CHEMICAL IMMOBILIZATION OF LEAD, ZINC, AND CADMIUM BASED ON RISK AND CONTAMINANT EXTRACTABILITY

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CHAPTER 1

IMMOBILIZATION OF LEAD, ZINC, AND CADMIUM IN SMELTER-CONTAMINATED SOIL: APPLICATION AMOUNT BASED ON CONTAMINANT EXTRACTABILITY

ABSTRACT

Immobilization is an *in-situ* remediation technique that reduces contaminant bioavailability and risk. In this study, the ability of diammonium phosphate (DAP) and other immobilization treatments (sodium phosphate, Na_2HPO_4; monoammonium phosphate, MAP; calcium carbonate, $CaCO_3$; and alkaline biosolids, AB) to reduce available lead (Pb), zinc (Zn), and cadmium (Cd) in contaminated soil was determined. Commonly, immobilization treatment amounts are determined empirically, making methods to determine the amount of an immobilization treatment based on chemical analysis of soil desirable. In this study, the ability of chemical extraction methods to determine the application amount of immobilization treatment for remediation of contaminated soils is evaluated. A soil contaminated with Pb (2250 mg kg^{-1}), Cd (278 mg kg^{-1}), and Zn (59000 mg kg^{-1}) from a smelter in northeastern Oklahoma was treated. Application amounts for phosphate-based treatments were based on: (1) metal extracted using 0.1 M $Ca(NO_3)_2$, (2) sum of metal sequentially extracted by 0.1 M Ca $(NO_3)_2$ and 1.0 M sodium acetate (NaOAc), (3) bioaccessible metal extracted by a simulated human gastrointestinal in vitro method, and (4) total metal measured by X-ray fluorescence. The $CaCO_3$ and AB treatments were applied at 100 g kg^{-1} and 200 g kg^{-1}, respectively. The application of DAP decreased extractable Zn by 82.1% at the total content amount, increased extractable Zn at all other application amounts, and decreased soil pH (from 7.2 to 6.2) with increasing application amounts. DAP reduced extractable Cd by 47.7% and 86.5% at the bioaccessible and total content amount, respectively. Na_2HPO_4 reduced extractable Zn by 99.5% and 94.4% at the bioaccessible and total content amount, respectively, and increased soil pH (from 7.2 to 10.8). Extractable Cd was reduced by 98.6 and 98.1% at the

bioaccessible and total content application amounts, respectively. MAP increased extractable Zn at all application amounts; decreased extractable Cd by 54.3 and 62.4% at the bioaccessible and total content amounts, respectively; and decreased soil pH (from 7.2 to 5.8). $CaCO_3$ reduced extractable Zn by 19.4%, reduced extractable Cd by 25.9%, and increased soil pH to 7.6. Alkaline biosolids reduced extractable Zn by 74.3%, reduced extractable Cd by 90.4%, and increased soil pH to 7.9. Applying phosphate treatments at the total content amount and the application of alkaline biosolids were most effective at reducing extractable Zn and Cd.

INTRODUCTION

Heavy metal contamination can degrade soil quality and pose risks to human and ecosystem health. Sources of heavy metal contamination include mining, industrial discharge, coal, gasoline, metal-smelting industries, and lead paint (Sparks, 1995). Lead (Pb), zinc (Zn), and cadmium (Cd) are heavy metals that are of environmental concern when present in amounts greater than regulatory levels. Excessive exposure to these metals can have severe human and ecological effects, such as pulmonary disease, renal tubular disease, mental retardation, and phytotoxicity (Klaassen, 1996).

Removal of contaminated soils by means of excavating and landfilling are common remediation practices. These practices are expensive (Cotter-Howells, 1996) and problematic due to the challenge of finding a hazardous landfill that is capable of accepting large quantities of contaminated soil (Pearson et al., 2000). For these reasons, the development of an effective *in-situ* remediation treatment is highly desirable. Past research of *in-situ* remediation has included soil washing, phytoremediation, and immobilization (Ma et al., 1993).

Immobilization is an *in-situ* remediation technique that does not remove the contaminant from the soil, but transfers the contaminant to a less bioavailable and/or available form. Reduction of availability/ bioavailability results in less risk for both humans and ecosystems.

The addition of apatite (hydroxyapatite ($[CA_{10}/PO_4)6(OH)_2]$) to contaminated soils is one technique of *in situ* immobilization (Ma et al., 1993). Apatite is considered an ideal amendment to soil for remediation of lead because of product abundance and low solubility of lead phosphates (Ma et al., 1993). Although very effective for Pb immobilization, the use of hydroxy apatite was much less effective on reduction of Cd and Zn solubility/availability. The chemical immobilization mechanism for

lead by apatite is isomorphic substitution, where ionic Pb^{2+} substitutes for calcium (Ca^{2+}) because they have a similar ionic radius. Cd and Zn divalent ions have much larger radii than Ca and do not substitute well into the apatite matrix.

Raising the pH of a Cd and/or Zn contaminated soil is the most commonly used method to immobilize these heavy metals for the remediation of the soil to plant pathway (Chen et al., 2000). A study by Pierzynski and Schwab (1993) used the addition of dry limestone to reduce Zn and Cd plant uptake from a contaminated soil collected near an abandoned mine and smelter site. By raising the pH with the application of limestone, the phytotoxicity produced by elevated levels of Zn and Cd was reduced. Raising the pH using alkaline materials, such as limestone, immobilizes metals by a chemical mechanism known as precipitation/specific adsorption (Sparks, 1995).

Previous research has shown the addition of organic materials, such as compost, not only provides "exchangeable sites for metal adsorption, but also specific binding sites from which metals are difficult to exchange; thus the solid organics are able to help in removing metals from the soil solution" (Shuman, 1999). Alkaline-treated sewage sludges can increase soil pH, which can result in precipitation and adsorption of metals. Also, addition of organic matter in the form of sewage sludge increases chelation sites of the soil, thus creating new sites for the adsorption of heavy metals (Petruzzelli et al., 1994). Organic matter not only increases adsorption sites for metal, but due to the presence of organic ligands, the chemical mechanism of chelating exists (Shuman, 1999). Chemical mechanisms that can result from the addition of organic matter to contaminated soil are precipitation, adsorption, and chelation. Little research has focused on treatments that would effectively and simultaneously immobilize Pb, Cd, and Zn.

Diammonium phosphate (DAP) is a water-soluble nitrogen and phosphorus fertilizer that has recently been evaluated as a chemical immobilization treatment (McGowen et al., 2001). The chemical immobilization mechanism for cationic heavy metals using DAP is formation of insoluble Pb, Cd, and Zn phosphate precipitates. Because of its high water solubility, DAP is very effective at immobilization of Pb, Cd, and Zn (McGowen et al., 2001). One disadvantage of DAP is that an excessive application of NH_4^+ can be oxidized in soil producing acidity and resulting in an acidic soil. Acidification of the soil would increase metal availability. Another soluble phosphate that can reduce mobility of heavy metals similarly to DAP is sodium phosphate (Na_2HPO_4). Na_2HPO_4 is an industrial product that is inexpensive

and plentiful. The main drawback of Na_2HPO_4 is excessive Na^+ application to soil can result in soil dispersion, loss of vegetation, and soil erosion (Brady and Weil, 1999). Other soluble phosphorus products that have been researched as immobilization treatments are KH_2PO_4, triple super phosphate fertilizer, and phosphoric acid (Hettiarachchi et al., 2001).

Currently, application amounts are determined empirically and are site-specific. Methods to determine the amount of immobilization treatments based on chemical analysis of soil are not commonly performed. However, application of apatite (hydroxyapatite) to immobilize Pb in contaminated soil based on a 3:5-P:Pb ratio that corresponds to the stoichiometric P/Pb ratio of chloropyromorphite [$Pb_5(PO_4)_3Cl$] has been recommended (Ma et al., 1993). However, recent work showed the amount of DAP required to reduce water soluble Cd, Pb, and Zn in smelter-contaminated study was «3/5 P/total metal (McGowen et al., 2001). Therefore, an accurate method to determine the application amount of immobilization treatment is needed. A method based on chemical analysis of contaminated soil is desirable. The objectives of this work were to evaluate the ability of DAP to reduce readily available Pb, Cd, and Zn in contaminated smelter-soils, to compare effectiveness of DAP with other treatments (Na_2HPO_4, $CaCO_3$, lime-stabilized sewage sludge (alkaline biosolids), and monoammonium phosphate), and to evaluate the ability of chemical extraction methods to determine the application amount of immobilization treatment needed for remediation of contaminated soils.

MATERIALS AND METHODS

The soil used for this project was collected from a zinc smelter in Northeastern Oklahoma. Elevated concentrations of Pb, Cd, and Zn were present in the soil. The soil was air-dried and sieved at <2 mm prior to all laboratory experiments. Soil pH, using a 1:2 soil:water ratio, was determined using a combination electrode. Total metal concentration in the soil was determined using X-ray fluorescence (Karathanasis and Hajek, 1996). Estimated potential bioavailability was determined with a 0.5M $Ca(NO_3)_2$ extraction (Basta and Gradwohl, 2000) and gastrointestinally available metal was determined using a modified version of the in vitro gastrointestinal procedure of Rodriguez et al. (1999).

The contaminated soil is a sandy loam with 67% sand, 29% silt, and 4% clay (McGowen et al., 2001). The contaminated soil had a pH of 6.6 and an electrical conductivity (EC) of 2.69 dS m^{-1}. Total metal content, in vitro gastrointestinal extractable (bioaccessible), and sequentially extractable

(Potentially Bio-Available Sequential Extraction-PBASE, Basta and Gradwohl, 2000) were determined for the contaminated soil and results are reported in Table 1. Background soil concentrations were exceeded for Pb, Zn, and Cd (Pierzynski et al., 2000).

Seven chemical treatments were evaluated to determine the reduction in extractable metal by the immobilization of Pb, Cd, and Zn. The seven chemical treatments included diammonium phosphate (DAP), sodium phosphate (Na_2HPO_4), lime-stabilized sewage sludge (alkaline bio-solids), $CaCO_3$, DAP + $CaCO_3$, DAP + biosolids, and monoammonium phosphate (MAP). The DAP, Na_2HP04, MAP, and CaCO3 were reagent grade chemicals purchased from Fisher Scientific. The alkaline biosolids are biosolids that were treated with CaOH (slaked lime), which is a procedure used to further reduce pathogens in the biosolids (USEPA, 1993). The calcium carbonate equivalency for the alkaline biosolids is 50% (Rund, 1984). The seven treatments were added at four-application amounts, with the exception of $CaCO_3$ and alkaline biosolids. The application amounts for phosphate-based treatments were based on four types of chemical extractions: (1) bioaccessible metal extracted using 0.1 M $Ca(NO_3)_2$ (E1), (2) sum of metal extracted by 0.1 M $Ca(NO_3)_2$ and 1.0 M sodium acetate (NaOAc), pH 5.0 determined by sequential extraction (Basta and Gradwohl, 2000) (E1E2), (3) metal extracted by simulated human gastrointestinal in vitro (IVG) method (Rodriguez et al., 1999), and (4) total metal measured by X-ray Fluorescence (Karathanasis and Hajek, 1996). The amount of P amendment added was based on the sum of P needed to react with Cd, Zn, and Pb. The amount of P required for Cd and Zn was based on a molar ratio of P:Zn or P:Cd of 1:1. However, the amount of P required for Pb was based on a molar ratio of P:Pb of 3:5 (Ma et al., 1993). The amounts of Pb, Cd, and Zn were summed for each application rate method and then divided by the percent P per chemical treatment. To ensure a calcareous soil environment and formation of metal carbonates, $CaCO_3$ treatment was applied at 100 g kg^{-1}. Alkaline biosolids treatment was applied at 200 g kg^{-1} based on its calcium carbonate equivalence (CCE) (Rund, 1984).

Contaminated soil (100 g), air-dried and sieved at <2 mm, was incorporated with each treatment and incubated in 500 g acid-washed I-CEM jars (Fisher Scientific). Each treatment, except for $CaCO_3$ and biosolids, was applied at four application amounts with three replications per treatment and control (Table 2). The control was untreated, contaminated soil. Application of DAP, MAP, and Na_2HPO_4, at the E1 and E1E2 amount, were made by addition of appropriate volumes of dissolved phosphate

solution to the contaminated soil. All other treatments and application amounts were dry when added to the soil. After all treatments were incorporated with the soil, 100 mL of deionized water was added to each jar and stirred. All jars were placed in a constant temperature room at 35°C. The jars were dried and re-wet with 100 mL of deionized water. This wet/dry process was repeated a total of three cycles. At the conclusion of the wet/dry cycling, the samples were made into a paste and allowed to incubate for 38 days. Combination treatments (DAP + $CaCO_3$ or DAP + alkaline biosolids) were performed sequentially. The DAP was added first, three wet/dry cycles, $CaCO_3$ and alkaline biosolids were added, followed by another three wet/dry cycles and the soil saturation paste procedure. Paste-like consistency and incubation were continued for 38 days. To maintain the paste consistency throughout the incubation period, each jar was stirred and watered on a daily basis. All jars were subsampled on days 1, 19, and 38.

Treated soils and controls were then evaluated for reduction of metal availability by the extraction of 1.0 g of treated soil with 20 mL of 0.1 M $Ca(NO_3)_2$ solution, which is the most available metal fraction according to a modified procedure of Basta and Gradwohl (2000). All extractions contained 1.0 gram of soil and 20.0 mL of 0.1 M $Ca(NO_3)_2$ solution in a 50-mL polycarbonate centrifuge tube. The tubes were shaken end-to-end for 16 hours. The supernatant, after centrifuging, was filtered through a 0.45μm membrane filter; extracted metal solutions were acidified with 1.0 mL of concentrated HCl, and stored in a refrigerator at 4°C. Determination of Pb, Zn, and Cd in the extracted solutions was performed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

Analysis of variance using a randomized complete block design and subsequent separation of means by Duncan's Multiple Range Test (SAS, 1988) was used to compare results between extractable metals and treatments.

RESULTS

Treatment effectiveness for the screening procedure was determined using 0.1M $Ca(NO_3)_2$ extraction (E1). Subsamples of soil were taken from each jar of the screening procedure at the beginning (day 1), middle (day 19), and conclusion (day 38) of the incubation period. Lead was below the detection limit of 0.8 mg kg^{-1} soil; therefore, numbers will only be reported for Zn and Cd. Statistical analysis of the screening procedure data was performed within each application amount to show differences between treatments for both Zn and Cd.

