In Situ Soil Treatments to Reduce the Phyto- and Bioavailability of Lead, Zinc, and Cadmium

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ABSTRACT

A study was established near a former Zn and Pb smelter to test the ability of soil amendments to reduce the availability of Pb, Zn, and Cd in situ. Soil collected from the field was amended in the lab with P added as 1% P-H_3PO_4, biosolids compost added at 10% (referred to hereafter as "compost"), and a high-Fe by-product (referred to hereafter as "Fe") + P-triple superphosphate (TSP) (2.5% Fe + 1% P-TSP) and incubated under laboratory conditions at a constant soil pH. Changes in Pb bioavailability were measured with an in vitro test and a feeding study with weanling rats. Field-amended and incubated soils using these plus additional treatments were evaluated using the in vitro extraction and tall fescue (*Festuca arundinacea* Schreb. cv. Kentucky-31) metal concentration. Reductions were observed across all parameters but were not consistent. In the feeding study, the 1% P-H_3PO_4 and compost treatments resulted in a decrease of 26% in rat tissue Pb concentration compared with the control soil. The 2.5% Fe + 1% P-TSP showed a 39% decrease. The 1% P-H_3PO_4 treatment caused the greatest reduction in in vitro extractable Pb from field samples (pH 2.2) with a measured reduction of 66%, while the compost treatment had a 39% reduction and the 2.5% Fe + 1% P-TSP treatment a 50% reduction. The in vitro extraction (pH 1.5) run on field samples showed no reduction in the compost or Fe treatments. The 1% P-H_3PO_4 treatment was the most effective at reducing plant Pb, Zn, and Cd.

As a result of hand to mouth play or through deliberate consumption of soil, children exposed to Pb-contaminated soil can exhibit elevated blood Pb concentrations. The quantity of Pb in soils has been strongly associated with children's blood lead levels (Mielke, 1999). In the Tri-State mining district of southwestern Missouri, soils have been contaminated with Pb, Zn, and Cd as a result of smelting locally mined ore. Children in Joplin, Missouri have exhibited high levels of blood Pb and soil remediation (removal and replacement) has occurred under the USEPA Superfund program.

In addition to the child health concern of elevated soil Pb there are implications that elevated soil Pb, Zn, and Cd can cause harm to native ecosystems (Beyer, 2000; Dodds-Smith et al., 1992; Gunson et al., 1982; Larison et al., 2000). In an extreme case, soil Pb contamination has been responsible for acute Pb toxicity in waterfowl that inadvertently ingested sediment as part of their diet (Beyer et al., 1998). Chronic and acute Pb poisoning in wildlife has also been observed in smelter-impacted areas (Beyer et al., 1985; Conder et al., 2001). Excess Cd in plant tissue can result in damage to wildlife (Beyer, 2000; Larison et al., 2000), although both the critical organ tissue Cd concentration and the precise concentrations of plant Cd associated with damage to herbivores is unknown. The primary risk associated with excess Zn in soils is to plants (Chaney, 1993). High-Zn sites will often be phytotoxic to most species (Brown et al., 2003b), resulting in poor or no plant growth.

Recent research has focused on the potential to change the bioavailability of soil Pb, Zn, and Cd in situ by altering the mineral forms of these elements, or providing excess adsorptive capacity for them in soils (Mench et al., 1994, 2000). The relationship between mineral form and bioavailability of Pb was demonstrated in both in vivo (using swine) and in vitro studies (Ruby et al., 1999). The range in bioavailability of total Pb in soil ranged from about 90% to less than 10% based on the mineral form of Pb present (Ruby et al., 1999). This understanding of the importance of bioavailability of soil Pb and the implication of mineral form on bioavailability has resulted in research focused on the potential of altering the mineral forms of the element in situ, or providing excess specific adsorptive capacity for them in soils. Much of this research has focused on the formation of chloropyromorphite [$Pb_5(PO_4)_3Cl$] through phosphorus addition. Formation of chloropyromorphite has been demonstrated under laboratory conditions with the addition of P as hydroxyapatite to various forms of Pb, including Pb salts, several Pb minerals, and Pb-contaminated soils (Ma et al., 1993; Ryan et al., 2001; Zhang et al., 1997; Zhang and Ryan, 1998, 1999).

In addition to the use of P to reduce the bioavailability of Pb in situ, work has suggested that increasing the adsorptive capacity of a soil system through the addition of high oxide minerals as well as biosolids composts can also reduce the bioavailability of soil Pb (Berti and Cunningham, 1997; Martinez et al., 1999; Brown et al., 2003a). Addition of up to 10% of an iron-rich material (a mineral by-product in the production of TiO_2, referred to hereafter as "Fe") reduced the leachability of Pb in three soils as measured by the toxic characteristic leaching procedure (TCLP) and an in vitro extraction method. In a rat feeding study, biosolids composts reduced the bioavailability of soil Pb in an urban soil (Brown et al., 2003a). Recent studies have shown that using combinations of treatments can improve their effectiveness compared with using them individually (Hettiarachchi et al., 2000; Hettiarachchi and Pierzynski, 2002). Although these laboratory studies have demonstrated that it is possible to alter Pb mineralogy and

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Abbreviations: TSP; triple superphosphate.

thereby reduce its extractability, it is important to replicate these findings under field conditions where greater variability of soil and environmental conditions exist. Additionally, achieving sufficient mixing is more problematic under field conditions.

When Pb contamination is accompanied by elevated concentrations of associated elements such as Zn and Cd, the effect of treatment addition on their availability is also important. Plant uptake of Zn and Cd are standard measures for the phytoavailability of these elements (Brown et al., 1998; Chaney, 1993; Chaney and Ryan, 1994). Plant uptake of Pb has also been used to measure reductions in Pb phytoavailability (Hettiarachchi and Pierzynski, 2002; Basta et al., 2001; Laperche et al., 1997). As a result of P (hydroxyapatite) addition to soil in a plant study, Pb concentrations in shoot tissue of sudax [*Sorghum bicolor* (L.) Moench] were reduced from 170 to 3 mg kg^{-1} (Laperche et al., 1997). Reductions were also observed in lettuce Cd, Zn, and Pb concentrations as a result of lime-stabilized biosolids treatments of smelter-contaminated soils (Basta et al., 2001). However, the observed reductions were not consistent across soils or elements (Basta et al., 2001). In a greenhouse study using soil collected from the same Joplin field site in this study, Hettiarachchi and Pierzynski (2002) observed decreased plant concentrations of Pb, Zn, and Cd as a result of P addition. Treatment effect, however, was not consistent across all elements or across all harvests. Hettiarachchi et al. (2000) and Hettiarachchi and Pierzynski (2002) combined Mn oxides with P and found that addition of Mn further reduced Pb bioavailability. The potential for combinations of treatments to be more effective than applied individually is largely unexplored.

