

Use of Diammonium Phosphate to Reduce Heavy Metal Solubility and Transport in Smelter-Contaminated Soil

S. L. McGowen, N. T. Basta,* and G. O. Brown

ABSTRACT

Phosphate treatments can reduce metal dissolution and transport from contaminated soils. However, diammonium phosphate (DAP) has not been extensively tested as a chemical immobilization treatment. This study was conducted to evaluate DAP as a chemical immobilization treatment and to investigate potential solids controlling metal solubility in DAP-amended soils. Soil contaminated with Cd, Pb, Zn, and As was collected from a former smelter site. The DAP treatments of 460, 920, and 2300 mg P kg⁻¹ and an untreated check were evaluated using solute transport experiments. Increasing DAP decreased total metal transported. Application of 2300 mg P kg⁻¹ was the most effective for immobilizing Cd, Pb, and Zn eluted from the contaminated soil. Metal elution curves fitted with a transport model showed that DAP treatment increased retardation (*R*) 2-fold for Cd, 6-fold for Zn, and 3.5-fold for Pb. Distribution coefficients (*K_d*) increased with P application 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. Increased *K_d* values with additional DAP treatment indicated reduced partitioning of sorbed and/or precipitated metal released to mobile metal phases and a concomitant decrease in the concentration of mobile heavy metal species. Activity-ratio diagrams indicated that DAP decreased solution Cd, Pb, and Zn by forming metal-phosphate precipitates with low solubility products. These results suggest that DAP may have potential for protecting water resources from heavy metal contamination near smelting and mining sites.

EXTRACTION and processing of metal ores has contaminated soil and water resources with heavy metals throughout the world. Natural weathering processes acting on contaminated land and mining wastes have dispersed metal contaminants beyond historic boundaries to surrounding soils, streams, and ground water (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.

Restoration of contaminated sites and the disposal of metal-contaminated soils and wastes are 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 (Vangronsveld and Cunningham, 1998). 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 ground water. 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 (Vangronsveld and Cunningham, 1998).

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 effective at reducing metal bioavailability associated with incidental ingestion of soil by humans (Lambert et al., 1994; Zhang et al., 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 shown that these treatments are mostly ineffective for reducing the release and transport of Cd and Zn from contaminated soils (McGowen, 2000).

Investigations of chemical immobilization treatments have mainly 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. Previous work has modeled metal transport through uncontaminated soil (Selim, 1992; Selim et al., 1990). However, traditional methods of researching heavy metal transport, described by Selim and Amacher (1996), are seldom applied to investigate contaminated soils. Investigations of metal mobility in contaminated soils have been addressed by describing metal content with depth (Scocart et al., 1983), modeling observed in situ metal transport in soil profiles (Cernik et al., 1994), observing distributions of metal in streams and ground water (Paulson, 1997), or describing metal mobility in soils using sequential extraction schemes (Li and Shuman, 1996).

Few studies have modeled metal transport from treated contaminated soils. 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

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Abbreviations: DAP, diammonium phosphate; PQL, practical quantitative limits; TCLP, toxicity characteristic leaching procedure; XRF, X-ray fluorescence.

phosphate fertilizers to arsenate-contaminated orchard soils. Of the recent research on amended contaminated soils, investigators have not applied transport models to evaluate heavy metal mobility and chemical immobilization treatments.

Soluble phosphate sources 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 (Santillan-Medrano and Jurinak, 1975) and induced the formation of heavy metal phosphate precipitates (Cotter-Howells and Capron, 1996). Investigation of soluble phosphate fertilizers, monoammonium phosphate (MAP) and diammonium phosphate (DAP), showed that MAP decreased and DAP increased the amount of Cd sorbed by the soil (Levi-Minzi and Petruzzelli, 1984). However, Pierzynski and Schwab (1993) found that DAP increased Cd and Zn bioavailability to soybean (*Glycine max* (L.) Merr.). Diammonium phosphate is a major source of P fertilizer and currently represents approximately 70% of the total US production of phosphate fertilizer products (U.S. Department 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. Additional research is needed to evaluate the reduction of heavy metal solubility, mobility, and transport in DAP-amended contaminated soils.

