., 1997). Increased sorption of metals to soil colloids can decrease mobile metals in solution and reduce metal transport in contaminated soils. Additionally, increased soil pH and carbonate buffering can allow the formation of metal-carbonate precipitates, complexes, and secondary minerals (Chlopecka and Adriano, 1996; McBride, 1989; Mench et al., 1994). Metal-carbonate minerals formed with addition of carbonate-rich limestone can decrease heavy metal solubility and reduce metal mobility and transport.

Additions of phosphate or having sufficient soil P status have proven to be extremely effective for reducing metal solubility. Ruby et al. (1994) indicated that adequate soil phosphate was responsible formation of insoluble complexes and the reduction in potential Pb. Experiments involving treatment of metal contaminated soils with rock phosphates (apatite and hydroxyapatite) have shown that formation of metal-phosphate precipitates and minerals reduced heavy metal solubility. Insoluble and geochemically stable lead pyromorphites such as hydroxypyromorphite [$Pb_5(PO_4)_3OH$] and chloropyromorphite [$Pb_5(PO_4)_3Cl$] have been found to control Pb solubility in apatite amended contaminated soils (Chen et al., 1997; Eighmy et al., 1997; Laperche et al., 1996; Ma et al., 1993; Ma et al.,1995; Ma and Rao, 1997; Zhang and Ryan, 1999). In addition to reducing metal solubility, phosphate amendments are also effective at reducing metal bioavailability associated with incidental ingestion of soil by

5

humans (Lambert et al., 1994; Zhang and Ryan, 1998). Rock phosphate treatments are also effective for reducing plant bioavailability of heavy metals (Basta and Gradwohl, 1998; Chlopecka and Adriano, 1996; Laperche et al., 1997). Although apatite treatments are effective for reducing metal solubility and bioavailability, more research is needed on its effectiveness for reducing the mobility and transport of heavy metals such as Cd, Pb, and Zn.

Other research has shown that phosphate sources with higher solubility than rock phosphate (i.e. phosphate salts) could be used to increase the efficiency of lead pyromorphite formation (Cooper et al., 1998; Hettiarachchi et al., 1997; Ma et al., 1993; Pierzynski and Schwab, 1993). Ma and Rao (1997) suggested that P sources with higher solubility could be mixed with rock phosphate to increase the effectiveness of lead immobilization in contaminated soils. Soluble phosphate has been shown to reduce Cd and Pb solubility (Santillian-Medrano and Jurinak, 1975). Other soluble phosphates have been shown to induce the formation of heavy metal phosphate precipitates. Materials such as $Na_2HPO_4$ (Cotter-Howells and Capron, 1996) and pyrophosphate (Xie and MacKenzie, 1990) are highly effective for forming precipitates and increasing sorption Pb and Zn. Another soluble phosphate source, diammonium phosphate $[(NH_4)_2HPO_4]$ (DAP), currently represents roughly 70% of the total US production of phosphate fertilizer products (US Dept. of Commerce, 1998). Research with DAP as a chemical immobilization treatment has shown decreased Cd solubility in soil cadmium suspensions (Levi-Minzi and Petruzzelli, 1984). A contrasting research result showed that DAP decreased soil pH via nitrification and was

6

therefore ineffective for reducing metal solubility in agricultural soils (Pierzynski and Schwab, 1993). Of the soluble P sources, commercial fertilizers and sodium phosphates are the most readily available materials in large quantities that may be needed for remediation of contaminated sites.

Most studies investigating chemical immobilization treatments have focused on reducing bioavailability (i.e. plants, gastrointestinal), solubility, or extractability (i.e. sequential extractions). Additional information is needed on the effect of chemical treatments for reducing the mobility and transport of Cd, Pb, and Zn. The objective of this study was to evaluate and compare the ability of agricultural limestone, rock phosphate, and diammonium phosphate treatments to reduce heavy metal solubility and transport in a smelter contaminated soil.

## MATERIALS AND METHODS

Surface soil (<20cm) with elevated residual concentrations of Cd, Pb, Zn, and As was collected from an inoperative smelter site in Northeastern Oklahoma. Soil was air-dried and sieved (<2mm) prior to use. Collected soils had recently been treated with coarse limestone. The soil exhibited effervescence with addition of 1M HCl indicating the presence of free carbonates. Soil pH (1:1, soil:water) was determined by combination electrode. Particle size analysis was determined using the hydrometer method (Gee and Bauder, 1986). Total metal contamination in the soil was determined by X-ray fluorescence (Karathanasis and Hajek, 1996). The contaminated soil was also tested to determine its

hazardous waste disposal status using the Toxicity Characteristic Leaching Procedure (TCLP, SW-846 Method 1311) (U.S. EPA, 1986). Furthermore, the soil was extracted with 0.5M $Ca(NO_3)_2$ at a 1:20 soil:solution ratio for 16 hours to estimate potential bioavailability (Basta and Gradwohl, 2000).

Three chemical treatment materials were evaluated for reducing the solubility and transport of Cd, Pb, and Zn: agricultural limestone (AL) (104% effective calcium carbonate equivalent (ECCE) as $CaCO_3$), mineral rock phosphate (RP) (12.4% P - carbonated fluorapatite North Carolina source - size 40 mesh), and reagent grade diammonium phosphate (DAP 23% P) $[(NH_4)_2HPO_4]$. Treatments were: check soil with no chemicals added, 10 g DAP $kg^{-1}$ (2300 mg P $kg^{-1}$), 90 g DAP $kg^{-1}$ (20700 mg P $kg^{-1}$), 60 g RP $kg^{-1}$, 180 g RP $kg^{-1}$, and 170 g AL $kg^{-1}$ mixed thoroughly with the with soil. An additional treatment included 180 g RP $kg^{-1}$ layered in the transport column. Phosphate amendments were based on providing a specific P/ total metal ($M_{total}$) molar ratios. Total metal was defined as the sum of total Cd, Pb, and Zn determined by XRF. This scheme was chosen because treatments were targeted to immobilize the total of these metals in the contaminated soil. A 3/5 P/$M_{total}$ ratio corresponds to the stoichiometric P/Pb ratio for chloropyromorphite $[Pb_5(PO_4)_3Cl]$ and has been reported as the basis of hydroxyapatite and apatite treatments to lead-contaminated soils (Laperche et al., 1996; Ma et al., 1993; Zhang et al., 1998; Zhang and Ryan, 1999). The 180 g RP $kg^{-1}$ treatment corresponds to an approximate 3/5 P/$M_{total}$ ratio, and the 60 g RP $kg^{-1}$ to a 1/5 P/$M_{total}$ ratio. These RP treatments were mixed thoroughly with the soil prior to repacking in the

transport columns. In addition to investigating RP treatments mixed with the contaminated soil, a layered treatment of 180 g RP kg$^{-1}$ was also investigated to simulate a reactive chemical barrier. This treatment involved layering RP on the top of the column and pumping soil solution upwards through the contaminated soil and then through the RP layer. With the low solubility of RP, the total applied phosphate does not correspond directly with total P in solution. Because of the high water solubility of DAP, the 3/5 P/M$_{total}$ molar ratio of the 90 g DAP kg$^{-1}$ (20700 mg P kg$^{-1}$) treatment supplies much more soluble phosphate per mass of treatment than RP. A lower rate of 10 g DAP kg$^{-1}$ (2300 mg P kg$^{-1}$) corresponding to a 1/15 P/M$_{total}$ ratio was also investigated. The agricultural limestone treatment was based on the formation of metal-carbonate precipitates with the form MCO$_3$, where M = M$_{total}$ as previously described. The actual rate of 170 g AL kg$^{-1}$ was 1.5 times the stoichiometric amount needed to convert M$_{total}$ to metal-carbonate precipitates. All DAP and AL amendments were mixed thoroughly with the soil prior to uniform repacking into acrylic transport columns.

Chemical immobilization treatments were evaluated using solute transport experiments with repacked soil columns similar to methods described by Selim and Amacher (1996) (Fig. 1). Column dimensions were 4 cm inside diameter by 7.5 or 10 cm in length. Teflon filters (0.45μm, Micron Separations, Inc., Westboro, MA) were placed between the soil matrix and end caps on each end of the column to prevent loss of fines from the soil column. An additional filter of the same type was placed between the soil matrix and the RP on the 180 g RP kg$^{-1}$ layered treatment. Soils were saturated with type 1 reagent grade water

(>18.0 MΩ•cm at 25°C) (ASTM, 1992) with continuous upward flow using a piston pump (Fluid Metering, Inc., Syosset, New York) until saturation and allowed to equilibrate for 48 hours prior to leaching. Eighmy et al. (1997) indicated that 24 hours was sufficient for pseudo-equilibrium and solid phase precipitation of metal phosphate compounds to occur with additions of soluble phosphate to combustion residues. Our preliminary studies showed that a steady state within the column was obtained after 24 hours of pre-equilibration. We selected a pre-equilibration period of 48 hours to ensure an equilibrated system. After the equilibration period, a saturated upward flow regime was resumed and soil solution fractions were collected with a fraction collector (ISCO Inc., Lincoln, Nebraska) through 60 pore volumes. Column effluent was passed through Teflon tubing and an in-line 0.45μm filter before collection into glass test tubes. Sample effluent pH was immediately analyzed after collection by combination electrode. Effluent was then acidified with trace metal grade $HNO_3$ (pH<2) (APHA, 1992) 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-AES). Metal eluted in solution was normalized to concentrations per 100 g of soil for comparison of treatments. Elution curves for As, Cd, Pb, P, and Zn were plotted for each column experiment. Numeric integration of metal mass eluted (through 60 pore volumes) per mass of soil was calculated and Darcy flux (q), and soil bulk density ($\rho_b$) were determined.

Following each metal elution experiment, 50 mg Br $L^{-1}$ solution was introduced as a conservative tracer to investigate the possibility of transport

10

related non-equilibrium. The tracer solution was introduced as a continuous flow until complete breakthrough was obtained. Collected effluent fractions were analyzed for Br⁻ by ion chromatography. Bromide tracer breakthrough curves were also plotted and fitted using the model COLUMN 1.4 (Brown et al., 1996) to examine the flow regime and determine the potential for transport related non-equilibrium.

Chemical analyses were performed using calibration curves determined from standards prepared from certified stock solutions. Sample blanks were analyzed to determine any matrix effects, which allowed for correction of instrument response. Trace metal control standards were used to assess instrument precision and accuracy. Limits of detection (LOD) were determined from the summation of three standard deviations ($3\sigma$) of the instrument response for seven repeated analyses of a sample blank solution. Practical quantitative limits (PQL) of detection were set at ten times the LOD (APHA, 1992). Solution concentrations below the PQL were assigned the value of zero in data analysis.

## RESULTS AND DISCUSSION

### Soil Properties and Contaminants

The contaminated soil was a sandy loam with 67% sand, 29% silt, and 4% clay with a soil pH of 6.8. The total levels of metal contamination in the soil as determined by X-ray fluorescence (XRF) and TCLP extractable levels are reported in Table 1. Total Cd, Pb, and Zn in the soil are well above background

soil concentrations (Holmgren et al., 1993). TCLP extractable Cd and Pb exceed

regulatory levels indicating the soil qualifies as a hazardous material that requires

remediation and disposal in a hazardous waste facility. The high amounts of Cd,

Pb, and Zn extracted with 0.5M $Ca(NO_3)_2$ indicate a large portion of the total

heavy metals in the soil is potentially bioavailable (Table 1) (Basta and Gradwohl,

2000). Total elemental content for each element in g $kg^{-1}$ (in parentheses) were:

Si (193), Al (38), Ca (24), Mg (2.5), K (6.1), Fe (47), Mn (1.9), Ti (3.2), P (0.39),

and Cr (0.27). As indicated by the Si to Fe ratio, the collected material exhibits

chemical properties of soil and not an iron-based smelting waste. Saturated

paste extractions were used to determine soluble anions and EC. Soluble anions

in mg $L^{-1}$ (in parenthesis) were: Cl (26.6), $SO_4$ (1556.6), and $NO_3$ (21.7). Soil EC

was 2.15 dS $m^{-1}$.


**Contaminant Transport**

Solution pH values varied only ±0.2 units ranging from 6.8 to 7.2

throughout the duration of all column elution experiments. Solution calcium

eluted over the course of all experiments was in excess of 0.005 M Ca (200 mg

Ca $L^{-1}$) indicating a well buffered system from the prior limestone amendments to

the soil. Because soil solutions were well buffered with Ca, the exclusion of

additional background electrolytes from the eluting solution likely had no adverse

effect on soil structure or aggregate stability during leaching. The experiment

values for bulk density, Darcy flux, and pore volume are given in Table 2. Soil

bulk densities ($\rho_B$) in the repacked columns ranged between 1.26 and 1.38 g cm$^{-3}$ and Darcy flux between 1.70 to 4.88 cm hr$^{-1}$.

Bromide breakthrough curves for all columns were sigmoid shaped and showed no apparent tailing, indicating homogenous packing and well-satisfied boundary conditions. Breakthroughs curves showed behavior representative of a conservative tracer in porous media and conformed to the assumption of local equilibrium with r$^2$ values above 0.99 for all fitted curves (data not shown). These results indicate that transport-related non-equilibrium was not a factor in any of the experiments.

Plotted elution curves for Cd (Fig. 2), Pb (Fig. 3), and Zn (Fig. 4) illustrate the differences in release and transport of heavy metals for each of the amendments. Numerical integration of observed solution Cd, Pb, and Zn eluted through 60 pore volumes allows for direct comparison of treatments for reducing the total mass metal transported (Table 3).

**Rock Phosphate Treatment**

Layered RP at 180 g kg$^{-1}$ showed 99.9% reduction in Pb eluted compared with the untreated check, but was not as effective for reducing Cd and Zn elution (<25% reduction in total Cd and Zn) (Table 3). Mixed RP treatments proved to be somewhat ineffective for reducing Cd, Pb, and Zn leached from the contaminated soil, with high percentages of (>73%) of total metals eluted in comparison to the untreated soil (Table 3). Phosphorus was not detected in effluent from any of the RP treated soils. Overall, metal elution curves for all RP

13

treatments, with the exception of the 180 g RP kg$^{-1}$ layered treatment and Pb

elution, closely followed the untreated soil metal elution curve but at slightly lower

concentrations (Figs 2-4). The improved efficiency of the layered RP treatment

over the mixed treatment could be due to a greater effective surface area and

increased contact time of soil solution that allows for the immobilization of Pb

within the RP matrix.


## Limestone Treatment

The agricultural limestone treatment was moderately effective at reducing

Cd and Pb elution but was much less effective for reducing the cumulative mass

of metals eluted form the soil. The AL treatment increased soil effluent pH from

6.8 to 7.2. This small increase in pH had only modest effects on metal solubility

and thus did not show a pronounced reduction in metal release and transport

from the contaminated soil. Although moderately effective for reducing Cd (45%)

and Pb (54.8%) over the untreated check, AL was a poor performer for removing

Zn from solution (Table 3).


## Diammonium Phosphate Treatment

Amendments of DAP were effective for decreasing the metal eluted from

the contaminated soil. Both DAP treatments decreased the amounts of Cd

eluted from the contaminated soil (Fig. 2). For the 90 g DAP kg$^{-1}$ treatment,

solution Cd fell below the instrument PQL (6 $\mu$g L$^{-1}$) at 4 pore volumes and

remained below measurable limits through 60 pore volumes. Compared with the

14

untreated soil, only 5.4% and 8.1% of the total Cd was eluted from 10 and 90 g

DAP kg$^{-1}$ treatments, respectively (Table 3). DAP also decreased the amounts of

Pb eluted (Fig. 3) with only 1.1% of the total eluted from the control soil for the 10

g DAP kg$^{-1}$ treatment (Table 3). Furthermore, eluted Pb in solution was reduced

below the instrument PQL (70 $\mu$g L$^{-1}$) after 2.5 pore volumes for the 90 g DAP kg$^-$

$^1$ and after 3.2 pore volumes for the 10 g DAP kg$^{-1}$ treatments. Eluted Zn was

also reduced by addition of DAP (Fig. 4), with Zn in solution falling below the

PQL (15 $\mu$g L$^{-1}$) after 4.6 pore volumes for the 90 g DAP kg$^{-1}$ treatment.

However, total reduction of Zn based on the untreated soil was far greater (4.2%)

for the 10 g DAP kg$^{-1}$ treatment than for the 90 g DAP kg$^{-1}$ treatment (24.7%).

Application of DAP released large amounts of As from the contaminated

soil (Fig. 5). Increasing DAP from 10 to 90 g kg$^{-1}$ elevated the total As eluted

from 0.13 to 29.5 mg kg$^{-1}$ over 60 pore volumes (Table 3), with As concentrations

in solution as high as 147 mg As L$^{-1}$. Phosphate additions increased As elution

apparently by phosphate-arsenate ligand exchange. Peryea and Kammereck

(1997) and Peryea (1991) reported similar phosphate induced release and

transport of As when P was added to orchard soils spiked or contaminated with

lead arsenate.

Elution curves of Cd, Pb, and Zn from the 90 g DAP kg$^{-1}$ treatment all

exhibited higher initial concentrations than the 10 g DAP kg$^{-1}$ treatment, but then

quickly decreased to solution concentrations below instrument detection. For the

90 g DAP kg$^{-1}$ treatment, solution collected from the first 5 to 7 pore volumes of

elution was dark colored at early times and faded to clear after approximately 10

pore volumes. The coloration of effluent fractions was unique to this treatment and may have indicated the formation of metal-organic complexes in this soil system. Phosphate compounds have long been used in extraction of soil organic matter for characterization (Swift, 1996). The high amounts of phosphate added could have allowed the formation of highly soluble and mobile metal-organic-phosphate complexes. In addition to the potential of complex formation, the Darcy flux for the 90 g DAP kg$^{-1}$ treatment was 2-times greater than for the 10 g DAP kg$^{-1}$ treatment. This higher flux could have further contributed to the chemical disequilibration in the system at early elution times and increased the solution concentration of heavy metals available for transport.