Application Amount Based on E1

The quantity of extractable Zn for this application amount decreased with the following treatments: MAP, DAP > control, Na_2HPO_4 > $CaCO_3$, DAP + $CaCO_3$ > alkaline biosolids, DAP + alkaline biosolids. The application of DAP at the E1 amount caused a significant increase of extractable Zn compared to the control (Table 3). The amount of zinc in the control increased from 268 to 437 mg kg^{-1} by the addition of DAP at the E1 application amount. The addition of Na_2HPO_4 to the contaminated soil at the E1 application amount had no effect on extractable Zn. The amount of Zn before the application of Na_2HPO_4 was 268 mg kg^{-1} and 278 mg kg^{-1} after the application of Na_2HPO_4 (Table 3). The pH of the soil was not affected by the application of Na_2HPO_4 at the E1 amount. When comparing the DAP and Na_2HPO_4 treatments at the E1 application amount, it was observed that the two treatments were significantly different from each other, but the DAP increased extractable Zn while Na_2HPO_4 had no effect on Zn concentration. The combination treatment of DAP + $CaCO_3$ at the E1 application amount decreased Zn from 268 mg kg^{-1} (control) to 219 mg kg^{-1} (Table 3). The pH of 7.2 was unaffected by the application of DAP + $CaCO_3$ (Table 4). Extractable Zn of 219 mg kg^{-1} was less after the addition of DAP + $CaCO_3$ than extractable Zn after the application of Na_2HPO_4 (278 mg kg^{-1}). DAP + alkaline biosolids reduced Zn from 268 mg kg^{-1} to 52.8 mg kg^{-1}. DAP + alkaline biosolids increased soil pH from 7.2 to 7.7 (Table 4). The DAP + alkaline biosolids treatment not only had significant difference from the control, but significant differences were also found between DAP, Na_2HPO_4, and DAP + $CaCO_3$ treatments and the DAP + alkaline biosolids treatment. The MAP treatment increased extractable Zn from 268 mg kg^{-1} to 453 mg kg^{-1}. The pH of the MAP treated soil was 6.8, which was lowered from that of the control. Compared to all other phosphate treatments, the addition of MAP and DAP at the E1 application amount caused the highest increase of extractable Zn. The application of $CaCO_3$ at the E1 amount increased the soil pH from 7.2 to 7.4, and reduced extractable Zn from 268 mg kg^{-1} to 198 mg kg^{-1}. The $CaCO_3$ treatment was significantly different from all other treatments, with exception to the DAP + $CaCO_3$ treatment. Biosolids treatment raised soil pH from 7.2 to 7.8 and reduced extractable Zn from 268 mg kg^{-1} to 87.6 mg kg^{-1}. The most effective treatment at lowering Zn was biosolids.

The quantity of extractable Cd for the E1 application amount decreased with the following treatments: MAP, DAP > control, Na_2HPO_4, > $CaCO_3$, DAP + $CaCO_3$, > alkaline biosolids, DAP +

alkaline biosolids. The application of DAP, as observed with the Zn data, caused an increase in extractable Cd from 24.3 mg kg^{-1} to 29.0 mg kg^{-1}. The addition of Na_2HPO_4 at the E1 application amount caused a small but significant decrease in extractable Cd from 24.3 mg kg^{-1} to 21.2 mg kg^{-1}. The pH was unaffected by the application of Na_2HPO_4. In comparison to DAP, the Na_2HPO_4 treatment decreased extracted Cd. The combined application of DAP + $CaCO_3$ decreased extractable Cd from 24.3 mg kg^{-1} to 16.9 mg kg^{-1}. No effect on pH was observed after the application of DAP + $CaCO_3$. The DAP + $CaCO_3$ treatment resulted in a Cd reduction of 24.3 mg kg^{-1} to 16.9 mg kg^{-1}. The DAP + $CaCO_3$ treatment had a Cd concentration that was significantly less than the Cd concentration of the Na_2HPO_4 treated soil. The DAP + alkaline biosolids treatment produced a reduction in extractable Cd from 24.3 mg kg^{-1} to 1.56 mg kg^{-1}. The DAP + alkaline biosolids was found to be significantly different from the DAP, Na_2HPO_4, and DAP + $CaCO_3$ treatments, and produced a reduction in extractable Cd of 24.3 mg kg^{-1} to 1.56 mg kg^{-1}. The MAP treatment resulted in the highest increase of ex-tractable Cd, with an increase of 24.3 kg mg^{-1} to 26.8 mg kg^{-1}. Monoammonium phosphate, like DAP, caused an increase in extractable Cd and a decrease in pH. The addition of $CaCO_3$ to the contaminated soil produced a higher pH (7.4) and significantly reduced the Cd concentration from 24.3 mg kg^{-1} to 17.7 mg kg^{-1}. The $CaCO_3$ treatment was significantly different from all other treatments except for the combined treatment of DAP + $CaCO_3$. Cadmium concentrations were decreased from 24.3 mg kg^{-1} to 2.34 mg kg^{-1} and soil pH was increased from 7.2 to 7.8 by the addition of alkaline biosolids. The alkaline biosolids treatment was not significantly different from the combined treatment of DAP + alkaline biosolids.

Application Amount Based on E1E2

The quantity of extractable Zn for this application amount decreased with the following treatments: DAP, MAP > control, Na_2HPO_4, DAP + $CaCO_3$ > $CaCO_3$ > DAP + alkaline biosolids, alkaline biosolids. As observed at the E1 application amount, the DAP treatment at the E1E2 application amount resulted in an increase in extractable Zn from 268 mg kg^{-1} to 467 mg kg^{-1}. The addition of DAP caused a decrease in soil pH from 7.2 to 6.9. Na_2HPO_4, when applied at the E1E2 amount, was found to have no significant difference from the control. The Na_2HPO_4 treatment increased soil pH from 7.2 to 7.5. The DAP + $CaCO_3$ treatment at the E1E2 amount showed no significant difference from the control.

The addition of DAP + alkaline biosolids decreased Zn concentration from 268 mg kg^{-1} to 60.1 mg kg^{-1}. The DAP + alkaline biosolids treatment was significantly different from all other phosphate treatments, and resulted in a decrease in Zn concentration from 268 mg kg^{-1} to 60.1 mg kg^{-1}. The MAP treatment at the E1E2 amount caused a significant increase in the Zn concentration. The Zn concentration was increased from 268 mg kg^{-1} to 498 mg kg^{-1} as a result of the application of MAP. The soil pH decreased from 7.2 to 6.9 after the addition of MAP. MAP and DAP have a similar effect on soil pH, but it was the application of MAP that caused the larger increase in extractable Zn. The $CaCO_3$ treatment at the E1E2 application amount raised the soil pH from 7.2 to 7.4 and decreased the amount of extractable Zn from 268 mg kg^{-1} to 220 mg kg^{-1}. This is similar to the reduction of Zn seen in the E1 application amount because $CaCO_3$ was added at the same amount for all application amounts. These similarities were also observed for alkaline biosolids, because they too were applied at one standard amount. Alkaline biosolids, as observed at the E1 rate, caused a reduction in extractable Zn and an increase in soil pH.

The quantity of extractable Cd for the E1E2 application amount decreased with the following treatments: DAP, MAP > control > Na_2HPO_4, DAP + CaCO3, $CaCO_3$ > DAP + alkaline biosolids, alkaline biosolids. The pattern of DAP that has been observed for all other application amounts of Zn are also present for Cd at the E1E2 application amount. DAP decreased soil pH and increased extractable Cd from 24.3 mg kg^{-1} to 28.8 mg kg^{-1}. Application of Na_2HPO_4 at the E1E2 amount resulted in a reduction of Cd from 24.3 mg kg^{-1} to 18.7 mg kg^{-1}. Soil pH was slightly increased from 7.2 to 7.5 by the application of Na_2HPO_4 at this amount. The DAP + $CaCO_3$ treatment at the E1E2 application amount caused a decrease in extractable Cd (24.3 mg kg^{-1} to 18.3 mg kg^{-1}) and a slight decrease of pH from 7.2 to 7.1. The DAP + alkaline biosolids treatment at the E1E2 application amount decreased the Cd concentration from 24.3 mg kg^{-1} to 1.35 mg kg^{-1}, as well as increased the soil pH from 7.2 to 7.8. Results of the DAP + alkaline biosolids treatment was significantly different from all other phosphate treatments. MAP caused a significant increase in Cd concentration from 24.3 mg kg^{-1} to 27.8 mg kg^{-1} for the E1E2 application amount. No significant differences were found between the treatments of Na_2HPO_4, DAP + $CaCO_3$ and $CaCO_3$. Because $CaCO_3$ and biosolids treatments were added at the same amount for all applications, the results are the same for the E1E2 application amount and Cd.

Application Amount Based on Bioaccessibility

The quantity of extractable Zn for this application amount decreased with the following treatments: DAP, DAP + $CaCO_3$, MAP > control, DAP + alkaline biosolids, $CaCO_3$ > Na_2HPO_4, alkaline biosolids. The treatment of DAP at the in vitro application amount caused an increase in extractable Zn from 268 mg kg^{-1} to 549 mg kg^{-1} and soil pH was decreased from 7.2 to 6.1. The application of Na_2HPO_4 at this amount decreased the Zn concentration from 268 mg kg^{-1} to 1.43 mg kg^{-1}, but caused a large increase in soil pH from 7.2 to 10.6. Addition of DAP + $CaCO_3$ at the in-vitro application amount resulted in an increase of extractable Zn from 268 mg kg^{-1} to 499 mg kg^{-1} and decreased soil pH from 7.2 to 6.3. The DAP + alkaline biosolids treatment showed no significant difference in Zn concentration from the control. MAP at the in-vitro application amount increased the Zn concentration from 268 mg kg^{-1} to 1440 mg kg^{-1} and decreased the soil pH from 7.2 to 5.8. Again, the application of $CaCO_3$ and biosolids are the same for all amounts; therefore, no variation in the data is reported for these treatments at this application amount.

The quantity of extractable Cd for the bioaccessible application amount decreased with the following treatments: control > $CaCO_3$ > DAP > DAP + $CaCO_3$, MAP > Na_2HPO_4, DAP + alkaline biosolids, alkaline biosolids. All treatments showed a significant difference from the control. DAP application at the bioaccessible amount decreased Cd concentrations from 24.3 mg kg^{-1} to 12.7 mg kg^{-1} and soil pH was decreased from 7.2 to 6.1. The Na_2HPO_4 treatment reduced the Cd level from 24.3 mg kg^{-1} to 0.33 mg kg^{-1}. The soil pH was elevated from 7.2 to 10.6 by the application of Na_2HPO_4. The Na_2HPO_4 treatment had no significant difference from that of the DAP + biosolids treatment. The DAP + $CaCO_3$ and treatment reduced extractable Cd from 24.3 mg kg^{-1} to 10.9 mg kg^{-1} and decreased soil pH from 7.2 to 6.3. The application of DAP + alkaline biosolids reduced Cd concentrations from 24.3 mg kg^{-1} to 1.11 mg kg^{-1} and decreased soil pH from 7.2 to 6.9. There was no significant difference between the Na_2HPO_4, DAP + alkaline biosolids and alkaline biosolids treatments. Unlike previous data, the application of MAP at the bioaccessible amount caused a decrease of 24.3 mg kg^{-1} to 11.1 mg kg^{-1} in extractable Cd. Soil pH was dropped to 5.8 after the addition of MAP. Again, no variation in data was observed for the $CaCO_3$ or biosolids treatments.

Application Amount Based on Total Contaminant Content

The quantity of extractable Zn for this application amount decreased with the following treatments: MAP > control > $CaCO_3$ > DAP, Na_2HPO_4, DAP + $CaCO_3$, DAP + alkaline biosolids, alkaline biosolids (Table 3). Addition of DAP at the total metal content application amount caused a reduction in extractable Zn from 268 mg kg^{-1} to 48 mg kg^{-1} and decreased the soil pH from 7.2 to 6.2. Application of Na_2HPO_4 at the total metal amount decreased the Zn concentration from 268 mg kg^{-1} to 15.0 mg kg^{-1} and increased the soil pH from 7.2 to 10.8. Application of DAP + $CaCO_3$ reduced extractable Zn from 268 mg kg^{-1} to 43.1 mg kg^{-1} and reduced soil pH from 7.2 to 6.3. DAP + alkaline biosolids lowered the extractable Zn level from 268 mg kg^{-1} to 66.3 mg kg^{-1} and reduced soil pH from 7.2 to 6.5. The combination treatment of DAP and alkaline biosolids was not statistically different from the alkaline biosolids treatment. Addition of MAP at the total metal content application amount increased extractable Zn from 268 mg kg^{-1} to 574 mg kg^{-1} and lowered soil pH from 7.2 to 5.8. Again, no variation in data was observed for the $CaCO_3$ or biosolids treatments. There was no significant difference between DAP, Na_2HPO_4, DAP + $CaCO_3$, DAP + alkaline biosolids, and alkaline biosolids treatments.

The quantity of extractable Cd for the total metal content application amount decreased with the following treatments: control > $CaCO_3$ > MAP > DAP, DAP + $CaCO_3$ > Na_2HPO_4, DAP + alkaline biosolids, alkaline biosolids. DAP applied at the total content amount reduced extractable Cd from 24.3 mg kg^{-1} to 3.28 mg kg^{-1} and reduced soil pH from 7.2 to 6.2. The addition of Na_2HPO_4 lowered the extractable Cd level from 24.3 mg kg^{-1} to 0.46 mg kg^{-1} and increased soil pH from 7.2 to 10.8. The application of DAP + $CaCO_3$ reduced extractable Cd levels from 24.3 mg kg^{-1} to 2.98 mg kg^{-1} and decreased soil pH from 7.2 to 6.3. Significant differences were observed between DAP + $CaCO_3$ and $CaCO_3$ treatments. The application of DAP + alkaline biosolids at the total content amount reduced Cd concentration from 24.3 mg kg^{-1} to 1.27 mg kg^{-1} and reduced soil pH from 7.2 to 6.5. No significant differences were observed between the DAP + alkaline biosolids and alkaline biosolids treatments. The addition of MAP at the total metal application amount reduced the extractable Cd level from 24.3 mg kg^{-1} to 9.14 mg kg^{-1} and reduced soil pH from 7.2 to 5.8. Cd concentrations for $CaCO_3$ and biosolids are consistent with other application amounts due to the standard application amount of the two treatments.