The objectives of this study were to evaluate the effectiveness of DAP as a chemical immobilization treatment to reduce heavy metal solubility and transport in a smelter-contaminated soil.

MATERIALS AND METHODS

Surface soil (<20 cm depth) with elevated residual concentrations of Cd, Pb, Zn, and As was collected at an inoperative smelter site in Oklahoma from an area that had recently been treated with coarse limestone. Soil was air-dried and sieved (<2 mm) prior to use. The soil exhibited effervescence with addition of 1 M HCl indicating the presence of free carbonates. Soil pH (1:1, soil to water) was determined by combination electrode. Particle size analysis was determined using the hydrometer method (Gee and Bauder, 1986). Total metal content 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 a modified toxicity characteristic leaching procedure (TCLP, SW-846 Method 1311) (USEPA, 1986). In this procedure, soil (5 g) was extracted with TCLP solution (0.1 M sodium acetate, pH 5.0) in a 125-mL polyethylene bottle on a reciprocal shaker for 18 h.

Furthermore, the soil was extracted with 0.5 M Ca(NO₃)₂ (1:20 soil to solution) for 16 h (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, (NH₄)₂HPO₄ (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 to M_{total} molar ratio treatment ($M_{\text{total}} = \Sigma$ of total Cd, Pb, and Zn determined by XRF). The 3:5 ratio corresponds to the stoichiometric P to Pb ratio of chloropyromorphite [Pb₅(PO₄)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 and Ryan, 1999; Zhang et al., 1998). Preliminary studies, used to determine the amount of DAP required to reduce soluble Cd, Pb, and Zn in the contaminated study soil used in this study, showed that DAP treatments <3:5 P to M_{total} were very effective. Also, phosphorus associated with the 3:5 P to M_{total} treatment released significant arsenic (McGowen, 2000). Both of these observations are attributed to the greater solubility of DAP compared with hydroxyapatite. Therefore, smaller P treatments of 460, 920, and 2300 mg P kg⁻¹ as DAP were selected for this study. These treatments corresponded to approximate P to 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. Teflon filters (0.45 μm) were placed between the soil matrix and end caps on each end of the column to prevent loss of fines from the soil column. The column had a 4-cm i.d. and was 7.5 cm long. Soils were saturated with Type 1 reagent grade water (>18.0 MΩ · cm at 25°C) (American Society for Testing and Materials, 1992) with continuous upward flow using a piston pump (Fluid Metering, Syosset, NY) until saturation and allowed to equilibrate for 48 h 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, Lincoln, NE) through 60 pore volumes. Column effluent was passed through Teflon tubing and an in-line 0.45-μm filter before collection into glass test tubes. Sample effluent pH and anion concentrations (F, Cl, Br, NO₃, PO₄, and SO₄) were immediately analyzed after collection by combination electrode and ion chromatography. Remaining effluent was acidified with trace metal grade HNO₃ (pH < 2) (American Public Health Association, 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 calculated as three standard deviations (3σ) of the instrument response for seven repeated analyses of a sample blank solution. Practical quantitative limits (PQL) of detection were set at 10 times the LOD (American Public Health Association, 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 (ρ_b), and volumetric water content were computed with the measured flow rate and column packing. Observed metal breakthrough curves were fitted using the transport model COLUMN 1.4 (Brown et al., 1997), and retardation (R) was determined for each metal species. The retardation factor is defined as:

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

where ρ_b is the soil dry bulk density and θ is the volumetric water content. The linear distribution coefficient, K_d , is defined as:

$$K_d = c^*/c \quad [2]$$

where c^* is the mass of solute adsorbed per dry mass of soils and c is the aqueous volume concentration.

