# AMENDMENTS FOR FIELD-SCALE PHYTOTREATMENT OF PB, CD AND ZN FROM AN INDIANA SUPERFUND SOIL

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ABSTRACT. A field study was conducted to determine the effectiveness of a mixed grass crop, sunflower (Helianthus annuus), or ragweed (Ambrosia trifida) and several amendments in revegetation and treatment of soil severely contaminated with lead, cadmium and zinc. Amendments included composted municipal solid waste, dried sewage sludge, citric acid, ethylenediaminetetraacetic acid (EDTA) (single and multiple applications), and control. The mixed grass crop was capable of growth on all treatments. Soil Pb and Zn occurred primarily in the carbonate, organic-bound and residual forms (23.1%, 31.8%, and 44.4%, Pb, respectively, and 11.4%, 26.5%, and 60.2% Zn, respectively) as determined by sequential extraction. The MSW and SS treatments resulted in greatest plant cover and dry matter production on the field plots. Dry matter production was significantly (P < 0.05) higher in the municipal solid waste (1.09 MT/ha) and dried sewage sludge (95 MT/ha) treatments. The single EDTA treatment resulted in significantly (P < 0.05) increased Pb uptake when compared to the other treatments. The EDTA, citric acid and municipal solid waste significantly (P < 0.05) increased Cd uptake by plants. In a growth chamber leaching study, soil Pb leached most from the 0.5 M EDTA treatment; the citric acid, mixed NPK fertilizer, municipal solid waste, sewage sludge and control treatments resulted in negligible leaching. Phytostabilization in combination with organic amendments may be the most appropriate technology to ensure stabilization of soil metals at this site.

Keywords: Cd, Pb, Zn, phytostabilization, revegetation, sewage sludge, municipal solid waste

Heavy metal contamination of soils at derelict industrial sites is a significant issue worldwide. Lead (Pb), cadmium (Cd) and zinc (Zn) are among the most commonly encountered heavy metals at contaminated facilities (Lasat 2007); and excess concentrations can be detrimental to plant growth. Such soils can also be adversely affected by poor drainage, low organic matter content, and diminished populations of indigenous microbes that cycle nutrients. Revegetation is essential to limit soil erosion by wind and water, including runoff of metallic sediments. A long-term goal for such sites is the development of a selfsustaining ecosystem that can support productive land use activities and is aesthetically appealing.

Plant species have been identified that have the capability to either immobilize or accumulate heavy metals. Recent research has examined the use of plants as either stabilizing or extractive tools for metal-contaminated soils (Pichtel & Bradway 2007; Mills et al. 2006; Tie et al. 2006; Datta & Sarkar 2005; Pichtel et al. 2000). During phytostabilization, mobility of contaminants is reduced by accumulation within roots, adsorption to root surfaces, or conversion to immobile species within the rhizosphere (Vangronsveld et al. 1995). In contrast, phytoextraction involves the engineered use of plants to remove contaminants from the soil.

Establishment of a long-term vegetative cover can retain contaminants in place, thus reducing dispersion to local environs (Pulford & Watson 2003). When revegetation is combined with application of soil amendments such as organic matter, the mobility of contaminants in the soil can be further reduced (Mench et al. 2000; Madejon et al. 2006).

For site revegetation to succeed, the degree of plant tolerance to metallic contaminants must be assessed. Recent research has documented effective plant stabilization or extraction of heavy metals (Wu et al. 2006; Li et al. 2005; Wilde et al. 2005); however, little is known regarding revegetation and/or treatment of highly toxic and/or infertile metalliferous wastes.

Metals on weathered metalliferous sites occur in complex forms and vary widely in solubility and bioavailability (Tie et al. 2006; Jensen et al. 2006; Selim & Kingery 2003). Chemical fractionation procedures have proven useful for segregating soil metals into various reactive forms (Almås et al. 2006; Bermond et al. 2005; Chagué-Goff 2005; Steele and Pichtel 1998). Each metal fraction is associated with a certain degree of mobility in the biosphere, and hence with bioavailability to plants.