**Phosphate Elution**

Large additions of P to the contaminated soil may increase the risk of eutrophication to phosphate-limited surface water bodies. Phosphorus elution curves for the DAP amended column experiments are shown in Figure 6. As P application increased, the mass of P eluted from the treated soil columns increased. Total phosphorus eluted from the DAP treatments through 60 pore volumes was 2.31 mg for the 10 mg DAP kg$^{-1}$ treatment and 335 mg for the 90 mg DAP kg$^{-1}$ (Table 2). The summation of total P eluted from the 10 mg DAP kg$^{-1}$ treatment corresponds to < 1% of the total P added to the system; however, P eluted from the 90 mg DAP kg$^{-1}$ represents 10.5% of the total P added. The low percentage of total P eluted from the 10 mg DAP kg$^{-1}$ treatment indicates an adequate pre-equilibration period for sorption and/or precipitation to occur. As

16

previously indicated, excessive As was released with the 90 mg DAP kg$^{-1}$ treatment which may have contributed to chemical non-equilibrium of heavy metals with this treatment. Additions of soluble phosphate >10 mg DAP kg$^{-1}$ (>2300 mg P kg$^{-1}$) have limited potential for improving reduction of eluted heavy metals from this soil and will likely increase eluted P and As. Soluble phosphate was not detected in the RP and AL treated experiments.

**Effects of Chemical Treatments on Soil pH**

Ammonium-based fertilizers can result in soil acidification (Sposito, 1989). Soil acidification from diammonium phosphate would increase solubility and mobility of heavy metals in soils. To investigate the effect of chemical treatments on soil acidification, amended soils were incubated at 0.22 % volumetric water content at 30° C for 6 months. Soil pH was monitored periodically using a 1:1 soil:water ratio and a combination pH electrode. For the DAP amended soils, soil pH values decreased from 7.1 to 6.5 after 2 months and then remained constant. The presence of free carbonates in the coarse limestone that was previously added to the soil (in the field) likely buffered the system. Other researchers have used liming materials along with soluble phosphate treatments to buffer against decreases in pH (Hettiarachchi et al., 1997, 1999; Brown et al., 1999) and many of the rock phosphate sources are carbonated forms of apatite that have some value as a liming materials. As expected, change in soil pH with the AL and RP treatments was negligible with pH values in the neutral (6.9-7.1) range after the incubation period.

# SUMMARY AND CONCLUSIONS

Overall, the 10 g DAP kg$^{-1}$ application was the most effective for immobilizing heavy metals eluted from the contaminated soil with only 5.4% of Cd, 1.1% of Pb, and 4.2 % of the Zn eluted when compared with the untreated soil. Application of DAP released As from the contaminated soil (via ligand exchange) and increasing DAP from 10 to 90 g kg$^{-1}$ elevated the total As eluted from 0.13 to 29.5 mg kg$^{-1}$ over 60 pore volumes. Total phosphorus eluted from the DAP treatments (60 pore volumes) was 2.31 mg (< 1% of the total added) for the 10 mg DAP kg$^{-1}$ treatment and 335 mg (10.5% of the total added) for the 90 mg DAP kg$^{-1}$ treatment. Layered RP at 180 g kg$^{-1}$ was the most effective treatment for reducing Pb transport with a 99.89% reduction over the untreated control; however, DAP treatments outperformed this treatment for Cd and Zn elution. Mixed RP at both treatments investigated was mostly ineffective in reducing Cd, Pb, and Zn elution from the contaminated soil. Limestone, although moderately effective for reducing Cd (45%) and Pb (54.8%) over the untreated check, was a poor performer for removing Zn from solution (Fig. 7).

Chemical immobilization of heavy metals using DAP provided the most effective method of reducing metal solubility and mobility. DAP treatments not only removed large amounts of Pb from solution, but were also highly effective at reducing Cd and Zn solubility and transport. Application schemes with DAP must be carefully planned to reduce As release and P elution, and co-application of liming materials with DAP may be necessary to offset potential soil acidification.

# REFERENCES

American Public Health Association (APHA). 1992. Standard methods for the examination of water and wastewater. Part 1030 Data Quality pp. 1-3 to 1-12 and Part 3000 Metals pp. 3-1 to 3-103. *In* A.E. Greenberg, L.S. Clesceri, and A.D. Eaton (eds.). 18th ed. American Public Health Assoc., Washington, DC.

ASTM. 1992. The American society for testing and material, vol. 11.01, sec. DH93-91.

Basta, N.T., and R. Gradwohl. 1998. Remediation of heavy metal-contaminated soil using rock phosphate. Better Crops Plant Food 82:29-31.

Basta, N.T., and R. Gradwohl. 2000. Estimation of Cd, Pb, and Zn bioavailability in smelter-contaminated soils by a sequential extraction procedure. J. Soil Contam. (in press).

Berti, W.R., and S.D. Cunningham. 1997. In-place inactivation of Pb in Pb-contaminated soils. Environ. Sci. Technol. 31:2673-2678.

Brown, G.O., H.T. Hseih, and Y.W. Lin. 1996. COLUMN for windows: User manual. Prepared for Sandia National Laboratories. Biosystems and Agricultural Engineering, Oklahoma State University, Stillwater, OK.

Brown, S.L., R. Chaney, and B. Berti. 1999. Field test of amendments to reduce the in-situ availability of soil lead. p. 506-507. *In* Proc. Extended Abstr., 5th Int. Conf. on the Biogeochem. Trace Elements (ICOBTE), Vienna, Austria, 11-15 July, 1999.

Chen, X., J.V. Wright, J.L. Conca, and L.M. Peurrung. 1997. Evaluation of heavy metal remediation using mineral apatite. Water Air Soil Pollut. 98:57-78.

Chlopecka, A. and D.C. Adriano. 1996. Mimicked in-situ stabilization of metals in a cropped soil: Bioavailability and chemical form of zinc. Environ. Sci. Technol. 30:3294-3303.

Cooper, E.M., D.G. Strawn, J.T. Sims, D.L. Sparks, and B.M. Onken. 1998. Effect of chemical stabilization by phosphate amendment on the desorption of P and Pb from a contaminated soil. p. 343. *In* 1998 Agronomy abstracts, ASA, Madison, WI.

Cotter-Howells, J., and S. Capron. 1996. Remediation of contaminated land by formation of heavy metal phosphates. Appl. Geochem. 11:335-342.

Eighmy, T.T., B.S. Crannell, L.G. butler, F.K. Cartledge, E.F. Emery, D. Oblas, J.E. Krzanowski, J.D. Eusden, Jr., E.L. Shaw, and C.A. Francis. 1997. Heavy metal stabilization in municipal solid waste combustion dry scrubber residue using soluble phosphate. Environ. Sci. Technol. 31:3330-3338.

Filius, A., T. Streck, and J. Richter. 1998. Cadmium sorption and desorption in limed topsoils as influenced by pH: Isotherms and simulated leaching. J. Environ. Qual. 27:12-18.

Fuge, R., F.M. Pearce, N.J.G. Pearce, and W.T. Perkins. 1993. Geochemistry of Cd in the secondary environment near abandoned metalliferous mines, Wales. Appl. Geochem., Suppl. Iss. 2:29-35.

Gee, G.W., and J.W. Bauder. 1986. Particle size analysis. p. 383-411. In A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agron. Monog. 9. ASA and SSSA, Madison, WI.

Hettiarachchi, G.M., and G.M. Pierzynski. 1999. Effect of phosphorus and other soil amendments on soil lead, cadmium and zinc bioavailability. p. 514-515. In Proc. Extended Abstr., 5th Int. Conf. on the Biogeochem. Trace Elements (ICOBTE), Vienna, Austria, 11-15 July, 1999.

Hettiarachchi, G.M., G.M. Pierzynski, J. Zwonitzer, and M. Lambert. 1997. Phosphorus source and rate effects on cadmium, lead, and zinc bioavailabilities in a metal-contaminated soil. p. 463-464. In Extended Abstr., 4th Int. Conf. on the Biogeochem. Trace Elements (ICOBTE), Berkeley, CA, 23-26 June, 1997.

Holmgren, G.G.S., M.W. Meyer, R.L. Chaney, and R.B. Daniels. 1993. Cadmium, lead, zinc, copper, and nickel in agricultural soils of the United States of America. J. Environ. Qual. 22:335-348.

Karathanasis, A.D., and B.F. Hajek. 1996. Elemental analysis by X-ray fluorescence spectroscopy. p. 161-223. In D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical Methods. SSSA Book Series no. 5. SSSA and ASA, Madison, WI.

Lambert, M., G. Pierzynski, L. Erickson, and J. Schnoor. 1994. Remediation of lead, zinc, and cadmium contaminated soils. Issues Environ. Sci. Technol. 7:91-102.

Laperche, V., T.J. Logan, P. Gaddam, and S.J. Traina. 1997. Effect of apatite amendments on plant uptake of lead from contaminated soil. Environ. Sci. Technol. 31:2745-2753.

Laperche, V., S.J. Traina, P. Gaddam, and T.J. Logan. 1996. Chemical and mineralogical characterizations of Pb in a contaminated soil: Reactions with synthetic apatite. Environ. Sci. Technol. 30:3321-3326.

Levi-Minzi, R., and G. Petruzzelli. 1984. The influence of phosphate fertilizers on Cd solubility in soil. Water Air Soil Pollut. 23:423-429.

Ma, Q.Y., T.J. Logan, and S.J. Traina. 1995. Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. Environ. Sci. Technol. 29:1118-1126.

Ma, Q.Y., S.J. Traina, and T.J. Logan. 1993. In situ lead immobilization by apatite. Environ. Sci. Technol. 27:1803-1810.

Ma, L.Q., and G.N. Rao. 1997. Effects of phosphate rock on sequential chemical extraction of lead in contaminated soils. J. Environ. Qual. 26:788-794.

Mench, M.J., V.L. Didier, M. Leoffler, A. Gomez, and M. Pierre. 1994. A mimicked in-situ remediation study of metal-contaminated soils with emphasis on cadmium and lead. J. Environ. Qual. 23:58-63.

McBride, M.B. 1989. Reactions controlling heavy metal solubility in soils. Adv. Soil Sci. 10:1-56.

McBride, M.B., S. Suave, and W. Hendershot. 1997. Solubility control of Cu, Zn, Cd, and Pb in contaminated soils. European J. Soil Sci. 48:337-346.

Paulson, A.J. 1997. The transport and fate of Fe, Mn, Cu, Zn, Cd, Pb, and $SO_4$ in a groundwater plume and in downstream surface water in the Coeur d'Alene mining district, Idaho, USA. Appl. Geochem. 12:447-464.

Peryea, F.J. 1991. Phosphate-induced release of arsenic from soils contaminated with lead arsenate. Soil Sci. Soc. Am. J. 55:1301-1306.

Peryea, F.J., and R. Kammereck. 1997. Phosphate-enhanced movement of arsenic out of lead arsenate-contaminated topsoil and through uncontaminated subsoil. Water Air Soil Pollut. 93:243-254.

Pierzynski, G.M., and A.P. Schwab. 1993. Bioavailability of zinc, cadmium, and lead in a metal-contaminated alluvial soil. J. Environ. Qual. 22:247-254.

Ruby, M.V., A. Davis, and A. Nicholson. 1994. In situ formation of lead phosphates as a method to immobilize lead. Environ. Sci. Technol. 28:646-654.

Santillian-Medrano, J., and J.J. Jurinak. 1975. The chemistry of lead and cadmium in soil: Solid phase formation. Soil Sci. Soc. Am. Proc. 39:851-856.

Selim, H.M., and M.C. Amacher. 1996. Reactivity and transport of heavy metals in soils. CRC Press, Boca Raton, FL.

Sposito, Garrison. 1989. The chemistry of soils. Oxford Univ. Press, New York.

Swift, R.S. 1996. Organic matter characterization. p. 1011-1069. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical Methods. SSSA Book Series no. 5. SSSA and ASA, Madison, WI.

U.S. Department of Commerce. 1998. Inorganic fertilizer materials and related products. Current Industrial Report, MA325B(98)-1, US Dept. of Com., Econom. and Stat. Div., U.S. Census Bureau.

U.S. Environmental Protection Agency. 1986. Test methods for evaluating solid wastes. SW-846, 3rd ed. U.S. Gov. Print. Office.

Vangronsveld, J., and S.D. Cunningham. 1998. Introduction to the concepts. *In* J. Vangronsveld and S.D. Cunningham (eds.) Metal-contaminated soils: In situ inactivation and phytorestoration. Springer-Verlag, Berlin.

Xie, R.J., and A.F. MacKenzie. 1990. Zinc sorption, desorption, and fractions in three autoclaved soils treated with pyrophosphate. Soil Sci. Soc. Am. J. 54:71-77.

Zhang, P, and J.A. Ryan. 1999. Formation of chloropyromorphite from galena (PbS) in the presence of hydroxyapatite. Environ. Sci. Technol. 33:618-624.

Zhang, P, J.A. Ryan, and J. Yang. 1998. In vitro soil Pb solubility in the presence of hydroxyapatite. Environ. Sci. Technol. 32:2763-2768.

Table 1. Total content, TCLP extractable, and 0.5M $Ca(NO_3)_2$ extractable Cd, Pb, As, and Zn for the smelter-contaminated soil.

| Element | Total Content † | TCLP Extractable | | 0.5M $Ca(NO_3)_2$ Extractable |
|---|---|---|---|---|
| -------- | mg kg$^{-1}$ | mg L$^{-1}$ | (reg. limit ‡) | mg kg$^{-1}$ |
| Cd | 1090 | 39.9 ± 1.59 | (1.0) | 155.7±4.44 |
| Pb | 5150 | 21.0 ± 0.58 | (5.0) | 12.3±.0.43 |
| As | 152 | 0.03 ± 0.002 | (5.0) | 0.25±0.02 |
| Zn | 69200 | 1171 ± 32 | (NA) | 585.5±17.8 |

† Total content determined by XRF
‡ Specified by U.S. EPA Method 1311 (U.S. EPA, 1986)

Table 2. Summary of transport parameters from untreated and amended soils.

| Amendment | Treatment | Length | Flux | $\rho_b$ | Pore Volume |
|---|---|---|---|---|---|
| | $g\ kg^{-1}$ | cm | $cm\ hr^{-1}$ | $g\ cm^{-3}$ | mL |
| Control | - | 7.5 | 1.70 | 1.31 | 39.4 |
| DAP | 10 | 7.5 | 2.43 | 1.29 | 40.1 |
| DAP | 90 | 10 | 4.84 | 1.26 | 5.4 |
| AL | 170 | 10 | 4.72 | 1.36 | 49.7 |
| RP | 180L† | 10 | 4.88 | 1.36 | 49.9 |
| RP | 60 | 7.5 | 2.06 | 1.34 | 38.1 |
| RP | 180M‡ | 7.5 | 2.46 | 1.38 | 36.5 |

† = Layered treatment (L)
‡ = Mixed treatment (M)

Table 3. Cumulative mass of As, Cd, Pb, Zn, and P collected from miscible displacement experiments and percent of metal eluted from the untreated column (in parentheses) through 60 pore volumes of elution.

| Treatment | As | Cd | | Pb | | Zn | | P |
|---|---|---|---|---|---|---|---|---|
| | mg kg$^{-1}$ | mg kg$^{-1}$ | | $\mu$g kg$^{-1}$ | | mg kg$^{-1}$ | | mg |
| Control | ND | 14.9 | (100) | 460 | (100) | 108 | (100) | 0.52 |
| DAP 10 | 0.13 | 0.8 | (5.4) | 5.2 | (1.1) | 4.5 | (4.2) | 2.31 |
| DAP 90 | 29.5 | 1.2 | (8.1) | 44.7 | (9.7) | 24.7 | (22.9) | 335 |
| AL | 0 | 6.7 | (45.0) | 252 | (54.8) | 84.4 | (78.1) | - |
| RP 180L | 0 | 7.0 | (47.0) | 0.5 | (0.11) | 81.6 | (75.6) | - |
| RP 60 | 0 | 12.7 | (85.2) | 418 | (91.0) | 94.1 | (87.1) | - |
| RP 180M | 0 | 10.9 | (73.2) | 376 | (81.7) | 79.3 | (73.4) | - |