The goal of this study was to determine if in situ treatments to a Pb-, Zn-, and Cd-contaminated soil could reduce metal phyto- and bioavailability as measured by in vitro and in vivo (using weanling rats) assays and plant concentrations. Combinations of treatments as well as treatments added singly were tested under both lab and field conditions. The relationship between results observed in the lab and the in the field was examined. The potential relationship between different measured endpoints was also examined.

MATERIALS AND METHODS

Field Site

Smelter emissions from a long-term Zn and Pb smelter operation in Joplin, MO, located in the Tri-State mining district, have contaminated the soils and resulted in it being listed on the USEPA National Priorities List as part of the Superfund program. A vacant lot near the center of the city was identified as an in situ field test site. For the laboratory portion of the study, a composite sample was collected from the field site before establishment of the field experiments. Analysis of the composite sample was conducted at the University of Missouri. Scanning electron microscopy (SEM) analysis suggested that the primary Pb minerals at the site were $PbCO_3$, PbO, and $PbSO_4$ (Yang et al., 2001). In addition to elevated Pb concentrations (>600 mg Pb kg^{-1}), the soil also has high concentrations of Zn (>3000 mg Zn kg^{-1}) and Cd (>15 mg Cd kg^{-1}). Characteristics of the composite sample are reported in Yang et al. (2001).

Laboratory Screening for Field Treatment Selection

Treatments for the field study were selected based on a series of laboratory incubations using the composite soil sample from the field site and a wide range of potential materials (Brown and Chaney, 1997). Treatments, at a range of application rates, were added to 50-g aliquots of the composite sample collected from the site. Samples were placed in specimen cups and deionized water (50 mL) was added to the samples, which were shaken side-to-side for 24 h. Samples were air-dried and then analyzed using an in vitro extraction procedure with an initial pH of 2.2 (Brown et al., 2003a). The laboratory treatments that showed the highest reduction in extractable Pb, based on the results of the in vitro procedure, were selected for use in the field study. Phosphate rock was included in the field experiment because of previous research indicating its potential efficacy (Laperche et al., 1997; Ma et al., 1993; Zhang and Ryan, 1998). Additionally, phosphoric acid was included based on a series of lab incubations conducted at the University of Missouri (Yang et al., 2001). Treatments used in the field study included phosphorus added to soils as triple superphosphate [TSP; $Ca(H_2PO_4)_2{\cdot}H_2O$], phosphate rock [$Ca_5(PO_4)_3F$], and phosphoric acid (H_3PO_4); iron-rich material (Fe) (donated by DuPont Chemical, Wilmington, DE); and Compro, a municipal biosolids compost high in both lime equivalent and Fe from Washington, DC (compost + Fe + lime, referred to hereafter as "compost") (Table 1). Each treatment had previously been shown to reduce Pb availability in in vivo or in vitro studies using laboratory-incubated soils (Berti and Cunningham, 1997; Brown et al., 2003a; Hettiarachchi and

Table 1. Total soil metals, pH (1998–1999), and bicarbonate-extractable P (1999) from the field site in Joplin, MO.†

Treatment	Soil Pb	Soil Zn	Soil Cd	Extractable P	Soil pH
	mg kg^{-1}				
Control (100 kg ha^{-1} N, P, K)	**2892 ± 680**	**4279 ± 1182**	**24.64 ± 6.05**	**85.5 ± 19**	**7.15**
1% P-TSP‡	**4056 ± 280**	**5118 ± 779**	**26.76 ± 3.29**	**245 ± 17**	**7.12**
3.2% P-TSP	**3340 ± 568**	**4572 ± 942**	**25.20 ± 5.02**	**353 ± 61**	**6.94**
1% P-phosphate rock	**2108 ± 433**	**3573 ± 1265**	**17.76 ± 8.16**	**61.4 ± 2.2**	**7.18**
1% P-H_3PO_4	**3263 ± 353**	**4476 ± 628**	**40.25 ± 18.3**	**615 ± 57**	**6.47**
1% Fe + 1% P-TSP	**3660 ± 801**	**5557 ± 1987**	**29.22 ± 13.7**	**129 ± 22**	**7.08**
2.5% Fe + 0.32% P-TSP	**2389 ± 827**	**2846 ± 827**	**13.94 ± 4.94**	**15.3 ± 4.4**	**7.07**
2.5% Fe + 1% P-TSP	**1861 ± 492**	**2742 ± 596**	**14.37 ± 3.15**	**33.3 ± 5.2**	**7.24**
Compost at 10%	**2617 ± 560**	**4236 ± 837**	**21.96 ± 5.79**	**18 ± 4**	**7.26**
Compost at 10% + 0.32% P-TSP	**1517 ± 507**	**2227 ± 600**	**12.30 ± 3.79**	**119 ± 27**	**7.24**
Compost at 10% + 1% P-TSP	**2965 ± 809**	**4099 ± 1020**	**21.92 ± 6.34**	**216 ± 41**	**7.08**

† Values are means ± standard error (n = 4).
‡ TSP, triple superphosphate.

Pierzynski, 2002; Yang et al., 2001). Characteristics of the Fe are presented in Berti and Cunningham (1997). Additional data on the compost are presented in Brown et al. (2003a). In addition to being added singly, treatments also were applied in several combinations. These included Fe + 0.32 and 1% P-TSP and compost + 0.32 and 1% P-TSP.

Rat Feeding Study

A feeding study using weanling rats was conducted with a subset of the laboratory-incubated samples. Treatments for the feeding study included a control, H_3PO_4 added at 1% P, 10% compost, and 2.5% Fe + 1% P-TSP. Soils were incubated moist for 30 d and then sieved to <1 mm before mixing with rat diets. Soils were added to AIN93G Basal Mix to comprise 5% of the mixture (Harlan Teklad [Indianapolis, IN] Catalog no. TD 96107). Diets were prepared and the feeding study was conducted according to the methodology outlined in Brown et al. (2003a).