DISCUSSION

Applications of DAP based on E1, E1E2, and bioaccessibility decreased soil pH and increased extractable Zn. However, the application of DAP based on total content, the largest amount of DAP applied, decreased extractable Zn. Although soil pH was decreased, the total content application amount of DAP was large enough to form phosphate precipitates and remove Zn from solution, thereby decreasing extractable Zn. Similar results were found for reduction of extractable Cd by DAP. Application of DAP based on E1, E1E2 decreased soil pH and increased extractable Cd. However, application of DAP based on bioaccessibility and total content, the two largest amounts of DAP applied, decreased extractable Cd. Although soil pH was decreased, the bioaccessibility and total content application amount of DAP were large enough to form phosphate precipitates and remove Cd from solution, thereby decreasing extractable Cd. However, less DAP was required to achieve these results for Cd than Zn. The contaminated soil had a Zn concentration that was much larger than that of the Cd concentration and required much larger amounts of phosphate to immobilize Zn than Cd.

A previous study conducted by McGowen et al. (2001) treated the same soil used in this study with DAP at 460, 920, 2300 mg kg^{-1} to reduce the mobility of Pb, Zn, and Cd. Treatment amounts used by McGowen et al. (2001) corresponded to $P:(Cd+Zn+Pb)_{Total}$ of 1:74, 1:37, and 1:15 on a molar basis. Treatment amounts in our study corresponded to $P:(Cd+Zn+Pb)_{Total}$ of 1:1 for the E1, E1E2, bioaccessibility, and total content. In general, much larger amounts of DAP were used in our study compared to McGowen et al. (2001). Metal mobility, measured in column effluent, was decreased by treatment with DAP. Zinc mobility was decreased at lowest application rate of 1:74 and increased applications did not further reduce Zn mobility. Reductions of mobile Cd was 1:15 > 1:37 > 1:74. Comparison of results between studies show much greater amounts of DAP were required to reduce E1 extractable Zn and Cd in this contaminated soil. Soil pH (6.5 to 6.9) of DAP-treated soil in McGowen et al. (2001) was similar to E1 and E1E2 treatments in our study. Differences in metal mobility and extractable Zn and Cd could not be attributed to differences in soil pH.

The application of Na_2HPO_4 caused a decrease in extractable Zn at all application amounts, except for the E1 application amount, which was not significantly different from the control. However, all application amounts of Na_2HPO_4 resulted in a reduction of extractable Cd. It is believed that not only did Na_2HPO_4 treatments provide a phosphorus source for the precipitation of Zn and Cd

phosphates but also caused an increase in soil pH. By increasing the pH, this treatment was capable of precipitating even more of the metals out of solution. The application of Na_2HPO_4 at the bioassessible and total metal amounts caused increases of the soil pH to greater than 10. Not only was an excessive pH produced by these two application amounts, but elevated EC values were observed. Previous work done by Cotter-Howells et al. (1996) used Na_2HPO_4 to form insoluble Pb and Zn phosphates. Cotter-Howells et al. (1996) applied Na_2HPO_4 at an amount of 100 g kg^{-1} of soil and the presence of heavy metal phosphates were characterized using an automated SEM image analysis program. In comparison to our research, our largest application of Na_2HPO_4 was 130 g kg^{-1} of soil and the treatment's ability to reduce heavy metals was measured using a 0.1 M $Ca(NO_3)_2$ extraction. Their research showed that use of Na_2HPO_4 as a soil amendment induced the formation of Pb and Zn phosphates in mine-waste contaminated soils, thereby reducing the availability of these metals to the ecosystem. Similarly, our study showed that an increase in Na_2HPO_4 application amounts causes a reduction in the level of Zn and Cd extractability. Cotter-Howells et al. (1996) did not report the effect of Na_2HPO_4 on the soil pH or EC. The application amount of 100 g kg^{-1} of soil used by Cotter-Howells et al. (1996) was between the bioaccessible and total content application amount used in our study. Thus it is suggested that elevated pH and EC levels might have existed in the Cotter-Howells et al. (1996) study; this could create problems for biological systems and cause soil dispersion.

The addition of MAP caused an increase in extractable Zn at all application amounts. However, applications of MAP at the E1 and E1E2 amount caused an increase in extractable Cd but a decrease in extractable Cd at the bioaccessible and total content application amounts. The soil pH decreased as the application amount of MAP increased. The acidifying nature of MAP is believed to be the reason for the increased extractable Zn at all application amounts and extractable Cd at the E1 and E1E2 application amounts. Decreasing soil pH causes an increase in metal solubility, thereby increasing the concentration of Zn and Cd in solution. To my knowledge, the use of MAP as an immobilization treatment to remediate heavy metal contaminated soil has not been reported.

The application of $CaCO_3$ to the contaminated soil was based on one standard amount (100 g of $CaCO_3$ kg^{-1} soil); therefore the amount of extractable Zn and Cd was consistent for all application amounts. The application of $CaCO_3$ reduced the Zn and Cd concentrations by raising the pH and precipitating the heavy metals from solution. Berti and Cunningham (1997) applied $CaCO_3$ at rates as

high as 10% (10 g $CaCO_3$ 100 g^{-1} of soil), which is identical to the application amount used in our study, and evaluation of treatment effectiveness was measured by sequential chemical extraction, Pb leach test (scaled-down version of the standard toxicity characteristic leaching procedure TCLP), and the physiologically-based extraction test (PBET) (Ruby et al., 1996). Results of the Berti and Cunningham (1997) study only reported $CaCO_3$ amended soil data for the Pb leach test and their findings were that $CaCO_3$, when applied at rates as high as 10%, were not as effective as phosphorus (from KH_2PO_4) for reducing leachable Pb. Our study examined treatment effectiveness, as measured by a 0.1 M $Ca(NO_3)_2$ extraction, and showed that both extractable Zn and Cd concentrations were reduced by the application of $CaCO_3$ and that the application of DAP at the total content amount and Na_2HPO_4 at the bioaccessible and total content amount were more effective at reducing Zn and Cd concentrations than that of $CaCO_3$. These findings are similar to Berti and Cunningham's study (1997). It is suggested that reductions in extractable Zn and Cd occurred due to the increased soil pH, which resulted in precipitation of Zn and Cd from solution.

Like the application of $CaCO_3$, the alkaline biosolids were added at one amount (200 g alkaline biosolids kg^{-1} of soil) across all application amounts. Extractable Zn and Cd concentrations were reduced by the addition of alkaline biosolids to the contaminated soil and soil pH was increased from 7.2 to around 7.9. It is believed that mechanisms for extractable metal reductions due to the application of alkaline biosolids were precipitation and chelation. Alkaline biosolids not only increase soil pH, which can result in the precipitation of heavy metals from solution, but also alkaline biosolids provide for chelation sites for the adsorption of heavy metals. A study conducted by Conder et al. (2001) applied lime-stabilized sewage sludge (i.e. alkaline biosolids) at an amount of 100 g kg^{-1} soil and examined treatment effectiveness by a 0.1 M $Ca(NO_3)_2$ extraction and an earthworm toxicity test. The sequential extraction results by Conder et al. (2001) suggested that an increase in soil pH, as a result of the addition of alkaline biosolids, increased adsorption and/or precipitation of Cd Pb, and Zn and decreased metal availability. Our study examined the effectiveness of alkaline biosolids at an application amount that was twice as large as the application amount used by Conder et al. (2001). As seen in the study conducted by Conder et al. (2001), our study suggests that alkaline biosolids have the ability to reduce Zn and Cd concentrations.

The combined treatment of DAP + $CaCO_3$ reduced extractable Zn at the E1 and total content application amount and increased extractable Zn at the bioaccessible application amount. However, this trend was not observed for extractable Cd. Addition of DAP + $CaCO_3$ at all application amounts reduced Cd concentrations. Comparison of DAP + $CaCO_3$ showed that DAP provided an additional decrease in extractable Zn and Cd. The combined treatment of DAP + alkaline biosolids reduced extractable Zn and Cd for all application amounts. In general, addition of DAP to alkaline biosolids did not further reduce extractable Zn (Table 3). When comparing Cd concentrations between DAP + alkaline biosolids treatment and alkaline biosolids treatment, no significant differences were found between the two treatments for all application amounts. Reductions in metal extractability in the alkaline biosolids treatments were due to the chelating ability of alkaline biosolids rather than formation of metal phosphates, which is typically observed with the application of DAP. No previous research has examined the use of combination treatments to remediate contaminated soil.

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Table 1. Total content, bioaccessible, and extractable Pb, Zn, and Cd measured by sequential extraction using 0.5 M $Ca(NO_3)_2$, 1.0 M NaOAc, 0.1 M Na_2EDTA, and 4.0 M HNO_3 for smelter-contaminated soil.

Element	Total Content	Bioaccessible	Sequential Extractant			
			$Ca(NO_3)_2$	NaOAc	Na_2EDTA	HNO_3
----	mg kg^{-1}	mg kg^{-1}	----------	mg kg^{-1}	----------	
Pb	2250	910	0	14.3	1310	511
Zn	59000	33900	609	179	36100	18100
Cd	278	131	31.5	15.2	69.7	79.8

Table 2. Treatments and application amounts for the screening procedure.

Treatments	Application Amounts			
----	E1	E1E2	Bioaccessible	Total Content
-----	----------	g kg^{-1} soil	----------	
DAP	1.26	1.65	69.0	120
Na_2HPO_4	1.40	1.80	74.4	130
DAP + $CaCO_3$	1.26 + 100	1.65 + 100	69.0 + 100	120 + 100
DAP + Biosolids	1.26 + 200	1.65 + 200	69.0 + 200	120 + 200
MAP	1.10	1.44	60.2	105
$CaCO_3$	100	100	100	100
Biosolids	200	200	200	200
Control	0	0	0	0

Table 3. Extractable Zn for immobilization treatments and application amounts.

Treatment	Extractable Zn of Application Amount			
	E1	E1E2	Bioaccessible	Total Content
	---------- mg kg^{-1} ----------			
Control	268 d†	268 c	268 b	268 c
DAP	437 e	467 d	549 c	48 a
Na_2HPO_4	278 d	255 c	1.43 a	15.0 a
DAP + $CaCO_3$	219 c	278 c	499 c	43.1 a
DAP + Biosolids	52.8 a	60.1 a	158 b	66.3 a
MAP	453 e	498 e	1440 d	574 d
$CaCO_3$	198 c	220 b	216 b	205 b
Biosolids	87.6 b	64.9 a	68.9 a	73.2 a

† Within a column, mean values followed by the same letters were not statistically different at the 5% level.

Table 4. Effect of treatment and application amount on soil pH.

Treatment	Soil pH of Treatment Application			
	E1	E1E2	In Vitro	Total Content
DAP	6.6	6.9	6.1	6.2
Na_2HPO_4	7.2	7.5	10.6	10.8
DAP + $CaCO_3$	7.2	7.1	6.3	6.3
DAP + Biosolids	7.7	7.8	6.9	6.5
MAP	6.8	6.9	5.8	5.8
$CaCO_3$	7.4	7.4	7.5	7.6
Biosolids	7.8	7.9	7.8	7.9
Control	7.2	7.2	7.2	7.2

Table 5. Extractable Cd for immobilization treatments and application amounts.

Treatment	Extractable Cd of Application Amount			
	E1	E1E2	Bioaccessible	Total Content
	mg kg^{-1}			
Control	24.3 d†	24.3 c	24.3 e	24.3 d
DAP	29.0 f	28.8 e	12.7 c	3.28 b
Na_2HPO_4	21.2 c	18.7 b	0.33 a	0.46 a
DAP + $CaCO_3$	16.9 b	18.3 b	10.9 b	2.98 b
DAP + Biosolids	1.56 a	1.35 a	1.11 a	1.27 a
MAP	26.8 e	27.8 d	11.1 b	9.14 c
$CaCO_3$	17.7 b	18.6 b	18.0 d	17.2 d
Biosolids	2.34 a	2.41 a	1.82 a	1.87 a

† Within a column, mean values followed by the same letter were not statistically different at the 5% level.

CHAPTER 2

IMMOBILIZATION TREATMENT EFFECTS ON THE REDUCTION OF RISK TO HUMAN AND ECOLOGICAL HEALTH

ABSTRACT

The use of DAP as an immobilization treatment to reduce risk of heavy metal-contaminated soil to the human soil ingestion pathway and/or earthworm survival has not been investigated. The objectives of this study were to evaluate the effectiveness of diammonium phosphate (DAP), sodium phosphate (Na_2HPO_4), calcium carbonate ($CaCO_3$), and alkaline biosolids (AB) to reduce lead (Pb), cadmium (Cd), and zinc (Zn) levels that pose risk to humans via soil ingestion and earthworms (*Eisenia andrei*). Contaminated soil (59,000 mg kg^{-1} Zn, 2250 mg kg^{-1} Pb and 278 mg kg^{-1} Cd) was treated with 69.0 g kg^{-1} or 120 g kg^{-1} of DAP, 74.4 g kg^{-1} or 129 g kg^{-1} of Na_2HPO_4, 100 g kg^{-1} of $CaCO_3$, and 200 g kg^{-1} of AB. Treatments were evaluated using an in vitro gastrointestinal method to determine bioaccessible Pb and Cd from soil ingestion and a 28-day earthworm (*Eisenia andrei*) toxicity test. Phosphate treatments based on total metal content and AB reduced bioaccessible Pb from 1130 mg kg^{-1} to 968 mg kg^{-1} and 1240 mg kg^{-1}, respectively. The following treatments reduced bioaccessible Cd (percent reduction): 120 g kg^{-1} DAP (22.1%), 74.4 g kg^{-1} Na_2HPO_4 (18.5%), 129 g kg^{-1} Na_2HPO_4 (27.5%), $CaCO_3$ (14.1%), and AB (39.2%). DAP treatment caused 100% earthworm mortality in the first 24 hours of the toxicity test as a result of elevated salinity (electrical conductivity, EC = 12 dS m^{-1}) and extractable NH_4 of 4800 mg kg^{-1}. Also, Na_2HPO_4 treatment resulted in 100% earthworm mortality due to salinity (EC = 18.1 dS m^{-1}). Soil treated with $CaCO_3$ and AB had <20% earthworm mortality throughout the 28-day toxicity test. In order for the phosphate treatments to reduce bioaccessible Pb, the application amounts must be based on total metal content. Extractable Cd was reduced by both the bioaccessible and total content application amounts.

Elimination of high salinity and high NH_4 from the phosphate treatments must be achieved to reduce earthworm mortality.

