

**REMEDICATION OF HEAVY METAL
CONTAMINATED SOIL BY
IN-SITU IMMOBILIZATION**

By

JERI LYNN ANDERSON

Bachelor of Science

Oklahoma State University

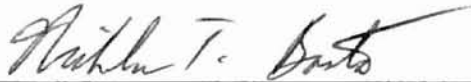
Stillwater, Oklahoma

1993

**Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
May, 1996**

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Thesis Approved:



Thesis Adviser







Dean of the Graduate College

ACKNOWLEDGMENTS

I extend my gratitude and appreciation to the Department of Agronomy at Oklahoma State University for the use of facilities and equipment and for funding of this research project. Special thanks to my major adviser Dr. Nicholas T. Basta for his time and dedication spent on the completion of this research. Also, I would like to thank my other committee members Drs. William R. Raun and Brian J. Carter for their input and time. My parents (Jerry and Linda Anderson) deserve more appreciation than words can say for their support (financially and emotionally) of my career goals. Others also deserving many thanks for their help and friendship are Leigh-Ann Barnes and David Edmondson.

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INTRODUCTION

This thesis is written in a style such that it will be submitted for publication in the *Journal of Environmental Quality*, an American Society of Agronomy publication.

REMEDICATION OF HEAVY METAL CONTAMINATED SOIL BY IN-SITU IMMOBILIZATION

ABSTRACT

In-situ immobilization is an inexpensive remediation technology to restore productivity and quality of contaminated soil. The objective of this work was to evaluate the ability of ten in-situ immobilization treatments to remediate a heavy metal contaminated soil. The incubation experiment was a completely randomized design with three replications of ten soil treatments and an untreated control. Contaminated soil was treated with amendments (100 g kg^{-1}) and incubated for 12 weeks. Remediation was evaluated by chemical speciation, U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP) extraction, and bioavailability to lettuce (*Lactuca sativa* L. 'Paris cos') of heavy metals. Chemical speciation involved sequential extraction of treated soils with $\text{Ca}(\text{NO}_3)_2$ (CaEx), NaOAc (AcEx), EDTA (EDEX), and HNO_3 (HEX). Treatments reduced CaEx Zn from > 2000 to $< 50 \text{ mg Zn kg}^{-1}$ and CaEx Cd from > 200 to $< 21 \text{ mg Cd kg}^{-1}$. Biosolids (lime-stabilized sewage sludge, LS; anaerobic-digested sewage sludge, SS; and NViro, NV), triple superphosphate (TSP), CKD (cement kiln dust), and bauxite red mud (RM) resulted in the largest reduction of CaEx Cd. Also, phosphate fertilizers, SS, and NV increased unavailable forms of Cd. Treatments reduced CaEx Pb from 20 to $< 1 \text{ mg Pb kg}^{-1}$. Biosolids and

TSP decreased potentially available AcEx Pb. Triple superphosphate converted available Pb to unavailable EDEx Pb. Most amendments decreased Cd and Pb TCLP values, but none below the 1.0 mg Cd L⁻¹ U.S. EPA regulatory level; LS, SS, and TSP, did however, reduce Pb below the 5.0 mg Pb L⁻¹ regulatory level. NViro, LS, CKD, and RM amended soil decreased Zn phytotoxicity and allowed revegetation of treated soil by lettuce. Cadmium (75 to 130 mg kg⁻¹) and Zn (499 to 852 mg kg⁻¹) lettuce tissue concentrations and Cd:Zn tissue ratios (0.098 to 0.20 mg kg⁻¹) were larger for lettuce grown in treated soils than lettuce produced in comparable baseline soils. Cadmium content of lettuce grown in treated soils was elevated more than 69 µg Cd g⁻¹ above baseline levels and is not recommended for human consumption. Amendments had little effect on Pb and Cu content in lettuce grown in treated soils. Overall, NV, LS, CKD, and RM were the most successful amendments in reducing availability, TCLP, bioavailability, and revegetating a highly contaminated soil. However, lime, zeolite, alum sludge, and rock phosphate may alleviate phytotoxicity in soils that have less Zn contamination than the soil used in this study and would allow revegetation and stabilization of contaminated sites.

INTRODUCTION

Mining of metal-ores, one of the most important and oldest industries in the world, can result in soil contamination by heavy metals. Copper, lead, and

zinc are the most extensively mined metals in the world and are the most commonly found metals in mining contaminated soils (Wong, 1986). Typical world production of these metals are 7,600 Cu, 3,500 Pb and 6,000 Zn ($\times 10^3$ tonnes) (Adriano, 1986). These metals often occur in mining-generated waste materials ranging from (in mg kg^{-1}) 30 to 15,400 Cu, 5700 to 29,900 Pb, and 1200 to 35,900 Zn. The total metal concentrations of these metals are associated with phytotoxicity and prevent establishing vegetation (Wong, 1986).

Most of the heavy metal contaminated soils in Oklahoma occur in the "Tri-State" area. The Tri-State Pb- and Zn-mining region includes portions of northeast Oklahoma, southeast Kansas, and the adjacent part of Missouri, extending over 158.4 km long by approximately 63.4 km wide. The Tri-State area is located near the industrial Midwest, the enormous oil and gas, and coal fields of the Southwest and the water resources of the Ozark Mountains. The Tri-State areas abundance of ore deposits, and its strategic location, made it one of the great mining districts of the world (Harbaugh, 1933).

Lead ores discovered near Joplin, MO in 1848 by William Tingle at Granby, MO ushered Pb mining in the Tri-State area (Ruhl, 1933). Zinc ore mining began in the 1870's which led to the construction of a railroad system in 1874 for better transportation facilities. Zinc became increasingly important and displaced Pb as the leader in mined ore production. In the 19th century, Peoria was the only Pb and Zn mining operation in Oklahoma. However, this area had only small amounts of ore-bodies and ore production was small. But, in 1906

and 1907, ore was discovered in northeastern OK and inaugurated a development that produced the great Picher camp and made OK the center of production for the entire Tri-State area. A few years later, the OK-KS field became the greatest zinc producer in the world (Ruhl, 1933).

The extensive Pb and Zn sulfide ore mining and smelting that occurred in this area from the mid 1800's to the 1950's resulted in soil contamination. Waste rock, tailings, and slag mixed with soil and deposition of airborne heavy metal particles in plume emissions from smelters onto soil resulted in Cd, Pb, and Zn contamination (Pierzynski and Schwab, 1993).

Heavy metal contamination of soil near smelters may constitute a significant health risk to the surrounding population. Elevated Cd, Pb, and Zn soil levels lead to human and animal exposure through the food chain, ingestion of wind-blown dusts, or direct ingestion of soil (Pierzynski and Schwab, 1993). Heavy metal contamination of soil may diminish soil productivity and soil quality in polluted sites (Geiger et al., 1993). Contamination of soil and groundwater from past industrial management is a high priority national environmental concern. Although many soils have been affected by past mining operations, cleanup of contaminated sites has generally been limited to areas designated as Superfund sites (Enlow, 1990). Reclamation costs for Superfund sites often range from tens to hundreds of million U.S. dollars, because most reclamation projects involve costly solidification technologies (Logan, 1992). Although

solidification technologies (adding a cementing agent to solidify the soil) are effective, they do not restore soil productivity or soil quality.

One inexpensive alternate remediation approach that may restore soil productivity and quality is in-situ immobilization. In-situ immobilization involves addition of amendments to soil to reduce the solubility and availability of soil contaminants by enhancing their sorption, precipitation, or complexation (Logan, 1992).

Heavy metal availability in soil is reduced by precipitation or specific adsorption reactions (Logan and Chaney, 1983; McLean and Bledsoe, 1992). Heavy metals form insoluble carbonate and phosphate precipitates thus reducing their availability and mobility (McLean and Bledsoe, 1992). Many studies have documented chelation by organic matter and surface complexation by Fe and Mn oxides limit heavy metal availability in soil (McKenzie, 1980; McBride, 1989; Kinniburgh and Jackson, 1981). Soil pH is one of the most important soil properties that control heavy metal solubility (Lindsay, 1979; Logan and Chaney, 1983). Increased soil pH promotes precipitation and specific adsorption reactions and reduces heavy metal bioavailability (McBride, 1989; Harter, 1983).

Lime containing amendments have been used for in-situ immobilization because it is well known that raising pH decreases heavy metal availability. Pierzynski and Schwab (1993) found limestone and limestone suspension decreased Zn in soybean [*Glycine max* (L.) Merr.] tissue and increased yield of

soybean grown in Zn contaminated soil. Czupyrna et al. (1989) found hydrated lime was one of the most effective in-situ immobilization amendments in reducing soluble Cd, Cu, Cr, Ni, and Zn in soils treated with heavy metals.

Phosphorus fertilizers react with heavy metals in soil to form insoluble phosphate precipitates (Lindsay, 1979), and may serve as effective in-situ immobilization soil treatments. Pierzynski and Schwab (1993) found K_2HPO_4 decreased Zn in soybean tissue and increased yield of soybean grown in Zn contaminated soil. In-situ immobilization using hydroxyapatite reduced soluble and resin-extractable Pb in contaminated soil (Ma et al., 1993).

Organic amendments (plant residues, manures, sewage sludge, composts, municipal solid waste, and peat) may immobilize cationic heavy metals by chelation and precipitation of metals (Adriano, 1986). However, information on in-situ immobilization using organic amendments is limited. Pierzynski and Schwab (1993) found cattle manure, NViro (a mixture of cement kiln dust and sewage sludge) and poultry litter immobilized Zn and decreased KNO_3 -extractable Zn in contaminated soil. Organic amendments also decreased Zn in soybean tissue and increased soybean yield in this study.

Iron oxides strongly adsorb heavy metals (McLean and Bledsoe, 1992), however few studies have evaluated the ability of iron oxide to remediate contaminated soils. Bauxite red mud, a waste product consisting of aluminum and iron oxides, is generated in large amounts from bauxite mining and aluminum production. Cocke et al. (1994) reported using bauxite red mud mixed

with cement in stabilization/solidification of heavy metals in contaminated soils. No information is available on the use of bauxite red mud for in-situ immobilization.

Other materials including alum sludge (waste from drinking water treatment plants), zeolite, and cement kiln dust (waste from cement production industry) may be useful amendments and immobilize heavy metals in contaminated soils but no information on the use for in-situ remediation is available.