SOLUTION
RESERVOIR

HIGH PRESSURE
PUMP

REPACKED
COLUMN

FRACTION
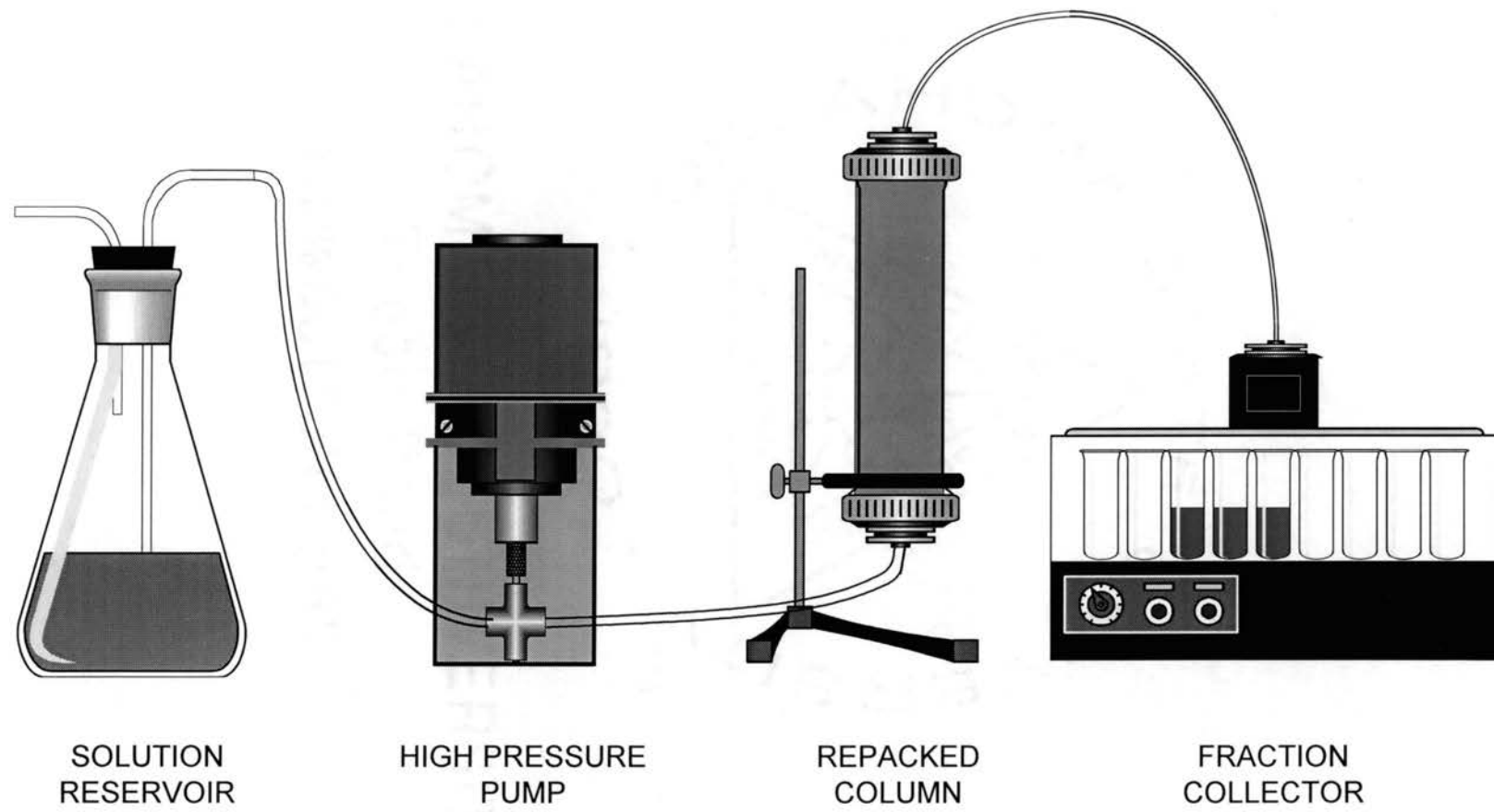COLLECTOR

Figure 1. Schematic of solute transport apparatus.
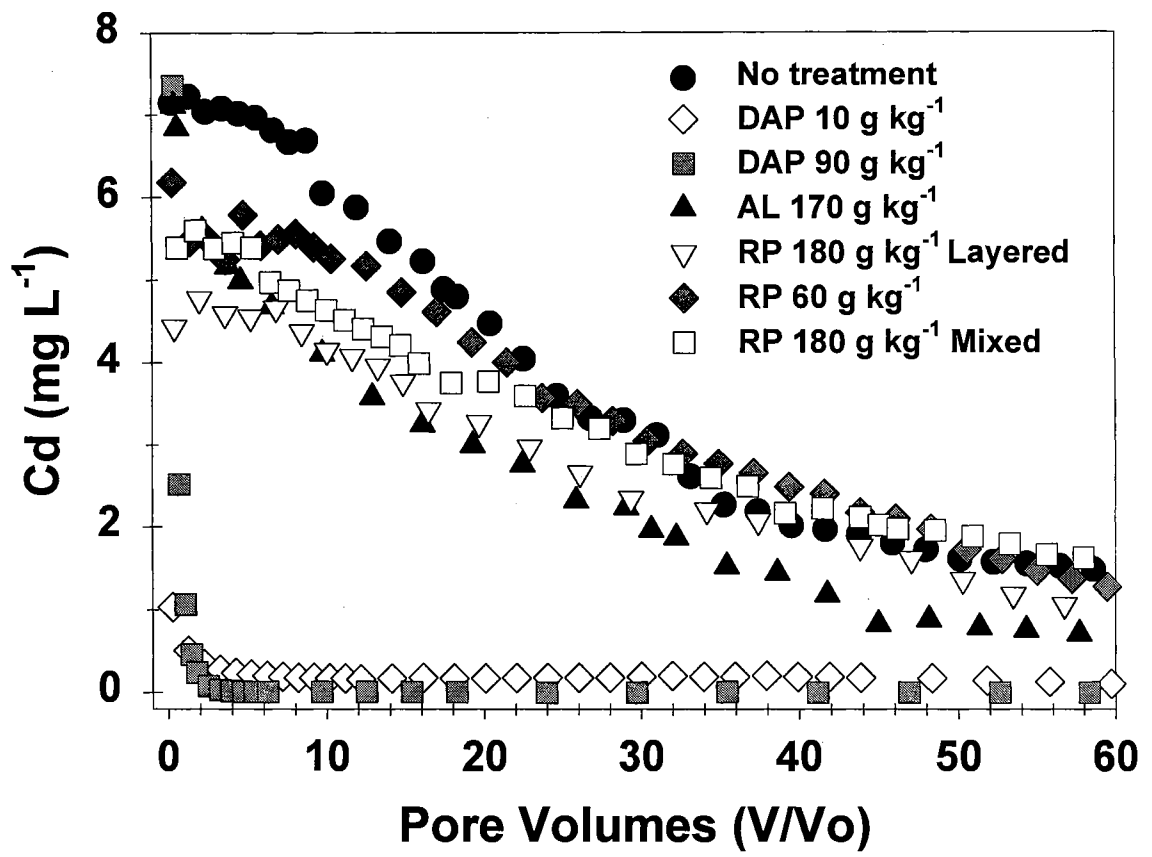
Figure 2. Cadmium elution curves for untreated and amended soils.
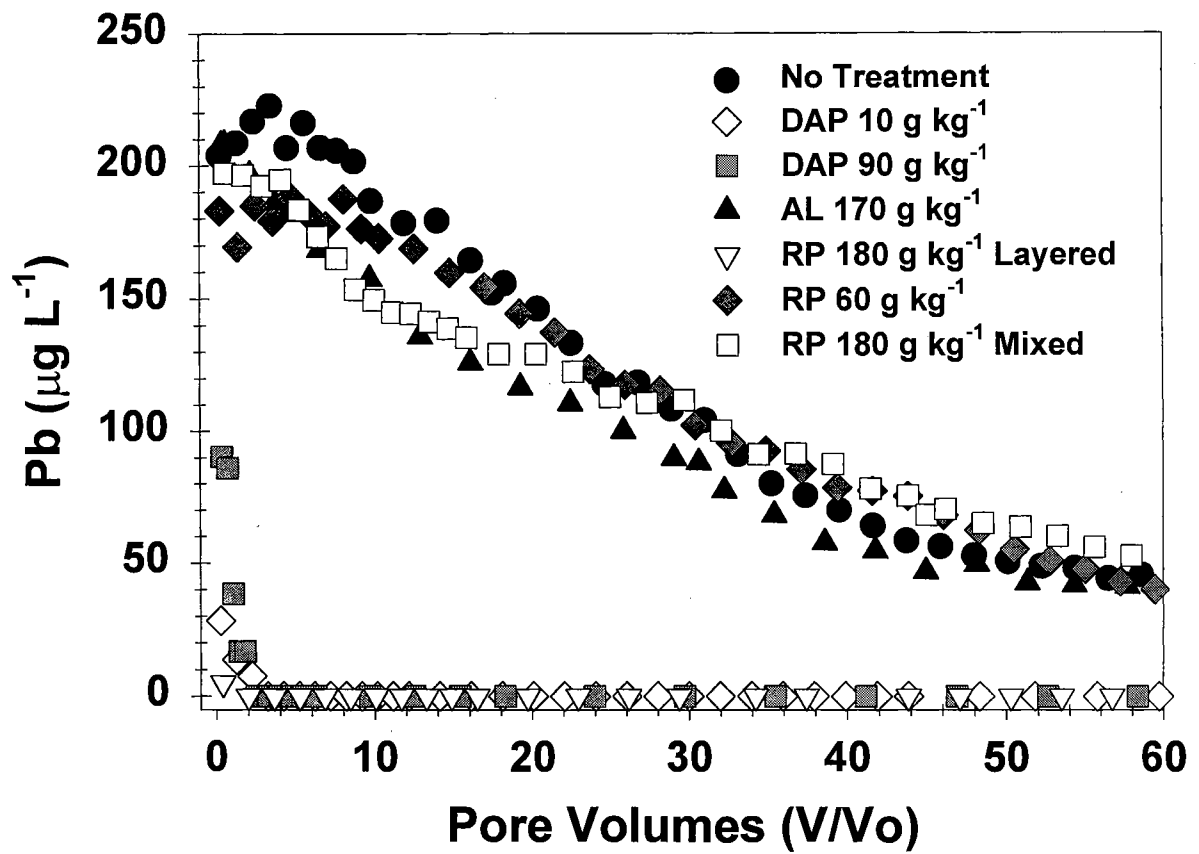
Figure 3. Lead elution curves for untreated and amended soils.
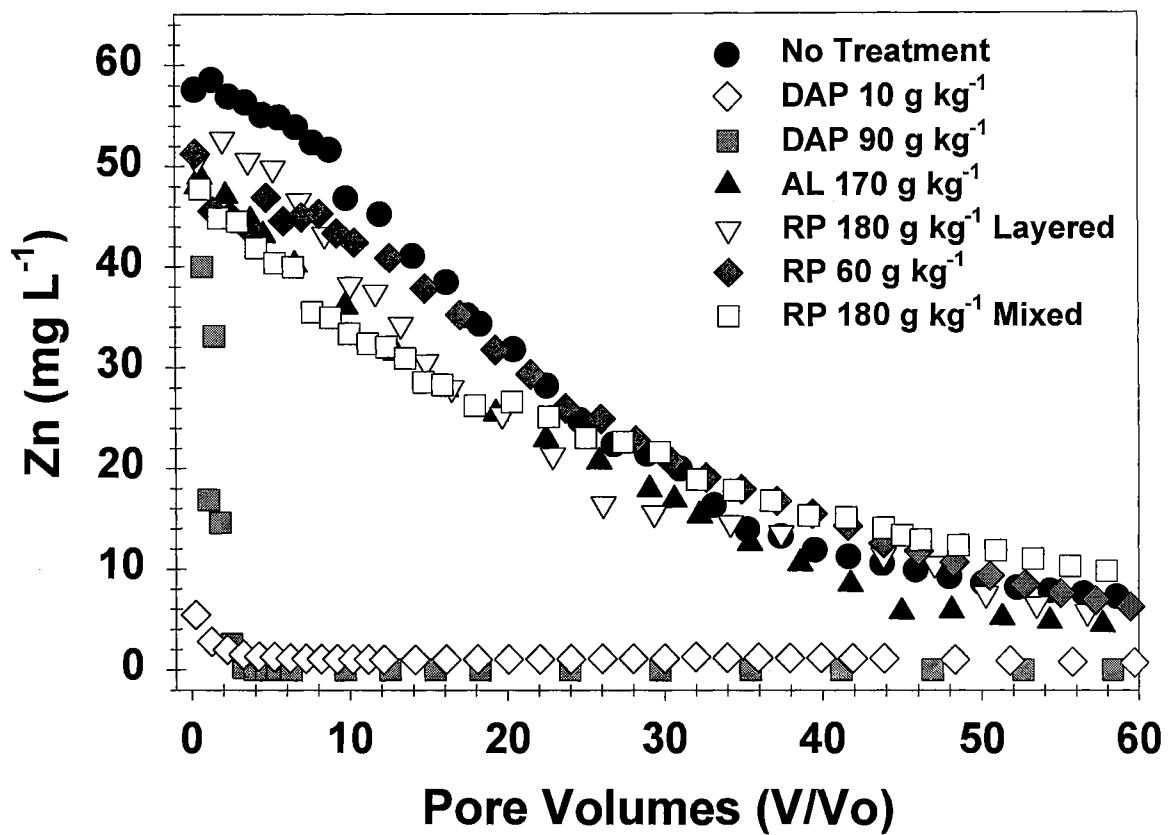
Figure 4. Zinc elution curves for untreated and amended soils.
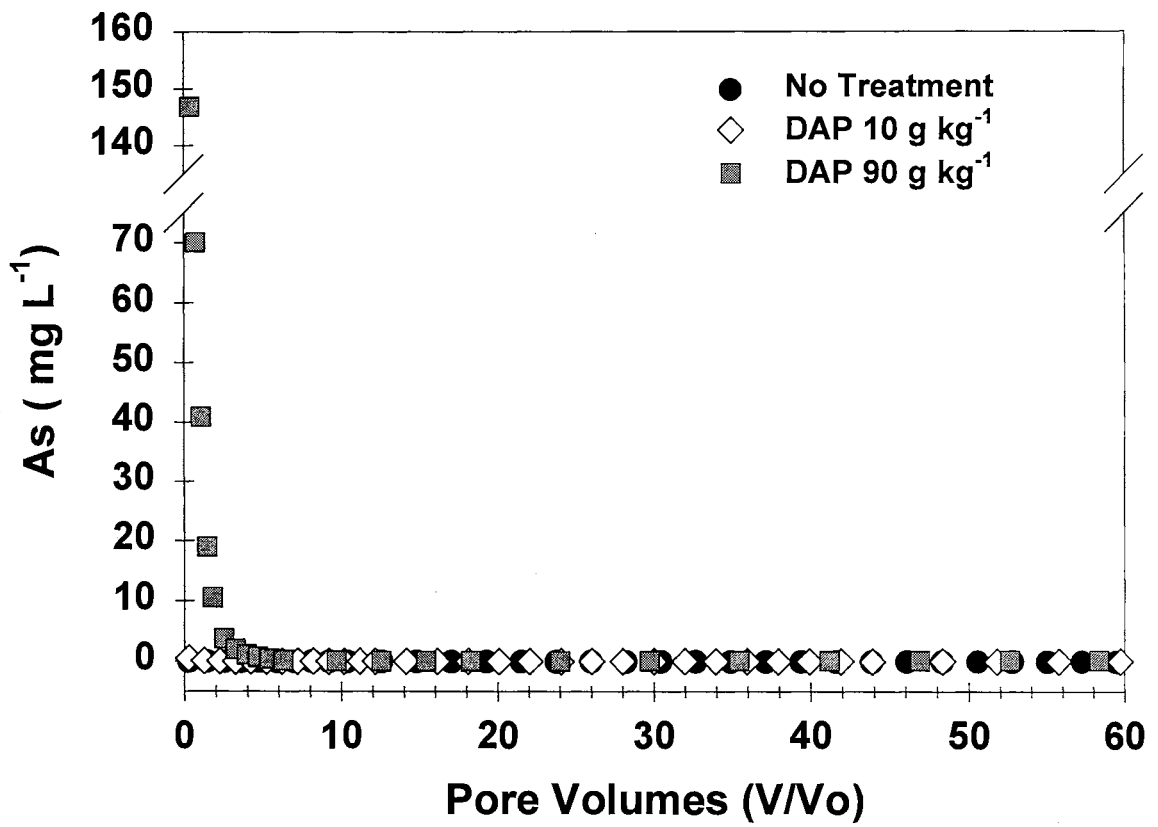
Figure 5. Arsenic elution curves for untreated and DAP amended soils.
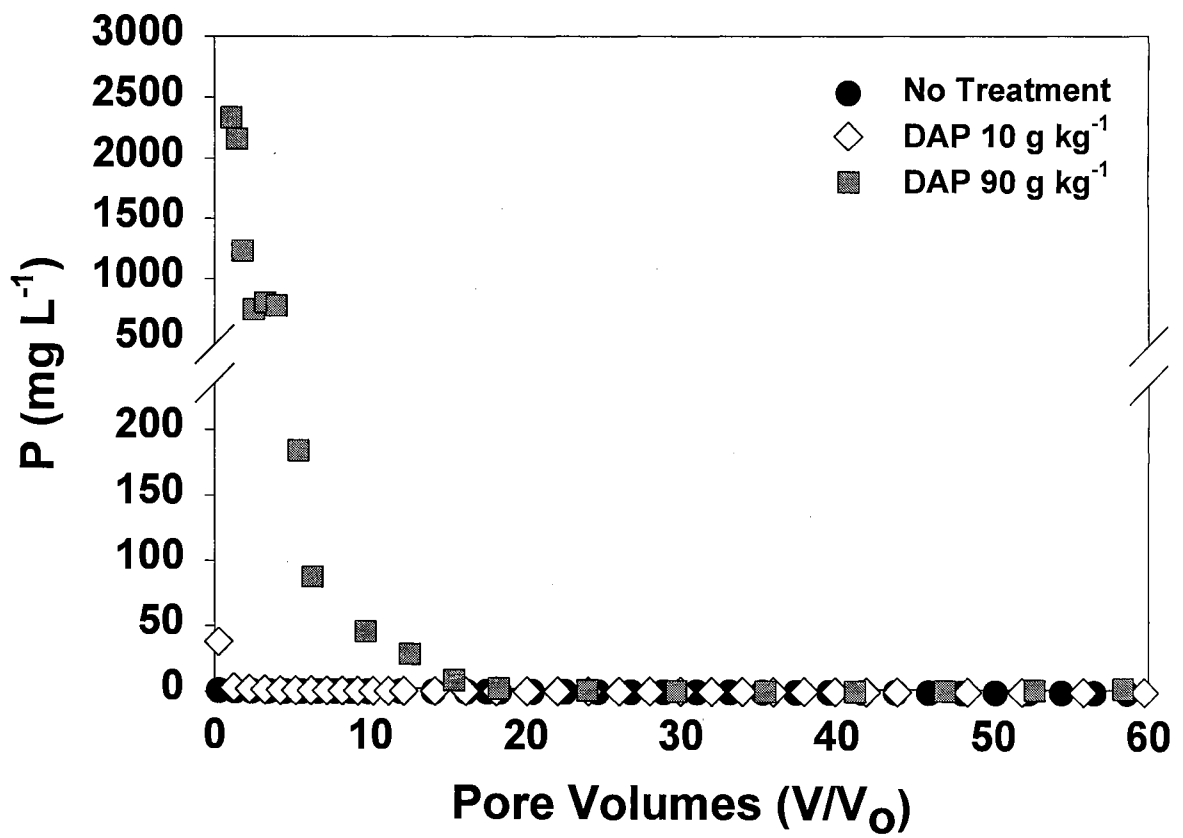
Figure 6. Phosphate elution curves for untreated and DAP amended soils.
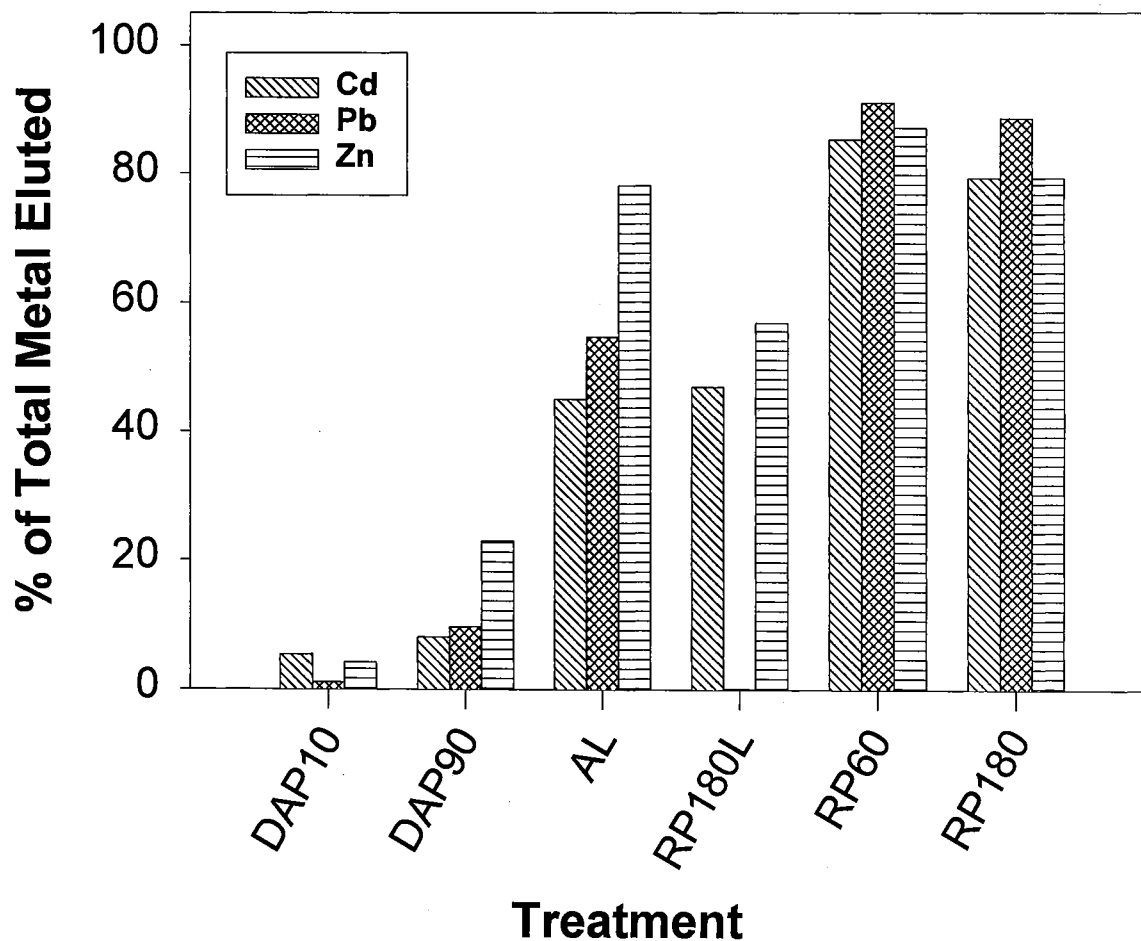
Figure 7. Percent of total Cd, Pb, and Zn eluted through 60 pore volumes from the amended soils based on totals from the control soil (100%). DAP10 - diammonium phosphate 10 g kg$^{-1}$; DAP90 - diammonium phosphate 90 g kg$^{-1}$; AL - agricultural limestone 170 g kg$^{-1}$; RP180L - rock phosphate 180 g kg$^{-1}$ layered; RP60 - rock phosphate 60 g kg$^{-1}$ mixed; RP180 - rock phosphate 180 g kg$^{-1}$ mixed.