An Indiana Superfund site (40°10'34"N, 85°25'36"W) was the focus of study. As a result of uncontrolled disposal of industrial wastes, the site is contaminated by Pb, Cd, Zn and other metals. The site is bordered on one side by the White River and by numerous residences on the opposite side. The soil has a massive structure and is classified as 'Made Land'. Remediation at the site as directed by the EPA Record of Decision (issued 2001) has involved isolation rather than removal of contaminants; steel sheet pilings have been installed along the riverbank. The site has subsequently been removed from the EPA National Priorities List (U.S. EPA 2006); however, soil material is still enriched with heavy metals. Due to proximity of the site to residential dwellings, loss of metals to groundwater or via airborne dispersal is still a concern.

If revegetation of the site is to succeed, a cover crop must be able to withstand potentially toxic soil conditions. Selected soil amendments may enhance plant establishment and enhance ecosystem sustainability. The purpose of the reported study was to assess revegetation of the toxic metalliferous soil at the site, and to study the influence of soil amendments on plant growth and plant stabilization and/or uptake of soil metals.

## METHODS

Field study.—Three test blocks were established in March 2006 at a Superfund site located in Delaware County, Indiana. Plots measuring  $2 \times 4$  m were set within each block. The following treatments were applied to the plots at the initiation of the study (three replicates each): composted municipal solid waste (MSW); dried sewage sludge (SS); citric acid (as Fisher-grade product); ethylenediaminetetraacetic acid (EDTA) (as Na<sub>2</sub>EDTA) (two application rates, e.g., EDTA1 and EDTA2); and control (no treatment applied). The MSW and SS were each applied at 25 MT/ha (metric tons per hectare). Throughout the growing season, citric acid and EDTA1 were applied to the plots at monthly intervals (May, June, July, and August) at 2 mmol/kg soil. The EDTA2 was provided as a single application of 500 mmol/kg. These concentrations were adapted from Blaylock et al. (1997) and from previous studies conducted in our laboratories. The source of the MSW was Bedminster Corp., Sevierville, Tennessee, and the dried sewage solids (recovered from belt press) were obtained from the Muncie, Indiana Bureau of Water Quality.

Seeds of a grass mixture (smooth meadowgrass, Poa pratensis; red fescue, Festuca rubra; and perennial ryegrass, *Phleum pratense*) (each approx. 10 kg/ha) were sown onto tilled soil by broadcast seeding. Both red clover (Trifolium pretense) and sunflower (Helianthus annuus) seeds were sown at the site, and ragweed (Ambrosia trifida) was transplanted from two-week old plants. All species except the grass mixture failed within the first 30-60 days, however. In June above-ground grass tissue and surface soil (0-20 cm) were sampled from each plot. Tissue was cut approximately 5 cm above the ground surface to limit contamination by soil material and was subsequently rinsed in deionized water to remove attached soil particles. Soil was sampled from 4-5 random points from the surface 20 cm of each plot using a stainless steel sampling tube. Soil material was composited, air-dried, and sieved through a 2 mm mesh sieve. At the conclusion of the growing season grass shoots were again harvested and surface soil sampled to assess changes in heavy metals content over the course of the growing season. Percentage vegetative cover was visually determined by two of the researchers.

Plant tissue samples were dried in a gravity convection oven (Baxter model DS-64) at 80°C for 48 h and weighed to determine total above-ground dry matter. Tissue was then ground in a Wiley mill (Bel-Art, Pequannock, New Jersey), and digested with hot (440°C)  $H_2SO_4$  and  $H_2O_2$  in a Hach Digesdahl<sup>®</sup> digestion apparatus. The digestate was diluted to 100 ml with deionized water. Flame atomic absorption spectroscopy (FAAS) using a Perkin Elmer AAnalyst 200 was utilized to determine levels of Pb, Cd, and Zn.

Soil was analyzed for total organic carbon (TOC) using loss on ignition (LOI) (360°C for

2 h) (Nelson & Sommers 1982). Soil pH was measured using an AB15 Accumet<sup>®</sup> Basic pH meter in a 1:1 soil:water suspension. Total N was measured using the method of Bremner & Mulvaney (1986). Soil samples were analyzed for extractable (in 1N ammonium acetate) Ca, Mg and K using the method of Lanyon & Heald (1986), and total Pb, Cd and Zn concentrations using the Hach Digesdahl<sup>®</sup> apparatus followed by FAAS analysis as described above for plant tissue.