INTRODUCTION

Immobilization of contaminants by in situ treatment of soil is an area of growing interest in the field of environmental and soil science. Research has focused on understanding chemical methods in soil, such as sorption, precipitation, chelation, and ion exchange that occur when various treatments are applied to the soil to reduce the availability of heavy metals. On the other hand, little research has been published about evaluation of the effectiveness of soil treatments to reduce risk to humans and the ecosystem. Past research has primarily focused on reduction of metal availability for crop yields and plant tissue metal concentration (Pierzynski and Schwab, 1993).

The question then arises: are immobilization treatments reducing the bioavailable fraction of contaminants that pose a risk to humans and the ecosystem? In-vivo animal models are one approach to determine the effect of contaminant bioavailability associated with soil ingestion by humans and to evaluate potential risk. Animal models have been used as surrogate methods to estimate human bioavailability. The expense and time constraints associated with animal models have increased interest in in-vitro chemical methods that simulate the gastrointestinal environment (Rodriguez et al., 1999). The development of a standard in vitro chemical method would give researchers a less expensive and quicker tool to use when evaluating the effectiveness of immobilization treatments on the reduction of metal bioavailability. In-vitro methods have been used for Pb (Ruby et al., 1999) and As (Rodriguez et al., 1999) to estimate oral bioavailability to humans. For a contaminant to pose a risk, it must first dissolve in the gastrointestinal fluid followed by subsequent absorption of the contaminant across the intestinal epithelium into the bloodstream. In order for an immobilization treatment to be considered effective, it must have the ability to reduce the fraction of contaminant that becomes soluble in the gastric solution of the stomach (i.e., bioaccessible fraction). Bioaccessibility is defined as the solubility of a metal in simulated stomach and intestinal solutions of the physiologically based extraction test (PBET) relative to the total metal in the soil (Berti and Cunningham, 1997). If a treatment can successfully bind with the bioavailable fraction of a chemical, it will reduce dissolution in the stomach and, in turn, reduce the amount of chemical that is available for absorption into the bloodstream. The development and validation of such an extraction method would allow for the risk from metals in soil to

be assessed on the basis of the site-specific fraction of bioavailable metals (Ruby et al., 1999). Basing soil amendment efficiency on the ability to reduce risk of Pb in soil is common practice because Pb often "drives the risk" associated with a contaminated site. In order to advance in situ remediation technologies, research must show that these treatments can reduce the risk that contaminated soils pose to humans.

Earthworm toxicity tests are another tool for researchers to use when evaluating the effectiveness of immobilization treatments for reduction of risk to ecosystems. Earthworms have been proposed as a good model for ecosystem risk because they are organisms that not only consume soil, but they are also in constant contact with the soil media. Few studies have used a soil invertebrate species to examine the reduction in bioavailability due to phosphorus or organic material amendments to the soil (Pearson et al., 2000). Earthworm bioassays are unique because they give the researcher the opportunity to examine several endpoints, such as mortality, contaminant accumulation (bio-accumulation) within the organism, and the potential for reproduction of the species. Soil amendments have the ability to immobilize a contaminant, but if the amendment itself is toxic to earthworms, remediation of the soil is incomplete. Earthworms are an invertebrate species found at the bottom of the trophic pyramid. If a treatment causes mortality to this species, the effects will be detrimental to all other species that rely on earthworms as a food source and effects will be observed upward throughout the trophic transfer model. The goal of remediation is to not only restore soil quality, but to restore an ecosystem by revegetating the land and promoting the return of wildlife to the area.

McGowen et al. (2001) showed that the application of diammonium phosphate (DAP) to a smelter-contaminated soil resulted in a reduction of Pb, Zn, and Cd mobility. No work to date has examined the use of DAP as an immobilization treatment to reduce the risk metal-contaminated soils pose to the human soil ingestion pathway and/or earthworm survival. The objectives of this experiment were to evaluate the effectiveness of DAP, Na_2HPO_4, $CaCO_3$, and lime-stabilized sewage sludge (alkaline biosolids) to reduce lead, cadmium, and zinc concentrations that pose risk to humans and the ecosystem by performing an in vitro gastrointestinal extraction method and an earthworm toxicity test.

MATERIALS AND METHODS

The soil used for this project was collected from a zinc smelter in northeastern Oklahoma. Elevated concentrations of Pb, Cd, and Zn were present in the soil. The soil was air-dried and sieved (<2 mm) prior to all laboratory experiments. The total metal contents for this smelter-contaminated soil were 2250 mg kg^{-1} of Pb, 59000 mg kg^{-1} of Zn, and 278 mg kg^{-1} of Cd (Table 1). The background levels for each of these chemicals are 20 mg kg^{-1} Pb, 50 mg kg^{-1} Zn, and 0.5 mg kg^{-1} Cd (Lindsey, 1979). The bioaccessible fractions of heavy metals in this soil, as determined by the in vitro gastrointestinal extraction (Rodriguez et al., 1999), were 910 mg kg^{-1} of Pb, 33900 mg kg^{-1} Zn, and 131 mg kg^{-1} Cd. The percentages for the amount of total metal content that is bioaccessible, divided by the total metal content, were 40.4% Pb, 57.5% Zn, and 47.1% Cd. The 0.1 M $Ca(NO_3)_2$ extractable metal in the contaminated soil is 0 mg kg^{-1} of Pb, 609 mg kg^{-1} of Zn, and 31.5 mg kg^{-1} of Cd. When comparing the total metal content with that of the background levels, it is clear that this contaminated soil needs to be remediated.

The treatments selected for this experiment, considered successful immobilization treatments from previous work (Chapter 1 of this thesis), were diammonium phosphate (DAP), sodium phosphate (Na_2HPO_4), $CaCO_3$, and lime-stabilized sewage sludge (i.e. alkaline biosolids). The treatment application amounts were based on bioaccessible and total metal content. Bioaccessible Pb and Cd were determined using a modified version of the in vitro gastrointestinal procedure of Rodriguez et al. (1999). Total metal concentration in the soil was determined using X-ray fluorescence (Karathanasis and Hajek, 1996). These application rates were found to be the most successful at immobilizing Pb, Cd, and Zn (Chapter 1 of this thesis).

Soil (1 kg) was treated in 2.5-quart plastic containers. The DAP and Na_2HPO_4 treatments were applied at the bioaccessible and total metal content amounts, while the $CaCO_3$ was applied at a 10% of weight basis (100 g kg^{-1}) and the alkaline biosolids were applied a 20% of weight basis (200 g kg^{-1}). There were four replications per treatment and control. Treatments were added dry and incorporated with the soil by manual stirring (Table 2). After all treatments were blended with the contaminated soil, 1 L of deionized water was added to each container and stirred. All containers were placed in a constant temperature room at 35°C. The containers were dried (2 days), then re-wet with 1000 mL of deionized water and stirred. This wet/dry cycle continued until three cycles were complete. At this

point, the soils remained in a paste-like consistency for the remainder of the incubation period. Paste-like consistency and incubation continued for thirty-two days. The chosen period of incubation was 32 days, because a preliminary study showed after 19 days little change in 0.1 M $Ca(NO_3)_2$ extractable Zn was observed. To maintain the paste consistency throughout the incubation period, each container was watered and stirred on a daily basis.

The incubation period for the full-scale immobilization experiment ended on day 32. Evaluation of treatment effectiveness was measured by in vitro gastrointestinal extraction, earthworm bioassay, lettuce germination study, and lettuce growth study.

Bioaccessible Pb and Cd

The in vitro extraction is an indirect measure of gastrointestinal availability. The modified in vitro gastrointestinal extraction, which contains no food ("dough") (Rodriguez et al., 1999), was used in this experiment. In this method, soil (4 g) is added to 600 mL of a simulated gastrointestinal solution containing 1% pepsin in 0.15M NaCl, with the pH adjusted and maintained to 1.8. The soil and solution were combined in 1L glass canning jar, which served as the reactor vessel. The reactor vessels were then placed into a water bath at 37°C and an individual paddle stirrer was installed in each vessel at a speed of approximately 100 rpm. Each vessel contained one combination pH electrode and one argon (Ar) gas dispersion apparatus. Ar gas was diffused into the vessel throughout the entire extraction to maintain an anaerobic atmosphere. Once the pH electrode and Ar gas diffuser were attached to the reactor vessel, the pH was adjusted to and maintained at 1.8 for one hour. At the end of one hour, two-20 mL aliquots of extraction were removed from each vessel and centrifuged at 10,000 rpm for 15 minutes. The supernatant was then syringe-filtered through a 0.45 μm filter. Extracted samples were filtered into vials and refrigerated until analysis by ICP.

Earthworm Bioassay

For the earthworm bioassays, 200 g of soil was weighed into mason jars. The Standard Guide for Conducting Laboratory Soil Toxicity Tests With the Lumbricid Earthworm *Eisenia fetida* (ASTM E 1676-97) was followed for all earthworm bioassays, except *Eisenia andrei* earthworms were substituted for *Eisenia fetida.* The toxicity test was conducted on all treatments and applications, plus a control and an artificial soil. Each jar received 60 mL of deionized water, except for the artificial soil, which received 70

mL of water. All jars were moistened to approximately 80% water holding capacity 24 hours prior to the addition of the earthworms. Earthworms were obtained from in-house cultures and allowed to depurate any food or culture bedding from the gastrointestinal tract for 24 hours before introduction to the test jars. Ten mature (clitellate) earthworms were placed into each jar. Three small holes were punched in each lid. The earthworm bioassay was conducted in controlled chambers with a temperature of 20°C (± 1°C) and constant light. Each jar was tested in four replications per treatment, control, and artificial soil. The earthworm toxicity test was conducted for 28 days. All jars were checked and counted daily for the first seven days of the test and once a week after seven days. During each jar check, any deceased earthworms were removed immediately, cleaned with deionized water, laid flat on aluminum foil, rolled, and stored in the freezer. Earthworms were considered dead when no movement resulted from gentle contact was observed. Earthworms were fed horse manure every seven days throughout the entire 28-day study. All earthworms that survived the duration of the toxicity test were rinsed thoroughly, laid flat on aluminum foil, rolled, and stored in the freezer. The soil from each jar was stored in the freezer.

The DAP treatment was successful at immobilizing the Pb, Cd, and Zn in the contaminated soil but was toxic to earthworms. An experiment was designed to determine if ammonium or salinity was causing mortality in the earthworms for the DAP treated soils. The design of this experiment had three treatments: a low salinity/high NH_4 soil, a high salinity/low NH_4 soil, a low salinity/low NH_4 soil, and a control (Table 3). These treatment combinations were achieved by the addition of NH_4Cl, KCl to uncontaminated, low NH_4, low salinity soil (Richfield soil), and leached DAP treated soil. To achieve a low salinity/high NH_4, 7.61 grams of NH_4Cl was added to 200 g of clean (non-contaminated) soil and then this combination was leached with deionized water. A combination of 5.45 grams of KCl and 200 grams of clean soil created the high salinity/low NH_4 soil. The DAP treatment at the bioaccessible application amount was leached in order to produce a soil with low salinity/low NH_4. Once desired salinity and NH_4 levels were achieved, a 7-day earthworm bioassay was performed. The control for this experiment was a noncontaminated soil from Richfield (Aridic Argiustolls). Each treatment and control were tested in triplicate. The procedure for a seven-day earthworm toxicity test was identical to that of the 28-day earthworm toxicity test, except for the duration time of the test. Each jar contained 200 grams of the spiked soils, noncontaminated soil, and artificial soil. Soils were moistened to 1/3 bar, which was approximately 70 mL of deionized water per jar,

24 hours prior to the beginning of the test. After 24 hours of depuration, 10 mature (clitellate) earthworms were added to each jar and placed in to a controlled chamber at 20°C (± 1°C). Earthworms were counted daily for survival and, if needed, water was added to the jar. Any deceased earthworms found during the test and worms remaining at the completion of the test were cleaned with deionized water, laid on aluminum foil, rolled, and stored in the freezer. The toxicity test lasted for seven days.

After discovering that both ammonium and soluble salt have fatal effects on earthworms, an experiment was designed to formulate a sequence of treatments, in combination with the DAP treatment, that would reduce ammonium levels to a concentration that would not be toxic to earthworms. Three additional treatments were added to the DAP treated soil. The three treatments were $CaCO_3$, CaO, and lime-stabilized sewage sludge (biosolids). A small screening procedure was performed with these three treatments to determine which treatment in combination with the DAP could eliminate the ammonium problem. The screening procedure involved the treatment of 50 grams of soil in 500 g acid-washed I-CHEM jars (Fisher Scientific). The soil was treated and incubated with 6.01 grams of DAP per 50 grams of soil. The soil and DAP was then saturated with 50 mL of deionized water. Three jars were prepared in this manner and incubated at 37.8°C for 24 hours. After 24 hours, the jars were administered the second treatment. Jar one received 10.0 grams of $CaCO_3$, jar two received 10.0 grams of CaO, and the third jar received 10.0 grams of alkaline biosolids. All jars received 50 mL of deionized water and incubated at 37.8°C for one week. Soil samples from each jar were removed and ammonium and pH was measured.

Because the CaO treatment had the greatest reduction in ammonium, this treatment was evaluated by an earthworm bioassay. In this study, 1 kg of contaminated soil was treated with 120 grams of DAP. The DAP was incorporated with the contaminated soil first, and then 1 L of deionized water was added and stirred. The full-scale study was done in triplicate and the first treatment, DAP, was allowed to incubate at 37.8°C for one week. At the end of one week, the second treatment, CaO (200 g kg^{-1}), was added to each replicate of DAP treated soil. Once the CaO was adequately incorporated, 1 L of deionized water was added to each replicate. After the addition of CaO, the treated soils were incubated at 37.8°C for three weeks. At the end of three weeks, subsamples were taken from each replicate and pH and ammonium were measured.

Because of the high pH (pH > 10) of the CaO and DAP treated soil, a titration was performed on the treated soil to determine the amount of acid required to lower the pH to 7. For the titration, 200 grams of

treated soil was combined with 500 mL of deionized water in a 1L glass canning jar (2 replications). A paddle stirrer was placed in each jar and a combination pH electrode was attached to the side of each jar. A 3M HCl solution was prepared and used for the titration. The initial pH for each jar was approximately 12.5. The amount of acid required to adjust the pH from 12.5 to 7.0 was determined to be 167 mL of 3M HCl. The titration was conducted for six days and changes in pH were recorded daily after each addition of acid.