When effluent metal concentrations were below the PQL, a minimum R value may be estimated. The total mass of metal, M_T , is given by:

$$M_T = \theta_c + \rho_b c^* \quad [3]$$

Note that the first effluent must be in equilibrium with the initial total mass, M_{T0} . Thus, setting $M_T = M_{T0}$ and substituting back into Eq. [1], [2], and [3] yields:

$$R \geq M_{T0}/PQL\theta \quad [4]$$

Distribution coefficients (K_d) were determined from the fitted and estimated minimum R values using Eq. [5]:

$$K_d = (R - 1)\theta/\rho_b \quad [5]$$

where ρ_b is the soil dry bulk density and θ is the volumetric water content.

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 R and K_d .

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

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). Graphic 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 metal 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

The contaminated soil was a sandy loam with 67% sand, 29% silt, and 4% clay and with a soil pH of 6.8. Selected soil properties and levels of metal contamination in the soil as determined by X-ray fluorescence

Table 1. Total content, toxicity characteristic leaching procedure (TCLP)-extractable, and 0.5 M Ca(NO₃)₂-extractable Cd, Pb, As, and Zn for the smelter-contaminated soil.

Element	Total content [†]	TCLP extractable		0.5 M Ca(NO ₃) ₂ extractable
	mg kg ⁻¹	mg L ⁻¹	reg. limit [‡]	mg kg ⁻¹
Cd	1 090	39.9 ± 1.59	1.0	156 ± 4.44
Pb	5 150	21.0 ± 0.58	5.0	12.3 ± 0.43
As	152	0.03 ± 0.002	5.0	0.25 ± 0.02
Zn	69 200	1171 ± 32	none	586 ± 17.8

[†] Total content determined by X-ray fluorescence (XRF).

[‡] Regulatory limit specified by USEPA Method 1311 (USEPA, 1986).

(XRF), TCLP extraction, and 0.5 M Ca(NO₃)₂ extraction are reported in Table 1. Total Cd, Pb, and Zn in the soil were well above background soil concentrations (Holmgren et al., 1993). The 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 Cd, Pb, and Zn extracted with 0.5 M Ca(NO₃)₂ indicate that a large portion of the total heavy metals in the soil is relatively soluble, potentially bioavailable, and mobile (Basta and Gradwohl, 2000). Total elemental contents, 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 anions determined from saturated paste extract in mg L⁻¹ (in parentheses) were: Cl (26.6), SO₄ (1560), and NO₃ (21.7). Soil electrical conductivity (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 Ca concentrations in eluent fractions were in excess of 0.005 M Ca (200 mg Ca L⁻¹) through 60 pore volumes elution for all experiments, indicating a well-buffered system from the prior limestone amendments to the soil. The Ca concentrations measured in solution were in excess of 0.005 M Ca over the duration of all experiments. Therefore, the exclusion of additional background electrolytes probably had no adverse effect on 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.

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. 1A). 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. 1B). Like-