A chemical fractionation procedure (Sposito et al. 1982) was used to determine soil metal fractions. The soluble fraction was determined by mixing 2.0 g (dry weight) soil with 25 ml DI H<sub>2</sub>O and then shaking in a reciprocating shaker (Eberbach 6010) for 2 h. The soil slurry was centrifuged (International Centrifuge Universal Model UV) for 15 min at 3000 rpm and the supernatant decanted. The procedure was repeated three times and the supernatants combined. The exchangeable fraction was determined by mixing the soil residue with 25 ml of 0.5 M KNO<sub>3</sub> for 16 h. The solution was then centrifuged and the supernatant decanted. The organic fraction was assessed by mixing the soil residue with 25 ml of 0.5 M NaOH for 16 h. The carbonate fraction was determined by mixing the soil residue with 25 ml of 0.05 M Na<sub>2</sub>EDTA for 6 h. The sulfide/residual fraction was assessed by mixing the soil residue with 13 ml of 4 M HNO<sub>3</sub> and heating for 16 h with 12 ml of 4 M HNO<sub>3</sub> added at the end of heating. All solutions were centrifuged and the supernatant decanted, and all supernatants were analyzed for Pb, Cd, and Zn using FAAS.

Metal mobility study.—A growth chamber study was conducted to determine the effectiveness of different amendments for their ability to mobilize soil Pb, Cd, and Zn. Surface soil from the Superfund site was packed into 45 cm length PVC columns (5.1 cm i.d.), with a final density of approx. 1.1 g/cm<sup>3</sup>. The columns (five replicates each) were exposed to the following treatments: EDTA (0.001 M, 0.01 M, 0.1 M, 0.5 M); citric acid (0.1 M), NPK solution (2.5 mM KNO<sub>3</sub> and 0.5 mM KH<sub>2</sub>PO<sub>4</sub>); MSW; SS; and control. The MSW and SS were applied at field-equivalent rates. The MSW, SS and control were leached with deionized H<sub>2</sub>O only. The columns were leached for 20 pore volumes using a Masterflex® peristaltic pump and the leachate was Table 1.—Selected chemical properties of the Superfund soil. TOC = Total organic carbon.

Parameter	Méan	Range	
рН	8.3		
TOC, %	5.4	5.3-5.5	
Total N, mg/kg	0.11	0.07-0.17	
CEC, cmol/kg	8.4	_	
Extractable, mg/kg			
Ca	3681	3785-3578	
Mg	241.5	229-254	
ĸ	61.5	59-64	
Total metals, mg/kg			
Pb	39,864	35,040-49,520	
Cd	10.1	8.2-11.8	
Zn	1512	1000-2800	
Sand, %	64.5		
Silt, %	14.1		
Clay, %	21.5		

collected and stored in Nalgene<sup>®</sup> bottles with two drops of concentrated nitric acid (HNO<sub>3</sub>) added. Leachates were then analyzed for total Pb, Cd and Zn using FAAS.

**Statistical analysis.**—Data was analyzed statistically with analysis of variance (ANO-VA) using SPSS<sup>®</sup> (SPSS, 2006). The ANOVA was followed by *post-hoc* Bonferroni *t*-tests.

### **RESULTS AND DISCUSSION**

Soil characterization.—Soil pH measured 8.3, and TOC and total N contents were 5.4% and 0.11 mg/kg, respectively (Table 1). The high TOC values are a result of disposal of hydrocarbon solvents and used oil to the site. Total soil Pb, Cd, and Zn concentrations averaged 39,860, 10.1, and 1512 mg/kg, respectively. Concentration ranges of Pb, Cd, and Zn in uncontaminated soil are approximately 10-84 mg/kg, 0.06-1.1 mg/kg, and 10-80 mg/kg, respectively (Sigel et al. 2005; McBride 1994). Metal levels in the current study varied widely, a result of the heterogeneity of soil materials at the site. Pichtel et al. (2000) measured soil Pb concentrations of 29,400 mg/kg at the site, and Hee (2005) measured from 1,900 to 6,050 mg/kg. Pichtel et al. (2000) measured average soil Cd concentrations up to 7.8 mg/kg at the site.

**Soil metal fractionation.**—The majority of the control soil Pb occurred in the residual (45.7%) and carbonate (37.2%) fractions (Table 3). Soil Pb occurring in the soluble and exchangeable fractions was negligible (0.5

Table 2.—Selected chemical properties of the organic amendments used in this study. MSW = municipal solid waste, SS = dried sewage sludge; TOC = total organic carbon; <sup>1</sup>extracted by 1 N ammonium acetate; <sup>2</sup>Pichtel & Anderson 1997.