Field Study

Treatments were installed at the field site in March 1997 using a randomized block design with four replicates. Each plot measured 2 × 4 m. Plots were tilled to a 12.5-cm depth using a tractor-pulled rototiller before treatment application. Trenches were dug around each plot and high-density polyethylene (HDPE) plastic barriers were installed to reduce the potential for inter-plot contamination. Treatments were weighed on a per plot basis and evenly applied to the surface of the tilled soil. For the field study, TSP and H_3PO_4 were purchased at a local fertilizer dealer. Phosphate rock was donated by Occidental Chemical (Dallas, TX). Applications were made on a dry weight basis with the assumption that the dry weight of 1 m^3 of soil = 1050 kg. Application rates of P treatments were calculated on the basis of total P addition. Treatments were then tilled into the soil with a minimum of three passes of the rototiller. The final treatments used at the field site are listed in Table 1. Average metal concentrations, extractable P, and pH for each of the treatments are also presented in this table.

After treatment, plots were covered with a commercial landscape fabric for 8 wk. After removing the fabric, $Ca(OH)_2$ (71% purity) was applied evenly and rototilled into each plot to bring the pH to 7. The amount of lime required ranged from 157 kg per plot (3.2% P-TSP) to 39.4 kg per plot (10% compost + 0.32% P-TSP) and no lime for the compost alone treatment. This corresponds to approximately 200 Mg lime ha^{-1} for the 3.2% P-TSP and 50 Mg lime ha^{-1} for the compost + 0.32% P-TSP treatment. After lime treatment, tall fescue seed was hand-scattered over the surface of the plots.

Plant Samples

Tall fescue grass samples (five subsamples per plot) were collected from the plots in September 1997, April 1998, October 1998, September 1999, and September 2000. This corresponds to 6 mo and 1, 1.5, 2.5, and 3.5 yr after treatment addition. Plants were analyzed for total metals. After harvest, samples were washed in a 0.3% sodium lauryl sulfate solution, rinsed in deionized water, and dried at 70°. One- to four-gram samples of plants were ashed in glass beakers at 480°C for 16 h. The ash was dissolved with concentrated HNO_3 and refluxed in 3 *M* HCl. Samples were brought to a final volume of 25 mL using 0.1 *M* HCl and analyzed for total metals using an inductively coupled plasma–atomic emission spectrophotometer (ICP–AES). Cobalt was used as an internal standard.

Soil Samples

Soil samples were collected from the plots immediately after treatment addition, in the fall of 1997, 1998, 1999, and 2000. Soil pH was measured using a 1:2 soil to deionized water slurry with a combination pH electrode. Total metals were measured using an aqua regia digestion (McGrath and Cunliffe, 1985). The in vitro extractions were conducted using the same procedure as was used in the lab-incubated samples with the exception that a 0.4 *M* glycine solution, adjusted to pH 1.5 and 2.2 with 0.1 *M* HCl, was used instead of a gastric fluid solution (Ruby et al., 1999). A lab comparison between the two extracting solutions (pH 2.2 ± enzymes) showed no difference (data not shown). Extractions were performed at pH 1.5 for soils collected in 1997 and 1998, and at pH 2.2 for all field-collected soils. In some cases both the <2-mm and the <250-μm particle size soil fractions were used for the procedure at pH 2.2. An evaluation of the effect of particle size was conducted using analysis of variance (ANOVA). There was no difference in results as a function of particle size ($p < 0.29$). As a consequence, results from extracts done with the different particle sizes have been combined. Metal concentrations in the total metal and in vitro procedures were measured using a flame atomic adsorption spectrophotometer. Soils from the 1999 sampling were also analyzed for available P using the Bray procedure (Kuo, 1996) (Table 1).

Data Analysis

For plant and soil samples, standard reference materials from the National Institute of Standards and Technology (NIST), method blanks, and laboratory standards were routinely included in analysis. Standard recovery was within 15% of the reported values. Statistics were calculated using SAS Version 6.12 for MacIntosh (SAS Institute, 1996). The significance of treatment and time for in vitro Pb and plant tissue metal concentrations was tested using the GLM procedure. The Duncan–Waller means separation procedure was then used to separate the effects of treatment and time for both plant metals and in vitro extractable Pb. To account for the differences in total soil metals, statistics were performed on the ratio of plant or in vitro Pb, Zn, and Cd to total soil Pb, Zn, or Cd for each plot. Data was log-transformed using the natural log (ln) so that the data followed a normal distribution. Both the actual value for each variable as well as the ratio of plant metal to total soil metal × 100% are presented.

RESULTS AND DISCUSSION

Laboratory-Treated Soils

In Vitro Extractions

All treatments tested in the laboratory in vitro screening process showed significant reductions in bioaccessibility (defined as the in vitro extractable fraction, which was developed to be a surrogate for in vivo or bioavailability studies) compared with the control soil (Table 2). These ranged from 21% for the 0.1% P-TSP treatment to 89% for 3.2% P-TSP treatment. The 3.2% P-TSP addition was the most successful treatment. However, adding this quantity of P to the soil reduced soil pH to 3.42, which is below agronomically acceptable values. Because of this reduction, soil treated with these levels of TSP would require liming before plants could be grown. The amount of lime ($CaCO_3$) required to return the pH to control levels for 3.2% P-TSP was approximately 200 Mg ha^{-1}, based on laboratory titrations.

Compost and Fe treatments were not associated with a similar decrease in pH. Of the four separate compost treatments initially tested at 10% dry weight, the compost from Washington, DC, which was high in Fe and lime, showed the highest reduction (65%). This material had been used previously as a treatment for a Pb-contaminated soil from Baltimore, MD. Added at 10% in a laboratory study, compost showed a 54% reduction of in vitro Pb and a 29% reduction in bone Pb in a rat feeding study (Brown et al., 2003a).

The Fe treatments tested in the laboratory showed an effect on bioaccessibility with the highest reductions in availability (bioaccessibility) when Fe was added at 2.5%. The addition of TSP with Fe caused a greater reduction in bioaccessibility than Fe alone. For example, adding 2.5% Fe resulted in a 44% reduction in availability (bioaccessibility). This increased to 71% when 1% P-TSP was included in the treatment. Addition of 1% P-TSP singly resulted in a 53% reduction compared with the control soil.

Rat Feeding Study

A few of the laboratory-treated soils were fed to weanling rats. All treatments tested in the rat feeding study reduced Pb bioavailability compared with the control soil (Table 3). For the feeding study, Pb concentrations in blood, kidney, liver, and bone were measured. Reductions were observed for all measured organs (significant for blood and bone); the degree of reduction varied between organs. Values were averaged by treatment to determine an overall reduction. Of the treatments tested, 2.5% Fe + 1% P-TSP was the most effective, showing a 39% reduction over the control. Both the compost and 1% P-H$_3$PO$_4$ showed a 26% reduction. Reductions in the feeding study were not as pronounced as those observed in the in vitro extract (Table 2). This could be the result of differences in the soil incubation used before extraction verses feeding or to a difference in the measured endpoint. Before the in vitro extraction, soils were mixed as a wet slurry on a side to side shaker. For the feeding study, soils were incubated moist with intermittent mixing. It may also be explained by differences between the in vitro and in vivo tests. In the same manner that soils extracts are designed to predict plant availability of nutrients, the in vitro extract has been designed to predict in vivo bioavailability. Data is only now being accumulated to test the validity of this extraction.