A large plastic container with lid was used to treat the soil. Diammonium phosphate and CaO treated soil (1 kg) was placed in a plastic container with lid and deionized water and 835 mL of 3M HCl was added. The soil was allowed to shake for one day. The lid to the container was frequently opened to release any accumulated gas. After shaking the solution for one day, the container was allowed to settle and the solution was removed for the container. The soil was then dried and pH and salinity was determined to be 66.0 dS/m. In order to reduce the EC, the soil was leached with 500 mL of deionized water until the salinity was less than 1 dS m^{-1}. A 7-day acute earthworm bioassay was performed, as previously described, on the treated soil.

Analysis of variance using a randomized complete block design and subsequent separation of means by Duncan's Multiple Range Test (SAS, 1988) was used to compare results between in vitro extractable metals of the control and treatments.

RESULTS

The effectiveness of the immobilization treatments was evaluated by an in vitro gastrointestinal (bioaccessibility) extraction and an earthworm bioassay. Treatment effects on soil pH and EC are reported in Table 4. The pH of the control (no treatment) was 7.45. Soil pH, after the application of DAP, $CaCO_3$, and biosolids, ranged from 7.33 to 7.85. The Na_2HPO_4 treatment at the in vitro application amount raised the pH to 10.34, while the total content application amount raised the pH to 10.89. The pH values were raised in these treatments due to the excessive amount of sodium that was added to the soil. $CaCO_3$ and biosolids had little effect on EC. The EC before treatment was 2.66 dS m^{-1}, which increased to 2.69 dS m^{-1} after the application of $CaCO_3$ and 2.94 dS m^{-1} after the application of biosolids. The application of DAP and Na_2HPO_4 at both application amounts raised the EC to a level that inhibited earthworm survival. The EC for DAP at the in vitro amount was 11.8 dS m^{-1} and 13.4 dS

m^{-1} for the total content amount. Na_2HPO_4 at both application amounts had an even stronger effect on EC. The EC for the in vitro amount was raised to 18.1 dS m^{-1} and 27.0 dS m^{-1} for the total content amount.

Bioaccessible Pb and Cd

The effect of remediation treatments on lead (Fig. 1) and cadmium (Fig. 2) extracted by the in vitro gastrointestinal method was determined. Treatments that reduced in vitro extractable lead ($P < 0.05$, Fig. 1) were DAP applied at the total content amount, Na_2HPO_4 applied at the total content amount, and alkaline biosolids applied at 200 g kg^{-1}. The DAP treatment (at the total content application amount) reduced bioaccessible Pb 27.2% to 968 mg kg^{-1}. Bioaccessible Pb was reduced 18.2% to 1090 mg kg^{-1} by the addition of Na_2HPO_4 at the total content application amount. Biosolids had the largest reduction of bioaccessible Pb with a 37.6% reduction to 828 mg kg^{-1}. All other treatments and application amounts had no effect on in vitro gastrointestinal available Pb.

Bioaccessible cadmium was reduced by four of the six remediation treatments (Fig. 2). Reduction of bioaccessible cadmium occurred in the following treatments and application amounts: DAP (total content amount), Na_2HPO_4 (in vitro and total content amounts), $CaCO_3$ (100 g kg^{-1} soil), and biosolids (200 g kg^{-1} soil). The bioaccessible Cd of the untreated contaminated soil (166 mg kg^{-1}) was reduced: 22.1% to 129 mg kg^{-1} by DAP at total content application amount, 18.6% to 135 mg kg^{-1} by Na_2HPO_4 at the in vitro application amount, 27.5% to 120 mg kg^{-1} by Na_2HPO_4 at the total content application amount, 14.1% to 143 mg kg^{-1} by $CaCO_3$, and 39.2% to 101 mg kg^{-1} by alkaline biosolids. The addition of DAP at the bioaccessible amount was the only remediation treatment that did not have significant reduction of cadmium from that of the control.

Earthworm Bioassay

The results of the earthworm bioassay are reported in Table 5. Results are presented in a mean percentage cumulative mortality value (averaged for all four replications) over a period of 672 hours (28 days). Both the DAP and Na_2HPO_4 treatments at the bioaccessible and total content application amounts were toxic to the earthworms, resulting in 100% mortality of the 10 worms per jar within the first 24 hours of the study. The $CaCO_3$ treated soil had a 7.5% mortality value at the conclusion of the procedure. Thirty-seven of the 40 worms (4 replications with 10 worms per jar) survived within the

$CaCO_3$ treated soil. At the completion of the earthworm bioassay, the biosolids treatment had 17.5% cumulative mortality. Of the 40 worms exposed to the biosolids treatment, 33 worms survived the bioassay in the treatment. The cumulative mortality was 0% for the artificial soil. The artificial soil is a negative control in the experiment; therefore, 0% mortality is expected and desired. The contaminated soil, with which no remedial treatments have been applied, had a cumulative mortality of 7.5%. The contaminated soil without treatment (positive control) is labeled as control in Table 5. As observed in the $CaCO_3$ treatment, 37 of the 40 worms survived in the control soil.

Due to the high mortality rate that resulted from the DAP and Na_2HPO_4 treatments, further investigation was conducted to identify what caused the 100% mortality of earthworms in these two treatments. The DAP treated soils had elevated NH_4 levels and high salinity values, while the Na_2HPO_4 treated soils had high salinity values. It was unclear as to whether the earthworm mortality was a result of the elevated levels of NH_4, high salinity, or both. Further investigation was made to determine the effect of NH_4 and/or salinity of the DAP treatment and if it could be reduced to a level that would not be toxic to the earthworms. The unleached DAP treatment had a cumulative mortality of 100% (10 dead worms) within the first 24 hours of the seven day test. The unleached bioaccessible DAP treated soil was saline (12.0 dS m^{-1}) and had a large extractable NH_4 content of 4800 mg kg^{-1}. The leached bioaccessible DAP treatment, which was characterized by having a low salinity (0.70 dS m^{-1}) and a high NH_4 (900 mg kg^{-1}), had 60% (6 of 10 worms were deceased) mortality in the first 24 hours of the earthworm toxicity test. The combination of the Richfield soil and KCl produced a soil that was characterized by a high salinity (14.0 dS m^{-1}), similar to salinity of DAP-treated soil, and a low NH_4 (13.0 mg kg^{-1}). The addition of KCl to the Richfield soil resulted in 100% (10 dead worms) earthworm mortality in the first day of the study. Treating the Richfield soil with NH_4Cl, followed by a leaching procedure, produced a soil that had a low salinity (0.50 dS m^{-1}) and a high NH_4 (580 mg kg^{-1}). This soil, like all other treated soils, had 100% earthworm mortality within the first 24 hours of the earthworm procedure. The Richfield soil (control) was classified as having a low salinity (0.91 dS m-1) and a low NH_4 (10.5 mg kg^{-1}). The control had no earthworm mortality within the 7-day toxicity test.

Results of the earthworm toxicity test determined that both high salinity and NH_4 associated with DAP or high salinity associated with Na_2HPO_4 was responsible for earthworm mortality. However, DAP with $CaCO_3$ reduced NH_4 from 4800 mg kg^{-1} to 2910 mg kg^{-1} (1 M KCl extraction) after one week of

incubation. The addition of alkaline biosolids to the DAP treated soil reduced NH_4 from 4800 mg kg^{-1} to 3110 mg kg^{-1}. The most successful removal of NH_4 was from the addition of CaO to the DAP treated soil. The NH_4 level was reduced from 4800 mg kg^{-1} to 8.09 mg kg^{-1} by the addition of CaO.

The addition of CaO to the DAP- treated soil reduced excess NH_4, but resulted in an excessive soil pH of 11.5. Acid (3 M HCl) was added to the CaO treated soil to lower the pH to 6.8. HCl addition increased the salinity to 66.0 dS m^{-1}. Leaching with deionized water reduced salinity to 0.609 dS m^{-1}.

Earthworm mortality in the leached DAP, CaO, and 3M HCl (leached) treated soil was determined. Mortality did not occur in the treated soil until day 5 (120 hours). A cumulative mortality of 6.7% was calculated on day 5 for the treated soil. The cumulative mortality increased to 16.7% on day 6, and increased to 20.0% for the last day of the test (day 7). The remaining worms were active and burrowed in the treated soil. The artificial soil had a 0% cumulative mortality throughout the duration of the 7-day test.

DISCUSSION

In order to produce a significant difference in the reduction of bioaccessible Pb, it was observed that the application amount had to be based on total metal content for the phosphate treatments. The only phosphate treatments that produced a reduction significantly different from the control was DAP and Na_2HPO_4 at the total metal application amount. The excessive amount of phosphorus applied at the total content amount of DAP and Na_2HPO_4 provided enough phosphorus to produce Pb and Cd phosphates and this elevated formation of precipitates were able to withstand the acidic environment of the gastric phase of the in vitro gastrointestinal extraction method. Bioaccessibility of Pb was also reduced by the application of alkaline biosolids. Application of 200 g kg^{-1} of alkaline biosolids to contaminated soil apparently resulted in the chelation of Pb. The reduction of bioaccessible Pb was likely due to insoluble Pb organic matter chelates that were not dissolved in the acidic environment of the simulated gastric phase extraction. Different results were observed for the reduction of bioaccessible Cd. All treatments, except for the application of DAP based on the in vitro extractable amount, were able to significantly reduce the bioaccessibility of Cd. Again, the mechanism believed to be responsible for the immobilization of bioaccessible Cd by the application of phosphorus fertilizers is the formation of insoluble Pb and Cd phosphates. It is believed the application of $CaCO_3$ elevated the soil pH to a level that was capable of precipitating Cd from solution, which suggests that the elevated

pH neutralized the acidic conditions of the gastric phase; therefore, dissolution of the precipitates did not occur.

Previous research has primarily focused on assessing reductions in Pb bioaccessibility by the in vitro gastrointestinal method and not bioaccessible Pb and Cd. Berti and Cunningham (1997) reported that phosphorus (P) (added at the rate of 0.5% P as KH_2PO_4) was highly effective in reducing Pb bioaccessibility in the stomach phase (PBET method; Ruby et al., 1996). Reduction of approximately 20% of bioaccessible Pb was found in the KH_2PO_4-treated soil. However, results from the Berti and Cunningham (1997) study only examined the reduction of Pb and no data were presented about the Cd and Zn levels of the contaminated soil or if any reduction in Cd bioaccessibility occurred. Hettiarachchi et al. (2001) examined the effect that phosphorus amendments had on the reduction of bioaccessible Pb, using the PBET method (Ruby et al., 1996). This study differs from Berti and Cunningham's study (1997) because Hettiarachchi et al. (2001) used triple superphosphate (TSP), a soluble P fertilizer, to treat Zn, Cd, and Pb-contaminated soil. Hettiarachchi et al. (2001) reported that application of TSP fertilizer at 5 g P kg^{-1} soil to reduced bioavailable Pb by 23%. The results from our study showed a 27.2% decrease in bioaccessible Pb after a P addition of 28 g kg^{-1} as DAP and an 18.2% decrease in bioaccessible Pb after a 28 g kg^{-1} P addition as Na_2HPO_4. Our applications of P were greater than those used by Berti and Cunningham (1997) and Hettiarachchi (2001). A higher application of P was used because the application amount was based on the total amount of Pb, Zn, and Cd concentrations in the contaminated soil. It is unclear if P additions were based on Pb or Pb, Cd, and Zn in the other studies. Berti and Cunningham (1997) did not report Cd or Zn concentrations for the contaminated soils used in their study. However, the study conducted by Hettiarachchi et al. (2001) reported Cd and Zn concentrations that were less than the concentrations found in our soil. The Cd concentration of our soil was 278 mg kg^{-1} and the Zn concentration was 59000 mg kg^{-1}. Hettiarachchi et al. (2001) reported Cd concentrations as high as 189 mg kg^{-1} and Zn concentrations as high as 42592 mg kg^{-1}. We had similar reductions in bioaccessible Pb, although we used a high application of phosphorus. It is likely the greater amounts of Zn in our soil required more P application to precipitate Zn and reduce bio-accessible Pb.

Alkaline biosolids reduced bioaccessible Pb by 37.6%. It is likely the reduction of bioaccessible Pb was due to the chelation of Pb by the alkaline biosolids. Basta et al. (2001) applied lime-stabilized

sewage sludge (alkaline biosolids) at four different amounts: 10, 30, 100, and 300 g kg^{-1} soil. After analysis of the amended soil by the PBET method (Ruby et al., 1996), it was determined that no significant differences existed between the control and the alkaline biosolids at any of the previously mentioned application amounts. Basta et al. (2001) suggested that the products of the alkaline biosolids (i.e., carbonates, chelates) were not stable under acidic conditions (pH 2.0) of the gastric solution of the PBET procedure. Our research applied alkaline biosolids at an amount of 200 g kg-1 contaminated soil, and observed a 37.6% decreased in bioaccessible Pb. It is believed that formation of chelates in our soil were able to remain stable in the acidic environment of the gastric phase of the PBET extraction (Ruby et al., 1996) and the chemical composition of our alkaline biosolids was different from that of the previous study conducted by Basta et al., (2001). It is noted that the alkaline biosolids used in these two studies were collected at different times and different facilities, thereby explaining why differences were observed between the two experiments.

The high earthworm mortality rate associated with the DAP and Na_2HPO_4 treatments was attributed to the elevated extractable NH_4 and salinity. Both high salinity and extractable NH_4 level could cause earthworm mortality. Untreated contaminated soil had less than 8% earthworm mortality, suggesting that elevated metal levels were not toxic to the earthworms. The actual addition of DAP and Na_2HPO_4 to the contaminated soil was more toxic to the earthworms than the untreated soil. Elimination of the high salinity and high NH_4 levels of the DAP treatment resulted in reduced toxicity to the earthworms. The effort to reduce excess NH_4 in the DAP treated soil resulted in a variety of treatments and procedures that exceed the ability of use as an in situ remediation treatment. An earthworm toxicity test conducted by Conder et al. (2001) examined the effect of certain soil amendments on earthworm mortality. The amendments tested in this experiment were lime-stabilized sewage sludge (alkaline biosolids), rock phosphate, municipal sewage sludge biosolids, and no treatment. It was observed from this experiment that alkaline biosolids (15% mortality) was the only treatment that did not result in 100% earthworm mortality by the end of the test (14 days). Similar results were observed in our experiment. The application of $CaCO_3$ and alkaline biosolids resulted in less than 20% mortality throughout the duration of the test, while the phosphate treatments, at all amounts, caused 100% mortality within the first 24 hours of the test. Conder et al. (2001) performed a 14-day acute study, while our experiment used a 28-day toxicity test. It is noted that the control of our

study had less than 8% earthworm mortality by the end of the test, while Conder et al. (2001) had 100% earthworm mortality in the control soil at the conclusion of the 14-day study. Possible explanations for this difference between control mortalities were that the $Ca(NO_3)_2$ concentrations for Pb, Zn, and Cd in the Conder et al. (2001) study were larger than the $Ca(NO_3)_2$ concentrations in our study (Table 7) and the Conder et al. (2001) study used the *Eisenia fetida* earthworm, while our study used the *Eisenia andrei* earthworm. It is possible that one species is more sensitive or tolerant to Zn and other heavy metals. It was also observed that our concentrations were higher than the calculated incipient lethal level (ILL) determined by Conder et al. (2001). Our concentrations were above the ILL, but our percent mortality of the control was less than Conder et al. (2001) (Table 7). Again, this difference can be attributed to the use of different earthworm species. More research is needed in the area of species sensitivity. It is suggested that phosphate treatments may be efficient at immobilizing heavy metals in contaminated soils, but these treatments are often more toxic to the soil wildlife than the contaminated soil itself.