# CHAPTER II


# DIAMMONIUM PHOSPHATE AMENDMENTS FOR REDUCING

# HEAVY METAL SOLUBILITY AND TRANSPORT

# IN SMELTER-CONTAMINATED SOILS


## ABSTRACT

Phosphate treatments can reduce metal release and transport from contaminated soils to safeguard natural resources; however, diammonium phosphate (DAP) has received little research attention as a chemical immobilization treatment. The objectives of this study were (i) to evaluate DAP as a chemical immobilization treatment, (ii) to identify chemical processes responsible for metal transport in DAP amended soils, and (iii) to investigate the potential solids controlling metal solubility in DAP amended soils.

Soil contaminated with Cd, Pb, Zn, and As was collected from a defunct smelter site. DAP treatments of 460, 920, 2300 mg P kg$^{-1}$, and an untreated check were evaluated using solute transport experiments. Increasing DAP decreased the total amount of metal transported. Application of 2300 mg P kg$^{-1}$ was the most effective for immobilizing Cd, Pb, and Zn eluted from the contaminated soil. Observed metal elution curves were fitted with a transport

model for quantitative comparisons of retardation (R) and distribution coefficients ($K_d$). Increased R-values with increased DAP treatment indicated slowed metal breakthrough with increasing P application. Increased $K_d$ values indicated slower partitioning rates of sorbed metal to mobile metal phases, and a decrease in concentration of mobile metal species with increasing DAP treatment

Chemical speciation of equilibrated soil solutions revealed a decrease in the total mass of highly mobile Cd, Pb, and Zn species with DAP treatment. Activity-ratio diagrams showed DAP shifted the mineral controlled solubility of Cd, Pb, and Zn to sparingly soluble metal-phosphate minerals. Chemical immobilization treatments using DAP are efficient at reducing the solubility and transport of Cd, Pb, and Zn in smelter contaminated soils.

## INTRODUCTION

Extraction and processing of metal ores has contaminated soil and water resources throughout the world with heavy metals. Highly contaminated land exposed to natural weathering processes has dispersed metal contaminants beyond historic boundaries to surrounding soils, streams, and groundwater (Fuge et al., 1993; Paulson, 1997). The redistribution of metal contaminants through transport processes endangers the quality of waters used for human consumption and threatens the welfare of surrounding ecosystems. Zinc is an essential plant nutrient, but excessive soil concentrations are phytotoxic to most plants (Adriano, 1986) and prevent the establishment of vegetation. Such barren

sites result in increased redistribution of metal contaminants through wind and water erosion (Dudka and Adriano, 1997). A nutritionally essential metal, ingestion of Zn by mammals in surplus of dietary needs is unlikely to cause chronic health effects. Unlike Zn, other metalloids and metals including As, Cd, and Pb are not essential nutrients and are toxic to mammals at elevated concentrations. Ingestion of Cd and Pb through contaminated vegetation, water, or indirect ingestion of soil can lead to renal dysfunction, carcinogenesis, loss of Ca in bone (Itai-Itai disease), chronic neuropathy, hypertension, and other disorders (Goyer, 1996). Effects are more pronounced in high-risk individuals (i.e. children and the elderly).

Restoration of contaminated sites and the disposal of metal contaminated soils and wastes is labor-intensive and expensive. Remediation technologies based on the excavation and landfilling of metal contaminated soils and wastes are highly effective at lowering risk to humans and the environment; however, these methods are costly due to the high price of disposal in hazardous waste landfills and the transport of waste and backfill soil. In-situ chemical immobilization is a remediation technique that involves addition of chemicals to contaminated soil to reduce the solubility of metals through metal sorption and/or precipitation. Decreased metal solubility and mobility will reduce heavy metal transport from contaminated soils to surface and groundwater. Compared with other remediation techniques, in-situ chemical immobilization is less expensive than excavation and landfilling, and may provide a long-term remediation solution through the formation of stable metal minerals and/or precipitates.

Chemical immobilization research using phosphate addition has included mineral apatite and synthetic hydroxyapatite materials. These materials have proven to be effective at reducing the solubility and bioavailability of heavy metals through the formation of metal-phosphate minerals (Chen et al., 1997; Ma et al., 1995; Ma and Rao, 1997). In addition to reducing metal solubility, rock phosphate amendments are also effective at reducing metal bioavailability associated with incidental ingestion of soil by humans (Lambert et al., 1994; Zhang and Ryan, 1998) and associated with plant phytotoxicity (Basta and Gradwohl, 1998; Chlopecka and Adriano, 1996; Laperche et al., 1997). Although apatite treatments are effective for reducing metal solubility and bioavailability, research on metal mobility and transport have proven it mostly ineffective for reducing the release and transport of Cd and Zn from contaminated soils (McGowen, 2000).

Soluble sources of phosphate could provide an abundance of solution phosphorus and increase the efficiency of metal-phosphate mineral formation (Berti and Cunningham, 1997; Cooper et al., 1998; Hettiarachchi et al., 1997; Ma et al., 1993). Metal-phosphate minerals were shown to control metal solubility in soil suspensions when soluble phosphorus was added (Santillian-Medrano and Jurinak, 1975), and induced the formation of heavy metal phosphate precipitates (Cotter-Howells and Capron, 1996). Investigation of soluble the phosphate fertilizers, monoammonium phosphate (MAP) and diammonium phosphate (DAP), showed that that MAP decreased and DAP increased the amount of Cd

fixed by the soil (Levi-Minzi and Petruzzelli,1984). Pierzynski and Schwab (1993) found DAP ineffective for reducing metal bioavailability to soybeans.

Research efforts investigating chemical immobilization treatments have focused on reducing the bioavailability (i.e. plants, gastrointestinal), solubility, or extractability (i.e. sequential extractions) of metals; however, information is needed on the effect of treatments for reducing the mobility and transport of Cd, Pb, and Zn. Extensive work has been done to model metal transport through soil (Jurinak and Santillian-Medrano, 1974; Selim et al., 1990; Selim, 1992; Selim and Amacher, 1996). Methods used for these studies involved the addition of metals to uncontaminated soils using batch equilibration techniques and addition of pulses of metal in solution through repacked uncontaminated soils in miscible displacement experiments.

When investigating metal mobility in contaminated soils, most studies describe changes in metal content with depth (Scocart et al., 1983), model metal transport observed in soil profiles (Cernik et al., 1994), report observed distributions of metal in solution (Paulson, 1997), or endeavor to describe metal mobility in soils using sequential extraction schemes (Li and Shuman, 1996). Studies conducted on the release and transport of metals from amended contaminated soils are few. Jones et al. (1997) investigated the transport of As in contaminated mine tailings following liming. Peryea and Kammereck (1997) investigated the release and movement of As with additions of phosphate fertilizers to arsenate-contaminated orchard soils. Although extremely insightful, these studies did not apply transport models as part of their evaluations.

Research on diammonium phosphate [$(NH_4)_2HPO_4$] (DAP) as a chemical immobilization treatment has been minimal. DAP is a major source of P fertilizer and currently represents approximately 70% of the total US production of phosphate fertilizer products (US Dept. of Commerce, 1998). Commercially available in large quantities, DAP could prove to be an economical (currently US$250-275 per Mg) and effective metal immobilization treatment. Further research is needed on the reduction of heavy metal solubility, mobility, and transport in DAP amended smelter-contaminated soils.

The objectives of this study were (i) to evaluate the effectiveness of DAP as a chemical immobilization treatment to reduce heavy metal solubility and transport in a smelter contaminated soil, (ii) to identify chemical processes responsible for metal transport in DAP amended soils, and (iii) to investigate the potential solids controlling metal solubility in DAP amended soils.

## MATERIALS AND METHODS

Surface soil (<20 cm) with elevated residual concentrations of Cd, Pb, Zn, and As was collected at an inoperative smelter site in Northeastern Oklahoma from an area that had recently been treated with coarse limestone. Soil was air-dried and sieved (<2mm) prior to use. The soil exhibited effervescence with addition of 1M HCL indicating the presence of free carbonates. Soil pH (1:1, soil:water) was determined by combination electrode. Particle size analysis was determined using the hydrometer method (Gee and Bauder, 1986). Total metal

contamination in the soil was determined by X-ray fluorescence (XRF) (Karathanasis and Hajek, 1996). The contaminated soil was also tested to determine its hazardous waste disposal status using the Toxicity Characteristic Leaching Procedure (TCLP, SW-846 Method 1311) (U.S. EPA, 1986). Furthermore, the soil was extracted with 0.5M $Ca(NO_3)_2$ (1:20 soil:solution) for 16 hours (Basta and Gradwohl, 2000) to estimate potential metal bioavailability.

Diammonium phosphate treatments were evaluated using solute transport experiments with repacked soil columns similar to methods described by Selim and Amacher (1996). Reagent grade diammonium phosphate, $(NH_4)_2HPO_4$ (23 %P), was added as an amendment to the contaminated soils based on the total molarity of Cd, Pb, and Zn metal in the soil. Phosphate amendments were based on preliminary experiments (McGowen, 2000) that included a 3/5 $P/M_{total}$ molar ratio treatment ($M_{total}$ = $\Sigma$ of total Cd, Pb, and Zn determined by XRF). The 3/5 ratio corresponds to the stoichiometric P/Pb ratio of chloropyromorphite $[Pb_5(PO_4)_3Cl]$ and has been reported as the basis of hydroxyapatite and apatite treatments to lead-contaminated soils (Zhang and Ryan, 1999; Ma et al.,1993; Laperche et al., 1996; Zhang et al., 1998). Because DAP supplies much more soluble phosphate than apatites, lower rates were selected for this study and the 3/5 $P/M_{total}$ treatment was omitted due to high P (335 mg P) and As (29.5 mg As $kg^{-1}$) released through 60 pore volumes of elution (McGowen, 2000). DAP was added to the soil at 460, 920, and 2300 mg P $kg^{-1}$. These treatments correspond to approximate $P/M_{total}$ ratios of 1/74, 1/37, and 1/15 respectively. Phosphate amendments were mixed thoroughly with the soil prior to uniform repacking into

acrylic transport columns (Fig. 1). Teflon filters (0.45μm) were placed between the soil matrix and end caps on each end of the column to prevent loss of fines from the soil column. Column dimensions were 4 cm inside diameter by 7.5 cm in length. Soils were saturated with type 1 reagent grade water (>18.0 MΩ•cm at 25°C) (ASTM, 1992) with continuous upward flow using a piston pump (Fluid Metering, Inc., Syosset, New York) until saturation and allowed to equilibrate for 48 hours prior to further leaching. After the equilibration period, a saturated flow regime was resumed and soil solution fractions were collected with a fraction collector (ISCO Inc., Lincoln, Nebraska) through 60 pore volumes. Column effluent was passed through Teflon tubing and an in-line 0.45μm filter before collection into glass test tubes. 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) (APHA, 1992) 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-AES).

Chemical analyses were performed using calibration curves determined from standards prepared from certified stock solutions. Sample blanks were analyzed to determine any matrix effects, which allowed for correction of instrument response. Trace metal control standards were used to assess instrument precision and accuracy. Limits of detection (LOD) were determined from the summation of three standard deviations (3σ) of the instrument response for seven repeated analyses of a sample blank solution. Practical quantitative

40

limits (PQL) of detection were set at ten times the LOD (APHA, 1992). Solution concentrations below the PQL were assigned the value of zero in data analysis.

Elution curves for As, Cd, Pb, P, and Zn were plotted for each column experiment. Metal eluted in solution was normalized to concentrations per 100 g of soil for comparison of treatments. Numeric integration of metal mass eluted (through 60 pore volumes) per mass of soil was calculated. Darcy flux (q), soil bulk density ($\rho_b$), and volumetric water content were determined. Observed metal breakthrough curves were fitted using the transport model COLUMN 1.4 (Brown et al., 1996) and retardation (R) was determined. When metal concentrations in solution fell below the detection limit of the instrument, a minimum R for the metal species was estimated using the instrument PQL and the empirical calculation indicated with equation [1].


$$R = M_T / PQL \bullet \theta \hspace{4cm} [1]$$


Where $M_T$ is the total mass of eluted metal species per volume of media leached, PQL is the practical quantitative limit of the metal species, and $\theta$ is the volumetric water content of the transport apparatus (See Appendix 1 for derivation). Distribution coefficients ($K_d$) were determined from the fitted and estimated retardation values using equation [2].


$$K_d = (R-1)\theta / \rho_b \hspace{4cm} [2]$$

Where $\theta$ is the volumetric water content and $\rho_b$ is the bulk density.


41

Following each metal elution experiment, 50 mg Br $L^{-1}$ tracer solution was introduced as a conservative tracer to define flow parameters and investigate the possibility of transport related non-equilibrium. The tracer solution was introduced as a continuous flow until complete breakthrough was obtained. Collected effluent fractions were analyzed for Br⁻ by ion chromatography. Bromide tracer breakthrough curves were also plotted and fitted using the model COLUMN 1.4 to determine retardation (R) and dispersion coefficients (D).