Although immobilization mechanisms such as sorption, ion exchange, and precipitation have been identified as potential in-situ approaches (Sims et al., 1986), little information is available on the effectiveness of these amendments to reduce heavy metal bioavailability and solubility. Successful remediation must also insure long-term stability of immobilized metal (Raghavan et al., 1989). The objectives of this work are to identify and evaluate soil amendments capable of in-situ remediation of heavy metal contaminated soils. Specifically, to evaluate the ability of soil amendments to reduce heavy metal solubility, bioavailability, and affect chemical speciation and long-term stability.

MATERIALS AND METHODS

The ability of ten soil amendments to precipitate or adsorb (immobilize) heavy metals was determined. In general, amendments were mixed with

contaminated soil and incubated under constant temperature and moisture for 12 weeks. The success of remediation was evaluated by chemical speciation, U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP) extraction, and bioavailability to lettuce (*Lactuca sativa* L. 'Paris cos') of heavy metals in treated soils.

Contaminated Soil and Amendments

Surface (10 cm) samples of contaminated Kirkland silt loam (Fine, mixed, thermic Udertic Paleustoll) were collected from areas adjacent to a Pb and Zn smelter. Soil samples were air dried and crushed to pass a 2 mm sieve with a stainless steel flail arm grinder. Soil pH was determined in 1:2 soil:0.01M CaCl₂ using a glass electrode (McLean, 1982). The soil had a water content of 0.17 kg kg⁻¹ soil at approximately 0.03 MPa. Soil electrical conductivity (EC) was determined to be 0.7 dS m⁻¹ in 1:5 soil:deionized water solution (Rhoades, 1982).

Total soil metal content was estimated by summation of metal measured by successive sequential extraction steps. Total soil metal content, expressed in mg kg⁻¹, is: 340 Cd, 754 Cu, 1185 Pb, and 24700 Zn.

Most amendments were classified into three categories: biosolids, alkaline materials, phosphorus fertilizers or a combination of categories (Table 1). Alkaline containing wastes (NViro, NV; cement kiln dust, CKD; and agricultural lime, L) and phosphate fertilizers (rock phosphate, RP and triple

superphosphate, TSP) were selected because these wastes should reduce heavy metal availability by precipitation. Amendments derived from biosolids (lime-stabilized sewage sludge, LS; anaerobic-digested sewage sludge, SS; and NV) that contained significant amounts of organic matter (Table 2) were selected to chelate heavy metals. Other amendments that contained large amounts of Fe and Mn oxides (bauxite red mud, RM) or Al oxides (zeolite, Z and alum sludge, AS) were selected to adsorb and precipitate heavy metals. Bauxite red mud, which contains lye and is highly corrosive, was treated with gypsum and leached with deionized water to remove excess lye and sodium as follows. Twenty-one kg of bauxite red mud residue was mixed with 4.1 kg of gypsum and then placed into a 20.3 cm PVC leachate column fitted with a wire mesh. Deionized water (64 L) was leached through the column until the electrical conductivity (EC) was $< 2 \text{ dS m}^{-1}$.

Amendments investigated in this study had a wide range of properties and chemical composition (Table 2). Amendment pH was determined in 1:2 amendment:0.01M CaCl_2 using a glass electrode (McLean, 1982). Electrical conductivity (EC) was determined in 1:5 amendment:deionized water by using a dip type probe (Rhoades, 1982). Calcium carbonate equivalent (CCE) was determined by reaction with HCl and backtitration as described by Rund (1972). Total trace metal content of each amendment was determined by wet digestion using HNO_3 and HClO_4 (Burau, 1982) as follows. Ten mL of concentrated HNO_3 was added to each amendment (10 g) and heated until near dryness. Fifteen

mL of HClO_4 was added to the amendment digest and refluxed for 90 minutes after the appearance of white fumes. Digests were diluted with deionized water, filtered through 0.45 micron membrane filters and analyzed for Cd, Cu, Pb, and Zn using inductively coupled plasma atomic emission spectroscopy (ICP). Unless otherwise specified, all chemical analyses of amendments and soil were performed in triplicate.

In-Situ Immobilization

A preliminary study was conducted to determine the application rate of soil amendments. Contaminated soil (2 g) was mixed with 50, 100, 200, 330, 670, and 1000 g kg^{-1} of amendment and shaken with 50 mL of 0.01 M $\text{Ca}(\text{NO}_3)_2$ for 24 h. One application rate (100 g kg^{-1}) was selected for detailed study.

The incubation experiment was a completely randomized design with ten soil treatments and an untreated control. Each treatment and control soil had three replications. Each amendment (100g) was mixed with contaminated soil (1000 g), both on dry-weight basis in plastic cups. Treated soils were incubated at 25 °C and 0.03 MPa for 12 weeks. After incubation, soils were air dried and crushed (< 2 mm) in plastic sampling bags with a stainless steel rolling pin.

Soil pH was determined for treated soil in 1:2 soil:0.01M CaCl_2 using a glass electrode (McLean, 1982). Electrical conductivity was determined in 1:5 soil:deionized water solution for each treated soil (Rhoades, 1982).

Chemical Speciation by Sequential Extraction

Chemical speciation of heavy metals in soil, by sequential extraction based on adsorption affinity and metal solubility, was performed to determine the effect of soil amendments on heavy metal availability and provide information on long-term stability (Basta et al., 1994) (Table 3). Trace metal or Ultrex® grade reagents were used to prepare extraction solutions. Metals were speciated into exchangeable and soluble (step 1), specific adsorbed and susceptible to pH changes (step 2), strong specific adsorption by Fe and Mn oxides and organic matter (step 3), and insoluble/occluded precipitates (step 4). Soil (1g) was shaken with 20 mL of chemical extractant (Table 3) in a 50 mL centrifuge tube. The mixture was centrifuged (2260 X g) for 10 min and solution was decanted through 0.45 µm membrane filter. Soil residue was carried to the next step of the extraction sequence (Table 3). Heavy metals in extracted solutions were measured by ICP.

Extraction of Heavy Metals by TCLP

Treated and control soils were extracted by U.S. EPA TCLP (Method 1311; U.S. EPA, 1990). In this procedure 2 g of soil were shaken with 40 mL of extracting solution for 1 h. Pretreatment tests for pH, specified by this method were used to select extraction solution. Noncalcareous soils (pH < 7.5) were extracted with 0.20 M HOAc (pH 5.0) and calcareous soils (pH > 7.5) were extracted with 0.20 M HOAc (pH not adjusted, pH 2.88).

Heavy Metal Bioavailability in Soil

Plant metal tissue concentrations are very useful for comparing differences in availability of metals between various amended soils. Leafy vegetables, such as cabbage and lettuce, accumulate more cadmium than root crops such as carrots or radishes (Davis and Carlton-Smith, 1980). Lettuce was selected for this study because it is a Cd accumulator and is used to assess risk to the food chain in human populations (Chaney and Ryan, 1994).

Bioavailability of heavy metals was determined by measuring metal content of lettuce grown in treated soils in a growth chamber. Lettuce was grown for 70 days (until maturity) in plastic pots containing approximately 400 g of treated soil. The growth chamber experiment was a completely randomized design with ten soil treatments and an untreated control. Two replicate pots of treated and untreated soil were planted with eight to ten lettuce seeds and thinned to five lettuce plants shortly after emergence. Growth chamber conditions were 16 h of light at 25 °C and 80% RH. In a preliminary study, burning along the margins of the leaves was apparent for several treatments shortly after emergence. Pots of treated soil were leached with deionized water until excess salt was removed (soil leachate EC < 0.5 dS m⁻¹). Twenty five percent, v/v, vermiculite was mixed in each pot for aeration. Two replicate pots of each treated soil were replanted with eight to ten lettuce seeds and thinned to five lettuce plants shortly after emergence. All pots received supplemental

fertilization by adding approximately 20 mL of a dilute water solution (1.0 g L^{-1}) of (Miracle Gro®) every third day. After maturity (70 days), the vegetative above-ground growth was harvested, dried in a forced-air oven at $70 \text{ }^{\circ}\text{C}$ for 48 h, and ground in a stainless steel Wiley mill (Jones, Jr. and Case, 1992). Dried plant tissue (1 g) was wet digested with concentrated trace metal grade HNO_3 in an aluminum digestion block at $140 \text{ }^{\circ}\text{C}$ for 2 h followed by Cd, Cu, Pb, and Zn analysis by ICP (Zarcinas et al., 1987). Bioavailability was defined as heavy metal content of above ground growth of lettuce and not metal in roots.

Treatment effects on measured parameters were evaluated by using multiple comparison of means by Duncan's Multiple Range Test (Steele and Torrie, 1980). Statistical analysis of data was performed using appropriate procedures given by the SAS Institute (SAS, 1988).

RESULTS AND DISCUSSION

Chemical speciation and TCLP for the contaminated Kirkland silt loam soil were performed (Table 4). Total metal contents are estimated as: (in mg kg^{-1}), 340 Cd, 754 Cu, 1185 Pb, and 24700 Zn. Geometric mean heavy metal contents in baseline U.S. soils are (in mg kg^{-1}): 0.27 Cd, 29.6 Cu, 12.3 Pb, and 56.5 Zn (Holmgren et al., 1993). Heavy metal contents greatly exceed baseline soil levels and confirm the Kirkland soil was highly contaminated. Chemical speciation of Cd, Cu, Pb, and Zn involved sequential extraction of treated soils

with $\text{Ca}(\text{NO}_3)_2$ (CaEx), NaOAc (AcEx), EDTA (EDEX), and HNO_3 (HEX). This sequential extraction method is based on adsorption affinity and solubility of heavy metals in soil (Basta et al., 1994). Heavy metal availability and plant bioavailability decreases with each successive sequential extraction. Most soil Cd was readily available (Table 4). Small amounts of Cu and Pb were in the CaEx fraction, but large amounts were in the AcEx form which is potentially available. Although Zn CaEx fraction is small compared to other fractions, CaEx fractions greater than 1000 mg kg^{-1} are associated with Zn phytotoxicity (Basta et al., 1994). This contaminated soil would be considered hazardous waste because it exceeded Cd and Pb U.S. EPA TCLP regulatory limits (Table 4).