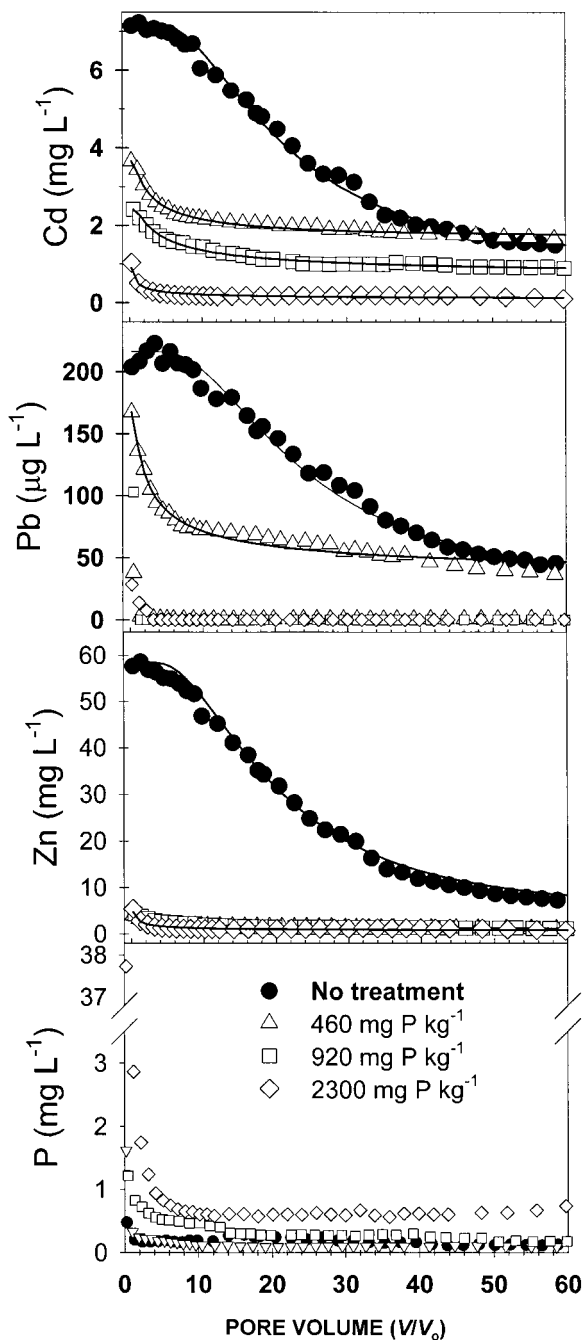


Fig. 1. Elution curves for Cd, Pb, Zn, and P for untreated and diammonium phosphate (DAP)-amended soils. Symbols represent observed elution data and lines represent model-fitted elution curves.

wise, P addition reduced the amount of Zn eluted with only slight differences observed for the Zn elution curves from the P-amended soils (Fig. 1C). Numerical integration (through 60 pore volumes) of eluted Cd, Pb, and Zn in Fig. 1A–C indicated that increasing DAP application decreased the total amount of metal transported. 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 beyond 460 mg kg⁻¹. 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.

Additions of excessive amounts of P to a contaminated soil may increase the risk of leaching and eutrophication to sensitive surface water bodies. Phosphorus elution curves for all column experiments are shown in Fig. 1D. 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, and 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 Fig. 1A–C. Experiment parameters (bulk density, Darcy flux, and water content), calculated *R*, and *K_d* are given in Table 3. Soil bulk densities (ρ_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 h⁻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 *R* with increasing P application (Table 3). Retardation factors increased by approximately twofold for Cd and sixfold 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. 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.

Table 2. Cumulative mass[†] of As, Cd, Pb, Zn, and P collected from miscible displacement experiments and expressed as 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		μg kg ⁻¹	mg kg ⁻¹	mg column ⁻¹
0	<0.001	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; P expressed on mass basis (mg column⁻¹).

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 diammonium phosphate (DAP)-amended soils.

P treatment	Length	Flux	ρ _b	θ	Cd			Pb			Zn		
					<i>R</i>	<i>K_d</i>	<i>r</i> ²	<i>R</i>	<i>K_d</i>	<i>r</i> ²	<i>R</i>	<i>K_d</i>	<i>r</i> ²
mg P kg ⁻¹	cm	cm h ⁻¹	g cm ⁻³	%	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.

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, *K_d* values 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. Using this definition, increasing *K_d* values indicate increased solute sorbed onto soil and less solute in solution 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 rep-

resentative 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 (Fig. 2). These results indicate that transport-related non-equilibrium was not a factor in any of the experiments.