Preliminary studies showed that metals within the transport apparatus reached steady state after 24 hours of pre-equilibration. We selected a pre-equilibration period of 48 hours to ensure the first solution fraction eluted was an accurate representation of the soil solution in an equilibrated soil system. Because the soil within each column was saturated and equilibrated for 48 hours prior to leaching, the first solution eluted is an adequate representation of the soil solution at equilibrium. Eighmy et al. (1997) indicated that 24 hours was sufficient for pseudo-equilibrium and solid phase precipitation of metal phosphate compounds to occur with additions of soluble phosphate to combustion residues.

Chemical analyses obtained from the first fraction samples were input into the chemical equilibrium speciation model MINTEQA2 (Allison et. al, 1991) to predict species activity in solution. To investigate the potential formation of metal phosphate precipitates or minerals formed from the immobilization treatments, activity-ratio diagrams were constructed (Sposito, 1994). Graphical methods such as activity-ratio diagrams can be used to describe and qualitatively interpret mineral solubility data to determine potential minerals controlling metal solubility

and their relative solubility with respect to other minerals. Dissolution equilibria of probable minerals controlling metals solubility and transport in contaminated soils were used to construct the diagrams. Chemical speciation data obtained from the first fraction of each column effluent were plotted on the diagrams to identify minerals potentially controlling heavy metal solubility.

## RESULTS AND DISCUSSION

### Soil Properties and Contaminants

Selected soil properties and levels of metal contamination in the soil as determined by X-ray fluorescence (XRF), TCLP extractable, and 0.5M $Ca(NO_3)_2$ extractable are reported in Table 1. Total Cd, Pb, and Zn in the soil are well above background soil concentrations (Holmgren et al., 1993). TCLP extractable Cd and Pb exceeded regulatory levels indicating the soil qualifies as a hazardous material and requires remediation and disposal at a hazardous waste facility. The high amounts of Cb, Pb, and Zn extracted with 0.5M $Ca(NO_3)_2$ indicate a large portion of the total heavy metals in the soil is relatively soluble, potentially bioavailable, and mobile (Basta and Gradwohl, 2000). Total elemental content, determined by XRF, for each element in g $kg^{-1}$ (in parentheses) were: Si (193), Al (38), Ca (24), Mg (2.5), K (6.1), Fe (47), Mn (1.9), Ti (3.2), P (0.39), and Cr (0.27). As indicated by the Si to Fe ratio, the collected material exhibits chemical properties of a soil material and not an iron-based smelting waste. Soluble

43

anions (in parentheses) determined from saturated paste extract were: Cl (26.6 mg L$^{-1}$), SO$_4$ (1556.6 mg L$^{-1}$), and NO$_3$ (21.7 mg L$^{-1}$). Soil EC was 2.15 dS m$^{-1}$.

## Contaminant Transport

Typically, weak electrolytes (0.01 to 0.001 M Ca) are included in the eluting solution to maintain ionic strength and aggregate stability of the soil system (Selim and Amacher, 1996). To accurately determine solution chemical speciation and probable mineral phases controlling metal solubility, background electrolytes were excluded from eluting solutions used in the metal transport experiments. Soluble calcium concentrations in eluent fractions was in excess of 0.005 M Ca (200 mg Ca L$^{-1}$) through 60 pore volumes for all experiments, indicating a well-buffered system from the prior limestone amendments to the soil. With the Ca concentrations measured in solution in excess 0.005M Ca over the duration of all experiments, the exclusion of additional background electrolytes probably did not adversely effect soil structure or aggregate stability. Solution pH values varied only ±0.2 units ranging from 6.8 to 7.2 throughout the duration of all column elution experiments.

Plots of metal elution curves show that DAP amendments decreased the metal eluted from the contaminated soil. Increasing P additions incrementally decreased the amounts of Cd eluted from the contaminated soil (Fig. 2). Similarly, P additions decreased the amounts of Pb eluted; however, treatments of 920 and 2300 mg P kg$^{-1}$ displayed similar Pb elution curves (Fig. 3). Likewise, P addition reduced the amount of Zn eluted, but only slight differences were

44

observed for the Zn elution curves from the P amended soils (Fig. 4). Numerical

integration (through 60 pore volumes) of observed solution Cd, Pb, and Zn eluted

(symbols in Figs. 2-4) indicated increasing DAP application decreased the total

amount of metal transported (Table 2). The mixture of DAP with the

contaminated soil at 460 mg P kg$^{-1}$ decreased the Cd and Pb transported by

roughly half and also produced a 19-fold decrease in the amount of Zn

transported (Table 2). A concomitant decrease in Cd and Pb transported was

realized with the 920 mg P kg$^{-1}$ application, but little difference in Zn elution was

shown by increasing applied P. Increasing the DAP application from 920 to 2300

mg P kg$^{-1}$ further reduced Cd and Pb eluted but also increased As eluted from

0.003 to 0.13 mg kg$^{-1}$ over 60 pore volumes. Phosphate additions increased As

elution apparently due to phosphate-arsenate ligand exchange. Peryea (1991)

and Peryea and Kammereck (1997) reported similar phosphate induced release

and transport of As when P was added to orchard soils spiked or contaminated

with lead arsenate. Only slight increases in total As eluted with P added were

observed in treatments < 2300 mg P kg$^{-1}$. Furthermore, the 2300 mg P kg$^{-1}$

application showed little improvement for further reducing Zn elution over the 460

mg P kg$^{-1}$ treatment. Overall, the 2300 mg P kg$^{-1}$ application was the most

effective for immobilizing heavy metals eluted from the contaminated soil with

only 5.4% of Cd, 1.1% of Pb, and 4.2 % of the Zn eluted when compared with the

untreated soil (Table 2).

Large additions of P to the contaminated soil may increase the risk of

eutrophication to sensitive surface water bodies. Phosphorus elution curves for

all column experiments are shown in Figure 5. As P application increased, the mass of P eluted from the treated soil columns increased. Total phosphorus eluted from the DAP treatments through 60 pore volumes was 0.32, 0.78, and 2.31 mg for the 460, 920, 2300 mg P $kg^{-1}$ treatments, respectively (Table 2). These summations of total P eluted correspond to < 1% of the total P added to each of the repacked soil columns. Furthermore, the low percentages of total P eluted indicate an adequate pre-equilibration period for sorption and/or precipitation to occur.

Model-fitted elution curves for Cd, Pb, and Zn are shown as solid lines in Figs. 2-4. Experiment parameters (bulk density, Darcy flux, and water content), best-fit retardation (R), and calculated distribution coefficients ($K_d$) are given in Table 3. Soil bulk densities ($\rho_B$) in the repacked columns ranged between 1.26 and 1.31 g $cm^{-3}$ and Darcy flux between 1.70 to 2.43 cm $hr^{-1}$. Fitted metal elution curves for most treatments had $r^2$ >0.9 and were well described by the COLUMN model. Elution of Pb from the 920 and 2300 mg P $kg^{-1}$ treatments resulted in only a few fractions with concentrations above detection limits; therefore, these datasets were not fitted with the model.

Model-fitted metal elution curves showed increasing retardation (R) with increasing P application (Table 3). Retardation factors increased by approximately 2-fold for Cd and 6-fold for Zn between the untreated soil and the 2300 mg P $kg^{-1}$ treatments. Lead retardation factors increased approximately 3.5 fold with the addition of 460 mg P $kg^{-1}$. These increases in R with added DAP indicate that metal breakthrough is slowed by increasing P applications.

Accordingly, distribution coefficients calculated for each metal indicate slower rates of metal partitioning from sorbed/precipitated phases to mobile phases, with rates that decrease with corresponding increases in DAP treatment. Calculated distribution coefficients increased from 4.0 to 9.0 L $kg^{-1}$ for Cd, from 2.9 to 10.8 L $kg^{-1}$ for Pb, and from 2.5 to 17.1 L $kg^{-1}$ for Zn (Table 3).

Lead elution from the 920 and 2300 mg P $kg^{-1}$ treatments resulted in only a few measured samples above the PQL. For these Pb elution curves the calculated minimum R does not follow the trend of increasing retardation values (and increasing $K_d$) with increased applied P (Table 3). This could be due to the variability of Pb concentrations measured (above the PQL) in the samples that were used to make the estimations for minimum Pb retardation.

With the exception of the two estimated values for Pb, model-fit R and calculated $K_d$ values increased with increasing P treatment. In general, increased retardation (R) values indicate slowed metal movement through the soil column (Fetter, 1993). This condition concurs with the diminished total metal transported through the column with increasing P application. By definition, distribution coefficients ($K_d$) relate the ratio of mass of solute sorbed on soil to the concentration of solute in solution at equilibrium with the mass of solute sorbed on soil (Fetter, 1993). Using this definition, increasing $K_d$ values indicate increased solute sorbed onto soil and less solute in solution. Therefore, increases in calculated distribution coefficients ($K_d$) indicate slower partitioning rates of sorbed (or precipitated) metal to mobile metal phases and an overall decrease in mobile metal available for transport.

Bromide breakthrough curves for all columns were sigmoid shaped and showed no apparent tailing, indicating homogenous packing and well-satisfied boundary conditions. Breakthrough curves showed behavior representative of a conservative tracer in porous media and conformed to the assumption of local equilibrium with $r^2$ values above 0.99 for all fits (Figure 6). These results indicate that transport-related non-equilibrium was not a factor in any of the experiments.

## Metal Speciation and Mobility

Solution speciation data was used to investigate the formation of ion pairs and complexes in the amended soils. Complexation of dissolved lead, cadmium, or zinc with other anions at smelter sites (i.e. Cl and $SO_4$) that results in uncharged or anionic chemical species may increase heavy metal mobility (McLean and Bledsoe, 1992). Similarly, chemical treatments that reduce formation of anionic or uncharged dissolved metal chemical species can reduce heavy metal mobility in contaminated soils. Because the formation of metal-ion pairs influences metal mobility in soils, determining the form of metal in soil solution can provide inference to potential leaching hazards. Assuming negative charges dominate the soil surfaces, low mobility species were defined as cationic species with +1 or +2 valence ($M^{2+}$, $MOH^+$), and high mobility species were defined as uncharged and/or anionic species with -1 or -2 valence [$MSO_4^0$, $M(SO_4)_2^{2-}$, etc.].

Chemical speciation of equilibrated soil solutions revealed an increase in the percentage of high mobility metal species (anionic and uncharged species)

with increased DAP treatment (Table 4). Phosphate addition could have increased solution sulfate (through ligand exchange) and formed the $MSO_4^0$ and $M(SO_4)_2^{2-}$ complexes, increasing their percentage of the total species in solution. The increase in highly mobile soluble species with phosphate addition appears to indicate that DAP treatments may increase heavy metal mobility through soil. This would directly contradict results obtained from the metal elution curves. However, closer inspection reveals that the concentration of high mobility species decreased with increasing DAP treatment (Table 4). Although the percentage of high mobility species is increased, the total concentration of high mobility species in solution is decreased by increasing DAP treatment. Species percentages are relative to the total concentration in solution. When the percentages of high mobility species are multiplied by the total metal concentration, the total mass of high mobility species is progressively decreased with DAP amendments. Consequently, treatment of contaminated soil with DAP *reduced* the *total mass* of anionic or uncharged dissolved metal chemical species in solution and decreased heavy metal mobility through the contaminated soil.

**Probable Mineral Solid Phases and Metal Solubility**

Chemical immobilization treatments decrease metal solubility through the formation of metal-phosphate precipitates and increase long-term stability by forming less soluble and more stable metal-phosphate minerals (Mench et al., 1998). Long-term geochemical stability of the solid phases formed by chemical immobilization must be evaluated to determine the potential long-term

effectiveness of such treatments. Decreased partitioning rates, indicated by increased $K_d$ values (Table 3), are likely due to the formation of metal phosphate precipitates or minerals. Probable Cd, Pb, and Zn mineral phases investigated using the geochemical speciation model MINTEQA2 (Allison et al., 1991) are listed in Table 5.

The Cd-$H_2PO_4$ activity-ratio diagram (Fig. 6) indicates that octavite (CdCO$_3$ log $K_{SP}$ = -12.8) may control Cd solubility in soils without added P. However, when P is added as DAP, the diagram suggests that cadmium phosphate $Cd_3(PO_4)_2$ (log $K_{SP}$ = -38.1) becomes the mineral controlling Cd solubility. This indicates that DAP application shifted the mineral controlled solubility of Cd from a relatively soluble Cd-carbonate (octavite) to a sparingly soluble Cd-phosphate. The much lower solubility product of $Cd_3(PO_4)_2$ implies that a less soluble Cd solid phase is formed with addition of DAP. Other research results have shown that $Cd_3(PO_4)_2$ can control Cd solubility in phosphate sufficient soils or soils amended with phosphate (Santillian-Medrano and Jurinak, 1975; Street et al., 1977).

The Pb-$H_2PO_4$ activity ratio diagram (Fig. 8) indicates that anglesite (PbSO$_4$ log $K_{SP}$ = -7.79) may control Pb solubility in soils without added P. With the addition of P as DAP, the diagram implies that hydroxypyromorphite (log $K_{SP}$ = -76.8) becomes the mineral controlling Pb solubility. Similar to the results obtained for Cd, this suggests that DAP shifted the mineral controlled solubility from a relatively soluble PbSO$_4$ to the sparingly soluble Pb-hydroxypyromorphite. Hydroxypyromorphite has been recognized as a mineral controlling Pb solubility

in many soils amended with phosphate materials. Other researchers have verified the presence of hydroxypyromorphite in chemical immobilization studies using solubility diagrams (Santillian-Medrano and Jurinak, 1975), and spectroscopic instruments including XRD and SEM-EDX (Laperche et al., 1997; Laperche et al., 1996; Ma et al., 1993; Ruby et al., 1994; Cotter-Howells and Capron, 1996).

From the activity-ratio diagrams for Zn minerals (Fig. 9), predicted solubility of Zn was apparently controlled by the phosphate mineral hopeite $(Zn_3(PO_4)_2*4H_2O)$ in soils with no added phosphate. For phosphate treatments of 460 and 920 mg P $kg^{-1}$ the mineral potentially controlling Zn solubility is Zn-pyromorphite (log $K_{SP}$ = -63.1). Therefore, further reduction in metal solubility occurring with addition of DAP could be due to excess phosphate precipitating metal ions as metal phosphates. As with Cd and Pb, the shift from hopeite to Zn-pyromorphite indicates that addition of shifted the mineral controlled solubility of Zn to a less soluble mineral phase. This would effectively reduce Zn concentration in solution and reduce total amounts available for transport. For the 2300 mg P $kg^{-1}$ treatment, hopeite is the predicted mineral controlling Zn solubility; however the solubility lines are converging near the values of $H_2PO_4$ = $10^{-4}$. With the close convergence of these solubility lines, Zn-pyromorphite could possibly be the mineral controlling Zn solubility for this treatment as well.

**Effect of Diammonium Phosphate Addition on Soil pH**

Application of ammonium-based fertilizers can potentially acidify the soil (Sposito, 1989). Reduction in soil pH from application of diammonium phosphate would increase metal solubility and mobility. To investigate the effect of DAP on soil acidification, soils were incubated at 0.22 % volumetric water content at 30°C for 6 months. Soil pH was monitored periodically using a 1:1 soil:water ratio and a combination pH electrode. Soil pH values decreased from 7.1 to 6.5 after 2 months and then remained constant. The presence of free carbonates present in the limed soil likely buffered the system pH and prevented acidification to pH < 6.5. Researchers investigating soluble phosphates have often included liming materials to buffer against drastic decreases in pH (Hettiarachchi et al., 1997, 1999; Brown et al., 1999). Additions of liming materials with soluble phosphate chemical amendments are crucial for maintaining desirable pH and controlling metal solubility.


# SUMMARY AND CONCLUSIONS


Soluble phosphate as DAP provided effective immobilization of heavy metals in a smelter contaminated soil. The 2300 mg P kg$^{-1}$ 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/M$_{total}$ ratio of 1/15, where M$_{total}$ = $\Sigma$ total Cd, Pb, and Zn determined by XRF. DAP treatments <2300 mg P kg$^{-1}$ had a similar effect on reducing metal transport

but with lower efficiency. Model fitted metal elution curves showed increased retardation factors (R) and distribution coefficients ($K_d$) with increased DAP application. Increased R factors indicated slowed metal transport with DAP treatment. Increased $K_d$ values were likely due to the formation of metal phosphate precipitates and/or increased sorption.

Chemical speciation of effluent fractions indicated that the total mass of highly mobile heavy metal species (anionic and/or uncharged) decreased with DAP treatment. Chemical immobilization treatments reduced solubility and mobility of heavy metal species in contaminated soils by forming less soluble solid-phase minerals or metal-phosphate precipitates. Activity-ratio diagrams showed DAP application shifted the mineral controlled solubility of Cd from $CdCO_3$ to less soluble $Cd_3(PO_4)_2$. Predicted minerals controlling Pb solubility were shifted from $PbSO_4$ to less soluble Pb-hydroxypyromorphite. Activity-ratio diagrams predicted phosphate minerals as controlling Zn solubility with and without added P. However, treatment with DAP changed the probable solid phases controlling Zn from hopeite to Zn-pyromorphite.

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 $kg^{-1}$ 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 (Vangronsveld and Cunningham, 1998). The optimum $P/M_{total}$ ratio of 1/15 observed for this

study soil may differ with varying concentrations of reactive metals in other contaminated soils and wastes. Co-application of liming materials with DAP may be necessary to offset potential soil acidification.

# REFERENCES

Adriano, D.C. 1986. Trace elements in the terrestrial environment. Springer-Verlag, Berlin.

Allison, J.D., D.S. Brown, and K.J. Novo-Grdac. 1991. MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: Version 3.0 user's manual. USEPA Rep. 600/3-91/021. Environ. Res. Lab., Athens, GA.