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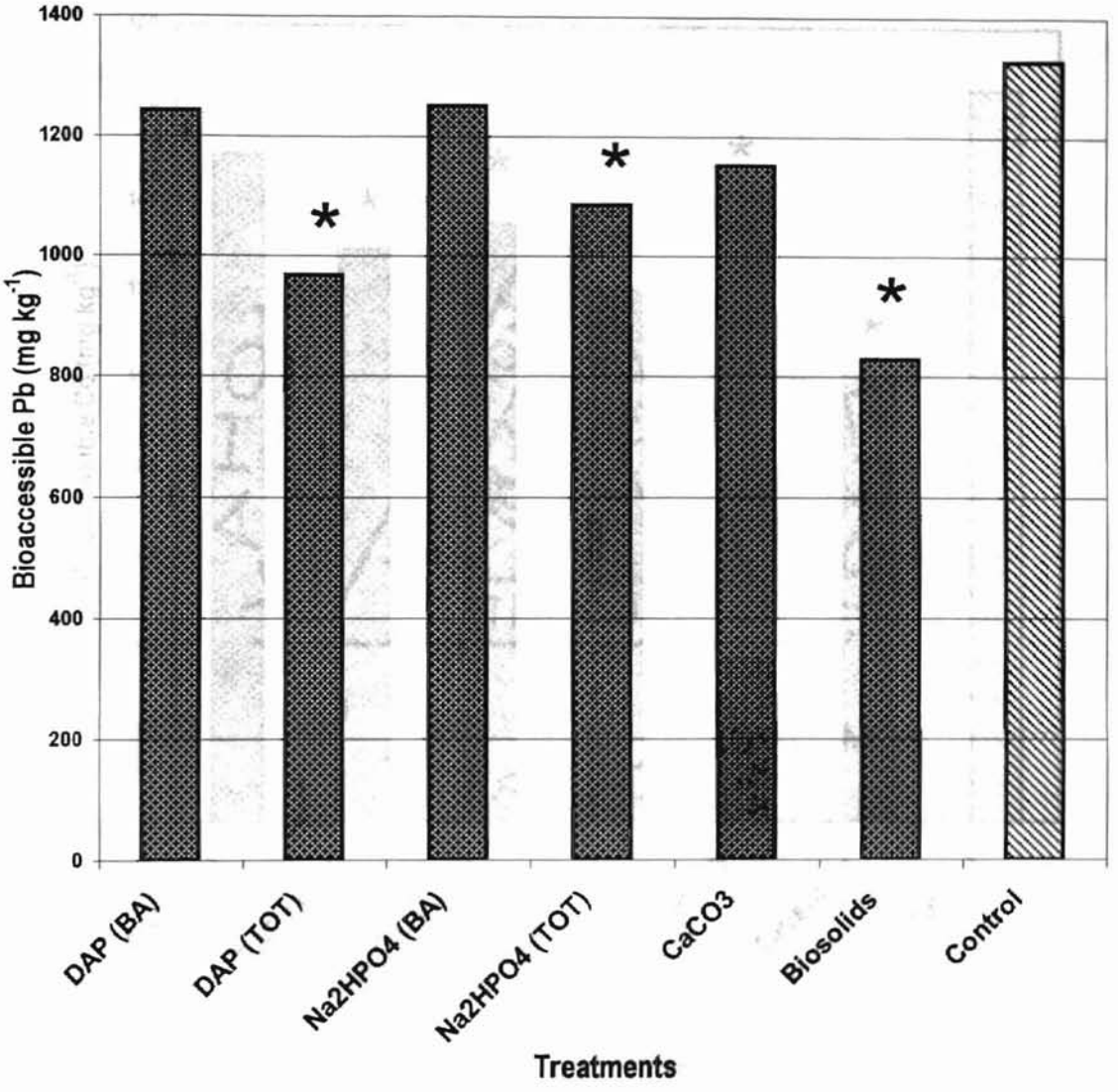
Table 1. Characterization of Pb, Zn, and Cd in contaminated soil used to evaluate effectiveness of immobilization treatments.

Element	Background Level	Total Content	Bioaccessible Metal	Percent Bioaccessibility	0.1 M $Ca(NO_3)_2$ Extractant
	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	%	mg kg^{-1}
Pb	20†	2250	910	40.4	0
Zn	50	59000	33900	57.5	609
Cd	0.5	278	131	47.1	31.5

† (Lindsay, 1979)

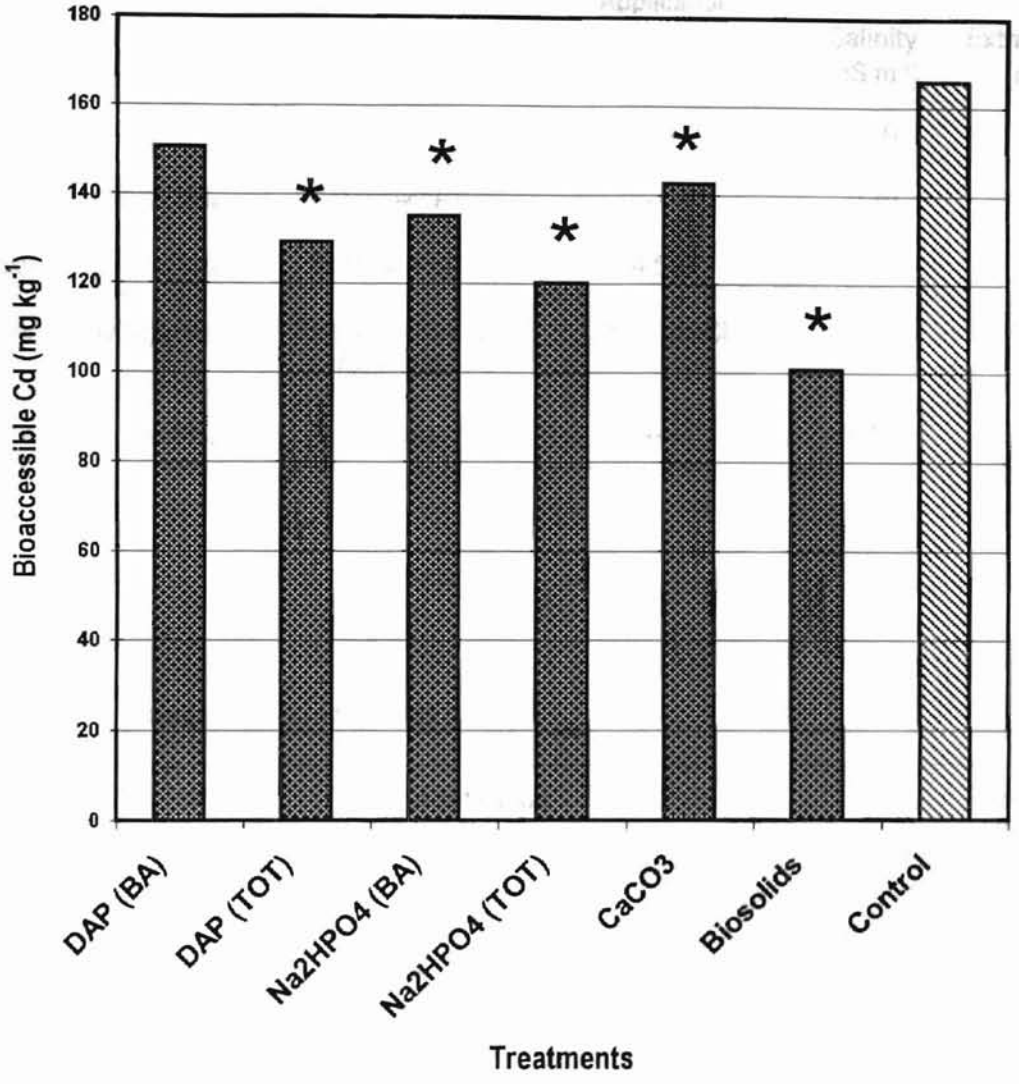
Table 2. Treatments and application amounts used to treat contaminated soil.

Treatments	Application Amounts	
----	Bioaccessibility	Total Content
------	----------g kg^{-1} soil----------	
DAP	69.0	120
Na_2HPO_4	74.4	129
$CaCO_3$	0.0	100
Biosolids	0.0	200
Control	0.0	0.0



* = Significant difference for the control at 0.05 level.

Figure 1. Effect of remediation treatments on bioaccessible Pb. Designations in parentheses are BA = amount added based on bioaccessible Pb and TOT = amount added based on Pb present in contaminated soil by XRF.



* = Significant difference for the control at 0.05 level.

Figure 2. Effect of remediation treatments on bioaccessible (BA) Cd. Designations in parentheses are BA = amount added based on bioaccessible and TOT = amount added based on Cd present in contaminated soil by XRF.

Table 3. Application amounts, salinity, and 1 M KCl extractable NH_4 level for ammonium spiking experiment.

Classification	Treatment	Application Amount (g kg^{-1})	Salinity (dS m^{-1})	Extractable NH_4 (mg kg^{-1})
High salinity/high NH_4	DAP (unleached)	-----	12.0	4800
Low salinity/high NH_4	DAP (leached)	-----	0.70	900
High salinity/low NH_4	Richfield + KCl	54.5 KCl	14.0	13.0
Low salinity/high NH_4	Richfield + NH_4Cl (leached)	76.1 NH_4Cl	0.50	580
Low salinity/low NH_4	Richfield	-----	0.91	10.5

Table 4. Treatment effects on soil pH and salinity.

Treatment	Application Amount	pH	Salinity (dS m^{-1})
Control	0	7.45	2.66
DAP	Bioaccessible	7.52	11.8 (0.25)
DAP	Total	7.33	13.4 (0.37)
Na_2HPO_4	Bioaccessible	10.3	18.1 (1.27)
Na_2HPO_4	Total	10.9	27.0 (0.76)
$CaCO_3$	100 g kg^{-1}	7.85	2.69
Biosolids	200 g kg^{-1}	7.53	2.94

Table 5. The effect of soil treatment on cumulative mortality of earthworms.

Treatments	Application Amount	Mean Percent Cumulative Mortality											
---	---	h											
---	---	0	24	48	72	96	120	144	168	240	360	540	672
DAP	Bioaccessible	0	100	100	100	100	100	100	100	100	100	100	100
DAP	Total Content	0	100	100	100	100	100	100	100	100	100	100	100
Na_2HPO_4	Bioaccessible	0	100	100	100	100	100	100	100	100	100	100	100
Na_2HPO_4	Total Content	0	100	100	100	100	100	100	100	100	100	100	100
$CaC0_3$	100 g kg^{-1}	0	0	0	0	0	2.5	2.5	2.5	2.5	5.0	5.0	7.5
Biosolids	200 g kg^{-1}	0	0	0	0	5.0	10.0	12.5	12.5	15.0	15.0	17.5	17.5
Artificial Soil	No treatment	0	0	0	0	0	0	0	0	0	0	0	0
Control	No treatment	0	0	0	0	0	0	0	2.5	5.0	5.0	5.0	7.5

Table 6. Mean percent cumulative mortality for earthworm toxicity test.

Treatment	Mean Percent Cumulative Mortality (%)							
	Hours							
----	0	24	48	72	96	120	144	168
DAP (unleached)	0	100	100	100	100	100	100	100
DAP (leached)	0	60	100	100	100	100	100	100
Richfield + KCl	0	100	100	100	100	100	100	100
Richfield + NH_4Cl	0	100	100	100	100	100	100	100
Richfield	0	0	0	0	0	0	0	0
DAP/CaO/3 M HCl (leached)	0	0	0	0	0	6.70	16.7	20.0
Artificial Soil	0	0	0	0	0	0	0	0

Table 7. Comparison of bioavailability and toxicity of Zn, Cd, and Pb to earthworms

	E1 Zn (mmol kg^{-1})	E1 Cd (mmol kg^{-1})	E1 Pb (mmol kg^{-1})
Our study	9.4	0.28	0.0
Conder et al. (2001)	15.8	1.39	0.007
ILL†	6.3	9.8	1.16

† ILL is the incipient lethal level, which is a time-based LC_{50} (lethal concentration that results in 50% mortality).

CHAPTER 3

RISK ASSESSMENT INVESTIGATION FOR THE INCIDENTAL INGESTION OF SOIL TO HUMANS

ABSTRACT

Risk assessment is a process used to quantitatively estimate the risks associated with the exposure of humans to various substances in the environment. The objective of this study was to evaluate risk reductions in human health for the incidental ingestion of soil for lead and cadmium concentrations, based on the potentially bioavailable concentrations measured by an in vitro gastrointestinal (bioaccessible) method, as a result of the application of the immobilization treatments DAP, Na_2HPO_4, $CaCO_3$, and biosolids. The amount of bioaccessible Pb in the control soil (untreated soil) had a calculated blood Pb level of 13.3 μg dL^{-1}. The treatment of DAP at the total content application and bioaccessible application amounts resulted in a calculated blood Pb level of 10.7 μg dL^{-1} and 12.8 μg dL^{-1}, respectively. Additions of Na_2HPO_4 at the total content and bioaccessible amounts resulted in calculated blood Pb levels of 11.6 μg dL^{-1} and 12.8 μg dL^{-1}, respectively. The application of $CaCO_3$ had a calculated blood Pb level of 12.1 μg dL^{-1}. The lowest calculated blood Pb level (9.6 μg dL^{-1}) resulted from the application of alkaline biosolids. The Center for Disease Control (CDC) has defined an elevated blood Pb level as ≥10 μg dL^{-1} for children. The application of alkaline biosolids was the only treatment to reduce blood Pb levels to < 10 μg dL^{-1}. Noncancer hazard quotient (HQ) for Cd was calculated by dividing the CDI by the RfD for (1) an adult with a lifetime (70 years) and residential (30 years) exposure, (2) a child with 6 years of exposure, and (3) worker with 25 years of exposure. The US EPA defines a HQ >1 as having potential for significant effects as a result of exposure to contaminants. Untreated and treated contaminated soils all had an HQ <1 for Cd.