Probable Mineral Solid Phases and Metal Solubility

Chemical immobilization treatments may 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 should be evaluated to determine the potential long-term effectiveness of such treatments. Increased *K_d* values (Table 3) are probably due to the formation

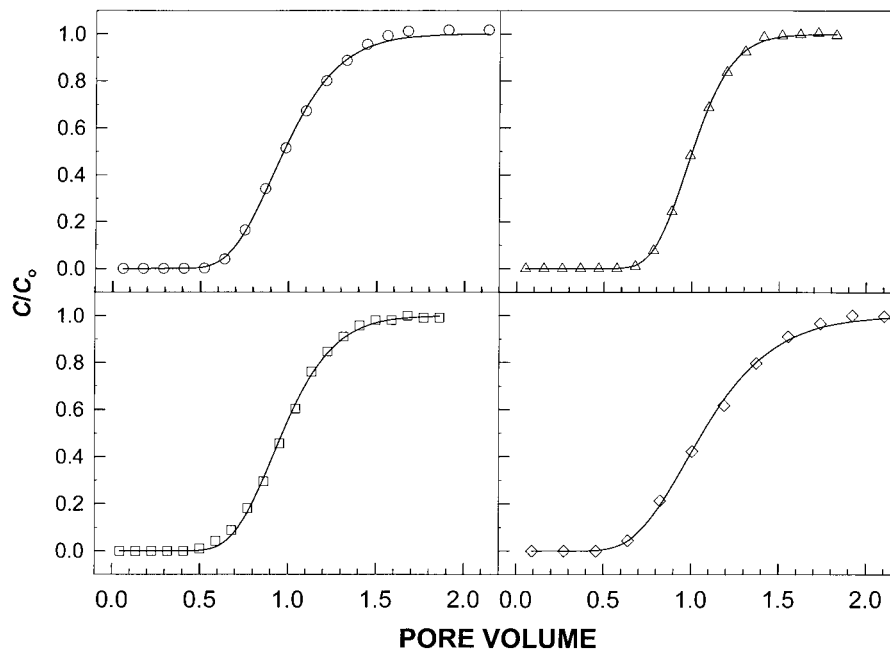


Fig. 2. Observed (symbol) and fitted (line) bromide breakthrough curves.

Table 4. 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	Jurinak and Santillian-Medrano, 1974
Cd(OH) ₂	$Cd(OH)_2 \rightleftharpoons Cd^{2+} + 2OH^-$	-14.7	Jurinak and Santillian-Medrano, 1974
Cadmium phosphate	$Cd_3(PO_4)_2 \rightleftharpoons 3Cd^{2+} + 2PO_4^{3-}$	-38.1	Jurinak and Santillian-Medrano, 1974
Soil cadmium	$Soil-Cd \rightleftharpoons Cd^{2+}$	-7.00	Lindsay, 1979
Anglesite	$PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$	-7.79	Lindsay, 1979
Lead phosphate	$PbHPO_4 \rightleftharpoons Pb^{2+} + HPO_4^{2-}$	-11.43	Nriagu, 1972
Cerrusite	$PbCO_3 \rightleftharpoons Pb^{2+} + CO_3^{2-}$	-12.8	Santillian-Medrano and Jurinak, 1975
Lead hydroxypyromorphite	$Pb_5(PO_4)_3OH \rightleftharpoons 5Pb^{2+} + 3PO_4^{3-} + OH^-$	-76.8	Nriagu, 1972
Lead chloropyromorphite	$Pb_5(PO_4)_3Cl \rightleftharpoons 5Pb^{2+} + 3PO_4^{3-} + Cl^-$	-84.4	Nriagu, 1973
Smithsonite (calamine)	$ZnCO_3 \rightleftharpoons Zn^{2+} + CO_3^{2-}$	-9.9	Nriagu, 1984
Zincite	$ZnO + 2H^+ \rightleftharpoons Zn^{2+} + H_2O$	11.16	Lindsay, 1979
Hopeite	$Zn_3(PO_4)_2 \cdot 4H_2O \rightleftharpoons 3Zn^{2+} + 2PO_4^{3-} + 4H_2O$	-35.4	Kuo, 1986
Zinc pyromorphite	$Zn_5(PO_4)_3OH \rightleftharpoons 5Zn^{2+} + 3PO_4^{3-} + OH^-$	-63.1	Nriagu, 1984

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 4.