Parameter	MSW	SS
pH	6.8	7.2
TOC, g/kg	390	605
Total P, g/kg	6.2	8.2
Extractable, mg/kg1		
Ca	6850	1460
Mg	608	690
К	1620	3480
Total metal content, mg/kg <sup>2</sup>		
Cr	21	57
Cu	28	40
Pb	210	340
Zn	655	770

and 0.2%, respectively). Using SEM-EDAX and x-ray diffraction analysis, Pichtel et al. (2001) identified both PbSO<sub>4</sub> (anglesite) and metallic Pb in soil from this site. Steele & Pichtel (1998) found a majority of soil Pb to occur in the organic (31%), carbonate (31%), and residual (35%) fractions of a Superfund soil. Zinati et al. (2004), Chlopecka et al. (1996), and Heil et al. (1996) all found soil Pb from contaminated sites to occur primarily in the carbonate and residual fractions.

A substantial portion of control soil Cd occurred in the soluble (21.0%) and exchangeable (11.3%) fractions; however, the majority occurred in the less-available carbonate and residual fractions (48.7%) (Table 3). Jaradet et al. (2006) found 33% of soil Cd to occur in the exchangeable form, and Sanchez et al. (1999) found the greatest proportion of soil Cd to occur in the exchangeable fraction. Steele and Pichtel (1998) found a majority of soil Cd to occur in the residual (54.6%) and carbonate (36.9%) fractions of a Superfund soil.

Soil Zn occurred predominantly in the residual (60.4%) and carbonate (29.6%) fractions (Table 3). Soil Zn in the soluble and exchangeable fractions measured 1.5 and 0.1%, respectively. Li et al. (2005) found a preponderance of soil Zn in residual and organicbound fractions. Soil Zn speciation is strongly influenced by pH; as pH increases the relative proportions of Zn in the exchangeable fraction will decrease. The pH of the soil (8.3, Table

Table 3.—Chemical fractions of Pb, Cd, and Zn in the Superfund soil. Values shown are mean values  $\pm$  standard deviation.

Treatment	Soluble	Exchangeable	Organic	Carbonate	Residual
Pb, %					
EDTA	$0.7 \pm 0.1$	$0.3 \pm 0.05$	$27.2 \pm 9.8$	$27.4 \pm 2.9$	$44.4 \pm 13.8$
Citric acid	$0.8 \pm 0.1$	$0.2 \pm 0.05$	$18.9 \pm 5.2$	$31.2 \pm 7.6$	$49.0 \pm 10.1$
MSW	$0.2 \pm 0.02$	$0.2 \pm 0.01$	$23.5 \pm 11.0$	$29.0 \pm 12.4$	$47.1 \pm 10.7$
SS	$0.4 \pm 0.04$	$0.3 \pm 0.02$	$29.5 \pm 8.6$	$34.1 \pm 7.1$	$35.7 \pm 10.6$
Control	$0.6 \pm 0.1$	$0.2 \pm 0.04$	$16.3 \pm 4.6$	$37.2 \pm 11.8$	$45.7 \pm 12.1$
Mean	$0.5 \pm 0.07$	$0.25 \pm 0.03$	$23.1 \pm 7.8$	$31.8 \pm 9.9$	$44.4 \pm 11.5$
Cd, %					
EDTA	$20.0 \pm 2.1$	$11.9 \pm 2.9$	$20.4 \pm 1.0$	$21.9 \pm 3.3$	$25.8 \pm 3.3$
Citric acid	$22.3 \pm 5.7$	$8.1 \pm 1.9$	$20.3 \pm 3.1$	$18.9 \pm 5.7$	$30.5 \pm 1.5$
MSW	$24.1 \pm 2.4$	$11.6 \pm 1.1$	$16.0 \pm 2.1$	$22.5 \pm 3.4$	$25.8 \pm 3.1$
SS	$21.4 \pm 1.5$	$17.3 \pm 2.9$	$13.9 \pm 2.0$	$19.5 \pm 3.2$	$27.9 \pm 2.0$
Control	$21.0 \pm 2.2$	$11.3 \pm 1.7$	$16.8 \pm 0.4$	$23.8 \pm 3.5$	$27.1 \pm 0.2$
Mean	$21.8 \pm 2.8$	$12.0 \pm 2.1$	$17.5 \pm 1.7$	$21.3 \pm 3.8$	$27.4 \pm 2.0$
Zn, %					
EDTA	$1.7 \pm 0.2$	$0.2 \pm 0.04$	$12.4 \pm 2.0$	$28.7 \pm 6.6$	$57.0 \pm 15.2$
Citric acid	$1.7 \pm 0.1$	$0.1 \pm 0.01$	$11.3 \pm 1.8$	$23.9 \pm 7.0$	$63.0 \pm 15.4$
MSW	$1.5 \pm 0.2$	$0.3 \pm 0.1$	$10.6 \pm 2.4$	$23.2 \pm 7.8$	$64.3 \pm 18.6$
SS	$1.7 \pm 0.2$	$0.3 \pm 0.1$	$14.5 \pm 3.7$	$27.0 \pm 7.2$	$56.5 \pm 16.0$
Control	$1.5 \pm 0.2$	$0.1 \pm 0.02$	$8.4 \pm 2.0$	$29.6 \pm 6.3$	$60.4 \pm 13.2$
Mean	$1.3 \pm 0.2$	$0.2 \pm 0.1$	$11.4 \pm 2.4$	$26.5~\pm~7.0$	$60.2 \pm 15.7$