INTRODUCTION

Heavy metal contamination of soil can lead to the exposure of pollutants in a variety of pathways and affect one or more receptors. One way to summarize the dangers imposed by contaminated soils to humans and ecosystems is to perform a risk assessment. Environmental risk assessment is defined as, "the process used to estimate quantitatively the risks associated with exposure of any organism to various substances in the environment" (Pierzynski et al., 2000). Examples of routes of exposure used in environmental risk assessment include ingestion, dermal contact, inhalation, and drinking water (Basta et al., 2002). Possible receptors of concern when performing environmental risk assessment are adults and children living near or on the contaminated area, on-site workers, groundwater, plants, soil invertebrates, and vertebrates (Menzie et al., 2000).

The three main human exposure pathways are inhalation, dermal absorption, and ingestion (Pierzynski et al., 2000), with ingestion being the most significant exposure pathway for metal-contaminated soil. Soil ingestion is the result of hand-to-mouth activities that lead to the incidental ingestion of soil (Pierzynski et al., 2000). Young children, usually six months to six years of age, are the most susceptible group to the ingestion exposure pathway. Children within this age group are considered Highly Exposed Individuals (HEI) (Dudka and Miller, 1999). Children are of the greatest concern for the ingestion pathway because "their toys are often in contact with the floor or the ground and they have a tendency to place their hands in their mouths" (Pierzynski et al., 2000). It is estimated that young children consume 30 milligrams of soil per day (Pierzynski et al., 2000), but 200 mg day^{-1} is the default value used for most risk assessments. *Pica* children, or children with an abnormal craving for nonfood substances, are considered to be of greatest risk when considering soil ingestion of contaminants (Pierzynski et al., 2000), because it is assumed they will consume well above the 30 milligrams of soil per day for non-*Pica* children.

A simple algebraic equation is used to calculate a chronic daily intake (CDI). The following equation is used to calculate the CDI for the incidental ingestion pathway (Benjamin and Belluck, 2001):

$$CDI = \frac{(CS)\,(IR)\,(CF)\,(FI)\,(EF)\,(ED)}{(BW)\,(AT)}$$

where:

CDI = chronic daily intake (mg kg^{-1} day^{-1})

CS = chemical concentration in soil (mg kg^{-1})

IR = ingestion rate (mg soil day^{-1})

CF = conversion factor (10^{-6} kg mg^{-1})

FI = fraction ingested from contaminated source (unitless)

EF = exposure frequency (days yr^{-1})

ED = exposure duration (yr)

BW = body weight (kg)

AT = averaging time (period over which exposure is average-days)

Current risk assessment methodologies for heavy metal contaminated soils base chemical concentrations in the soil (CS) on total metal content, rather than bioavailable concentrations. Bioavailability of a chemical is defined "as the fraction of an administered dose that reaches the central (blood) compartment from the gastrointestinal tract" (Ruby et al., 1999). Bioavailable concentrations of chemicals can be determined in a number of ways including in vivo studies using an animal model, chemical extraction methods, such as the Potentially BioAvailable Sequential Extraction (PBASE) method (Basta and Gradwohl, 2000), or an in vitro gastrointestinal (IVG) extraction (bioaccessible) method. Current risk assessment calculations for CDI also assume that the target organisms will absorb all the metal measured by total metal analysis. Therefore, risk assessment calculations not only overestimate risk but also fail to consider the behavior of the chemical in the soil. Alexander (2000) points out that although early findings and their importance have been obscured with the passage of time, awareness now is growing among environmental toxicologists, risk assessors, and regulatory agencies that the total concentration of a toxicant in a contaminated environment frequently overestimates the risk of pollutants to humans, animals, and plants. One way to avoid the overestimation of risk is to account for a metal's bioavailability in risk assessment calculations. The benefits of considering bioavailability in risk assessment calculations include more accurate estimates of exposure, better guidance in the selection of appropriate and protective remedial measures, reduction of uncertainty, reduction of overly conservative nature of risk assessments, and providing risk managers with a more reasonable and site-specific baseline risk estimate (Basta et al., 2002; Menzie et al., 2000).

Lead (Pb) and cadmium (Cd) are two heavy metal contaminants that commonly co-occur on smelter sites (Pearson et al., 2000). Lead is a concern of human health because overexposure can result in neurological, neurobehavioral, and developmental effects in children and neuropathy (any disease of the nervous system) in adults (Klaassen, 1996). Pulmonary disease, emphysema, and renal tubular disease can result from an overexposure of cadmium (Klaassen, 1996). The Environmental Protection Agency (EPA) created the Integrated Risk Information System (IRIS) to provide risk assessors with a summary of EPA risk assessment and risk management information for chemical substances. The goal of IRIS is to provide quality information that will be consistent in EPA risk assessment and risk management decisions. IRIS identifies lead as having both noncarcinogenic and carcinogenic effects. In order to quantify the hazard that exist from a noncarcinogen, the EPA calculates a hazard quotient (HQ). Noncarcinogenic effects are different from carcinogenic effects in that noncarcinogens are not expressed as a probability of an individual suffering an adverse effect, such as cancer. Noncarcinogenic effects are calculated using the following equation (Benjamin and Belluck, 2001):

$$\text{Noncancer HQ} = \frac{\text{Chronic Daily Intake (CDI) or Exposure Level}}{\text{RfD or RfC for a given period of time}}$$

where HQ is the hazard quotient; CDI is the chronic daily intake (mg kg^{-1} day^{-1}); and RfD or RfC are the regulatory concentrations for noncarcinogens. RfD or RfC values are unique to each chemical and can be obtained for IRIS. When the HQ is greater than one, the potential for significant effects as a result of exposure to a contaminant exist (Benjamin and Belluck, 2001). Carcinogens, on the other hand, are calculated and expressed as a probability of an individual developing cancer. Carcinogenic risk is quantified by the following equation (Benjamin and Belluck, 2001):

$$\text{Risk} = \text{Chronic Daily Intake (CDI)} \times \text{Slope Factor (SF)}$$

where:

Risk = unitless probability of an individual developing cancer

CDI = chronic daily intake averaged over 70 years (mg kg^{-1} day^{-1})

SF = numerical expression of upper-bound probability of an individual developing cancer as a result of a lifetime of exposure to a particular level of a carcinogen

The SF value, like the reference dose (RfD) for noncarcinogens, is unique to each chemical and is generally obtained from the IRIS. The risk for carcinogens is based on the assumption that SF is a constant and risk is directly related to intake (Benjamin and Belluck, 2001). The SF is a probabilistic value that provides information of the slope of a dose-response curve. When a chemical has a large slope factor, the slope or curve of the dose-response is steep, which indicates that a small amount of chemical causes a relatively large toxic response above a threshold concentration. In contrast, a small slope factor reflects a shallow dose-response curve, which indicates that a relatively small toxic response results at concentrations above the threshold. These dose-response relationships only exist with a slope factor and not an RfD or RfC.

As previously mentioned, an HQ greater than one indicates the potential for significant non-carcinogenic risks. The range of risk for a carcinogen often varies between a one-in-ten thousand and one-in-one-million excess lifetime cancer risk level.

Uncertainty also exists in risk assessment due to the lack of a sufficient toxicity test that restricts the EPA on the establishment of reference doses and slope factors for many contaminants. The EPA classifies both Pb and Cd as probable cancer-causing chemicals, yet no slope factors have been established for either pollutant. EPA uses a weight of evidence classification, which characterizes Pb as a B2 probable carcinogen and Cd as a B1 probable human carcinogen. The EPA weight-of-evidence classification system for carcinogenicity defines group A chemicals as human carcinogens, group B chemicals as probable human carcinogens, group C chemicals as possible human carcinogens, group D chemicals as not classifiable, and group E chemicals as having negative evidence. Group B is further broken down into B1, which indicates that limited human data are available; and B2, which indicates sufficient evidence in animals and inadequate or no evidence in humans. The EPA uses information from animal (rat, dog, hamsters, etc.) toxicity tests to establish acceptable hazard levels. The same problems exist with noncarcinogens. EPA will classify a chemical as hazardous, but due to the lack of research needed to establish reference doses, a hazard quotient cannot be properly calculated. The approach of immobilization treatments is to decrease exposure by decreasing the dose. Most of the research using immobilization treatment to remediate contaminated soil does not include the reduction of contaminants in a risk context. The objective of this study was to evaluate risk reductions in human health for the incidental

ingestion of soil for lead and cadmium concentrations, based on the potentially bioavailable concentrations measured by an in vitro gastrointestinal (bioaccessible) method, as a result of the application of the immobilization treatments DAP, Na_2HPO_4, $CaCO_3$, and biosolids.

MATERIALS AND METHODS

The soil used for this project was collected from a zinc smelter in northeastern Oklahoma. Elevated concentrations of lead (Pb), cadmium (Cd), and zinc (Zn) were present in the soil. The soil was air-dried and sieved at <2 mm prior to all laboratory experiments. The total metal contents for this smelter-contaminated soil are 2250 mg kg^{-1} of Pb and 278 mg kg^{-1} of Cd. The background levels for each of these chemicals are 20 mg kg^{-1} Pb and 0.5 mg kg^{-1} Cd (Lindsey, 1979). The bioaccessible fractions of heavy metals in soil, as determined by the in vitro gastrointestinal extraction (Rodriguez et al., 1999), are 910 mg kg^{-1} of Pb and 131 mg kg^{-1} Cd. The percentages of total metal content that are bioaccessible, divided by the total metal content, are 40.4% Pb and 47.1% Cd.

The treatments used for the risk assessment calculations were diammonium phosphate (DAP), sodium phosphate (Na_2HPO_4), $CaCO_3$, and lime-stabilized sewage sludge (alkaline biosolids). The application amounts of these treatments, except for $CaCO_3$ and biosolids, were based on: (1) metal extracted by simulated human gastrointestinal in vitro (IVG) method (bioaccessible) (Rodriguez et al., 1999); and (2) total metal measured by X-ray fluorescence (Karathanasis and Hajek, 1996).

Contaminated soil (1000 g) was incorporated with each treatment in 2.5-quart plastic containers. DAP and Na_2HPO_4 treatments were applied at two application amounts, while $CaCO_3$ and alkaline biosolids were applied at an amount of 100 g $CaCO_3$ per kg contaminated soil and 200 g alkaline biosolids per kg contaminated soil. DAP application amounts were based on bioaccessible metal extracted by a simulated human gastrointestinal in vitro method (69.0 g DAP kg^{-1} soil) and total metal measured by X-ray fluorescence (120 g DAP kg^{-1} soil). Na_2HPO_4 treatments were also based on bioaccessible and total metal in the contaminated soil and application amounts were 74.4 g kg^{-1} soil (bioaccessible) and 129 g kg^{-1} soil (total metal). All treatments and application amounts were added to the contaminated soil dry. After all treatments were stirred with the soil, 1000 mL of deionized water was added to each container and stirred again. All containers were placed in a constant temperature room at 35°C. The containers were dried and

re-wet with 1000 mL of deionized water. This wet/dry process was repeated a total of three cycles. At the conclusion of the wet/dry cycles, the containers were made into a paste and allowed to incubate for 38 days. The paste consistency was maintained by daily watering and stirring of the test containers.

After day 38, all containers were dried. Three replicates of 4 g of soil each were removed from each container to analyze by in vitro gastrointestinal extraction method (Rodriguez et al., 1999). The in vitro extraction is an indirect measure of gastrointestinal availability. The modified in vitro gastrointestinal extraction, which contained no dosing vehicle ("dough") (Rodriguez et al., 1999), was applied for this experiment. The procedure used 4 g of soil and 600 mL of a pepsin/sodium chloride solution (1% pepsin in 0.15M NaCl). The soil and solution were combined in 1L canning jar, known as the reactor vessel. The reactor vessels were then placed into a water bath at 37°C and an individual paddle stirrer was installed in each vessel at a speed of approximately 100 rpm. Each vessel contained one combination pH electrode and one argon (Ar) gas dispersion apparatus. Ar gas was diffused into the vessel throughout the entire extraction to maintain an anaerobic atmosphere. Once the pH electrode and Ar gas diffuser were attached to the reactor vessel, the pH was adjusted to and maintained at 1.8 for one hour. At the end of one hour, two 20-ml aliquots of extraction were removed from each vessel and centrifuged at 10,000 rpm for 15 minutes. The supernatant was then syringe filtered through a 0.45 μm filter. Extracted samples were filtered into vials and refrigerated until analysis by ICP.

The amount of Pb, Zn, and Cd found in the in vitro extraction method was considered potentially bioavailable and was used in the risk assessment calculations as soil concentrations instead of total metal concentrations. Only Pb and Cd were used in the risk assessment calculations because Zn is nontoxic to humans and is considered an essential component of human health. The receptors of concern for the risk associated with Cd were adults, children, and site workers and the exposure pathway of concern was incidental ingestion of soil. Children and incidental ingestion of soil were the receptors and pathway of concern for the risk associated with Pb. Both Pb and Cd were considered to have noncarcinogenic and probable carcinogenic effects, but neither Pb nor Cd has a slope factor listed in the Integrated Risk Information System (IRIS) of the United States Environmental Protection Agency (US EPA); therefore a carcinogenic risk was not calculated. The EPA has only a reference dose (RfD) listed for Cd and not Pb; therefore, CDI values and hazard quotients were calculated for Cd only.

Total content determined by XRF and bioaccessible values for the controls and treated soils were used to quantify risk posed by soil Pb. Because the US EPA has yet to agree on a slope factor or reference dose for Pb, both carcinogen and noncarcinogen effects of Pb were not calculated. However, the conversion of bioaccessible Pb concentrations to an equivalent blood Pb level, using the IEUBK (Integrated Exposure Uptake Biokinetic Model for Lead in Children) model provided by the US EPA was performed. All defaults of the IEUBK model were used except for bioavailability information. In order to make adjustments to the bioavailability information, all bioaccessible values were converted to a percentage. This percentage was determined by dividing the bioaccessible Pb value by the total Pb value, then multiplied by 100. Adjustments to the model were made to the percent accessible for soil and dust. The IEUBK model had Pb bioavailability default values of 30% for soil and dust. The model assumes soil is ingested by two exposure pathways: direct ingestion of soil and ingestion of household dust that is composed of 45% contaminated soil. The model also assumes the percent bioavailability of Pb in drinking water is 50%. This means that only half of the water soluble Pb ingested in drinking water is absorbed into the blood stream. The bioaccessible values in our study were a measure of Pb in solution. We assumed 50% of the dissolved bioaccessible Pb would be absorbed into the blood stream (i.e. similar to Pb in water). We calculated a relative bioavailable Pb, to adjust our in vitro values for 50% absorption into blood, by multiplying bioaccessible values by 0.50. Similarly, bioavailability of Pb in household dust was adjusted by multiplying the percentage of soil in dust (i.e. 45%) by 0.50. The total concentration of Pb in the untreated soil was used as the soil Pb concentration in the model. The Centers for Disease Control (CDC) has defined elevated blood Pb level as $\geq 10\ \mu g\ dL^{-1}$ for children.