Table 2. Effect of different treatments on laboratory-incubated samples of soil collected from the field plot as part of treatment selection process on soil pH and in vitro extractable Pb (pH 2.2).

Treatment†	Solution Pb‡	Reduction§	Soil pH¶
	mg kg^{-1}	%	
Control	13.40 ± 0.23		6.97
Compost (10%)			
Compost	7.76 ± 0.42	42	6.74
Compost + lime	6.10 ± 0.25	54	6.75
Compost + Fe	7.30 ± 0.55	46	6.60
Compost + Fe + lime	4.69 ± 0.84	65	6.93
Fe (iron-rich)			
0.5%	8.12 ± 0.98	39	6.90
1.0%	8.60 ± 0.46	36	6.86
2.5%	7.54 ± 0.71	44	6.89
P (TSP)			
0.1%	10.61 ± 2.50	21	6.04
0.32%	7.25 ± 4.29	46	5.09
1.0%	6.25 ± 0.03	53	4.31
3.2%	1.53 ± 0.17	89	3.42
Fe 0.5% + P (TSP)			
0.1%	9.24 ± 0.26	31	6.03
0.32%	7.87 ± 0.79	41	5.19
1.0%	6.18 ± 0.08	54	4.38
3.2%	1.76 ± 0.14	87	3.44
Fe 1.0% + P (TSP)			
0.1%	8.28 ± 0.39	38	6.12
0.32%	7.19 ± 0.37	46	5.18
1.0%	5.50 ± 0.05	59	4.44
3.2%	2.18 ± 0.07	84	3.44
Fe 2.5% + P (TSP)			
0.1%	7.04 ± 0.70	48	6.20
0.32%	5.62 ± 0.28	58	5.50
1.0%	3.92 ± 0.07	71	4.61
3.2%	2.18 ± 0.02	84	3.50

† The compost section included four different biosolids composts from different composting operations. The compost + Fe + lime (referred to in the text as "compost") was the specific compost selected for use in the field study. TSP, triple superphosphate.

‡ Values are means ± standard errors ($n = 3$).

§ Percent reduction is the change in solution Pb in the treated soils over the control soil.

¶ Soil pH is the measured pH of the soil following the 24-h incubation with the treatments.

Field-Treated Soils

Variables measured in the field study included plant uptake of Pb, Zn, and Cd and in vitro extractable Pb. Plant toxicity is the primary concern for elevated Zn in soil, whereas the potential for risk to the herbivores is the primary concern with elevated soil Cd. Human health concerns focus on Pb for which the most pertinent pathway is direct ingestion of soil. The results from the field in vitro extractions are the most useful to evaluate treatment effectiveness regarding direct soil Pb inges-

Table 3. Rat diet Pb concentrations, bone, blood, kidney, and liver Pb concentrations (dry weight), and observed reduction in bioavailability for weanling rats fed laboratory incubated soils from the Joplin site that had been amended with 10% compost, 2.5% Fe + 1% P, or 1% P as H$_3$PO$_4$.

Treatment	Rat diet	Bone	Kidney	Liver	Blood	Reduction†
	mg Pb kg^{-1}					%
Control	88a‡	152.5e	22.9	5.4	439de	
10% Compost	100ab	133.1ef	17.7	5.0	358ef	26
2.5% Fe + 1% P-TSP§	89.6c	89.8g	13.6	3.6	273f	39
1% P-H$_3$PO$_4$	87.5ab	106.8fg	15.1	4.1	357ef	26

† Reduction was calculated as (control organ Pb/control diet Pb − amended organ Pb/amended diet Pb)/control organ Pb/control diet Pb, and has been averaged across all organs.

‡ Numbers in columns followed by the same letter are not significantly different ($p = 0.05$).

§ TSP, triple superphosphate.

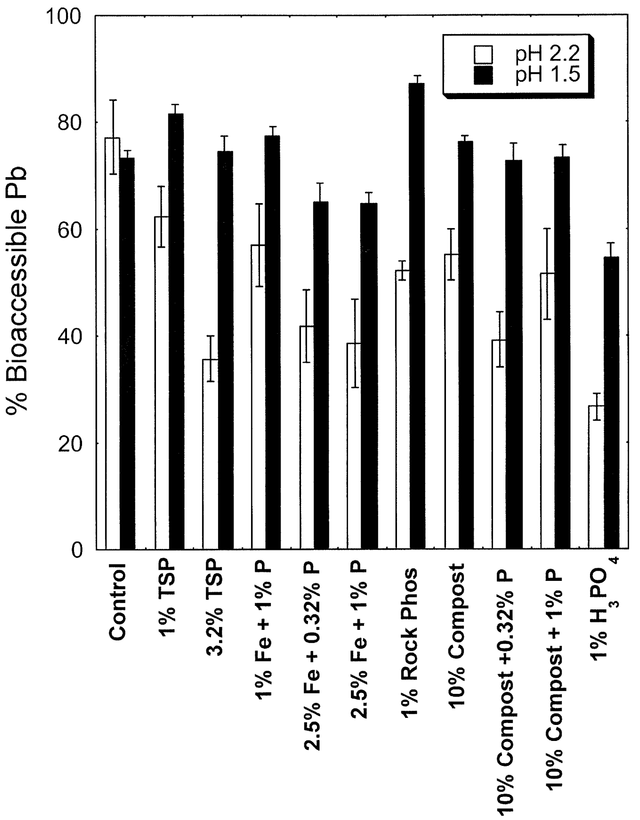

Fig. 1. In vitro extractable Pb for field-collected samples. Data shown are means ± standard errors for samples collected in 1997 and 1998 (0.5 and 1.5 yr after amendment addition).

tion. The reductions in in vitro Pb may also be mirrored by reductions in plant Pb.