American Public Health Association (APHA). 1992. Standard methods for the examination of water and wastewater. Part 1030 Data Quality pp. 1-3 to 1-12 and Part 3000 Metals pp. 3-1 to 3-103. In A.E. Greenberg, L.S. Clesceri, and A.D. Eaton (eds.). 18th ed. American Public Health Assoc., Washington, DC.

ASTM. 1992. The American society for testing and material, vol. 11.01, sec. DH93-91.

Basta, N.T., and R. Gradwohl. 1998. Remediation of heavy metal-contaminated soil using rock phosphate. Better Crops Plant Food 82:29-31.

Basta, N.T., and R. Gradwohl. 2000. Estimation of Cd, Pb, and Zn bioavailability in smelter-contaminated soils by a sequential extraction procedure. J. Soil Contam. (in press).

Berti, W.R., and S.D. Cunningham. 1997. In-place inactivation of Pb in Pb-contaminated soils. Environ. Sci. Technol. 31:2673-2678.

Brown, G.O., H.T. Hseih, and Y.W. Lin. 1996. COLUMN for windows: User manual. Prepared for Sandia National Laboratories. Biosystems and Agricultural Engineering, Oklahoma State University, Stillwater, OK.

Brown, S.L., R. Chaney, and B. Berti. 1999. Field test of amendments to reduce the in-situ availability of soil lead. p. 506-507. In Proc. Extended Abstr., 5th Int. Conf. on the Biogeochem. Trace Elements (ICOBTE), Vienna, Austria, 11-15 July, 1999.

Cernik, M., P. Federer, M. Borkovec, and H. Sticher. 1994. Modeling of heavy metal transport in a contaminated soil. J. Environ. Qual. 23:1239-1248.

Chen, X., J.V. Wright, J.L. Conca, and L.M. Peurrung. 1997. Evaluation of heavy metal remediation using mineral apatite. Water Air Soil Pollut. 98:57-78.

Chlopecka, A. and D.C. Adriano. 1996. Mimicked in-situ stabilization of metals in a cropped soil: Bioavailability and chemical form of zinc. Environ. Sci. Technol. 30:3294-3303.

Cooper, E.M., D.G. Strawn, J.T. Sims, D.L. Sparks, and B.M. Onken. 1998. Effect of chemical stabilization by phosphate amendment on the desorption of P and Pb from a contaminated soil. p. 343. *In* 1998 Agronomy abstracts, ASA, Madison, WI.

Cotter-Howells, J., and S. Capron. 1996. Remediation of contaminated land by formation of heavy metal phosphates. Appl. Geochem. 11:335-342.

Dudka, S., and D.C. Adriano. 1997. Environmental impacts of metal ore mining and processing: A review. J. Environ. Qual. 26:590-602.

Eighmy, T.T., B.S. Crannell, L.G. butler, F.K. Cartledge, E.F. Emery, D. Oblas, J.E. Krzanowski, J.D. Eusden, Jr., E.L. Shaw, and C.A. Francis. 1997. Heavy metal stabilization in municipal solid waste combustion dry scrubber residue using soluble phosphate. Environ. Sci. Technol. 31:3330-3338.

Fetter, C.W. 1993. Contaminant Hydrogeology. MacMillan Pub. Co., New York.

Fuge, R., F.M. Pearce, N.J.G. Pearce, and W.T. Perkins. 1993. Geochemistry of Cd in the secondary environment near abandoned metalliferous mines, Wales. Appl. Geochem., Suppl. Iss. 2:29-35.

Gee, G.W., and J.W. Bauder. 1986. Particle size analysis. p. 383-411. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agron. Monog. 9. ASA and SSSA, Madison, WI.

Goyer, R.A. 1996. Toxic effects of metals. p. 691-736. *In* C.D. Klaassen (ed.) Caserett & Doull's toxicology: the basic science of poisons. McGraw-Hill, New York.

Hettiarachchi, G.M., G.M. Pierzynski, J. Zwonitzer, and M. Lambert. 1997. Phosphorus source and rate effects on cadmium, lead, and zinc bioavailabilities in a metal-contaminated soil. p. 463-464. *In* Extended Abstr., 4th Int. Conf. on the Biogeochem. Trace Elements (ICOBTE), Berkeley, CA, 23-26 June, 1997.

Hettiarachchi, G.M., and G.M. Pierzynski. 1999. Effect of phosphorus and other soil amendments on soil lead, cadmium and zinc bioavailability. p. 514-515. *In* Proc. Extended Abstr., 5th Int. Conf. on the Biogeochem. Trace Elements (ICOBTE), Vienna, Austria, 11-15 July, 1999.

Holmgren, G.G.S., M.W. Meyer, R.L. Chaney, and R.B. Daniels. 1993. Cadmium, lead, zinc, copper, and nickel in agricultural soils of the United States of America. J. Environ. Qual. 22:335-348.

Jones, C.A., W.P. Inskeep, and D.R. Neuman. 1997. Arsenic transport in contaminated mine tailings following liming. J. Environ. Qual. 26:433-439.

Jurinak, J.J., and J. Santillian-Medrano. 1974. The chemistry and transport of lead and cadmium in soils. Report 18, Utah Agric. Exp. Sta. Logan, UT.

Karathanasis, A.D., and B.F. Hajek. 1996. Elemental analysis by X-ray fluorescence spectroscopy. p. 161-223. In D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical Methods. SSSA Book Series no. 5. SSSA and ASA, Madison, WI.

Kuo, S. 1986. Concurrent sorption of phosphate and zinc, cadmium, or calcium by a hydrous ferric oxide. Soil Sci. Soc. Am. J. 50:1412-1419.

Lambert, M., G. Pierzynski, L. Erickson, and J. Schnoor. 1994. Remediation of lead, zinc, and cadmium contaminated soils. Issues Environ. Sci. Technol. 7:91-102.

Laperche, V., T.J. Logan, P. Gaddam, and S.J. Traina. 1997. Effect of apatite amendments on plant uptake of lead from contaminated soil. Environ. Sci. Technol. 31:2745-2753.

Laperche, V., S.J. Traina, P. Gaddam, and T.J. Logan. 1996. Chemical and mineralogical characterizations of Pb in a contaminated soil: Reactions with synthetic apatite. Environ. Sci. Technol. 30:3321-3326.

Levi-Minzi, R., and G. Petruzzelli. 1984. The influence of phosphate fertilizers on Cd solubility in soil. Water Air Soil Pollut. 23:423-429.

Li, Z., and L.M. Shuman. 1996. Heavy metal movement in metal-contaminated soil profiles. Soil Sci. 161:656-666.

Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley & Sons Inc., New York.

Ma, Q.Y., T.J. Logan, and S.J. Traina. 1995. Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. Environ. Sci. Technol. 29:1118-1126.

Ma, Q.Y., S.J. Traina, and T.J. Logan. 1993. In situ lead immobilization by apatite. Environ. Sci. Technol. 27:1803-1810.

Ma, L.Q., and G.N. Rao. 1997. Effects of phosphate rock on sequential chemical extraction of lead in contaminated soils. J. Environ. Qual. 26:788-794.

McGowen, S.L. 2000. In-situ chemical treatments for reducing heavy metal solubility and transport in smelter contaminated soil. Ph.D. dissertation, Oklahoma State Univ., Stillwater, OK.

McLean, J.E., and B.E. Bledsoe. 1992. Behavior of metals in soils. EPA, Ground Water Issue, U.S. Environ. Protection Agency, EPA/540/S-92/018, U.S. Govt. Print. Office, Washington, DC.

Mench, M., J. Vangronsveld, N.W. Lepp, and R. Edwards. 1998. Physico-chemical aspects and efficiency of trace element immobilization by soil amendments. In J. Vangronsveld and S.D. Cunningham (eds.) Metal-contaminated soils: In situ inactivation and phytorestoration. Springer-Verlag, Berlin.

Nriagu, J.O. 1972. Lead orthophosphate I. Solubility and hydrolysis of secondary lead orthophosphate. Inorg. Chem 11:2499-2503.

Nriagu, J.O. 1973. Lead orthophosphates - II. Stability of chloropyromorphite at 25°C. Geochim. Cosmochim. Acta 37:367-377.

Nriagu, J.O. 1984. Formation and stability of base metal phosphates in soils and sediments. Ch. 10 In J.O. Nriagu and P.B Moore (eds.) Phosphate Minerals. Springer-Verlag, Berlin.

Paulson, A.J. 1997. The transport and fate of Fe, Mn, Cu, Zn, Cd, Pb, and $SO_4$ in a groundwater plume and in downstream surface water in the Coeur d'Alene mining district, Idaho, USA. Appl. Geochem. 12:447-464.

Peryea, F.J. 1991. Phosphate-induced release of arsenic from soils contaminated with lead arsenate. Soil Sci. Soc. Am. J. 55:1301-1306.

Peryea, F.J., and R. Kammereck. 1997. Phosphate-enhanced movement of arsenic out of lead arsenate-contaminated topsoil and through uncontaminated subsoil. Water Air Soil Pollut. 93:243-254.

Pierzynski, G.M., and A.P. Schwab. 1993. Bioavailability of zinc, cadmium, and lead in a metal-contaminated alluvial soil. J. Environ. Qual. 22:247-254.

Ruby, M.V., A. Davis, and A. Nicholson. 1994. In situ formation of lead phosphates as a method to immobilize lead. Environ. Sci. Technol. 28:646-654.

Santillian-Medrano, J., and J.J. Jurinak. 1975. The chemistry of lead and cadmium in soil: Solid phase formation. Soil Sci. Soc. Am. Proc. 39:851-856.

Scocart, P.O., K. Meeus-Verdinne, and R. DeBorger. 1983. Mobility of heavy metals in polluted soils near zinc smelters. Water Air Soil Pollut. 20:451-463.

Selim, H.M. 1992. Modeling the transport and retention of inorganics in soils. Adv. Agron. 47:331-384.

Selim, H.M., and M.C. Amacher. 1996. Reactivity and transport of heavy metals in soils. CRC Press, Boca Raton, FL.

Selim, H.M., M.C. Amacher, and I.K. Iskandar. 1990. Modeling the transport of heavy metals in soils. CRREL-Monograph 90-2, U.S. Army Corps of Engineers, Hanover, NH.

Sposito, Garrison. 1989. The chemistry of soils. Oxford Univ. Press, New York.

Sposito, Garrison. 1994. Chemical equilibria and kinetics in soils. Oxford Univ. Press, New York.

Street, J.J., W.L. Lindsay, and B.R. Sabey. 1977. Solubility and plant uptake of cadmium in soils amended with cadmium and sewage sludge. J. Environ. Qual. 6:72-77.

U.S. Department of Commerce. 1998. Inorganic fertilizer materials and related products. Current Industrial Report, MA325B(98)-1, US Dept. of Com., Econom. Stat. Div., U.S. Census Bureau.

U.S. Environmental Protection Agency. 1986. Test methods for evaluating solid wastes. SW-846, 3rd ed. U.S. Gov. Print. Office.

Vangronsveld, J., and S.D. Cunningham. 1998. Introduction to the concepts. In J. Vangronsveld and S.D. Cunningham (eds.) Metal-contaminated soils: In situ inactivation and phytorestoration. Springer-Verlag, Berlin.

Zhang, P, and J.A. Ryan. 1999. Formation of chloropyromorphite from galena (PbS) in the presence of hydroxyapatite. Environ. Sci. Technol. 33:618-624.

Zhang, P, J.A. Ryan, and J. Yang. 1998. In vitro soil Pb solubility in the presence of hydroxyapatite. Environ. Sci. Technol. 32:2763-2768.

# APPENDIX A

Estimate of minimum retardation (R) from Practical Quantitative Limit (PQL).

$$R = 1 + \frac{\rho_b}{\theta} \bullet K_d \qquad [1]$$

Therefore :

$$K_d = (R-1)\frac{\theta}{\rho_b} \qquad [2]$$

Also:

$$K_d = \frac{c^*}{c} \qquad \therefore \qquad c^* = K_d \cdot c \qquad [3]$$

$$M_T = c^* \rho_b + c\theta \qquad [4]$$

substitute equation [3] into equation [4]

$$M_T = K_d \cdot c \cdot \rho_b + c\theta \qquad [5]$$

substitute equation [2] into equation [5]

simplify

$$M_T = c[(R-1)\theta + \theta] \qquad [7]$$

rearrange

$$M_T = c\left[(R-1)\frac{\theta}{\rho_b} \bullet \rho_b + \theta\right] \qquad [6]$$

$$M_T = c\, \theta\, (R) \qquad [8]$$

$$R = \frac{M_T}{c\theta} \qquad \text{or} \qquad R = \frac{M_T}{PQL \bullet \theta} \qquad [9]$$

## Key to terms
R = retardation
$\rho_b$ = bulk density
$\theta$ = volumetric water content
$K_d$ = distribution coefficient
$M_T$ = total mass of eluted metal species per volume of media leached
$c^*$ = mass of solute adsorbed per dry weight of soil (total concentration in media)
c = concentration per aqueous volume (concentration of PQL)

Table 1. Selected soil properties and contaminant concentrations of the smelter-contaminated soil.

| Contaminant / Element | Total Content † | TCLP Extractable | | 0.5M Ca(NO$_3$)$_2$ Extractable |
|---|---|---|---|---|
| -------- | mg kg$^{-1}$ | mg L$^{-1}$ | (reg. limit ‡) | mg kg$^{-1}$ |
| Cd | 1090 | 39.9±1.59 | (1.0) | 155.7±4.44 |
| Pb | 5150 | 21.0±0.58 | (5.0) | 12.3±.0.43 |
| As | 152 | 0.03±0.002 | (5.0) | 0.25±0.02 |
| Zn | 69200 | 1171±32 | (NA) | 585.5±17.8 |

| Particle Size Fractions | | | pH (1:1) |
|---|---|---|---|
| Sand (0.05 to 2.0 mm) | Silt (0.05 to 0.002 mm) | Clay (<0.002mm) | |
| ------------------------------- % ------------------------------------- | | | 6.8 |
| 67 | 29 | 4 | |

† Total content determined by XRF
‡ Specified by U.S. EPA Method 1311(U.S. EPA, 1986)

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

| P Treatment | As | Cd | | Pb | | Zn | | P |
|---|---|---|---|---|---|---|---|---|
| mg P kg$^{-1}$ | mg kg$^{-1}$ | mg kg$^{-1}$ | | $\mu$g kg$^{-1}$ | | mg kg$^{-1}$ | | mg |
| 0 | ND | 14.9 | (100) | 460 | (100) | 108 | (100) | ND |
| 460 | 0.003 | 7.1 | (47.7) | 237 | (51.4) | 5.7 | (5.3) | 0.32 |
| 920 | 0.002 | 4.1 | (27.5) | 9.5 | (2.1) | 6.0 | (5.6) | 0.78 |
| 2300 | 0.13 | 0.8 | (5.4) | 5.2 | (1.1) | 4.5 | (4.2) | 2.31 |

† As, Cd, Pb, and Zn are expressed on a kg soil basis (mg kg$^{-1}$); P expressed on mass basis (mg)

Table 3. Summary of transport parameters, best-fit retardation (R), and calculated distribution coefficients ($K_d$) for Cd, Pb, and Zn elution from untreated and DAP amended soils.

| P Treatment | Length | Flux | $\rho_b$ | $\theta$ | Cd | | | Pb | | | Zn | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | R | $K_d$ | $r^2$ | R | $K_d$ | $r^2$ | R | $K_d$ | $r^2$ |
| mg P kg$^{-1}$ | cm | cm hr$^{-1}$ | g cm$^{-3}$ | % | | L kg$^{-1}$ | | | L kg$^{-1}$ | | | L kg$^{-1}$ | |
| 0 | 7.5 | 1.70 | 1.31 | 0.38 | 14.8 | 4.0 | 0.995 | 10.9 | 2.9 | 0.992 | 9.5 | 2.5 | 0.993 |
| 460 | 7.5 | 2.10 | 1.29 | 0.39 | 16.7 | 4.7 | 0.987 | 37.7 | 10.8 | 0.970 | 15.9 | 4.5 | 0.984 |
| 920 | 7.5 | 2.41 | 1.29 | 0.37 | 18.1 | 4.9 | 0.993 | 58.2† | 16.4 | - | 20.9 | 5.7 | 0.992 |
| 2300 | 7.5 | 2.43 | 1.29 | 0.38 | 31.4 | 9.0 | 0.923 | 30.6† | 8.74 | - | 58.8 | 17.1 | 0.903 |

† Estimated from equation based on practical quantitative limit (PQL) of instrument method.