Chemical Speciation and Extent of Remediation

Zinc. Most amendments significantly decreased CaEx Zn (Figure 1). Treatments grouped from left to right in all figures are biosolids (LS, SS, and NV), liming materials (CKD and L), phosphate fertilizers (RP and TSP), and others (RM, Z, and AS). Zinc in the CaEx fraction was decreased from $> 2000 \text{ mg kg}^{-1}$ in the control to $< 50 \text{ mg kg}^{-1}$ in CKD treatment. The four most effective treatments (LS, NV, CKD, and RM) at reducing CaEx Zn resulted in the largest increase in soil pH ($\text{pH} > 7.3$) (Figure 2). Although all four amendments decreased CaEx Zn by increasing pH, the reaction mechanisms are probably different. Chelation of metals in LS and NV, metal carbonate precipitation by LS, NV, and CKD, and specific adsorption by metal oxides in RM may account for

the reductions in Zn availability. Czupyrna et al. (1989) conducted an in-situ immobilization study using amendments to reduce soluble Cd, Cu, Cr, Ni, and Zn in soils treated with heavy metal salts. They reported hydrated lime and FeSO_4 as being viable treatments for immobilizing Cu, Ni, Cd, and Zn and reducing solubility of heavy metals in soil.

The AcEx fraction represents weak specific adsorbed and susceptible to pH changes (i.e. precipitated carbonates). Because future soil acidification may release heavy metal from the AcEx fraction and make it bioavailable, it is desirable to convert heavy metals to stable EEx and HEx fractions. Decreases in AcEx Zn and an increase in HEx Zn suggest CaEx and AcEx Zn fractions may have been converted to stable HEx Zn by NV. Pierzynski and Schwab (1993) investigated the effects of various soil amendments on Zn, Pb, and Cd bioavailability in a metal-contaminated alluvial soil. Cattle manure, NViro, and poultry litter immobilized Zn and decreased KNO_3 -extractable Zn in contaminated soil. They suggested limestone treatments converted readily available exchangeable Zn to a less available precipitated form. Results from previous studies agree with our findings where organic amendments and lime converted soluble and exchangeable Zn to less available forms of Zn. However, the other three amendments (LS, CKD, and RM) successful at increasing pH and reducing CaEx Zn, did not significantly change CaEx Zn to AcEx, EEx, and HEx fractions (Figure 1). Because the reduction in CaEx Zn is small compared

to the amounts of Zn in the other three fractions, CaEx may have been converted to less available forms not detected at $P < 0.05$.

Only TSP treatment increased CaEx Zn. The dissolution of TSP yields phosphoric acid which decreases soil pH (Lindsay 1979). The overall increase in CaEx Zn from TSP can be attributed to the large decrease in soil pH caused by TSP. Thus, TSP increased readily available Zn. Because metals in the AcEx fraction are "susceptible to acid", the lower pH induced by TSP likely dissolved acid labile AcEx forms of Zn (Figure 1). Triple superphosphate decreased the HEx Zn fraction but increased EDEX. Although HEx is more insoluble than EDEX forms of Zn, both of these fractions are associated with insoluble P precipitates and are considered unavailable to plants.

Cadmium. All amendments significantly decreased CaEx Cd (Figure 3). Cadmium was reduced from $> 200 \text{ mg kg}^{-1}$ in the control to $< 21 \text{ mg kg}^{-1}$ by NV. Biosolids (LS, SS, and NV), CKD, TSP, and RM were the most effective at reducing CaEx Cd. The decrease in CaEx Cd fraction from lime containing wastes suggests that there is a relationship between soil pH (Figure 2) and CaEx Cd. Because the chemistry of Cd and Zn in soil are similar (Logan and Chaney, 1983; Alloway, 1992), similar decreases between CaEx Cd and CaEx Zn by soil amendments were found. Chelation of metals in LS, SS, and NV, metal carbonate precipitation by LS, NV, and CKD, metal phosphate precipitation by TSP, and specific adsorption by metal oxides in RM may account for the reductions in Cd availability. Lime containing wastes (LS, NV,

CKD, RM, and AS) increased AcEx Cd and suggest CaEx Cd was converted into less available AcEx Cd forms. Most amendments increased EDEX Cd which suggests some CaEx Cd was converted into an unavailable form which is more insoluble than AcEx Cd. Phosphate fertilizers, SS, and NV possibly converted CaEx Cd into EDEX and/or HEx Cd fractions which are generally not plant available. Rock phosphate showed the greatest increase in both EDEX and HEx Cd. Rock phosphate was the only amendment that had a significant increase in HEx Cd. The conversion to EDEX or HEx Cd suggests SS and phosphate fertilizers decrease Cd availability more than lime containing wastes.

Lead. All amendments significantly decreased CaEx Pb (Figure 4). Reductions in CaEx Pb ranged from 20 mg kg⁻¹ in the control to < 1.0 mg kg⁻¹ by NV. The decrease in CaEx Pb fraction from addition of lime containing wastes to soil suggests that there is a relationship between soil pH and CaEx (Figure 2). Biosolids and TSP decreased potentially available AcEx Pb. Impressive results suggest TSP converted available forms of CaEx and AcEx Pb to unavailable EDEX Pb.

Other studies have reported phosphorus fertilizer decreased Pb availability (solubility) in contaminated soils (Ma et al. 1993; Ma et al. 1995). Readily available soluble and resin-extractable forms of Pb from contaminated soil were precipitated as Pb(OH)₂ and lead pyromorphite, a Pb analog of hydroxyapatite, from aqueous solution by hydroxyapatite. Lead pyromorphite is very insoluble and has a low bioavailability (Ruby et al., 1994). Formation of

insoluble phosphates may be responsible for the decrease in availability of Pb in soils amended with TSP and RP in our study. Conversion of Pb to the least available HEx form would be the most desirable effect of soil amendments. Unfortunately, conversion of soil Pb to HEx Pb forms was not apparent (Figure 4).

Copper. The Kirkland soil contained 754 mg kg^{-1} Cu which indicates slight Cu contamination. None of the amendments decreased CaEx Cu (Figure 5). However, TSP and LS increased CaEx Cu and Cu availability. Soil acidification induced by TSP may have increased CaEx forms of Cu. The organic matter composition (Sloan et al., 1995) of the three biosolids in this study were different. Lime-stabilized sewage sludge contained much greater amounts of soluble organic matter than SS and NViro. Perhaps soluble organic Cu complexes from LS additions increased the CaEx Cu fraction. Potentially available AcEx forms of Cu were decreased by biosolids and TSP. In general, the treatments did not affect EDEX or HEx Cu fractions.

Heavy Metal Hazard and Mobility (U.S. EPA TCLP)

The U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP) (U.S. EPA, 1990) is used to classify waste materials. Waste materials with metal concentrations in TCLP extracts that exceed regulatory criteria are considered hazardous waste. Regulatory levels for TCLP Cd are 1.0 mg L^{-1} and 5.0 mg L^{-1} for TCLP Pb. The contaminated soil used in this study is considered hazardous

waste because it exceeds Cd and Pb U.S. EPA TCLP regulatory limits (Table 4).

Because TCLP extraction solution is dilute (0.20 M) acetic acid, only forms of heavy metals in soils that are easily dissolved are extracted. Metals extracted by TCLP are considered more mobile than unextracted forms and constitute greater environmental hazard.

The ability of soil amendments to reduce heavy metal concentrations in TCLP extracts is presented in Figure 6. Cadmium TCLP concentrations were not reduced below U.S. EPA regulatory levels, but many amendments decreased TCLP extractable Cd. Reductions in heavy metal hazard are associated with reductions of TCLP Cd. The most significant decreases in TCLP Cd were from SS and TSP treatments.

The majority of amendments applied to the contaminated soil reduced TCLP extractable Pb. Lead TCLP values were reduced below U.S. EPA regulatory limit (Table 4) by LS, SS, and TSP. Rock phosphate and RM decreased TCLP Pb, but not below regulatory levels. The extracting solution used in the TCLP procedure depends on the treated soil pH. According to U.S. EPA TCLP procedure, noncalcareous soils ($\text{pH} < 7.5$) were extracted with 0.20 M HOAc adjusted to pH 5.0 and calcareous soils ($\text{pH} > 7.5$) were extracted with 0.20 M HOAc without pH adjustment (pH 2.88). Lime containing wastes (NV and CKD) that raised the soil $\text{pH} > 7.5$ (Figure 2) required the use of unbuffered acetic acid (pH 2.88). The more acidic unbuffered extraction solution may dissolve more Pb than the extraction solution buffered at pH 5.0. The control

soil was extracted with buffered TCLP solution. Perhaps the use of different TCLP extracting solutions caused the TCLP Pb concentration from the CKD (final extracting solution pH 4.3) treated soil to be larger than the TCLP Pb from the control soil (final extracting solution pH 5.0).

Four amendments (LS, SS, TSP, and RM) reduced TCLP extractable Zn. Although U.S. EPA regulatory levels have not been established for Zn, reductions in TCLP Zn reflect decreases in solubility and potential hazard from Zn. Lime containing wastes (NV and CKD) that raised the soil pH > 7.5 (Figure 2) required the use of unbuffered acetic acid (pH 2.88). Because Zn solubility increases with acidity, the use of different TCLP extracting solutions may have resulted in TCLP Zn concentration from the NV (final extracting solution pH 4.2) treated soil to be larger than the TCLP Zn from the control soil (final extraction solution pH of 5.0).

Most biosolids, TSP, and RM reduced TCLP extractable Cu. Although U.S. EPA regulatory levels have not been established for Cu, reductions in TCLP Cu reflect decreases in potential hazard from Cu. Increases in TCLP Cu, similar to increases in TCLP Zn and Cd, were found for NV and CKD treatments and may be due to the use of an extracting solution that resulted in a final pH more acidic than the control soil extracting solution.

Heavy Metal Bioavailability

Leaf burn along the margins of lettuce grown in several treated soils suggested a salinity problem. Electrical conductivity values (1:5 soil:water) of treated soils were increased by LS, NV, CKD, TSP, and RM (Figure 7). Treated soils were leached with deionized water until excess salt was removed (soil solution $EC < 0.5 \text{ dS m}^{-1}$) and lettuce was replanted. Leaf burn did not occur from any of the treatments after leaching and replanting of lettuce seeds.

Lettuce grew in LS, NV, CKD, and RM amended soil, but Zn toxicity prevented growth in other treated soils. Increased soil pH (Figure 2) from LS, NV, CKD, and RM decreased CaEx Zn and prevented Zn phytotoxicity. Zinc CaEx fractions greater than 1000 mg kg^{-1} are associated with Zn phytotoxicity (Basta et al., 1994). The effect of soil amendments on lettuce yield and tissue metal concentrations are shown in Table 5. Tissue Zn concentrations were 763 for LS, 499 for NV, 562 for CKD, and 852 mg kg^{-1} for RM. Zinc plant tissue concentrations in the amended soil were larger than lettuce produced in comparable baseline soils which ranged from 9.8 to 22.8 mg kg^{-1} Zn (Table 5) (Scott, 1994).