The Cd-H₂PO₄ activity-ratio diagram (Fig. 3) indicates that cadmium phosphate Cd₃(PO₄)₂ or octavite (CdCO₃ log K_{SP} = -12.8) may control Cd solubility in soils before DAP addition. Results from the 2300 mg kg⁻¹ P treatment suggest that cadmium phosphate Cd₃(PO₄)₂ (log K_{SP} = -38.1) is more likely the mineral controlling Cd than CdCO₃ solubility (Fig. 3). Other work has shown that Cd₃(PO₄)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-H₂PO₄ activity ratio diagram (Fig. 4) indicates that anglesite (PbSO₄, log K_{SP} = -7.79) or lead phosphates may control Pb solubility in soils before addition of DAP. Results from the 2300 mg kg⁻¹ P treatment suggest that lead hydroxypyromorphite is more likely than anglesite (Fig. 3). Lead hydroxypyromorphite has been recognized as a mineral controlling Pb solubility in many soils amended with phosphate materials (Santillian-Medrano and Jurinak, 1975) and its formation in phosphate-treated contaminated soil has been confirmed by XRD and SEM-EDX (Cotter-Howells and Capron, 1996; Laperche et al., 1996, 1997; Ma et al., 1993; Ruby et al., 1994).

Results for the untreated contaminated soil suggest that none of the Zn solid phases investigated were controlling the soluble Zn concentration. However, results from P-treated contaminated soil were consistent with zinc phosphate minerals controlling Zn solubility (Fig. 5).

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 220 g kg⁻¹ volumetric water content at 30°C for 6 mo. Soil pH was monitored periodically using a 1:1 soil to water ratio and a combination pH electrode. Soil pH values decreased from 7.1 to 6.5 after 2 mo and then remained constant. A large percentage (>60%) of the total NH₄ added to the contaminated soils was leached from the column apparatus and collected in solution. This lowered the NH₄ concentration and decreased the acidification potential in the soil during the incubation periods. Furthermore, the presence of free carbonates present in the limed soil probably buffered the system pH and prevented acidification to pH < 6.5. Researchers investigating soluble phosphates have

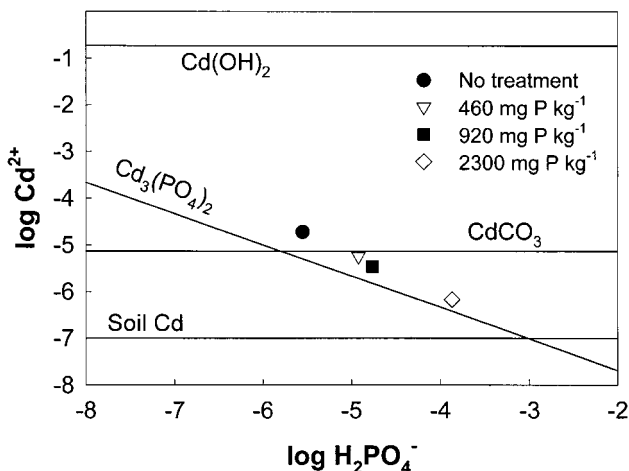


Fig. 3. Cadmium activity-ratio diagram with soil solution speciation data. CdCO₃ line assumes CO₂(g) = 10^{-3.5} M.