Table 4. Soil solution Cd, Pb, and Zn speciation data from untreated and DAP amended soils.

| Metal | P Treatment | Metal Species (% of total metal in solution) | | | | | $\Sigma$ % Low Mobility† | $\Sigma$ % High Mobility‡ | Total Conc. | High Mobility Conc. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $M^{2+}$ | $MOH^+$ | $MSO_4^0$ | $M(SO_4)_2^{2-}$ | Other | | | | |
| | mg kg$^{-1}$ | ------------------------------------------------ % -------------------------------------------------- | | | | | | | mg L$^{-1}$ | mg L$^{-1}$ |
| Cd | 0 | 54.6 | - | 38.0 | 5.5 | 1.9 | 54.6 | 43.5 | 7.2 | 3.1 |
| | 460 | 35.5 | - | 43.3 | 20.9 | 0.3 | 35.5 | 64.2 | 3.7 | 2.3 |
| | 920 | 39.1 | - | 43.0 | 17.1 | 0.8 | 39.1 | 60.1 | 2.4 | 1.5 |
| | 2300 | 22.4 | - | 36.5 | 38.8 | 2.3 | 22.4 | 75.3 | 1.0 | 0.78 |
| Pb | 0 | 44.5 | 4.8 | 45.4 | 4.1 | 1.2 | 49.3 | 49.5 | 0.20 | 0.10 |
| | 460 | 29.0 | 2.5 | 52.3 | 15.9 | 0.3 | 31.5 | 68.2 | 0.17 | 0.12 |
| | 920 | 30.1 | 8.4 | 48.9 | 12.3 | 0.3 | 38.5 | 61.2 | 0.11 | 0.06 |
| | 2300 | 18.9 | 3.5 | 45.5 | 30.6 | 1.5 | 22.4 | 76.1 | 0.04 | 0.03 |
| Zn | 0 | 58.6 | 6.5 | 30.9 | 3.6 | 0.4 | 65.1 | 34.5 | 58 | 20 |
| | 460 | 42.1 | 3.7 | 39.0 | 14.9 | 0.3 | 45.8 | 53.9 | 4.0 | 2.1 |
| | 920 | 41.7 | 12.0 | 34.8 | 11.0 | 0.5 | 53.7 | 45.8 | 4.3 | 2.0 |
| | 2300 | 27.9 | 5.2 | 34.5 | 29.2 | 3.2 | 33.1 | 63.7 | 4.4 | 2.0 |

† $\Sigma$ % Low Mobility includes cationic metal species ($M^{1+}$ $M^{2+}$)

‡ $\Sigma$ % High Mobility includes uncharged and anionic metal species ($M^0$ $M^{1-}$ $M^{2-}$)

64

Table 5. Metal phosphate minerals and their solubility products.

| Mineral | Equilibrium Reaction | Log $K_{sp}$ | Source |
|---|---|---|---|
| Octavite | $CdCO_3 \rightleftharpoons Cd^{2+} + CO_3^{2-}$ | -11.3 | † |
| $Cd(OH)_2$ | $Cd(OH)_2 \rightleftharpoons Cd^{2+} + 2OH^-$ | -14.7 | † |
| Cadmium Phosphate | $Cd_3(PO_4)_2 \rightleftharpoons 3Cd^{2+} + 2PO_4^{3-}$ | -38.1 | † |
| Soil Cadmium | $Soil\text{-}Cd \rightleftharpoons Cd^{2+}$ | -7.00 | ‡ |
| Anglesite | $PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$ | -7.79 | ‡ |
| Lead Phosphate | $PbHPO_4 \rightleftharpoons Pb^{2+} + HPO_4^{2-}$ | -11.43 | § |
| Cerrusite | $PbCO_3 \rightleftharpoons Pb^{2+} CO_3^{2-}$ | -12.8 | ¶ |
| Lead Hydroxypyromorphite | $Pb_5(PO_4)_3OH \rightleftharpoons 5Pb^{2+}+3PO_4^{3-}+OH^-$ | -76.8 | § |
| Lead Chloropyromorphite | $Pb_5(PO_4)_3Cl \rightleftharpoons 5Pb^{2+}+3PO_4^{3-}+Cl^-$ | -84.4 | # |
| Smithsonite (calamine) | $ZnCO_3 \rightleftharpoons Zn^{2+} + CO_3^{2-}$ | -9.9 | †† |
| Zincite | $ZnO+2H^+ \rightleftharpoons Zn^{2+} + H_2O$ | 11.16 | ‡ |
| Hopeite | $Zn_3(PO_4)_2 \bullet 4H_2O \rightleftharpoons 3Zn^{2+} + 2PO_4^{3-} + 4H_2O$ | -35.4 | ‡‡ |
| Zinc pyromorphite | $Zn_5(PO_4)_3OH \rightleftharpoons 5Zn^{2+}+3PO_4^{3-}+OH^-$ | -63.1 | †† |

† Jurinak and Santillian-Medrano, 1974; ‡ Lindsay, 1979; § Nriagu, 1972;
¶ Santillian-Medrano and Jurinak, 1975; # Nriagu, 1973; †† Nriagu, 1984; ‡‡ Kuo, 1986
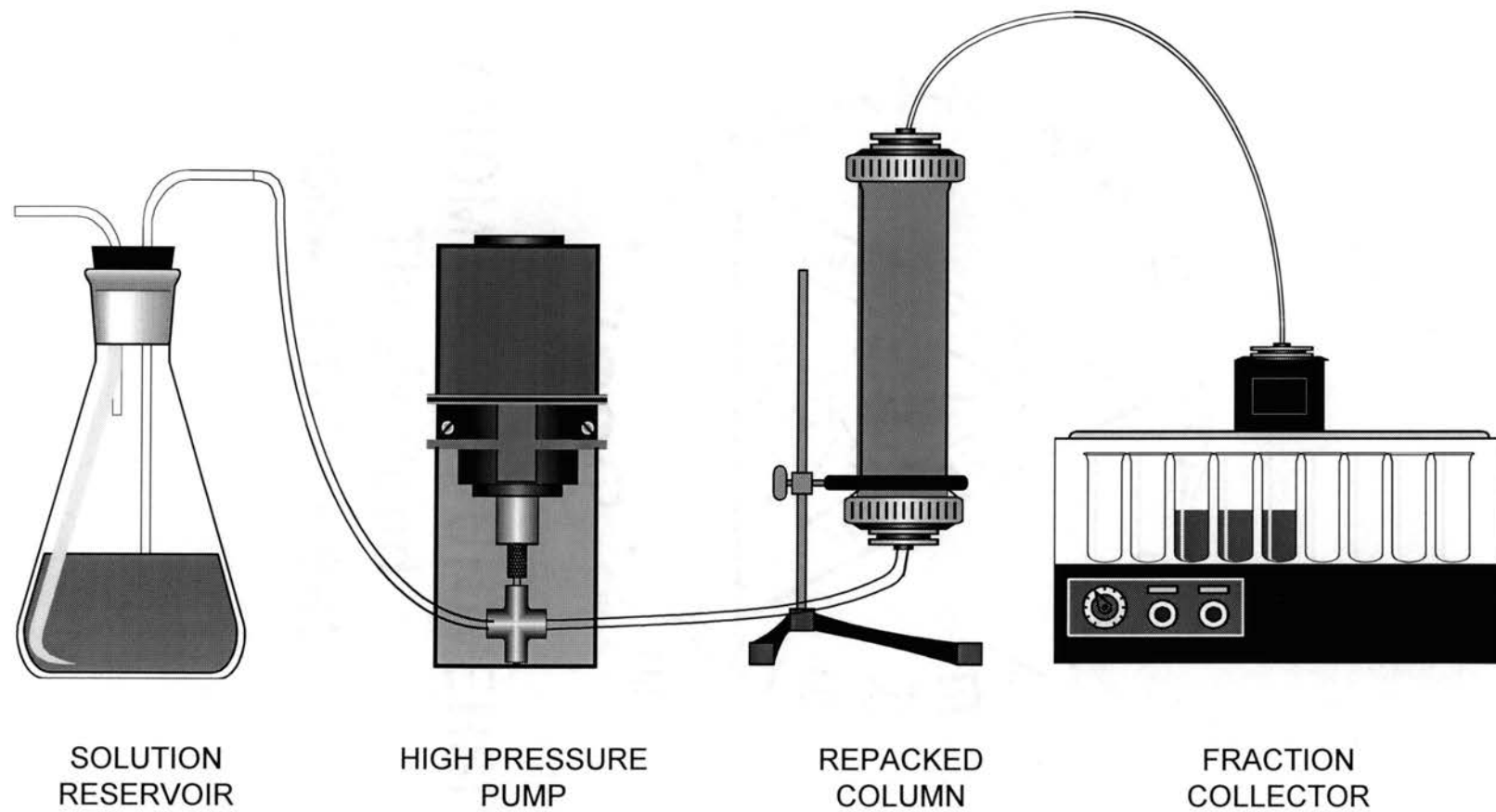
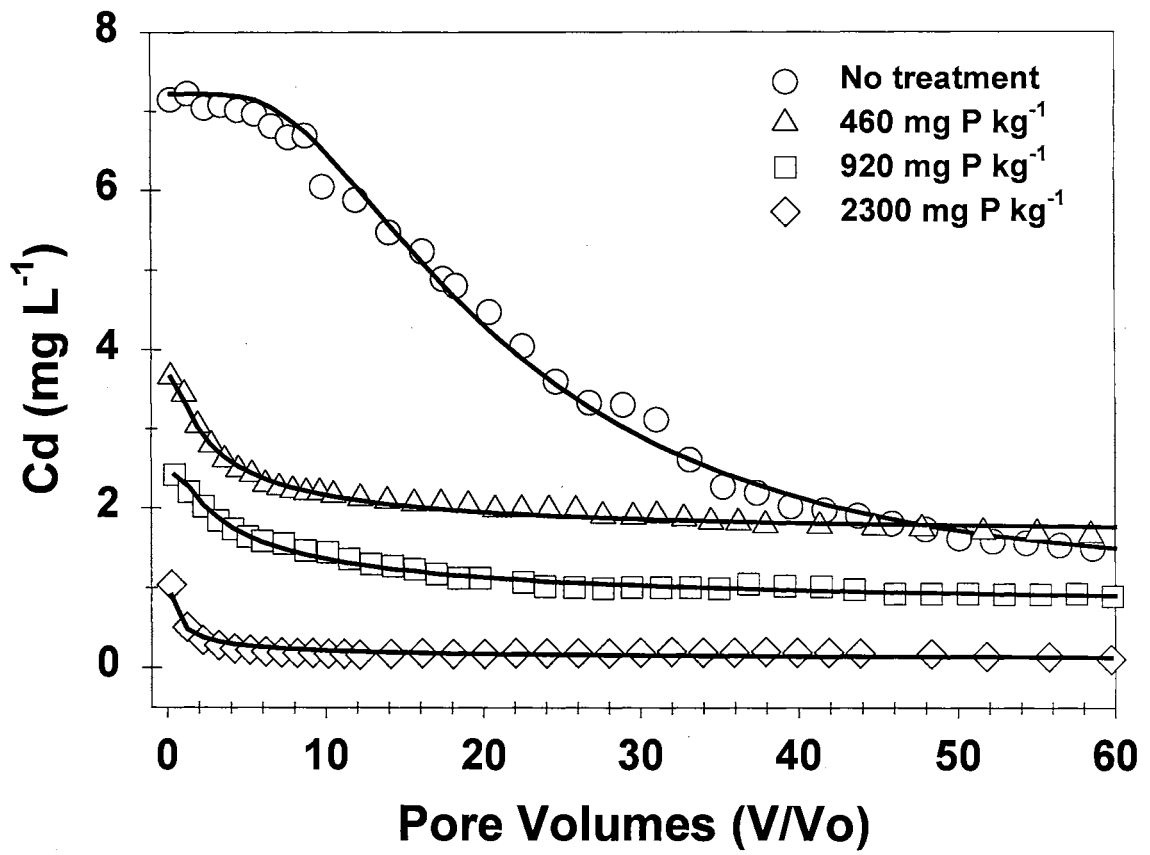Figure 1. Schematic of solute transport apparatus.

Figure 2. Observed (symbol) and fitted (line) cadmium elution curves for
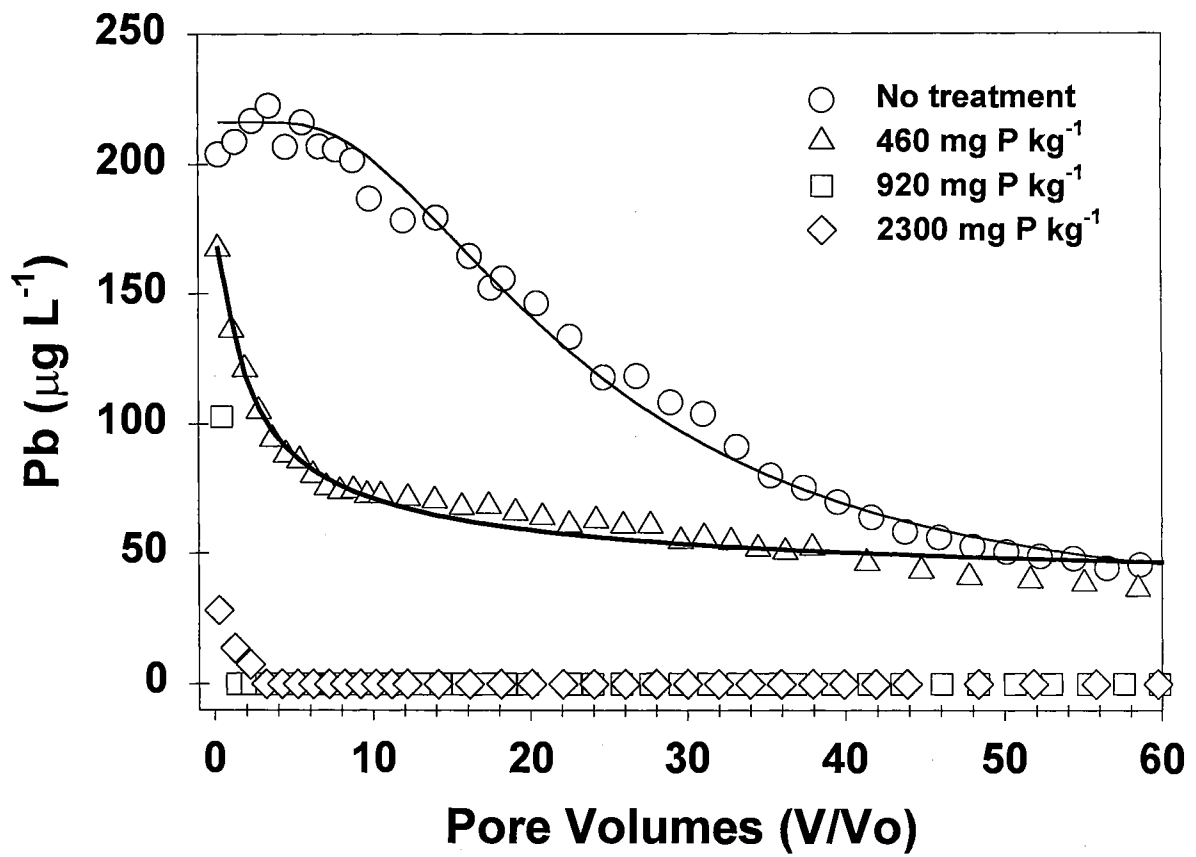untreated and DAP amended soils.

Figure 3. Observed (symbol) and fitted (line) lead elution curves for untreated
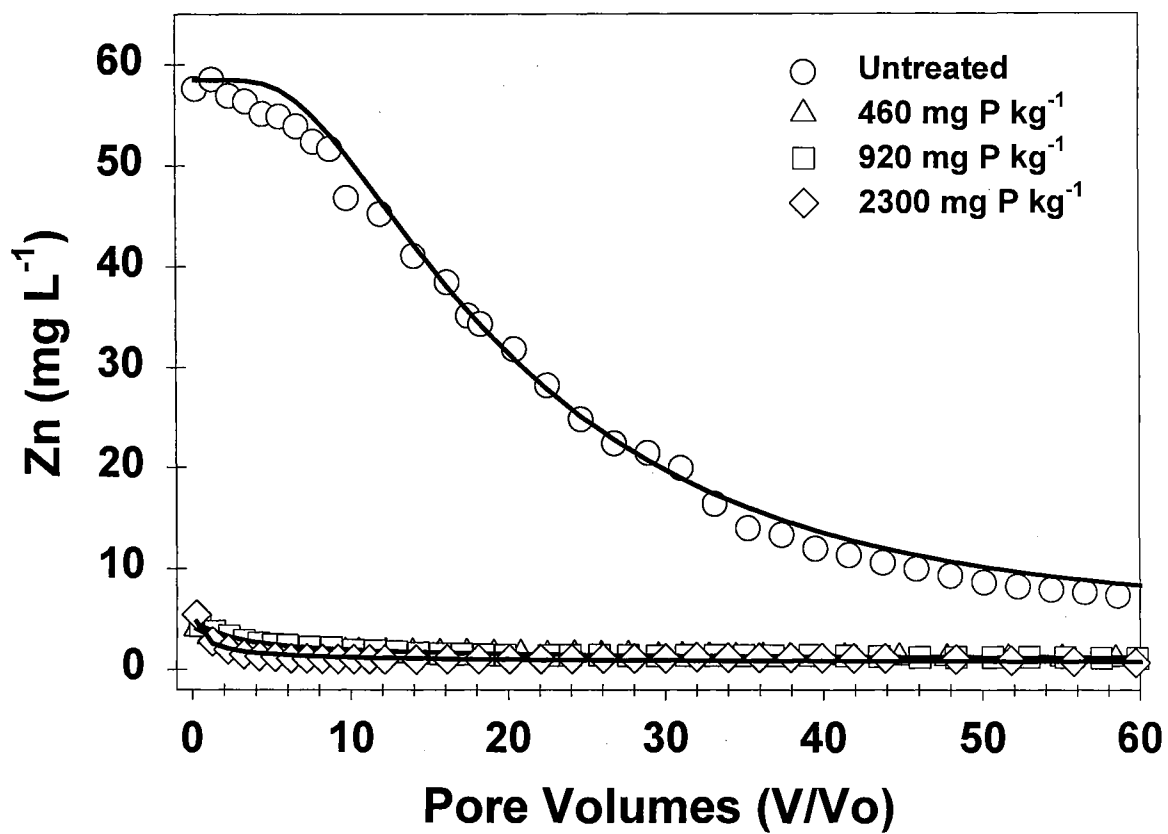and DAP amended soils.