Table 4.—Dry matter yields and percent vegetative cover on the treated plots. MSW = municipal solid waste; SS = dried sewage sludge; MT/ha =metric tons per hectare.

Treatment	Dry matter (MT/ha)	Coverage (%)
EDTA1	$0.42 \pm 0.07$	70
EDTA2	$0.13 \pm 0.03$	85
Citric acid	$0.58 \pm 0.07$	70
MSW	$1.09 \pm 0.20$	90
SS	$0.95 \pm 0.34$	90
Control	$0.54 \pm 0.15$	75

1) will promote Zn precipitation as carbonates and other insoluble minerals (Lindsay 1979); likewise, high soil pH will render humic materials more reactive with soil metals (Brady 2000).

**Field study.**—The grass mixture was the only plant treatment capable of survival on the site. Red clover, sunflower and ragweed grew early in the field experiment, but soon disappeared from all plots. The loss is explained primarily by the inability of these species to tolerate the toxic conditions of the site, combined, to a lesser extent, with the massive soil structure and poor drainage conditions.

Plant tissue dry matter yields ranged from 1.09 MT/ha (MSW) to 0.13 MT/ha (EDTA2) (Table 4). Dry matter yields were significantly highest (P < 0.05) for the MSW and SS treatments. The MSW and SS treatments resulted in the greatest vegetative cover (both approximately 90%). Cover was 70% on the EDTA1 and citric acid plots, 85% on the EDTA2 plots, and 75% on control plots. The increased growth on the MSW and SS treatments is at-

tributed in part to the added nutrient supply from both amendments, including Ca, Mg and K (Table 2). Conversely, the relatively lower yields in the EDTA and citric acid treatments may be a result of excess metal (including nutrient base) solubilization.

Amendment application did not significantly (P < 0.05) increase concentrations of soil Pb, Cd, or Zn in the soluble and exchangeable fractions when compared with the control (Table 3). Soil Pb was low in the soluble and exchangeable fractions (0.5% and 0.25% averaged over all treatments). These proportions are not significantly (P < 0.05) different from the control fractions (0.6% and 0.2%, respectively). Amendments did not significantly increase the presence of Cd in the soluble or exchangeable fractions; mean values for the amended plots were 21.8 and 12.0%, respectively, and those of the control averaged 21.0 and 11.3%, respectively. Soluble or exchangeable soil Zn fractions did not change significantly (P < 0.05) with amendment addition; mean values for the amended plots were 1.6% and 0.2%, respectively, whereas those of the control were 1.5% and 0.1%, respectively.

*Metal uptake:* Tissue Pb concentrations increased (P < 0.10) from June to October (31.7 to 51.6 mg/kg, respectively) (Table 5) for all treatments. The EDTA, citric acid and MSW treatments resulted in increased Pb uptake when compared to the control; however, by the October sampling only the EDTA2 data was significantly (P < 0.05) higher than for the other treatments. Addition of amendments did not significantly increase the amount of plant-available (e.g., soluble and exchangeable) soil Pb fractions (Table 3). The EDTA2

Table 5.—Grass shoot concentrations of Pb, Cd, and Zn, June and October samplings. Values shown are mean values  $\pm$  standard deviation. n.d. = not determined; MSW = municipal solid waste, SS = dried sewage sludge.