Tissue concentrations for Cd (Table 5) were 75.1 for LS, 87.3 for NV, 114.1 for CKD, and 130 mg kg^{-1} for RM. Cadmium plant tissue concentrations in the amended soil were larger than those obtained with lettuce produced in comparable baseline soils which ranged from 0.59 to 3.68 mg kg^{-1} Cd. Consumption of lettuce with Cd content elevated more than $69 \text{ } \mu\text{g Cd g}^{-1}$ above baseline lettuce Cd is possible without lifetime injury to the worse-case home

gardener who consumes 50% of lifetime garden foods as lettuce (Chaney and Ryan, 1994). Cadmium content of lettuce grown in treated soils was elevated more than $69 \mu\text{g Cd g}^{-1}$ above baseline levels (Table 5) and would not be recommended for human consumption. Other crop production may be less harmful since leafy vegetables tend to accumulate heavy metals more than other garden vegetables. Soils treated with LS, NV, CKD, or RM can be revegetated by plants that exclude Cd and other heavy metals. Revegetation will stabilize the contaminated site. However established vegetation should not be harvested for food or feed unless the metal levels in the established vegetation is not a hazard to the food chain.

Because Cd and Zn uptake mechanisms in people are similar, risk from Cd in food may be better related to Cd:Zn ratios than absolute amounts of Cd (Logan and Chaney, 1983; Chaney and Ryan, 1994). In addition, cadmium to zinc ratios (0.098 to 0.20) were increased in LS, NV, CKD, and RM amended soils versus comparable baseline soils which Cd:Zn ratios ranged from 0.044 to 0.062 (Table 5).

Tissue Pb concentrations (Table 5) were 4.89 for LS, 7.12 for NV, 6.84 for CKD, and 6.93 mg kg^{-1} for RM. Small increases in Pb concentrations were found in amended soils versus lettuce produced in comparable baseline soils which ranged from 2.32 to 4.10 mg kg^{-1} , but these increases were not significant at $P < 0.05$ (Table 5).

Tissue concentrations for Cu (Table 5) were 15.3 for LS, 17.6 for NV, 13.0 for CKD, and 17.3 mg kg⁻¹ for RM. Small increases in Cu concentrations were found in amended soils versus lettuce produced in comparable baseline soils which ranged from 3.14 to 5.95 mg kg⁻¹.

Lettuce was only produced in soils treated with lime-containing amendments (LS, NV, CKD, and RM) that resulted in pH > 7.3. Chemical speciation results showed CaEx Zn was reduced from phytotoxic levels in the control to non-toxic levels by the same four treatments. Similar amendments of limestone and limestone suspension decreased Zn in soybean and increased yield of soybean grown in Zn contaminated soil (Pierzynski and Schwab, 1993). In addition to limestone-containing amendments, organic amendments (poultry litter, NViro, and cattle manure) and K₂HPO₄ decreased Zn in soybean tissue and increased soybean yield in Zn contaminated soil. Lime, zeolite, alum sludge, and rock phosphate decreased plant available CaEx forms of Zn in our study (Figure 1). Lettuce growth occurred for the first three weeks after germination in L, Z, AS, and RP treated soils, but CaEx Zn was not reduced below phytotoxic levels and the plants were stunted and discolored as a result of the toxic soil conditions and did not grow to maturity. Total Zn content of 24700 mg kg⁻¹ in this Kirkland soil was much greater than the 1165 mg kg⁻¹ Zn in the contaminated alluvial soil studied by Pierzynski and Schwab (1993). Lime, zeolite, alum sludge, and rock phosphate may alleviate Zn phytotoxicity in soils that have less Zn contamination than the Kirkland soil used in our study.

SUMMARY

In general, all the amendments (LS, SS, NV, L, CKD, RP, TSP, RM, Z, and AS) decreased readily available Zn, Cd and Pb except TSP which increased readily available Zn. Zinc availability was decreased by NV and TSP to a stable unavailable form. NViro successfully converted (stabilized) Zn to highly unavailable (HEX) form. Acidity produced by TSP increased readily available Zn which made the soil more toxic. Many amendments contained alkaline materials and were effective at increasing pH which promoted precipitation and specific adsorption reactions and reduced heavy metal availability in amended soils.

Many alkaline containing amendments (LS, NV, CKD, RM, and AS) converted readily available Cd (CaEx) into less available (AcEx) forms. Most biosolids and phosphates increased the EDEx Cd (stabilized) fraction. NViro and RP amendments converted Cd into highly unavailable (stable) HEX forms. Because HEX forms tend to be chemically stable, RP proved most impressive in increasing highly unavailable Cd.

Biosolids and TSP decreased potentially available AcEx Pb. Apparently TSP converted available CaEx and AcEx Pb into unavailable (stable) EDEx Pb.

In general most biosolids, phosphate fertilizers, RM, and AS were the most effective in reducing Cd, Pb, Zn, and Cu TCLP in contaminated soils. Rock phosphate and TSP were quite successful at reducing TCLP Cd but the

reduction was not below U.S. EPA regulatory level. Three amendments (LS, SS, and TSP) decreased TCLP Pb to levels below U.S. EPA regulatory limit. Reductions in TCLP metal below the regulatory level changes the soil classification from hazardous to non-hazardous material. Amendments that reduce TCLP metal levels below U.S. EPA limits could be used to treat excavated soils prior to landfill disposal.

NViro, LS, CKD, and RM treatments increased soil pH, and decreased CaEx Zn and zinc phytotoxicity which allowed revegetation by lettuce. Zinc and Cd tissue concentrations ranging from 499 to 852 mg kg⁻¹ Zn and 75.1 to 130 mg kg⁻¹ Cd were elevated compared to lettuce produced in baseline soils (25.1 mg kg⁻¹ Zn and 1.86 mg kg⁻¹ Cd). Cadmium content of lettuce grown in treated soils was elevated more than 69 µg Cd g⁻¹ above baseline levels and would not be recommended for human consumption. Amendments had little effect on Pb and Cu content in lettuce grown in treated soils.

Overall NV, LS, CKD, and RM were the most successful amendments in reducing availability, TCLP, bioavailability, and revegetating a highly contaminated soil. However, L, Z, AS, and RP amendments used in this study may have the ability to alleviate Zn phytotoxicity in less contaminated soils and allow revegetation and stabilization of the contaminated site. The extent of remediation could be increased by using larger treatment rates. Unfortunately, applications of larger rates may not be practical due to mechanical limitations of field equipment. However, TSP was impressive in reducing available forms of

Pb and Cd; and increasing unavailable forms. Investigation using TSP with a liming material may provide a successful remediation treatment that decreases bioavailability and increases stability of all four metals (Cd, Cu, Pb, and Zn).

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Table 1. Classification of in-situ immobilization amendments.

Amendment	Acronym	Biosolid	Alkaline Material	Phosphorus Fertilizer	Other
Lime-stabilized sewage sludge	LS	X	X		
Anaerobic-digested sewage sludge	SS	X			
NViro soil	NV	X	X		
Cement kiln dust	CKD		X		
Agricultural Lime	L		X		
Rock phosphate	RP			X	
Triple superphosphate	TSP			X	
Bauxite red mud	RM				X
Zeolite	Z				X
Alum sludge	AS		X		X

Table 2. Chemical properties of soil amendments.

Property	Amendment									
	LS	SS	NV	CKD	L	RP	TSP	RM	Z	AS
pH†	12.3	7.1	7.9	12.6	nd‡	7.0	3.0	8.1	8.9	7.0
Total Content, mg kg ⁻¹										
Cd	8	41	11	2.98	0.1	15.3	1.82	6.6	0.43	0.57
Cu	272	685	124	7.48	10	4.04	1.48	27.3	4.70	24.8
Pb	63	274	<1	29.7	<1	2.85	3.87	56.4	6.98	14.0
Zn	415	1675	254	36.8	25	159	100	56.1	43.4	86.1
Fe oxide§, g kg ⁻¹	1.6	1.0	1.4	nd‡	nd‡	nd‡	nd‡	209	nd‡	21.6
CCE¶, %	21.4	<2.0	46.7	87.5	104	21.4	nd‡	24.2	10.4	40.8
EC, dS m ⁻¹	1.3	3.8	6.5	17.8	0.94	0.32	27.9	2.6	0.63	0.31
Organic Carbon, g kg ⁻¹	302	223	57	nd‡	nd‡	nd‡	nd‡	nd‡	nd‡	nd‡

† 1:2 amendment:0.01M CaCl₂.

‡ not determined.

§ Fe oxide contents are expressed on an elemental basis as Fe.

¶ calcium carbonate equivalent expressed in %.

Table 3. Experimental conditions and chemical forms of heavy metal determined by sequential extraction.

Extraction Sequence	Chemical Extractant	Acronym	Extraction Conditions	Chemical Form of Metal Extracted	Plant Availability	Reference
1	0.5 M Ca(NO ₃) ₂	CaEx	shake 16 h	exchangeable soluble	readily	Miller et al., 1986
2	1.0 M NaOAc, pH 5	AcEx	shake 5 h	weakly complexed carbonate precipitates "acid-labile"	potential	Gibson and Farmer, 1986
3	0.1 M Na ₂ EDTA, pH 7	EDEx	shake 6 h	complexed/precipitated with Fe, Mn oxides and organic matter surface precipitates	unavailable	Miller and McFee, 1983
4	4 M HNO ₃	HEx	shake 16 h, 80° C	insoluble/occluded precipitates	highly unavailable	Sposito et al., 1982

Table 4. Total and extractable heavy metals in contaminated Kirkland silt loam soil.

Parameter	Cd	Cu	Pb	Zn
	————— mg kg ⁻¹ —————			
Chemical Speciation †				
Ca(NO ₃) ₂	201	1.8	20.1	2220
NaOAc	57.7	250	460	9472
EDTA	14.4	266	348	5333
HNO ₃	66.7	236	357	7676
Total‡	340	754	1185	24700
	————— mg L ⁻¹ —————			
TCLP	9.3	3.9	8.7	299
U.S. EPA Regulatory Limit	1.0	nl§	5.0	nl§

† = Extraction solutions are used to designate sequential extraction fractions.