In Vitro

The in vitro procedure on soils collected from the amended field plots was performed using glycine–HCl buffered solutions at two pH values: 1.5 and 2.2. Treatment effects were more pronounced when the in vitro procedure was performed at the higher pH. Average bioaccessibility across all treatments was 70% at pH 1.5 and 44% at pH 2.2 (Fig. 1). Zinc and Cd concentrations in the extract were also analyzed. The in vitro procedure showed no treatment effect for either element, indicating either that it may not be an appropriate extract to evaluate changes in bioaccessibility for Cd or Zn or that no changes had occurred.

pH 1.5

At pH 1.5, both treatment and time affected bioavailable Pb concentrations; however, there was no significant treatment × time interaction. The average percent extractable fraction across all treatments of total soil Pb fell from 77 to 70 from 1997 (0.5 yr) to 1998 (1.5 yr). This decrease may be the result of sampling differences as it is likely that the in vitro test is insensitive to changes over time (due to the potential for reactions to occur during the extract). For both years, the 1% P-H_3PO_4 treatment was the most effective, reducing the fraction of total Pb that was extracted from 73% in the control soil to 55% (Fig. 1). At this pH, however, several of the treatments appeared to increase Pb availability over the control. These included 1% P-TSP (82%) and phosphate rock (87%). In addition, all of the other treatments showed no change in extractable Pb over the control soil. The in vitro extractable Pb in these treatments ranged from 76% in the compost treated soil to 65% in the 2.5% Fe + 1% P-TSP treated soil.

pH 2.2

Compared with pH 1.5, the in vitro extraction at pH 2.2 showed both a lower overall Pb availability and a more pronounced effect of treatment. As for the pH 1.5 extract, both year and treatment were significant and there was no interaction between the two variables. Average in vitro extractable Pb across all treatments was similar in the fall of 1997 (57% after Year 0.5) and 1999 (52% after Year 2.5) but was lower in 1998 (44% after Year 1.5). This suggests that changes over time did not follow a consistent pattern or that some reactions may have actually occurred during the extraction procedure.

At pH 2.2, all treatments significantly reduced the portion of total Pb that was extractable compared with the control soil (77%) (Fig. 1). The most effective treatment was 1% P-H_3PO_4 (26%), which corresponds to a 65% reduction compared with the control soil. The observed reduction over the control for the 1% P-H_3PO_4 treatment at pH 1.5 was 25%. The fraction of total Pb that was extracted from the 3.2% P-TSP treatment was 37%. This corresponds to a 52% reduction over the control. This treatment showed no decrease over the control at pH 1.5. Comparably effective treatments included 2.5% Fe + 1% P-TSP (41%), 2.5% Fe + 0.32% P-TSP (42%), and compost + 0.32% P-TSP (43%). Observed bioaccessibilities for the other treatment treatments ranged from 51% in the compost + 1% P-TSP treatment to 63% in the 1% P-TSP treatment.

Relationship between Laboratory- and Field-Treated Soils

The reduction in bioavailability observed in lab-incubated and field soil samples is shown in Fig. 2. All of the treatments were the same except for phosphate rock. In this case reagent-grade hydroxyapatite was used in the lab study instead of the phosphate rock ore that was applied to the field plots. Excluding phosphate rock, the lab-incubated samples showed greater reductions than the field-collected samples. The reduction observed in the lab sample was 15% (10% compost + 0.32% P-TSP) to 240% (1% P-TSP) greater than that observed in the field. This may be the result of several factors. Lab samples were mixed to maximize contact between treatments and Pb in the soil. This mixing resulted in more soil–amendment contact and more complete reactions. The decrease in pH following incubation (Table 1) may also have solubilized more Pb, allowing for more complete reactions. Although reaction time

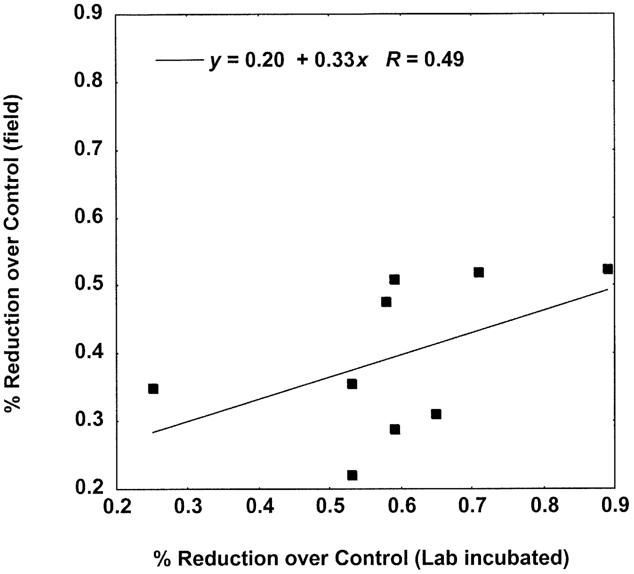

Fig. 2. The relationship between in vitro extractable Pb from lab-incubated and field-amended samples. Data shown were all extracted at pH 2.2.

for the laboratory treatments was 24 h, the conditions for the incubation would maximize reaction potential.

The wide range in results in the lab-incubated samples may be related to differences in the solubility of Pb as a result of treatment addition. For example, the pH of the slurry of the 1% P-TSP incubated sample was 4.31 whereas the pH in the compost samples was 6.74 (Table 1). The reduced pH may have solubilized more Pb. More Pb in solution would increase the potential for re-adsorption or precipitation in a less bioavailable mineral form. Although field soils were tilled after treatment addition and left to incubate for 8 wk before lime was added, it may be that additional mixing combined with irrigation would have improved the performance of the treatments in the field as it would increase the potential for dissolution and reprecipitation. It is also possible that lime addition following the 8-wk incubation altered the efficacy of the amendments in comparison with the lab-amended soils.

Relationship between In Vivo and In Vitro

The feeding study using lab-incubated samples showed a reduction in bioavailability for all treatments tested (Table 3). This was most pronounced for the 2.5% Fe + 1% P-TSP (39%) treatment, but it was also significant for the compost (26%) and 1% P-H_3PO_4 (26%) treatments. This reduction was also reflected in the in vitro analysis of the field-treated soils for the P treatment. For other treatments, reductions were not consistent between the in vivo and in vitro assays (Table 4). If results from the pH 1.5 in vitro extraction are used, compared with the control there was no reduction observed for compost, a 12% reduction for 2.5% Fe + 1% P-TSP, and a 25% reduction for 1% P-H_3PO_4 (Table 4). At pH 2.2, the in vitro extraction showed a 29% reduction for compost, 50% for 2.5% Fe + 1% P-TSP, and 66% for 1% P-H_3PO_4 compared with the control soil. While the feeding study was conducted on lab-treated samples, it is potentially more representative of a human response than the in vitro extraction procedure. Feeding tests of field-treated soils have also been conducted using both pigs and rats as human surrogates (Ryan et al., 2001). While all treatments have been fed to rats, only a few have been fed to swine. Lead in the 1% P-H_3PO_4 treated field soils showed a 38% reduction compared with control soils when fed to juvenile swine (Casteel et al., 2001). Complete results from the rat feeding studies will be published separately. However, for the in vitro extraction to be useful, the predicted changes in bioaccessibility need to be related to animal feeding tests (bioavailability) for a range of treatments. The in vitro test was developed to function as a rapid, inexpensive alternative to in vivo feeding studies (Ruby et al., 1999). The test aims to replicate the factors determining metal solubility in a human gastric environment. It would be equally useful if it over- or under-predicted these reductions, as long as it did so consistently across treatments. Initial results from this study do not indicate that it does. These inconsistencies may be the result of comparing field versus lab-incubated samples. They may also reflect problems in in vivo studies such as insensitivity to change over time (Ryan et al., 2004). Complete results from the field soil feedings will help to evaluate the in vitro procedure. Moreover, this study was done on amended soils from a single field site. Variability might be greater if treated soils from a range of sites are considered.