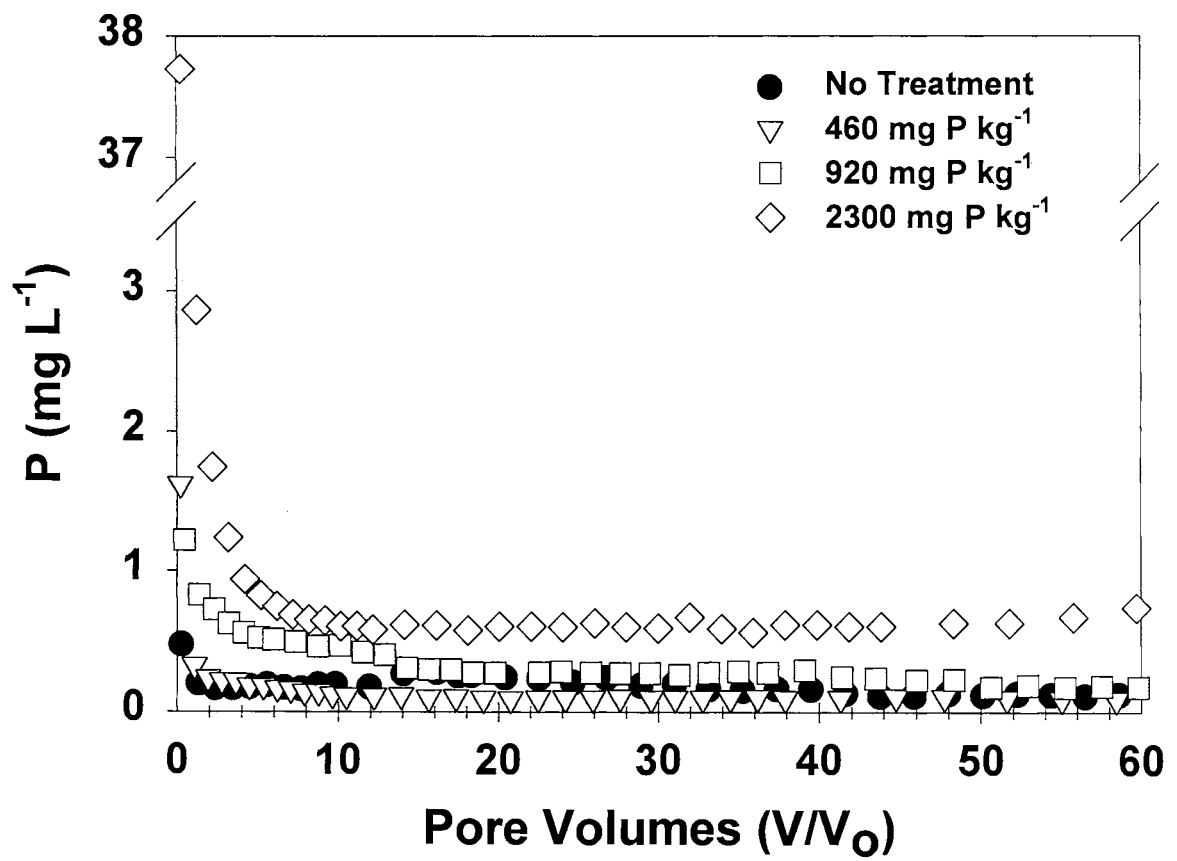Figure 4. Observed (symbol) and fitted (line) zinc elution curves for untreated and DAP amended soils.

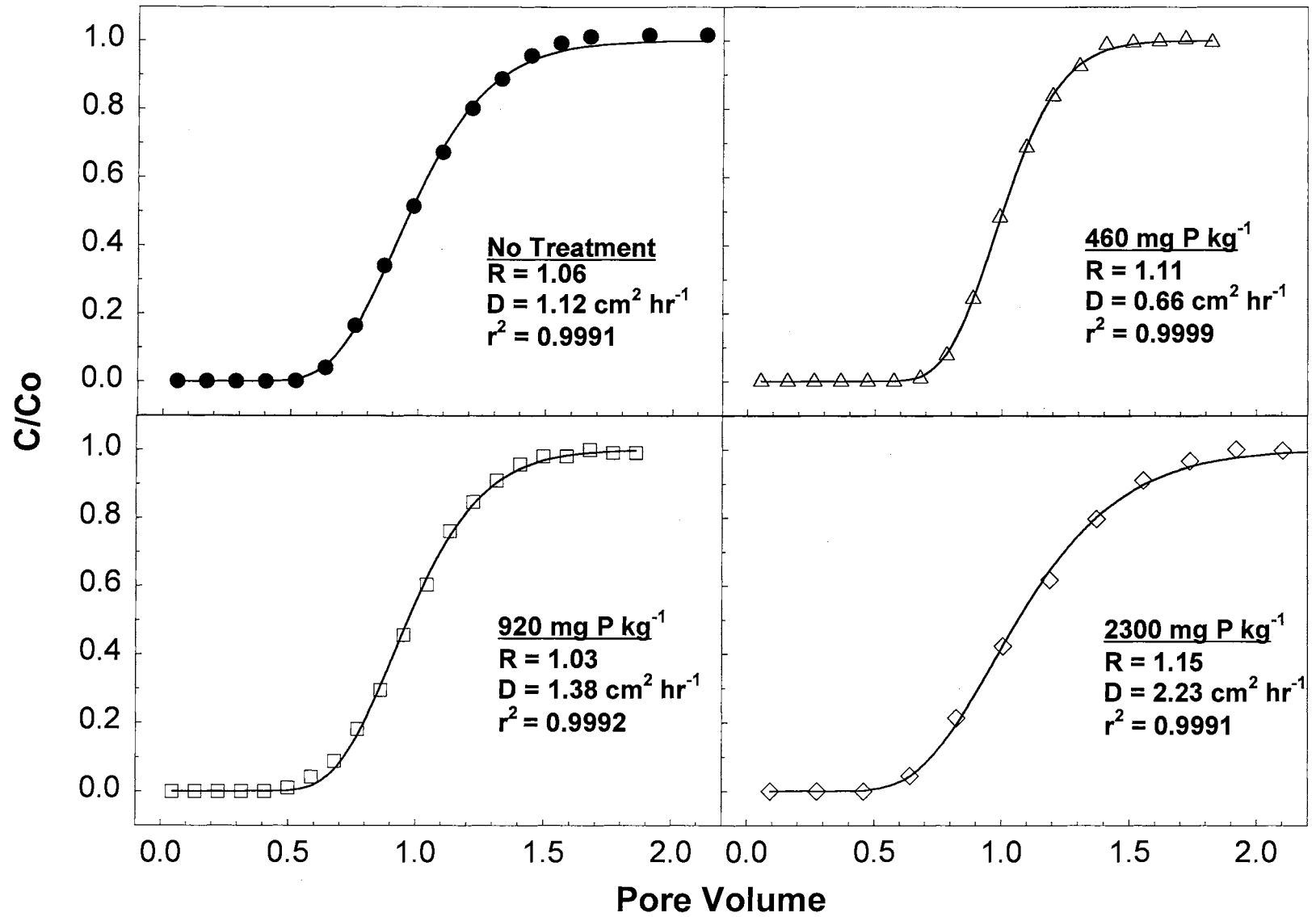Figure 5. Phosphorus elution curves for untreated and DAP amended soils.

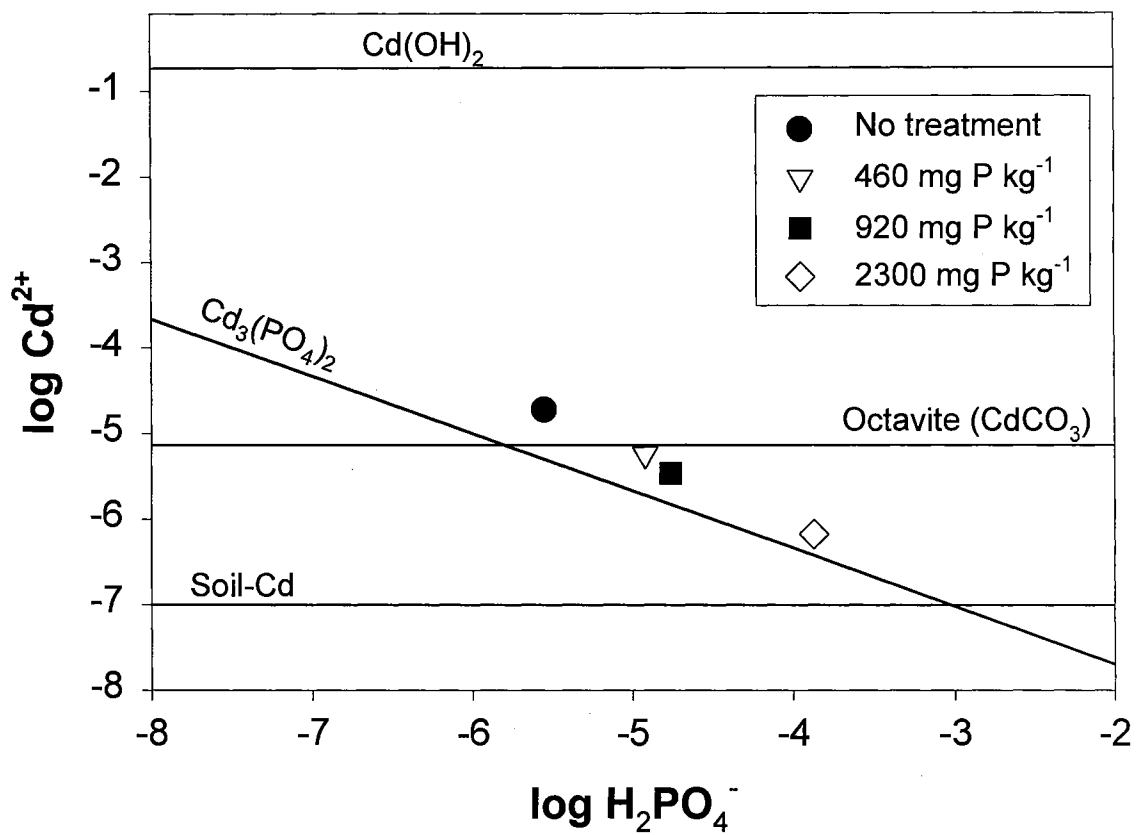Figure 6. Observed (symbol) and fitted (line) bromide breakthrough curves.

Figure 7. Cadmium activity-ratio diagram with soil solution speciation data. $CdCO_3$ line assumes $CO_2(g) = 10^{-3.5}$ M.
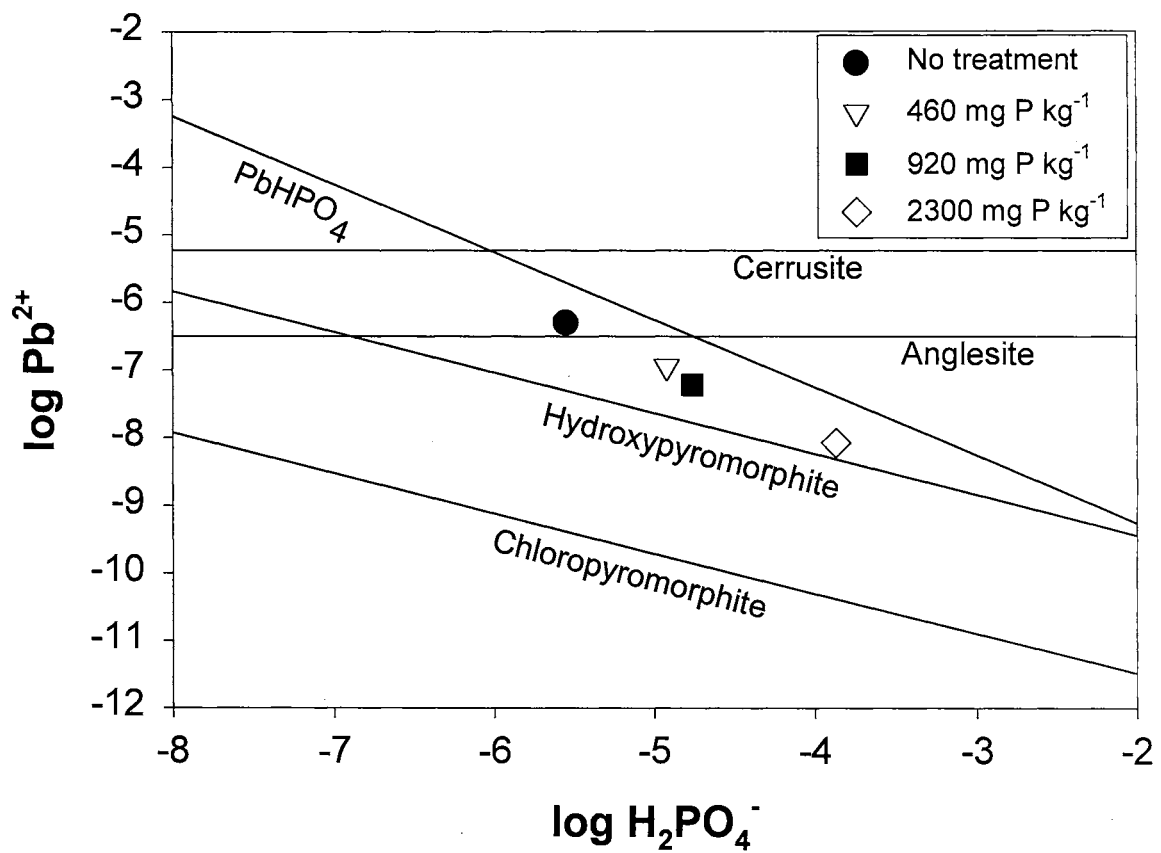
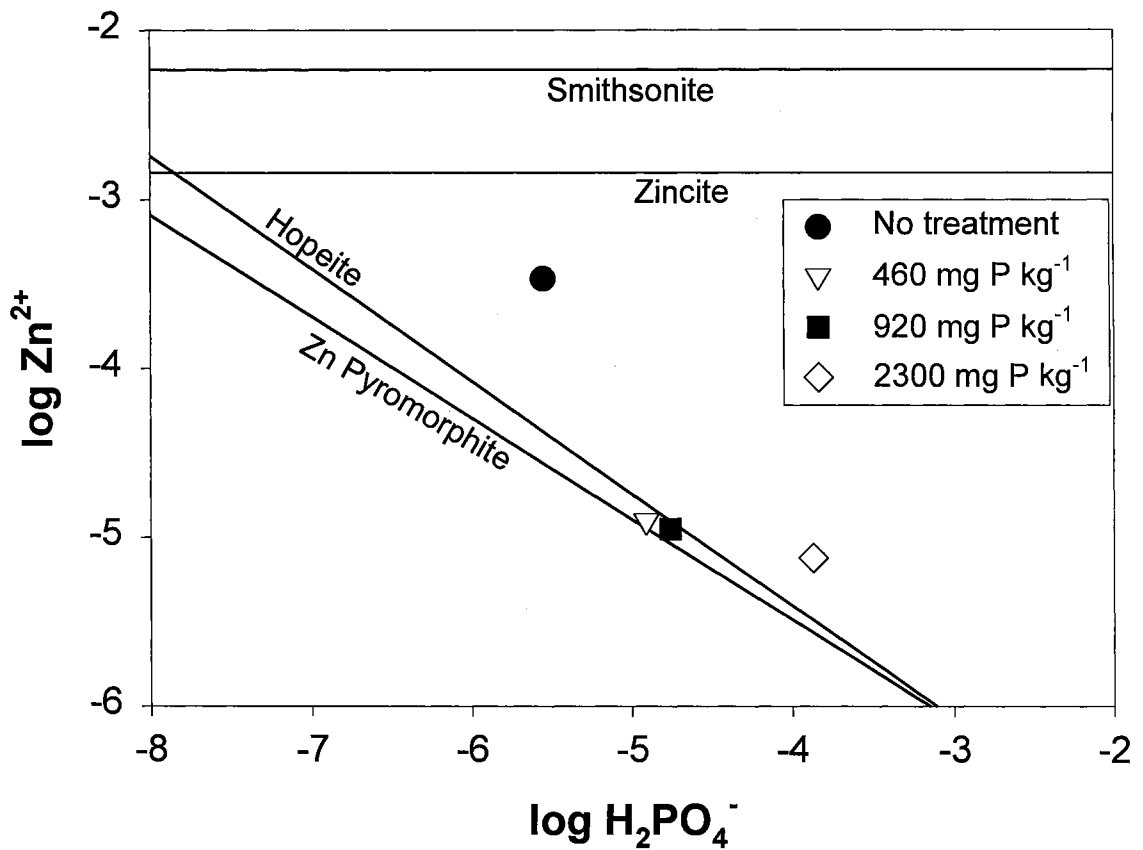Figure 8. Lead activity-ratio diagram with soil solution speciation data. Solution $Cl = 10^{-4}$ M, $SO_4 = 10^{-1.3}$ M, and $CO_2(g) = 10^{-3.5}$ M.

Figure 9. Zinc activity-ratio diagram with soil solution speciation data. Assumes amorphous $FeOH_3$ controls Fe solubility, $CO_2(g) = 10^{-3.5}$ M, and pH = 7.

74

# VITA

Steven Lynn McGowen

Candidate for the Degree of

Doctor of Philosophy

Dissertation: IN-SITU CHEMICAL TREATMENTS FOR REDUCING HEAVY
METAL SOLUBILTY AND TRANSPORT IN SMELTER
CONTAMINATED SOILS

Major Field: Soil Science

Biographical:

Personal Data: Born in Norman, Oklahoma, on December 10, 1971, the son of
Norbert J. and Patricia J. McGowen. Married Dia Dawn (Evetts)
McGowen on August 6, 1994.

Education: Graduated from Purcell High School, Purcell, Oklahoma in May
1990; received Bachelor of Science degree in Agronomy (Soil Science
option) from Oklahoma State University in July 1994; received Master of
Science degree in Agronomy from Louisiana State University, Baton
Rouge, Louisiana in July 1996. Completed the requirements for Doctor of
Philosophy degree in Soil Science at Oklahoma State University in May
2000.

Experience: Employed by Oklahoma State University, Department of Plant and
Soil Sciences from 1996 to 2000.

Professional Memberships: American Society of Agronomy, Soil Science Society
of America.