‡ = Total metal content estimated by summation of chemical speciation fractions.

§ nl = no regulatory level.

Table 5. Treatment effects on lettuce yield and tissue metal concentrations.

Treatment	Yield g pot ⁻¹	Tissue Concentrations				Ratio Cd:Zn
		Zn	Cd	Pb	Cu	
		mg kg ⁻¹				
LS	4.1	763a	75.1b	4.89a	15.3a	0.099c
NV	4.3	499b	87.3b	7.12a	17.5a	0.176ab
CKD	3.6	562b	114 a	6.84a	13.0a	0.203a
RM	1.8	852a	130 a	6.93a	17.3a	0.156b
LSD(0.05)		159	16.4	3.26	10.5	0.041
Baseline Soils†						
	mean	25.1	1.86	3.35	4.44	0.062
	min	13.4	0.59	2.32	3.14	0.044
	max	51.8	3.68	4.10	5.95	0.102

† Lettuce produced on baseline soils. (Scott, T. D. 1994.)

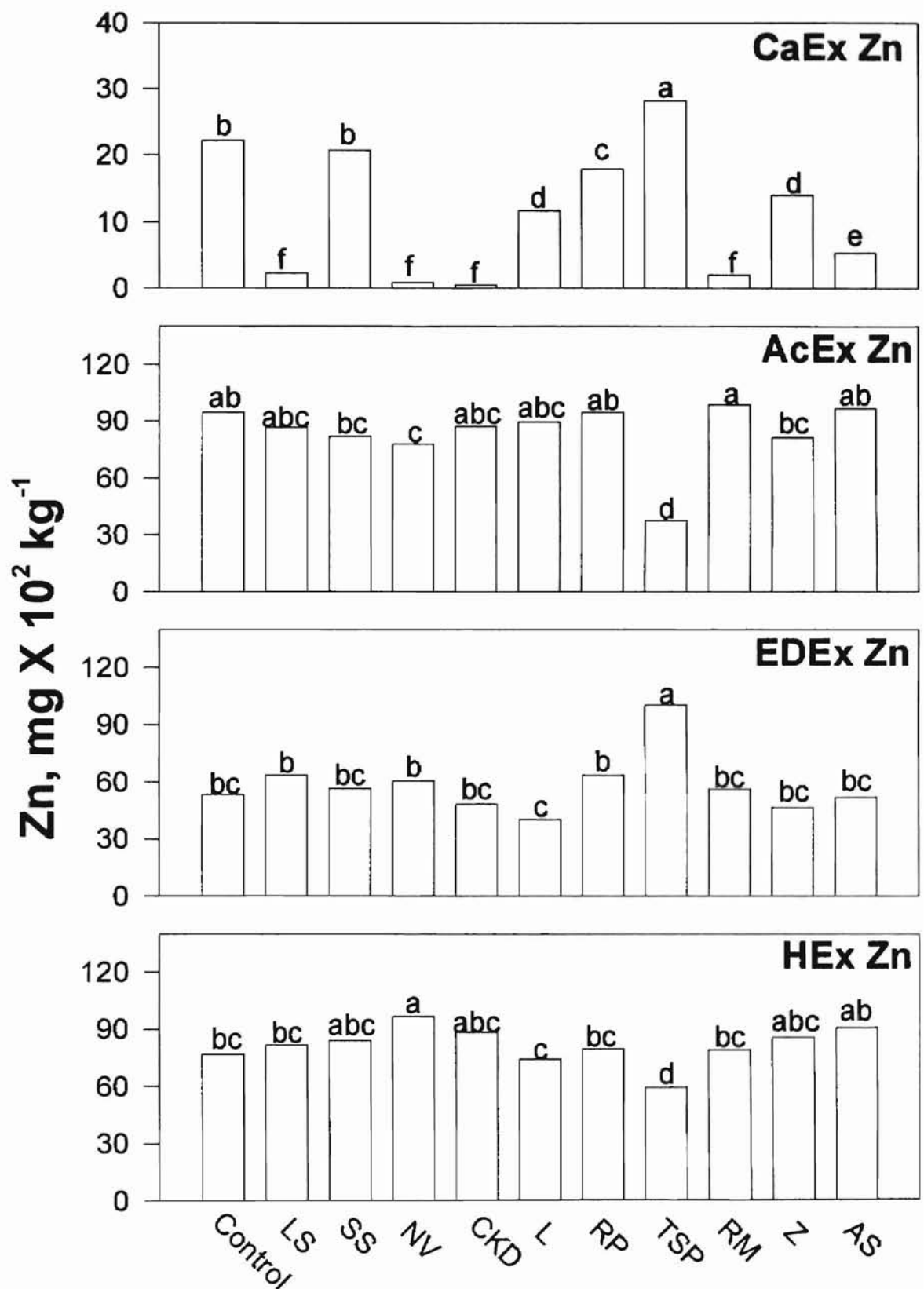


Figure 1. Zinc speciation after in-situ immobilization of contaminated soil. Columns with the same letter are not different at $P < 0.05$.

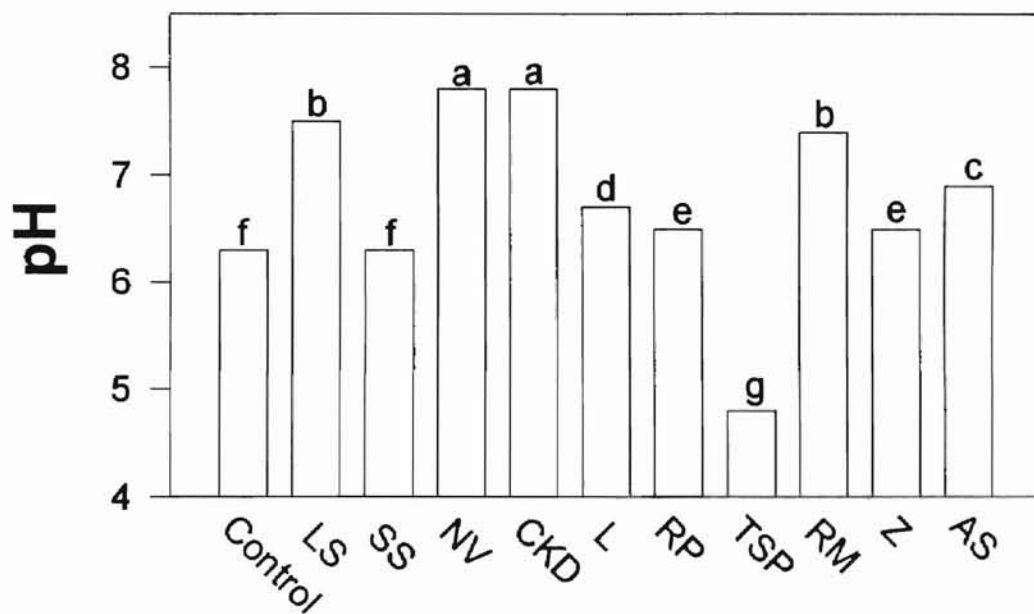


Figure 2. Soil pH after in-situ immobilization of contaminated soil. Columns with the same letter are not different at $P < 0.05$.

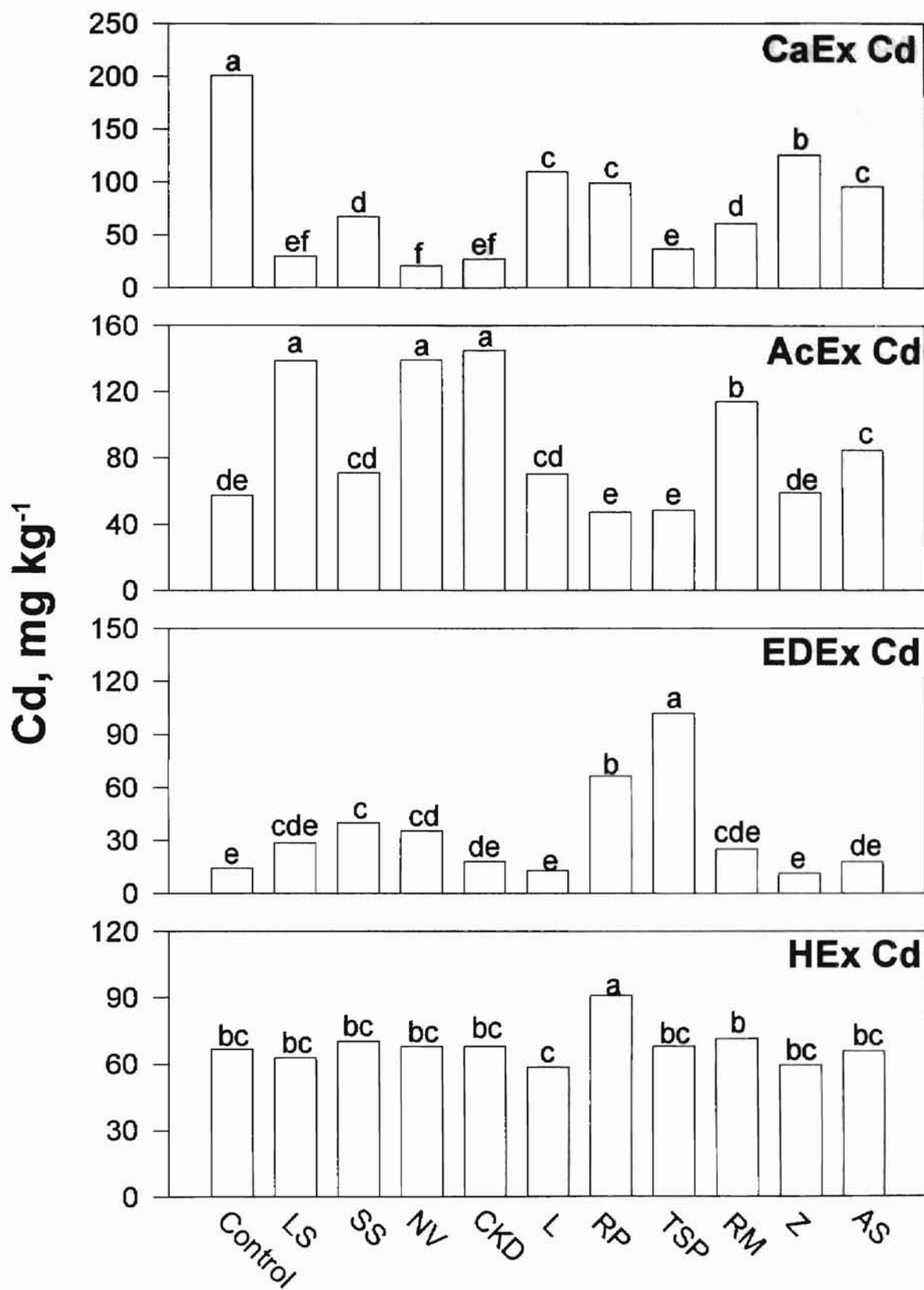


Figure 3. Cadmium speciation after in-situ immobilization of contaminated soil. Columns with the same letter are not different at $P < 0.05$.