Table 4. A comparison of the observed percent reduction in bioavailability, bioaccessibility, and phytoavailability in amended soil vs. control soil from the same field site using both lab- and field-amended samples as measured in vitro, in a rat feeding trial using lab-incubated soils, and in a plant (fescue) uptake study.

Study	Conditions	1% P-H_3PO_4	10% Compost	2.5% Fe + 1% P-TSP
			% reduction	
Rat feeding	lab-amended	26	26	39
In vitro				
	lab-amended		65	71
	field-amended			
	pH 1.5	25	1	12
	pH 2.2	66	29	50
Fescue	field-amended			
	Pb	65	7	62
	Cd	63	56	−8
	Zn	30	53	37

Plants

For Zn, Cd, and Pb in plant tissue, time was the most important factor in determining plant metal concentration. For all elements, the average tall fescue concentration across all treatments was highest in the year following treatment addition (1997, 0.5 yr after treatment; Table 5). For all elements, mean plant concentration decreased for all subsequent harvests. This was true for the control as well as the amended soils. It may be appropriate to look at variation after the first harvest to evaluate what would normally occur based on seasonal climate differences. The effect of these factors on soil

Table 5. Differences in tall fescue Zn, Cd, and Pb concentrations as a function of year.†

Year‡	Plant Zn	Plant Cd	Plant Pb
	mg kg^{-1}		
1997 (0.5)	288 ± 20	4.81 ± 0.34	13.4 ± 1.7
1998a (1)	191 ± 11	1.51 ± 0.09	3.27 ± 0.34
1998b (1.5)	145 ± 13	1.14 ± 0.13	7.56 ± 1.1
1999 (2.5)	106 ± 8	0.57 ± 0.09	6.10 ± 0.85
2000 (3.5)	107 ± 8	1.44 ± 0.12	4.55 ± 0.39

† Values are means ± standard errors ($n = 44$).
‡ Results for each year are averaged over all treatments. Numbers in parentheses indicate number of years after treatment addition.

partitioning and plant uptake of Zn and Cd has been previously noted (Almas et al., 2000; Brown et al., 1998).

For all treatments, plant concentrations of Zn, Cd, and Pb were below those associated with phytotoxicity or food chain risk (Table 6). The response to treatment addition observed in this study may not be indicative of the behavior that would be seen where metals in soil are sufficiently phytoavailable to result in phytotoxic tissue concentrations (Brown et al., 2003b; Li et al., 2000). Under these circumstances a more pronounced treatment effect has been observed.

Plant Lead

Treatment effects were not consistent across elements of concern or across harvests with treatment effect more pronounced for some years and less pronounced for others. The effect of the soil treatments was most significant for plant Pb and Cd uptake. Average plant Pb concentrations across all years, shown as the ratio of plant Pb to soil Pb, are presented in Fig. 3.

Phosphorus Treatments

Across all treatments, plant Pb to total soil Pb ratio was consistently lowest in the 3.2% P-TSP and 1% P-H_3PO_4 amended plots. Plant Pb in the 1% P-phosphate rock amended plots was not different from plant Pb in the control treatment for any harvest. For 1% P-TSP, plant Pb generally decreased over time. Concentrations were similar to the control treatment in 1997 (Year 0.5) and fall of 1998 (Year 1.5). Relative plant uptake began to decrease in 1999 (Year 2.5), and by the 2000 (Year 3.5) harvest, plant concentration of Pb in the 1% P-TSP treatment was as low as that observed in the 3.2% P-TSP treatment. The increased efficacy over time of the 1% P-TSP treatment may be related to increased pyromorphite formation. However, pyromorphite formation was also observed in the 1% P-phosphate rock treatment, and this had no effect on the phytoavailability of Pb for this treatment (Sheckel and Yang, 2001). When 3.2% P-TSP was added, the effect on plant Pb uptake was immediate and consistent across harvests.

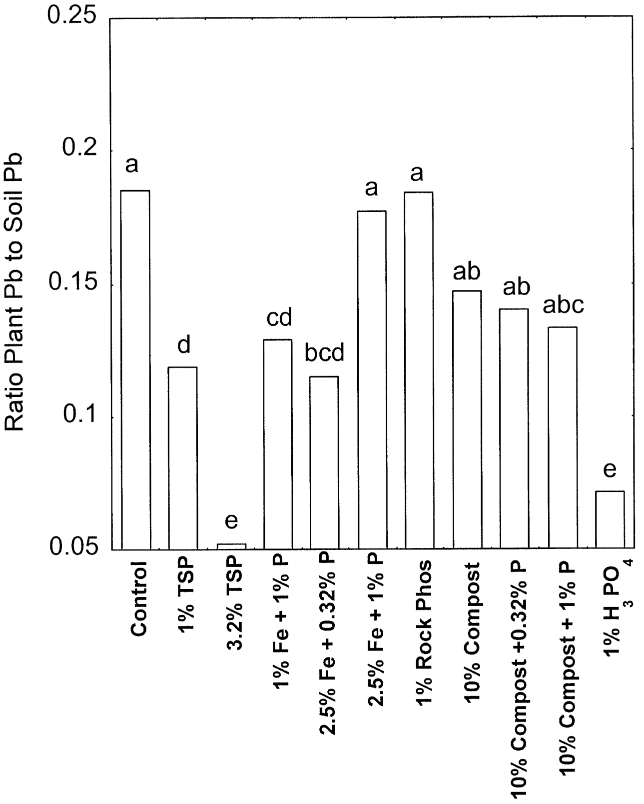

Fig. 3. The natural log (ln) of the ratio of plant Pb to soil Pb for tall fescue grown at the field site in Joplin, MO. Results are averaged across all harvests. Different letters above bars indicate significantly different values using the Duncan–Waller means separation procedure ($p < 0.05$).