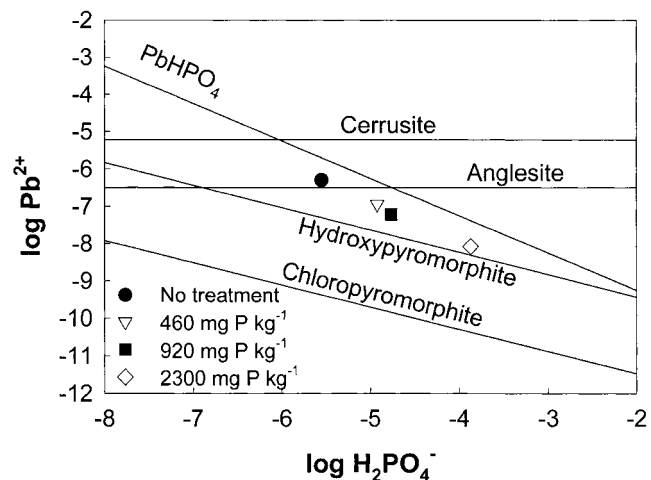


Fig. 4. Lead activity-ratio diagram with soil solution speciation data. Plotted lines assume Cl = 10⁻⁴ M, SO₄ = 10^{-1.3} M, and CO₂(g) = 10^{-3.5} M.

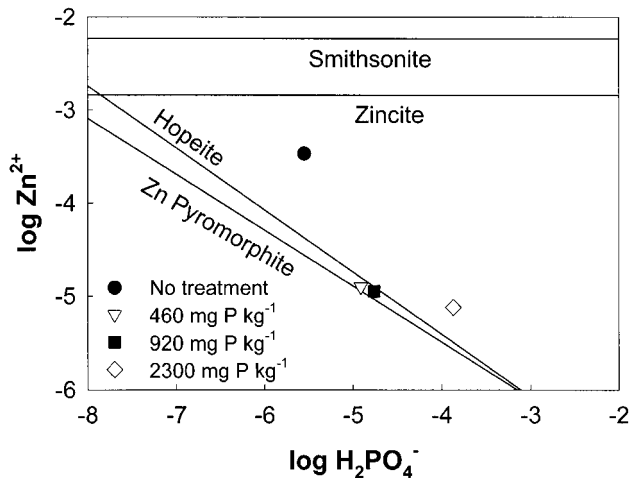


Fig. 5. Zinc activity-ratio diagram with soil solution speciation data. Assumes amorphous $\text{Fe}(\text{OH})_3$, controls Fe solubility, $\text{CO}_2(\text{g}) = 10^{-3.5} \text{ M}$, and $\text{pH} = 7$.

often included liming materials to buffer against drastic decreases in pH (Brown et al., 1999; Hettiarachchi et al., 1997; Hettiarachchi and Pierzynski, 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 $2300 \text{ mg P kg}^{-1}$ application was the most effective for immobilizing Cd, Pb, and Zn eluted from the contaminated soil when compared with the untreated check. This treatment corresponded to a P to M_{total} ratio of 1:15, where $M_{\text{total}} = \Sigma$ total Cd, Pb, and Zn determined by XRF. Diammonium phosphate treatments $< 2300 \text{ mg P kg}^{-1}$ had a similar effect on reducing metal transport but with lower efficiency. Model-fitted metal elution curves showed increased R and K_d values with increased DAP application. Increased R factors indicated slowed metal transport with DAP treatment. Increased K_d values were probably due to the formation of metal phosphate precipitates and/or increased sorption.

Chemical immobilization of heavy metals using DAP is an effective method of reducing metal solubility and mobility. Diammonium phosphate is inexpensive and commercially available in large quantities as a fertilizer. In situ treatment with DAP at the $2300 \text{ mg P kg}^{-1}$ treatment corresponds to estimated material costs of only $\text{US}\$2.5 \text{ m}^{-2}$ to 60 cm depth (assuming bulk density of 1.4 g cm^{-3}) compared with $\text{US}\$730 \text{ m}^{-2}$ to 60 cm depth for excavation and landfilling (Vangronsveld and Cunningham, 1998). The optimum P to M_{total} ratio of 1:15 observed in soil used in this study may differ with varying concentrations of reactive metals in other contaminated soils and wastes. Application of ammonium fertilizer as DAP did not result in soil acidification and remobilization of metals in this study. However, the contaminated soil in this study had received limestone

application. Co-application of liming materials with DAP may be necessary to offset potential soil acidification from ammonium fertilizer application in non-alkaline soils. Heavy metal phosphates, formed by DAP treatment of contaminated soil, should provide long-term reductions in metal solubility and transport.

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