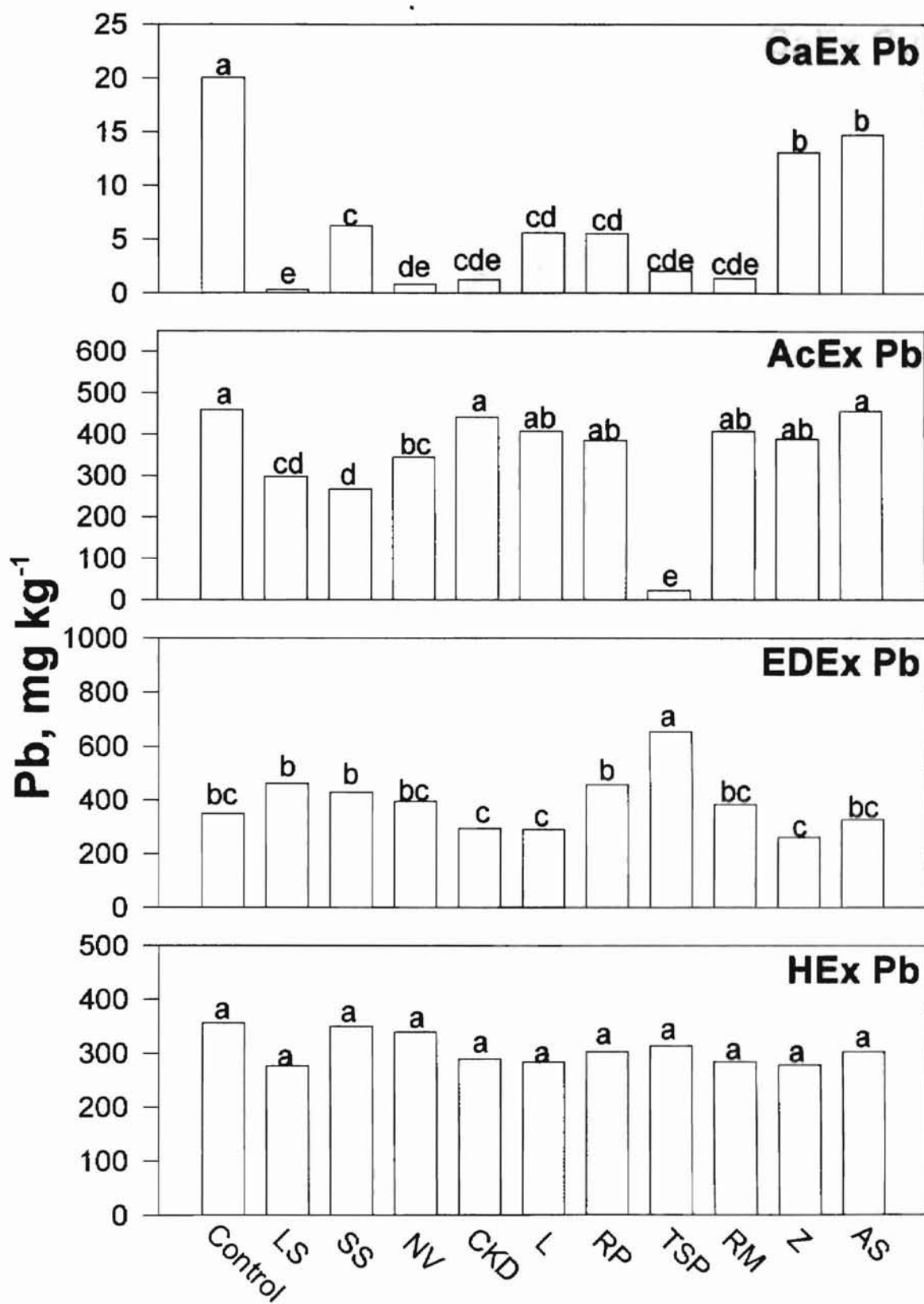


Figure 4. Lead speciation after in-situ immobilization of contaminated soil. Columns with the same letter are not different at $P < 0.05$.

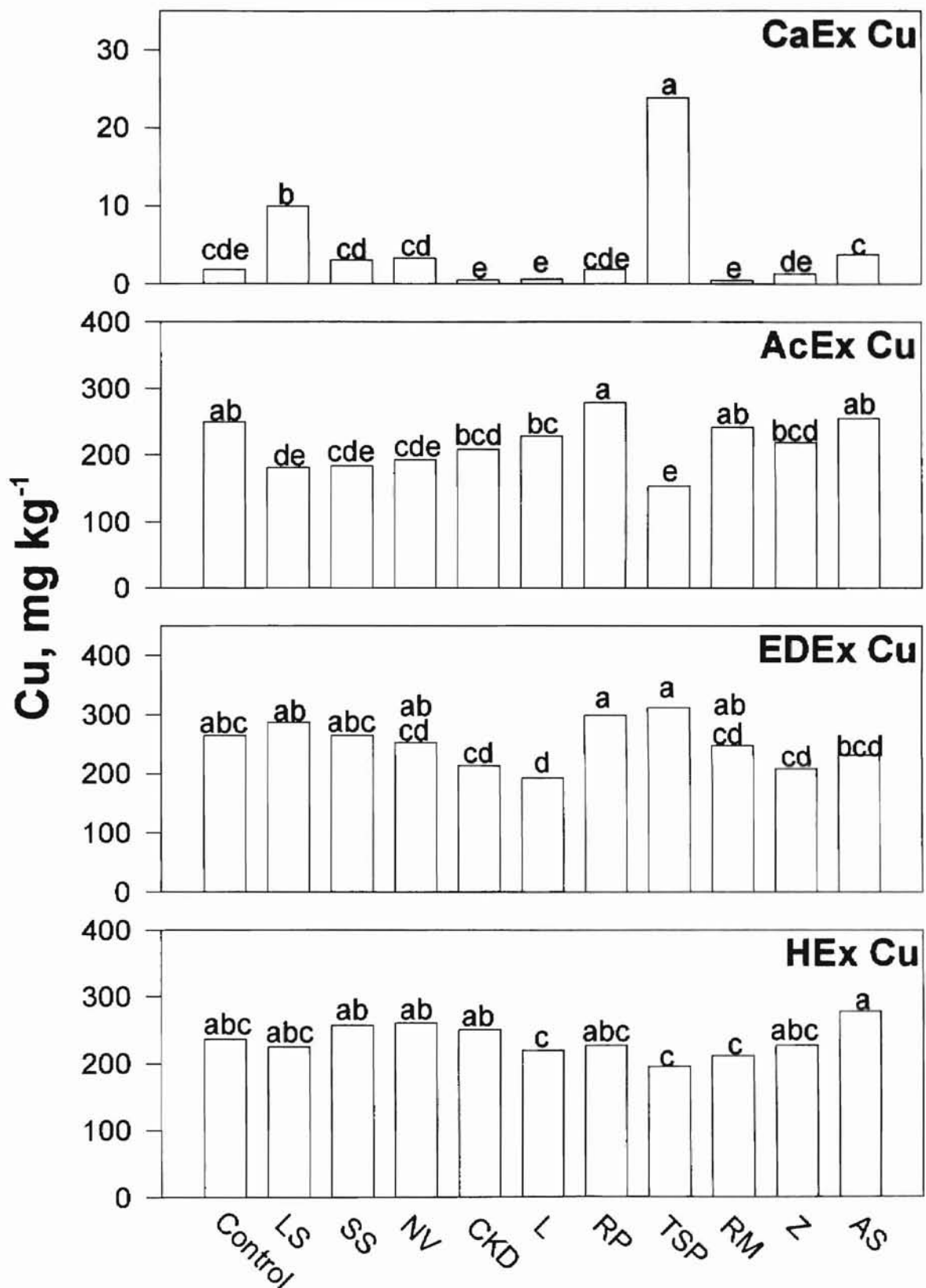


Figure 5. Copper speciation after in-situ immobilization of contaminated soil. Columns with the same letter are not different at $P < 0.05$.