The quantifying of risk associated with exposure to Cd was evaluated by calculating CDI values and hazard quotients. The calculation of the CDI values examined the differences between spending a lifetime on or near the contaminated site with only staying on or near the site for a residential period of 30 years. The following equation was used to calculate the chronic daily intake (CDI) values of Cd:

$$CDI = \frac{(CS)\,(IR)\,(CF)\,(FI)\,(EF)\,(ED)}{(BW)\,(AT)}$$

where:

CDI = chronic daily intake (mg kg^{-1} day^{-1})

CS = chemical concentration in soil (mg kg^{-1})

IR = ingestion rate (mg soil day^{-1})

CF = conversion factor (10^{-6} kg mg^{-1})

FI = fraction ingested from contaminated source (unitless)

EF = exposure frequency (days yr^{-1})

ED = exposure duration (yr)

BW = body weight (kg)

AT = averaging time (period over which exposure is average-days).

Chemical concentrations in soil (CS) were determined by the human gastrointestinal in vitro method. CDI values were calculated only for the noncarcinogenic effects of Cd. The ingestion rate (IR) of 100 mg day^{-1} was used for adults and workers and 200 mg day^{-1} for children. A unitless value of 1 was applied for the fraction ingested from the contaminated source (FI). Exposure frequency (EF) was 365 days a year for all adult calculations and 350 days a year for children. Workers are generally not on site 7 days a week; therefore 250 days a year was assumed for the EF of on-site workers. Values for exposure duration (ED) were dependent on whether or not the assessment was for a lifetime exposure (ED of 70 years) or residence exposure (ED of 30 years), with the exception of children for a residence exposure for which an ED of 6 years was used. An ED of 30 years was only used when calculating residential risk for non-carcinogenic effects. It was assumed that body weight (BW) of adults and worker was 70 kg and 16 kg for children. The averaging time (AT) is determined by multiplying ED by 365 days.

The second step of the risk assessment for Cd was to quantify risk associated with noncarcinogenic effects of Cd using the IRIS reference dose for Cd to calculate hazard quotients. The equation used to calculate the hazard quotients was the following:

$$HQ = \frac{CDI}{RfD}$$

where:

HQ = the noncancer hazard quotient;

CDI = the chronic daily intake (mg kg^{-1} day^{-1}); and

RfD = the reference dose (exposure duration toxicity factor).

Cd, like Pb, is considered a probable carcinogen, yet the US EPA has yet to determine an appropriate slope factor for Cd. The receptors and exposure durations of concern for the hazard quotient calculations of Cd were adults with 70 years of exposure, adults with 30 years of exposure, children with 6 years of exposure, and on-site workers with 25 years of exposure. Since hazard quotients were being calculated for one chemical only (Cd), the hazard quotients were not summed within each treatment. Risk assessors often sum hazard quotients if the receptor is exposed to more than one chemical at a time. This was not the case for this risk assessment; therefore each receptor and duration of exposure was individually assessed. Potential for significant effects was expressed when noncancer hazard quotients were greater than one.

RESULTS AND DISCUSSION

The results of the IEUBK model conversions are reported in Table 1. The control soil (untreated soil) had a calculated blood Pb level of 13.3 μg dL^{-1}. The CDC defines a child as having elevated blood Pb levels when blood Pb levels are ≥ 10 μg dL^{-1}. The treatment of DAP at the total content application and bioaccessible application amounts resulted in a calculated blood Pb level of 10.7 μg dL^{-1} and 12.8 μg dL^{-1}, respectively. Although DAP treatments resulted in significant decreases in calculated blood Pb, the IEUBK model still predicts exposure to the DAP-treated soil would result in >10 μg dL^{-1}. Additions of Na_2HPO_4 at the total content and bioaccessible amounts resulted in calculated blood Pb levels of 11.6 μg dL^{-1} and 12.8 μg dL^{-1}, respectively. The application of $CaCO_3$ had a calculated blood Pb level of 12.1 μg dL^{-1}. The lowest calculated blood Pb level (9.6 μg dL^{-1}) resulted from the application of alkaline biosolids. A calculated blood Pb level that is <10 μg dL^{-1} is the goal and this marker was met by the application of alkaline biosolids. All other treatments failed to reduce the blood Pb level to <10 μg dL^{-1}, but they did show a reduction in blood Pb levels from that of the untreated soil. It is noted that this risk assessment was performed for one soil and all soils are different; therefore, the application of these treatments at these

amounts could cause reduction of blood Pb level <10 μg dL^{-1} for a different soil. Each site must be assessed on a site-specific basis.

Chronic daily intakes (CDI) of Cd were calculated for the following receptors, effects, and exposure duration:

1. Cd-Adult-Noncarcinogenic effect—Lifetime (70 years)—Table 2
2. Cd-Adult-Noncarcinogenic effect—Residence (30 years)—Table 3
3. Cd-Child-Noncarcinogenic effect—Residence (6 years)—Table 4
4. Cd-Worker-Noncarcinogenic effect—25 years—Table 5

Noncancer hazard quotient (HQ) for Cd was calculated by dividing the CDI by the RfD for (1) an adult with a lifetime (70 years) and residential (30 years) exposure, (2) a child with 6 years of exposure, and (3) a worker with 25 years of exposure (Table 6). The US EPA defines an HQ >1 as having potential for significant effects as a result of exposure to contaminants. Untreated and treated contaminated soils all had a HQ < 1 for Cd. However, soil treatment reduced the HQ Cd value and followed the trend: control (XRF) > control (bioaccessible) > $CaCO_3$ > Na_2HPO_4 (bioaccessible) > DAP (bioaccessible) > DAP (total) > Na_2HPO_4 (total) > alkaline biosolids. Because calculated HQ for contaminants with similar modes of action are added to determine actual risk at a contaminated site, decreased Cd HQ values in treated soil may reduce HQ > 1 values to HQ < 1. Calculated HQ followed trend child > adult, residence and lifetime > adult, worker, suggesting the greatest risk of Cd exposure via soil ingestion is to children.

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Table 1. Bioaccessible Pb levels and converted blood Pb levels.

Treatment	Total Pb Content	Bio-accessible	Bio-accessible	Estimated Bioavailability in Soil †	Estimated Bioavailability in Dust ‡	Blood Pb Level
	mg kg^{-1}	mg kg^{-1}	%	%	%	µg dL^{-1}
Control	2245	1327.73	59.1	29.6	13.3	13.3
DAP – Total	2245	967.88	43.1	21.6	9.72	10.7
DAP – Bioaccessible	2245	1242.26	55.3	27.7	12.5	12.8
Na_2HPO_4 – Total	2245	1085.63	48.4	24.2	10.9	11.6
Na_2HPO_4 – Bioaccessible	2245	1251.15	55.7	27.9	12.6	12.8
$CaCO_3$	2245	1152.26	51.3	25.7	11.6	12.1
Biosolids	2245	828.34	36.9	18.5	8.33	9.60

† Percent bioaccessible multiplied by 0.5

‡ Estimated bioavailability multiplied by 0.45

Table 2. Calculated chronic daily intakes (CDI) for an adult receptor, lifetime exposure, and noncarcinogenic effects of Cd.

Treatment	CS (mg kg^{-1})	IR (mg day^{-1})	CF (kg mg^{-1})	FI (unit-less)	EF (days yr^{-1})	ED (yr)	BW (kg)	AT (day)	CDI (mg kg^{-1} day^{-1})
Control—Bioaccessible	165.79	100	0.000001	1	365	70	70	25550	2.37E-04
Control—XRF	278.50	100	0.000001	1	365	70	70	25550	3.98E-04
DAP—Total	129.23	100	0.000001	1	365	70	70	25550	1.85E-04
DAP—Bioaccessible	150.49	100	0.000001	1	365	70	70	25550	2.15E-04
Na_2HPO_4—Total	120.23	100	0.000001	1	365	70	70	25550	1.72E-04
Na_2HPO_4—Bioaccessible	135.04	100	0.000001	1	365	70	70	25550	1.93E-04
$CaCO_3$	142.46	100	0.000001	1	365	70	70	25550	2.04E-04
Biosolids	100.80	100	0.000001	1	365	70	70	25550	1.44E-04

Table 3. Calculated chronic daily intakes (CDI) for adult receptor, residential exposure, and noncarcinogenic effects of Cd.

Treatment	CS (mg kg^{-1})	IR (mg day^{-1})	CF (kg mg^{-1})	FI (unit-less)	EF (days yr^{-1})	ED (yr)	BW (kg)	AT (day)	CDI (mg kg^{-1} day^{-1})
Control—Bioaccessible	165.79	100	0.000001	1	365	30	70	10950	2.37E-04
Control—XRF	278.50	100	0.000001	1	365	30	70	10950	3.98E-04
DAP—Total	129.23	100	0.000001	1	365	30	70	10950	1.85E-04
DAP—Bioaccessible	150.49	100	0.000001	1	365	30	70	10950	2.15E-04
Na_2HPO_4—Total	120.23	100	0.000001	1	365	30	70	10950	1.72E-04
Na_2HPO_4—Bioaccessible	135.04	100	0.000001	1	365	30	70	10950	1.93E-04
$CaCO_3$	142.46	100	0.000001	1	365	30	70	10950	2.04E-04
Biosolids	100.80	100	0.000001	1	365	30	70	10950	1.44E-04

Table 4. Calculated chronic daily intakes (CDI) for child receptor, residential exposure, and noncarcinogenic effects of Cd.

Treatment	CS (mg kg^{-1})	IR (mg day^{-1})	CF (kg mg^{-1})	FI (unit-less)	EF (days yr^{-1})	ED (yr)	BW (kg)	AT (day)	CDI (mg kg^{-1} day^{-1})
Control—Bioaccessible	165.79	200	0.000001	1	350	6	16	10950	3.97E-04
Control—XRF	278.50	200	0.000001	1	350	6	16	10950	6.68E-04
DAP—Total	129.23	200	0.000001	1	350	6	16	10950	3.10E-04
DAP—Bioaccessible	150.49	200	0.000001	1	350	6	16	10950	3.61E-04
Na_2HPO_4—Total	120.23	200	0.000001	1	350	6	16	10950	2.88E-04
Na_2HPO_4–Bioaccessible	135.04	200	0.000001	1	350	6	16	10950	3.24E-04
$CaCO_3$	142.46	200	0.000001	1	350	6	16	10950	3.42E-04
Biosolids	100.80	200	0.000001	1	350	6	16	10950	2.42E-04

Table 5. Calculated chronic daily intakes (CDI) for an on-site worker receptor, residential exposure, and noncarcinogenic effects of Cd.

Treatment	CS (mg kg^{-1})	IR (mg day^{-1})	CF (kg mg^{-1})	FI (unit-less)	EF (days yr^{-1})	ED (yr)	BW (kg)	AT (day)	CDI (mg kg^{-1} day^{-1})
Control—Bioaccessible	165.79	100	0.000001	1	250	25	70	9125	1.62E-04
Control—XRF	278.50	100	0.000001	1	250	25	70	9125	2.73E-04
DAP—Total	129.23	100	0.000001	1	250	25	70	9125	1.26E-04
DAP—Bioaccessible	150.49	100	0.000001	1	250	25	70	9125	1.47E-04
Na_2HPO_4—Total	120.23	100	0.000001	1	250	25	70	9125	1.18E-04
Na_2HPO_4—Bioaccessible	135.04	100	0.000001	1	250	25	70	9125	1.32E-04
$CaCO_3$	142.46	100	0.000001	1	250	25	70	9125	1.39E-04
Biosolids	100.80	100	0.000001	1	250	25	70	9125	9.86E-05

Table 6. Reference doses (RfD) and hazard quotients for noncarcinogenic risk of Cd.

Treatment	Receptor	Exposure Duration (yr)	CDI (mg kg^{-1} day^{-1})	RfD	Hazard Quotient
Control – Bioaccessible	Adult	70	2.37E-04	0.001	0.237
	Adult	30	2.37E-04	0.001	0.237
	Child	6	3.97E-04	0.001	0.397
	Worker	25	1.62E-04	0.001	0.162
Control – XRF	Adult	70	3.98E-04	0.001	0.398
	Adult	30	3.98E-04	0.001	0.398
	Child	6	6.68E-04	0.001	0.668
	Worker	25	2.73E-04	0.001	0.273
DAP – Total	Adult	70	1.85E-04	0.001	0.185
	Adult	30	1.85E-04	0.001	0.185
	Child	6	3.10E-04	0.001	0.310
	Worker	25	1.26E-04	0.001	0.126
DAP – Bioaccessible	Adult	70	2.15E-04	0.001	0.215
	Adult	30	2.15E-04	0.001	0.215
	Child	6	3.61E-04	0.001	0.361
	Worker	25	1.47E-04	0.001	0.147
Na_2HPO_4 – Total	Adult	70	1.72E-04	0.001	0.172
	Adult	30	1.72E-04	0.001	0.172
	Child	6	2.88E-04	0.001	0.288
	Worker	25	1.18E-04	0.001	0.188
Na_2HPO_4 – Bioaccessible	Adult	70	1.93E-04	0.001	0.193
	Adult	30	1.93E-04	0.001	0.193
	Child	6	3.24E-04	0.001	0.324
	Worker	25	1.32E-04	0.001	0.132
$CaCO_3$	Adult	70	2.04E-04	0.001	0.204
	Adult	30	2.04E-04	0.001	0.204
	Child	6	3.42E-04	0.001	0.342
	Worker	25	1.39E-04	0.001	0.139
Biosolids	Adult	70	1.44E-04	0.001	0.144
	Adult	30	1.44E-04	0.001	0.144
	Child	6	2.42E-04	0.001	0.242
	Worker	25	9.86E-05	0.001	0.099

VITA

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