	Pb (mg/kg)		Cd (mg/kg)		Zn (mg/kg)	
Treatment	June	Oct.	June	Oct.	June	Oct.
EDTA1	$29.3 \pm 19.2$	$46.0 \pm 21.8$	17.7 ± 1.5	$21.9 \pm 5.1$	$220.5 \pm 60.8$	373.1 ± 188.8
EDTA2	$62.0 \pm 19.4$	$108.5 \pm 14.2$	$8.6 \pm 1.1$	$9.9 \pm 0.9$	n.d.	n.d.
Citric acid	$25.1 \pm 14.6$	$45.2 \pm 17.1$	$21.5 \pm 3.9$	$20.3 \pm 1.9$	$147.3 \pm 81.1$	358.8 ± 116.4
MSW	$36.9 \pm 31.8$	$59.3 \pm 33.8$	$16.7 \pm 5.7$	$23.1 \pm 2.6$	$118.3 \pm 38.8$	$437.1 \pm 24.7$
SS	$24.2 \pm 23.4$	$21.7 \pm 17.1$	$18.7 \pm 3.4$	$17.8 \pm 2.3$	$182.7 \pm 104.1$	$370.5 \pm 213.9$
Control	$12.9 \pm 11.0$	$29.0 \pm 15.5$	$10.2 \pm 3.2$	$13.7 \pm 2.9$	$117.5 \pm 37.0$	$387.3 \pm 68.7$
All treatments	31.7	51.6	15.6	17.8	157.3	385.4

treatment increased tissue Pb from 62.0 mg/ kg (June) to 108.5 mg/kg (October); the single EDTA application (EDTA2) apparently solubilized soil Pb and enhanced uptake and transport of Pb from roots to shoots. In contrast, the EDTA1 (multiple doses over the growing season) accumulated 46.0 mg/kg by October. The smaller EDTA applications (EDTA1) may have non-selectively reacted with soil Ca, Fe and other cationic metals instead of with Pb. Control tissue accumulated 12.9 mg/kg in June and 29.0 mg/kg in October.

Tissue Pb concentrations in the MSW treatment increased from 36.9 mg/kg (June) to 59.3 mg/kg (October). In the citric acid treatment Pb increased from 25.1 mg/kg (June) to 45.2 mg/kg (October). Elevated tissue Pb concentrations for both treatments (Table 5) could be explained by chelating effects. Zaccheo et al. (2002) and Chefet et al. (1998) determined the presence of a wide range of humic compounds in MSW compost, some of which may chelate metals and be of sufficiently low molecular size to be taken up by roots. The increase in tissue Pb for the citric acid treatment is further explained by its acidifying effects: decreasing soil pH will increase the proportion of Pb in soil solution. Shen et al. (2002) reported an increase in cabbage (Brassica rapa) tissue Pb concentration with application of citric acid to soil. Correlation coefficients  $(r^2)$  for tissue Pb versus Pb chemical fractions ranged from 0.007 (exchangeable) to 0.52 (organic), none of which were statistically significant.

Cadmium uptake: The grasses accumulated 15.6 mg/kg Cd in June and 17.8 mg/kg in October, averaged over all treatments (Table 5). Effectiveness of amendments for plant Cd uptake (combined data for June and October) followed the order: citric acid = MSW = EDTA1 > SS > control > EDTA2. Addition of citric acid resulted in slight soil acidification (pH 7.9 compared to 8.5 in control plots) which may have increased the soil Cd available for plant uptake. Soil pH is the single most important factor relating Cd mobility in soil and Cd plant-availability (McBride 2002). Citric acid additionally serves as an effective chelating agent (Patel and Subramanian 2006). The MSW and EDTA1 resulted in similar tissue Cd accumulation. The MSW may have increased available Cd concentrations due to possible chelating effects. Cadmium accumulation in the EDTA2 treatment was comparable to the control; this is explained by excessive losses from the profile; a substantial proportion of soil Cd initially occurred in the soluble fraction (Table 3). High EDTA concentrations may have accelerated Cd loss from the root zone. Correlation coefficients ( $r^2$ ) for tissue Cd in relation to Cd chemical fractions ranged from 0.18 (soluble) to 0.36 (residual) thus showing no statistical relationship (data not shown).