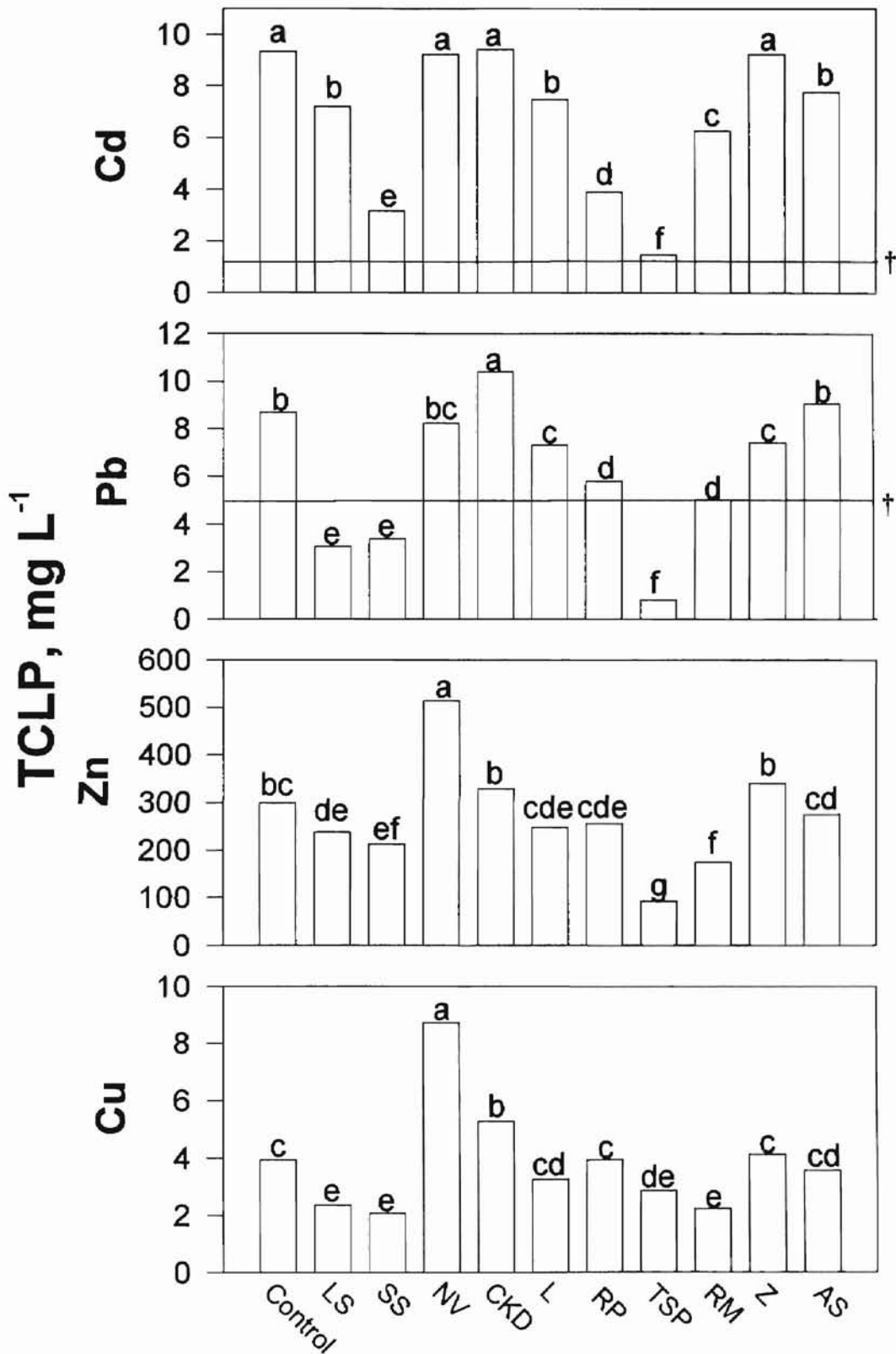


Figure 6. Heavy metals extracted by U.S. EPA TCLP from treated soil. † designates U.S. EPA regulatory limit for Cd and Pb. Columns with the same letter are not different at P < 0.05.

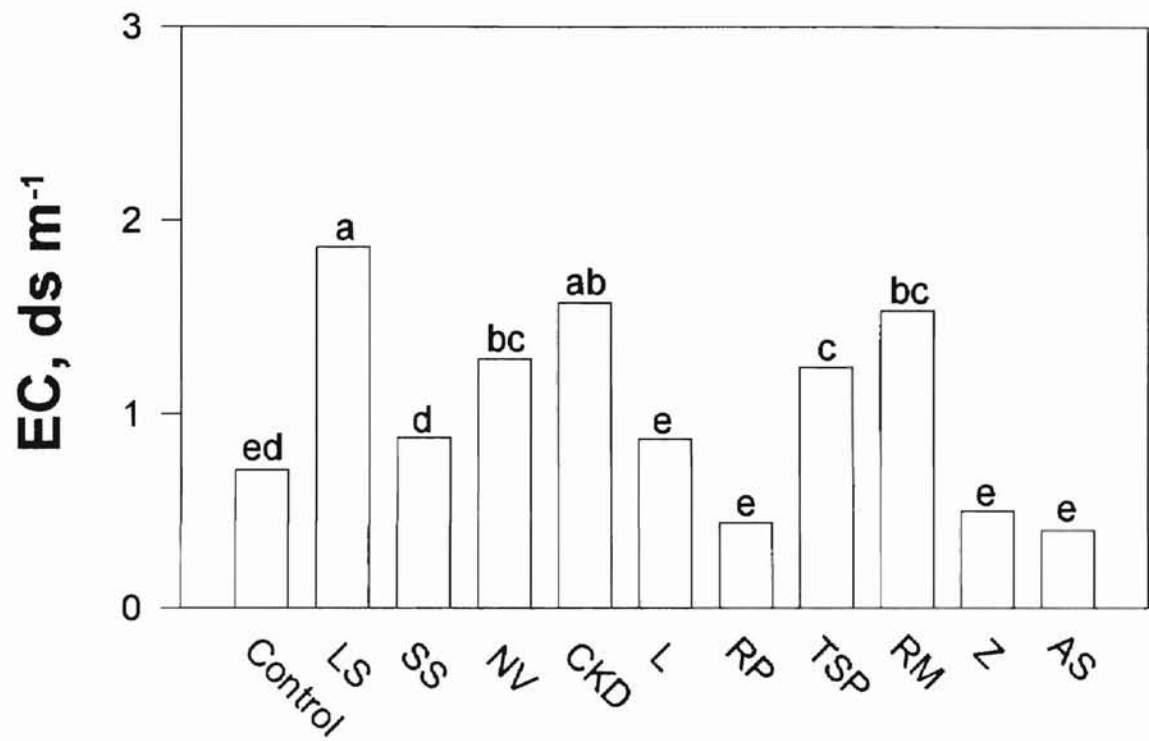


Figure 7. Soil electrical conductivity (EC) values after in-situ immobilization of contaminated soil. Columns with the same letter are not different at $P < 0.05$.

APPENDIX

Table A1. Chemical speciation ($\text{Ca}(\text{NO}_3)_2$) data of amended soil.

Amendment	Rep	Zn	Pb	Cd	Cu
		mg kg ⁻¹			
Alum Sludge	1	554.9	15	94.96	4.75
Alum Sludge	2	571.09	19.89	101.43	1.54
Alum Sludge	3	468.85	9.21	91.59	4.97
Zeolite	1	1196.91	12.78	124.89	1.4
Zeolite	2	1246.5	10.39	117.63	0.73
Zeolite	3	1754.64	16.11	134.7	1.78
NViro	1	87.65	0.79	19.17	3.55
NViro	2	79.39	0.81	21.42	2.99
NViro	3	77.29	0.77	21.68	3.45
TSP	1	2879.04	0.95	39.13	24.68
TSP	2	3007.16	1.71	38.66	26.35
TSP	3	2597.54	3.46	32.84	20.56
LSSS	1	210.09	0.11	27.88	9.51
LSSS	2	234.39	0.44	31.48	10.85
LSSS	3	228.6	0.33	29.1	9.43
Sewage Sludge	1	1928.9	5.72	66.26	3.04
Sewage Sludge	2	2212.96	7.3	77.07	3.14
Sewage Sludge	3	2081.73	5.77	58.68	2.87
Ag Lime	1	954.41	4.99	108.24	0.48
Ag Lime	2	1396.62	6.49	113.4	0.63
Ag Lime	3	1140.65	5.23	107	0.65
CKD	1	46.44	0.36	24.96	0.57
CKD	2	45.28	2.75	30.29	0.25
CKD	3	50.38	0.62	26.85	0.67
Red Mud	1	194.43	0.9	59.36	0.36
Red Mud	2	257.48	1.59	75.54	0.44
Red Mud	3	156.72	1.63	48.93	0.58
Rock PO ₄	1	1751.17	3.59	94.54	1.82
Rock PO ₄	2	1807.83	6.32	103.01	1.82
Rock PO ₄	3	1821.11	6.58	99.87	1.77
Control	1	2034.68	16.48	181.85	1.74
Control	2	2177.69	17.05	198.93	1.7
Control	3	2447.12	26.68	223.05	2.03

Table A2. Chemical speciation (NaOAc) data of amended soil.

Amendment	Rep	Zn	Pb	Cd	Cu
		mg kg ⁻¹			
Alum Sludge	1	9244	444.45	77.81	256.76
Alum Sludge	2	11390.77	536.82	92.04	307.94
Alum Sludge	3	8417.2	391.3	84.77	201.11
Zeolite	1	8550.27	408.86	64.58	227.51
Zeolite	2	8488.49	402.55	66.12	215.47
Zeolite	3	7410.34	355.21	46.56	212.12
NViro	1	7100.8	335.57	130.48	188.09
NViro	2	9103.66	406.72	143.23	234.85
NViro	3	7147.71	291.76	143.79	154.96
TSP	1	3753.4	17.96	48.07	147.37
TSP	2	3976.69	22.2	51.56	164.93
TSP	3	3565.51	28.75	45.56	146.99
LSSS	1	9164.84	315.94	147.96	196.69
LSSS	2	7768.59	253.52	122.3	151.98
LSSS	3	9060.24	322.19	146.1	194.75
Sewage Sludge	1	8332.37	286.11	68.7	187.51
Sewage Sludge	2	7781.71	245.1	65.23	172.55
Sewage Sludge	3	8474.73	267.61	79.02	190.9
Ag Lime	1	9227.85	423.38	76.82	239.42
Ag Lime	2	8199.62	382.08	65.39	208.37
Ag Lime	3	9484.29	414.79	69.11	238.09
CKD	1	8510.75	433.95	142.15	217.23
CKD	2	8171.25	379.55	141.77	191.8
CKD	3	9492.87	511.5	151.74	217.67
Red Mud	1	10067.21	386.76	119.65	235.13
Red Mud	2	10490.17	449.54	120.51	264.59
Red Mud	3	9076.19	387.22	101.97	225.89
Rock PO ₄	1	8947.89	356.29	40.66	270.86
Rock PO ₄	2	10188.62	433.75	53.88	296.17
Rock PO ₄	3	9293.77	366.4	46.95	270.02
Control	1	10188.93	449.89	52.75	262.53
Control	2	10003.47	483.18	66.09	255.31
Control	3	8223.8	446.7	54.34	232.16

Table A3. Chemical speciation (Na₂EDTA) data of amended soil.