Table 6. Average Cd, Pb, and Zn concentrations of tall fescue across all years of the field study.†

Treatment	Plant Cd	Plant Pb	Plant Zn
		mg kg^{-1}	
Control	3.38 ± 0.43	10.4 ± 1.84	298 ± 31
1% P-TSP‡	1.58 ± 0.31	9.67 ± 2.35	192 ± 29
3.2% P-TSP	0.92 ± 0.13	3.11 ± 0.48	129 ± 12
1% Fe + 1% P-TSP	2.33 ± 0.58	8.85 ± 2.18	197 ± 32
2.5% Fe + 0.32% P-TSP	1.81 ± 0.42	5.29 ± 1.12	128 ± 15
2.5% Fe + 1% P-TSP	2.12 ± 0.63	6.67 ± 1.44	120 ± 16
1% P-phosphate rock	1.90 ± 0.28	8.77 ± 2.53	190 ± 22
10% Compost	1.33 ± 0.26	8.77 ± 1.89	139 ± 11
10% Compost + 0.32% P-TSP	1.66 ± 0.47	3.84 ± 0.66	125 ± 18
10% Compost + 1% P-TSP	1.96 ± 0.51	8.24 ± 1.45	156 ± 19
1% P-H_3PO_4	2.02 ± 0.34	4.07 ± 1.19	218 ± 21

† Values are means ± standard errors. Values do not reflect variation in total metal concentrations by treatment.
‡ TSP, triple superphosphate.

Iron + Compost

For the treatments that included Fe, Pb concentration in plant tissue was highest during the first year of the study. Across all years, the 2.5% Fe + 1% P-TSP treatment was similar to the control. The two Fe treatments that included either lower application rates of Fe and/or P decreased plant Pb compared with the control soil. The Fe treatment that showed the lowest plant Pb concentrations across all years was the 2.5% Fe + 0.32% P-TSP treatment. The same rate of Fe addition coupled with 1% P-TSP had the highest plant Pb values for all treatments in 1997 (Year 0.5). It is possible that, initially, the binding capacity of the Fe was negated by the addition of the high rate of P. In the 1% P-TSP alone treatment, phytoavailability of Pb was also comparable with the control in the first year of the study. These results indicate that including TSP with Fe initially had little effect on Pb phytoavailability. Over time, however, the efficacy of the Fe treatments increased, with plant Pb level in the 1% Fe + 1% P-TSP treatment decreasing in respect to the other Fe treatments. By the 2000 harvest (Year 3.5), plant Pb in this treatment was not significantly different from plant Pb in the 3.2% P-TSP or 1% P-H_3PO_4 treatments. As the experimental design did not include a Fe alone treatment, it is also possible that the Fe addition negated the binding capacity of the P. The compost treatments did reduce plant Pb concentration compared with the control for all harvests. The higher rate of the TSP as well as the 1% P-H_3PO_4 treatments were the most consistent at reducing plant Pb concentrations.

Plant Zinc

Based on statistical analysis, the effect of soil treatment on plant Zn concentration was not as pronounced or consistent as for plant Pb. There was no treatment effect on plant Zn for two of the five harvests of the study (May 1998 [Year 1] and September 1999 [Year 2.5]). Plant Zn concentration decreased across all treatments from 1997 with overall Zn concentrations lowest in the 1999 and 2000 harvests (Table 5).

Phosphate Treatments

The primary similarities with the results observed for Pb was the efficacy of the 3.2% P-TSP treatment in lowering plant Zn (Fig. 4). Plant Zn increased over time in the 1% P-H_3PO_4 treatment, and it was similar to the control during the final year. This may be the result of the soil pH in this treatment. Although lime was added after treatment, the soil pH averaged 6.5 in 1998–1999 vs. 7.15 in the control treatment. Soil pH averaged 6.94 in the 3.2% P-TSP and 7.12 in the 1% P-TSP treatments over the same period. Plants grown in the 1% P-TSP treatment plots had decreasing Zn concentrations over time with average plant Zn similar in both TSP treatments. Plant Zn in the phosphate rock amended plots was comparable with the control treatment.

Iron + Compost Treatments

Average plant Zn to soil Zn ratio across all harvests in all Fe + P treatments was lower than the control treatment. Within the different Fe treatments, the 1% Fe + 1% P-TSP treatment appeared to be the most effective. Increasing the rate of Fe addition, however, also increased the rate of Zn uptake. Across all years, the ratio of plant Zn to soil Zn in plants grown in the compost alone treatment was similar to the ratio in the 1% P-TSP treatment. Adding P to the compost (0.32% P-TSP) resulted in an increase in plant Zn concentrations. For both the Fe and compost treatments, including P with these treatments did not result in increased efficacy of reducing plant Zn concentrations that had been expected. Overall, for treatments that included 1% P-TSP, the fraction of plant-available Zn was lowest in the 1% P-TSP treatment.

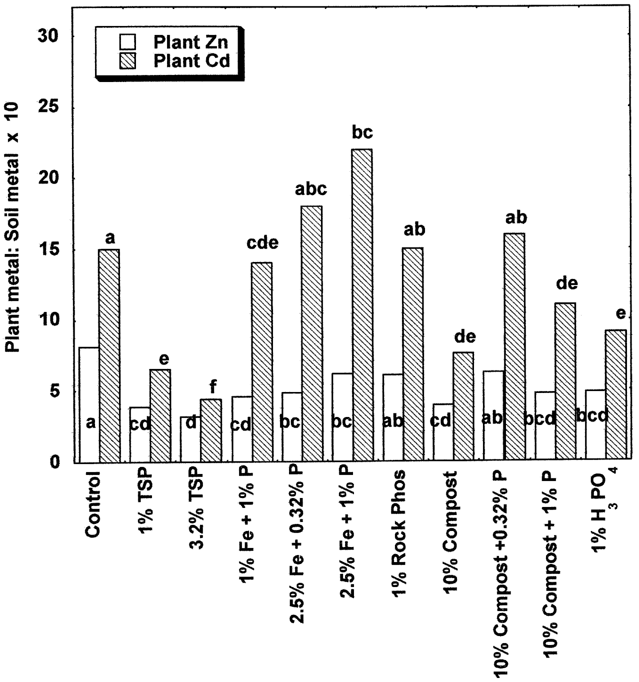

Fig. 4. The ratio of plant Zn and Cd to soil Zn and Cd for tall fescue grown on amended field plots in Joplin, MO. Results are averaged across five harvests. Different letters above bars indicate significantly different values using the Duncan–Waller means separation procedure ($p < 0.05$).