Zinc uptake: Averaged over all treatments, grasses at the site accumulated 157.3 mg/kg Zn (June 2005) and 385.4 mg/kg (October 2005) (Table 5), a significant (P < 0.01) increase. There was no significant effect of amendments on Zn accumulation, however. By the October sampling the greatest Zn accumulation occurred in the MSW treatment. This treatment also produced the highest biomass (Table 4), the highest October tissue Cd and the second highest October Pb tissue concentrations (Table 5). The ability of MSW to enhance Zn accumulation may be a result of possible chelating effects. Zinc availability increases with the addition of chelates (Fergusson, 1990). Correlation coefficients for tissue Zn in relation to Zn chemical fractions ranged from 0.55 (exchangeable) to 0.65 (residual), however, with no significant statistical relationship (data not shown).

Leaching study: With increase in EDTA concentration the amount of Pb leached increased (P < 0.01). A total of 557 mg Pb was leached in the 0.5 M treatment, compared with 203 mg for the 0.001 M treatment (Fig. 1). Luo et al. (2006) and Blaylock et al. (1997) found that EDTA addition to soil greatly increased Pb mobility. EDTA application increased soluble Pb concentrations from nondetectable to 4000 mg/l (Huang et al. 1997). Negligible Pb was leached with citric acid, NPK, MSW and SS treatments (Fig. 1). The complex organic molecules within amendments such as MSW and SS act to complex and chelate Pb; likewise, the pH values of the MSW and SS (6.8 and 7.2, respectively), rendered soil Pb immobile. The citric acid was apparently neutralized by the calcareous soil (pH 8.3, Table 1).

Increased EDTA concentration significantly (P < 0.01) increased the amount of Cd leached (Fig. 2). A total of 1.1 mg was leached with 0.5 M EDTA, compared with

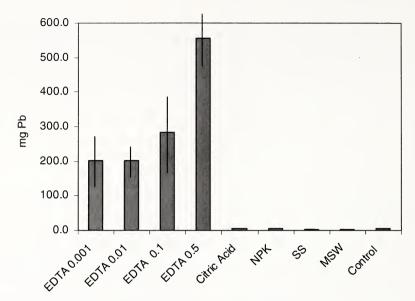


Figure 1.—Leaching of Pb from the Superfund soil as affected by extracting solution.

0.04 mg at 0.001 M EDTA. These data are consistent with Elkhatib et al. (2001), who found that EDTA was effective for increasing Cd mobility in soil. Cajuste & Laird (2001) found that increasing EDTA concentration (0.01 M to 0.1 M) increased Cd leached from 1.4 to 2.2 ug/g. The ability of EDTA to enhance Pb availability more than Cd was noted by Bucheli-Witschel & Egli (2001) and Blaylock et al. (1997). The citric acid, NPK, MSW, SS and control did not result in marked Cd leaching.

EDTA leached greater amounts of Zn compared with any other amendment (Fig. 3). The 0.1 and 0.5 M rates of EDTA resulted in similar Zn leaching rates (960 and 997 mg, respectively).

These data are consistent with those of Novillo et al. (2002), Greman et al. (2001), and Alvarez et al. (1996), who found that ad-

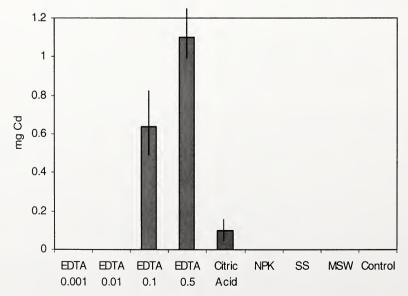


Figure 2.—Leaching of Cd from the Superfund soil as affected by extracting solution.

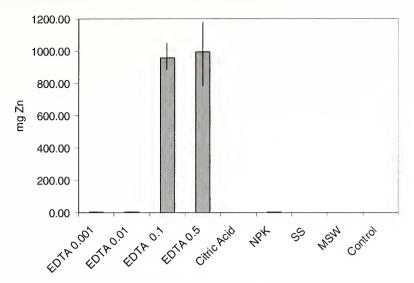


Figure 3.—Leaching of Zn from the Superfund soil as affected by extracting solution.

dition of EDTA was effective for increasing Zn mobility in soil. The citric acid, NPK, MSW, SS and control resulted in minimal Zn leaching.

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