Amendment	Rep	Zn	Pb	Cd	Cu
		mg kg ⁻¹			
Alum Sludge	1	4650.38	310.52	16.52	222.53
Alum Sludge	2	5464.83	324.45	17.71	241.01
Alum Sludge	3	5484.43	344.19	19.88	232.96
Zeolite	1	5356.26	304.01	14.63	248.99
Zeolite	2	4916.94	270.76	12.53	209.79
Zeolite	3	3755.78	206.15	7.14	165.13
NViro	1	4577.37	376.74	23.38	221.06
NViro	2	5340.79	344.89	27.51	229.25
NViro	3	8234.45	462.28	55.79	311.15
TSP	1	11582.62	733.74	122.29	345.31
TSP	2	10431.96	747.6	105	301
TSP	3	8053.29	477.54	77.63	289.38
LSSS	1	5409.25	372.75	21.14	252.14
LSSS	2	7267.77	511.39	37.56	312.4
LSSS	3	6393.94	498.25	27.22	297.17
Sewage Sludge	1	6809.39	548.53	51.47	321.64
Sewage Sludge	2	4961.67	356.17	37.14	231.22
Sewage Sludge	3	5180.31	381.87	31.55	245.36
Ag Lime	1	3606.63	256.61	11.7	176.34
Ag Lime	2	4352.97	321.59	14.34	208.4
Ag Lime	3	4149.87	289.88	12.54	193.27
CKD	1	4678.38	318.03	18.77	211.53
CKD	2	4707.91	272.46	15.15	204.65
CKD	3	5045.97	287.83	19.9	222.9
Red Mud	1	5699.66	384.01	26.15	239.3
Red Mud	2	5805.37	414.9	25.37	266.75
Red Mud	3	5331.41	383.33	23.89	240.02
Rock PO ₄	1	7236.47	516.44	73.6	337.48
Rock PO ₄	2	6258.13	478.31	70.22	306.74
Rock PO ₄	3	5492.92	373.36	55.9	252.37
Control	1	4995.59	332.89	13.77	261.17
Control	2	6287.11	382.34	16.23	304.16
Control	3	4717.1	328.8	13.18	232.89

Table A4. Chemical speciation (HNO₃) data of amended soil.

Amendment	Rep	Zn	Pb	Cd	Cu
		mg kg ⁻¹			
Alum Sludge	1	8323.58	291.08	58.73	332.42
Alum Sludge	2	9904.27	317.71	73.69	268.19
Alum Sludge	3	9005.78	298.78	65.26	232.63
Zeolite	1	9257.62	306.47	64.57	244.48
Zeolite	2	9109.12	293.71	59.89	243.9
Zeolite	3	7317.89	233.93	53.59	193.34
NViro	1	9224.29	390.53	62.6	284.61
NViro	2	10191.68	330.72	73.52	260.78
NViro	3	9523	295.99	67.4	236.94
TSP	1	5819.1	277.12	68.63	169.13
TSP	2	5975.32	328.64	69.45	197.26
TSP	3	5966.39	333.49	65.31	217.19
LSSS	1	7703.63	259.34	59.09	207.49
LSSS	2	8538.94	254.94	65.08	230.58
LSSS	3	8248.59	313.93	64.27	236.05
Sewage Sludge	1	8346.95	292.75	67.78	239.96
Sewage Sludge	2	8359.47	356.06	69.53	250.49
Sewage Sludge	3	8460.42	398.92	72.9	278.62
Ag Lime	1	6650.77	229.54	54.19	193.45
Ag Lime	2	6953.52	334.11	57.82	203.51
Ag Lime	3	8605.08	287.56	63.83	261.99
CKD	1	8391.39	271.56	62.71	242.4
CKD	2	8918.04	281.36	69.57	244.75
CKD	3	9165.87	314.22	71.43	265.17
Red Mud	1	7127.95	260.35	61.9	208.15
Red Mud	2	8189.1	300.34	77.16	218.67
Red Mud	3	8334.49	289.11	75.06	205.8
Rock PO ₄	1	9380.65	305.56	87.45	254.26
Rock PO ₄	2	6884.84	298.34	83.26	214.53
Rock PO ₄	3	7580.96	305.44	102.08	213.45
Control	1	7929.73	297.55	70.72	254.93
Control	2	8560.77	293.96	73.6	251.86
Control	3	6538.09	477.88	55.79	200.42

Table A5. U.S. EPA TCLP data of amended soil.

Amendment	Rep	Zn	Pb	Cd	Cu
		mg kg ⁻¹			
Alum Sludge	1	286.13	10.11	8.33	4.06
Alum Sludge	2	275.48	9.33	7.55	3.7
Alum Sludge	3	266.17	7.71	7.42	2.88
Zeolite	1	320.16	7.17	9.41	3.66
Zeolite	2	294.64	6.51	8.63	3.33
Zeolite	3	405.82	8.56	9.7	5.34
NViro	1	500.31	8.34	8.8	8.41
NViro	2	484.1	8.26	9.12	8.51
NViro	3	557.51	8.1	9.76	9.23
TSP	1	117.03	1.04	1.92	3.44
TSP	2	81.25	0.52	1.23	2.61
TSP	3	77.49	0.87	1.23	2.53
LSSS	1	230.14	3.07	7.35	2.44
LSSS	2	233.38	2.88	6.97	2.27
LSSS	3	248.22	3.26	7.23	2.38
Sewage Sludge	1	271.93	4.02	3.76	2.51
Sewage Sludge	2	181.03	2.99	2.73	1.82
Sewage Sludge	3	183.82	3.15	2.99	1.91
Ag Lime	1	225.57	6.36	6.93	2.91
Ag Lime	2	264.2	7.64	7.75	3.47
Ag Lime	3	255.07	7.95	7.74	3.39
CKD	1	324.01	10.06	9.33	5.23
CKD	2	335.44	10.64	9.62	5.39
CKD	3	326.39	10.51	9.25	5.22
Red Mud	1	173.24	4.95	6.12	2.26
Red Mud	2	187.67	5	6.78	2.32
Red Mud	3	162.66	5.11	5.89	2.11
Rock PO ₄	1	253.32	6.29	3.92	3.81
Rock PO ₄	2	259.88	5.47	3.88	3.81
Rock PO ₄	3	254.96	5.67	3.91	4.2
Control	1	285.03	8.12	9.08	3.94
Control	2	287.07	8.52	9.06	3.53
Control	3	324.87	9.39	9.86	4.36

Table A6. Lettuce metal tissue concentrations.

Amendment	Rep	Zn	Pb	Cd	Cu	Cd:Zn
		mg kg ⁻¹				
Alum Sludge	1
Alum Sludge	2
Alum Sludge	3
Zeolite	1
Zeolite	2
Zeolite	3
NViro	1	468.27	6.45	82.18	16.45	0.17
NViro	2	568.77	8.26	91.42	20.41	0.16
NViro	3	458.66	6.63	88.34	15.78	0.19
TSP	1
TSP	2
TSP	3
LSSS	1	775.67	5.01	71.30	15.01	0.09
LSSS	2	720.23	5.66	83.13	16.38	0.11
LSSS	3	792.20	3.97	70.90	14.56	0.08
Sewage Sludge	1
Sewage Sludge	2
Sewage Sludge	3
Ag Lime	1
Ag Lime	2
Ag Lime	3
CKD	1	562.63	7.19	102.99	11.71	0.18
CKD	2	556.33	6.47	124.99	14.31	0.22
CKD	3	565.85	6.85	114.17	12.975	0.20
Red Mud	1	999.46	10.6	138.53	29.75	0.13
Red Mud	2	863.51	5.23	118.02	10.56	0.13
Red Mud	3	693.79	4.95	133.11	11.65	0.19
Rock PO ₄	1
Rock PO ₄	2
Rock PO ₄	3
Control	1
Control	2
Control	3

Table A7. Amended soil pH values.

Amendment	Rep	pH
Alum Sludge	1	6.8
Alum Sludge	2	6.9
Alum Sludge	3	7
Zeolite	1	6.4
Zeolite	2	6.6
Zeolite	3	6.6
NViro	1	7.8
NViro	2	7.8
NViro	3	7.8
TSP	1	4.9
TSP	2	4.8
TSP	3	4.8
LSSS	1	7.4
LSSS	2	7.5
LSSS	3	7.4
Sewage Sludge	1	6.3
Sewage Sludge	2	6.3
Sewage Sludge	3	6.3
Ag Lime	1	6.7
Ag Lime	2	6.8
Ag Lime	3	6.7
CKD	1	7.7
CKD	2	7.9
CKD	3	7.9
Red Mud	1	7.4
Red Mud	2	7.3
Red Mud	3	.
Rock PO ₄	1	6.5
Rock PO ₄	2	6.5
Rock PO ₄	3	6.5
Control	1	6.3
Control	2	.
Control	3	6.3

Table A8. Amended soil electrical conductivity (EC) values.

Amendment	Rep	EC
Alum Sludge	1	0.47
Alum Sludge	2	0.33
Alum Sludge	3	.
Zeolite	1	.
Zeolite	2	.
Zeolite	3	0.5
NViro	1	1.38
NViro	2	1.07
NViro	3	1.39
TSP	1	1.3
TSP	2	1.14
TSP	3	1.28
LSSS	1	1.61
LSSS	2	1.88
LSSS	3	2.12
Sewage Sludge	1	1.11
Sewage Sludge	2	0.72
Sewage Sludge	3	0.81
Ag Lime	1	0.57
Ag Lime	2	0.45
Ag Lime	3	0.5
CKD	1	1.62
CKD	2	1.65
CKD	3	1.46
Red Mud	1	1.47
Red Mud	2	1.62
Red Mud	3	.
Rock PO ₄	1	0.43
Rock PO ₄	2	0.45
Rock PO ₄	3	.
Control	1	.
Control	2	0.73
Control	3	0.7

VITA 

Jeri Lynn Anderson

Candidate for the Degree of

Master of Science

Thesis: REMEDIATION OF HEAVY METAL CONTAMINATED SOIL BY IN-SITU
IMMOBILIZATION

Major Field: Agronomy

Biographical:

Personal Data: Born July 9, 1971, in Okemah, OK, a daughter of Mr. Jerry G.
and Ms. Linda J. (Jackson) Anderson.

Education: Graduated from Okemah High School, Okemah, OK, in May 1989;
received the Associate of Science degree in General Education from
Seminole Jr. College, Seminole, OK, in December, 1992; received the
Bachelor of Science degree in Agronomy (Soil Science option) from
Oklahoma State University, Stillwater, OK, in December, 1993;
completed the requirements for the Master of Science degree in Soil
Science from Oklahoma State University, Stillwater, OK, in May, 1996.

Professional Experience: Graduate Research Assistant, Department of
Agronomy, Oklahoma State University, January 1994 to December
1995. Field and Laboratory Assistant, OSU Soil Fertility Project, August
1992 to December 1994. Office Assistant and Tutor, Seminole Jr.
College, Seminole, OK January 1990 to August 1991, and May 1992 to
August 1992.

Professional Organizations:

American Society of Agronomy
Soil Science Society of America
Gamma Sigma Delta- Honor Society of Agriculture
Phi Theta Kappa- Honor Society among Jr. Colleges