Plant Cadmium

As was observed for both plant Pb and Zn, concentrations of plant Cd in the 3.2% P-TSP were lowest overall. The 1% P-TSP and 1% P-H_3PO_4 treatments also resulted in decreased plant Cd compared with the control treatment. Phosphate rock addition had no effect on plant Cd concentrations in comparison with the control.

Iron + Compost Treatments

Of all of the treatments that included Fe, only the 1% Fe + 1% P-TSP treatment was different from the control. Average plant Cd concentrations for two of the compost treatments were lower than the control. Combining P with compost did not have any consistent or significant effect on plant Cd concentrations. Compost added alone was the most effective of the compost treatments at reducing plant Cd and was similar in efficacy to the most effective P treatments.

Plant Zinc versus Plant Lead and Plant Cadmium

These results suggest that there is some relationship between the mechanisms controlling the phytoavailability of Pb, Cd, and Zn. As would be expected due to their similar characteristics, the relationship between plant Zn and plant Cd (r = 0.76) was stronger than the relationship between Zn and Pb (r = 0.61). For all elements, the addition of 3.2% P-TSP was the most effective treatment at reducing plant uptake. This might suggest a similar mechanism limiting solubility for all three elements. However, the 1% P-H_3PO_4 treatment, which was one of the most effective for reducing plant Pb and

Cd, was not comparably effective at reducing plant Zn. If pyromorphite formation was the primary mechanism reducing the solubility of Pb, formation of low-solubility Zn and Cd phosphate minerals should have produced similar results in reducing plant concentrations of these two elements. Hopeite [$Zn_3(PO_4)_24H_2O$], which has a log K of 3.8, is much more soluble in a soil system than pyromorphite, which has a log K of -25.05 (Lindsay, 2001). In addition, the potential for Zn– or Cd–phosphate complexes or surface precipitates (Kuo, 1986) may be more important in limiting Zn and Cd availability than the formation of Zn or Cd phosphate minerals. If surface complexation on functional groups is a primary factor controlling Zn availability, it would be expected that soil pH would be a dominant factor controlling the number of specific adsorption sites. These results suggest that this may be the case.

Inconsistencies in plant metal concentrations after soil treatment addition have been observed in greenhouse studies using smelter-contaminated soils (Basta et al., 2001; Hettiarachchi and Pierzynski, 2002; Mench et al., 1994). In one case, soil from the same field site was amended with P as phosphate rock (also from Occidental Chemical) and 0.5% P as TSP (Hettiarachchi and Pierzynski, 2002). As in the current study, phosphate rock did not reduce swiss chard (*Beta vulgaris* L.) concentrations of Pb, Cd, or Zn compared with that grown in the control soil. Triple superphosphate addition, however, did reduce Pb, Zn, and Cd concentrations in swiss chard. On the other hand, when sudax was grown in the same soils, treatment effects were not consistent over harvests dates for plant Cd. Plant Zn was also not reduced by phosphate rock addition. As in the current study, harvest date was a much more significant factor controlling plant uptake of Zn and Cd than treatment addition with Zn and Cd concentrations in plant tissue highest in the first cutting after soil treatment. In another pot study with smelter-contaminated soils from the Tri-State mining district, phosphate rock (added at 100 g kg^{-1}) did not reduce lettuce (*Lactuca sativa* L.) concentrations of Zn, Cd, or Pb over the untreated soil (Basta et al., 2001). Lime-stabilized biosolids (similar to the feedstock used to make compost used in this study) reduced lettuce Cd and Zn compared with the unamended soil. These results suggest that a range of factors, including plant species, soil moisture and temperature, soil tillage, and time are potentially as important as treatment composition in affecting plant concentrations of Pb, Zn, and Cd in contaminated but not phytotoxic soils.

Relationship between Plant and In Vitro Extraction

The lack of a strong relationship ($r = 0.18$) between plant-available Pb and soil Pb extracted by the in vitro (pH 2.2) method indicated that the two measures are not similar. The environment and range of interactions that occur in soil solution as they relate to phytoavailability are expected to be different from the human gastric system. In addition, the in vitro procedure reflects bioaccessibility (i.e., the amount potentially bioavailable for uptake into the blood from the GI tract of an animal) at a distinct time (30 min) under uniform conditions, whereas plant concentration is an integration of availability over the growing season. It is also possible that precipitation reactions are actually occurring during the in vitro extraction. It has also been shown that plants can solubilize pyromorphite under conditions of severe P deficiency (Laperche et al., 1997). Plants in this study averaged total P greater than 2 g kg^{-1} across all treatments, suggesting that P deficiency was not a concern. If reductions in bioaccessibility and plant concentrations are based on reduced solubility via the formation of discreet mineral phases, there is the potential for commonality between the two measurements of Pb availability when the plant nutrient supply is adequate. Similar results would also provide conformation in the success of the treatment. The absence of any relationship between the extracts suggests, despite adequate plant nutrients, that it may be necessary to use multiple tools to evaluate changes in bioaccessibility and phytoavailability for a range of endpoints.

CONCLUSIONS

Results from both lab- and field-treated soils indicate that it is possible to reduce the bioaccessibility and phytoavailability of soil Pb in situ. However, they also indicate that evaluating the magnitude of the reduction is not clear-cut (Table 4). Overall, additions of 3.2% P-TSP and 1% P-H_3PO_4 were the most effective treatments for reducing plant concentrations of Pb, Zn, and Cd and in vitro extractable Pb. The efficacy of the 1% P-TSP treatment appeared to increase over time. There was a relationship between plant Zn concentrations and Pb and Cd uptake. Despite potentially different adsorption–precipitation mechanisms for these elements, these results suggest that a single soil treatment may be suitable for reducing phytoavailability of the three elements. Although P addition was the most effective treatment tested in this study, the practicality of amending soils with these rates of P remains questionable. Excess P in soil and its potential effect on the eutrophication of surface waters remains a concern. In addition, in cases of co-contamination with As, P addition has been shown to solubilize soil As (Peryea, 1991). Other treatments can also effectively reduce phytoavailable Zn and Cd and bioavailable Pb. They may be of less concern than P loadings. Compost alone, for example, was an effective treatment across all measurement indices.

Across the measurement endpoints used in this study, all treatments tested were able to reduce the phyto- and bioavailability of Pb, Cd, and Zn. This suggests that the hazards associated with these contaminants can be simultaneously reduced for a range of different receptors. However, inconsistencies in measurements make it difficult to assess how effective these treatments are. Variability in results may increase as these types of amendments are used on a range of soil types with varied sources of contamination.

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