Field Test of In Situ Soil Amendments at the Tar Creek National Priorities List Superfund Site

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A range of soil amendments including diammonium phosphate fertilizer (DAP), municipal biosolids (BS), biosolids compost, and Al- and Fe-based water treatment residuals were tested on Pb-, Zn-, and Cd-contaminated yard soils and tailings at the Tar Creek NPL site in Oklahoma to determine if amendments could restore a vegetative cover and reduce metal availability in situ. For the yard soils, all amendments reduced bioaccessible (assessed with a physiologic-based extraction method) Pb, with reductions ranging from 35% (BS+Al, DAP 0.5%, DAP+Compost+Al) to 57% (Compost+Al). Plant Zn (*Cynadon dactylon* L.) and NH_4NO_3–extractable Cd and Zn were also reduced by a number of amendments. For the tailings, all amendments excluding BS reduced bioaccessible Pb, with the largest reductions observed in the DAP 3% and DAP3%+BS treatments (75 and 84%). Plant growth was suppressed in all treatments that contained DAP for the first season, with the highest growth in the treatments that included compost and biosolids. In the second year, growth was vigorous for all treatments. Plant Zn and Cd and extractable metal concentration were also reduced. A number of treatments were identified that reduced bioaccessible Pb and sustained a healthy plant with reduced metal concentrations. For the yard soil, Compost+Al was the most effective treatment tested. For the tailings, BS+DAP 1% was the most effective treatment tested. These results indicate that in situ amendments offer a remedial alternative for the Tar Creek site.

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Remedial activities at the Tar Creek, Oklahoma National Priorities List site in the US Environmental Protection Agency (EPA) Superfund Program have come under a great deal of public scrutiny (Barringer, 2004). The 104-km² site is located in the Tri-State mining district, which includes portions of southeastern Kansas and southwestern Missouri. Due to rich deposits of Zn and Pb ore, this area was extensively mined during the early to mid portion of the 20th century. Coarse material contaminated with Pb, Zn, and Cd from the milling operations, locally referred to as chat, was extensively used for fill for home gardens and driveways. Piles of mine tailings and chat are visible throughout the area. The area is economically depressed, and no clear solution for remediation of the mine wastes has been identified. One potential solution involves moving residents out of the area and flooding the area to create a wetland game preserve (USEPA, 2004). The cost of EPA remedial activities at the site to date is approximately $100 million (Barringer, 2004). The failure of initial remedial efforts, in combination with the cost of these activities and the depressed economy in the area, has resulted in negative public sentiment toward the EPA's remedial activities. In addition, the remaining millions of tons of chat and tailings piles are a visual nuisance and a source of fugitive dust. The aggregate is being mined for road-building materials and provides some income for residents in the area. Because of this, there is public opposition to removing the chat. In addition, the large volume of chat would be prohibitively expensive to move to a confined disposal facility.

In situ soil amendments offer the potential for a cost-effective remedial option to citizens and regulatory officials. Amendments are required to reduce the bioavailability of soil Pb in home gardens and/or establishing a plant cover on the mine waste materials. Previous studies on Pb and/or Zn mine waste materials have shown the ability of soil amendments to restore a plant cover on tailings and reduce the erosive potential of the wastes and the potential for fugitive dust (Brown et al., 2003: Brown et al., 2005). Application of municipal biosolids in combination with a lime source has also been shown to reduce the extractable and phytoavailable fraction of total soil metals for Pb-, Zn-, and Cd-contaminated soils. In Leadville,

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Abbreviations: BS, biosolids; DAP, diammonium phosphate; EC, electrical conductivity; WTR, water treatment residuals.

Colorado, a range of ecosystem function measures, including microbial respiration, earthworm (*Eisenia fetida*) toxicity tests, plant germination, metal content, and small mammal body burden tests, were performed on biosolids (BS)- and lime-amended mine tailings. The results indicate that the amendment was sufficient to restore ecosystem function to the site (Brown et al., 2005).

High rates of P addition to soils can reduce the availability of metals in situ. Diammonium phosphate (DAP) at 10 g kg^{-1} was effective for immobilizing the combination of Cd, Pb, and Zn, with reduction in contaminant mobility of 94.6%, 98.9%, and 95.8%, respectively (McGowen et al., 2001). DAP is the major source of commercial P fertilizer in the USA and represents 40% of the worldwide production of 23 × 10^6 kg DAP (PotashCorp, 2004). Commercially available in large quantities, DAP could prove to be an economical and effective metal immobilization treatment (US $250–275 per Mg).

Amendments have also been shown to reduce the fraction of total soil Pb that becomes soluble in a gastric system (Ma et al., 1993; Hettiarachchi and Pierzynski, 2004; Ryan et al., 2001, 2004). The primary focus of this research has centered on the addition of P to Pb solutions and Pb-contaminated soils to force the precipitation of pyromorphite, a highly insoluble Pb/P mineral (Ryan et al., 2004; Scheckel and Ryan, 2004). Although concerns have been expressed about the stability of pyromorphite in soils, it is very stable species from a thermodynamic perspective, indicating that it should be stable in a soil environment (Ryan et al., 2004). Other amendments, including biosolids composts and Fe-rich wastes, have been shown to reduce Pb availability in situ (Brown et al., 2003; Brown et al., 2004; Mench et al., 1994; Mench et al., 1997).

A field study was conducted at the Tar Creek site to determine the feasibility of using residuals and commercially available amendments to reduce the environmental risk from elevated Pb, Zn, and Cd of the mine wastes and contaminated yard soils. The study was conducted on mine wastes and excavated home garden soils in Picher, Oklahoma to test ability to reduce the bioavailability of soil Pb in situ and restore a plant cover on the metal-contaminated mine waste materials. Amendments that had been previously shown to achieve one or both of these goals were tested (Basta and McGowen; 2004; Brown et al., 2004, Brown et al., 2005). Amendments were used singly and in combination to maximize their efficacy.

Materials and Methods

The experiment consisted of two complete field trials. Each trial was set up on different contaminated substrates (yard and tailings). Both trials had a total of 12 treatments (five amendments with different amendment combinations and application rates) in plots that were set up using a completely randomized block design with three replicates. Soil properties, plant growth, and plant composition were monitored at 6 and 18 mo after amendment addition. This study was conducted as the field component of a cooperative interlaboratory research study (Brown et al., 2005). The mine wastes used in the interlab study were collected approximately 50 km east of the Tar Creek site and were from a similar ore body. The amendments used in the current study were similar to those used in the interlaboratory study with the exception that locally available materials were used and amendments were combined for several treatments.

The field site was established as two sets of replicated plots: The first set was on mine tailings in a sedimentation basin (tailings), similar to those used in the interlab study, and the second set was on soils excavated from home gardens (yard). Excavating Pb-contaminated yard soils and replacing the soils with clean material is the current standard remedial action for areas included in the EPA Superfund Program (Hettiarachchi and Pierzynski, 2004). The two sets of experimental plots were installed in the spring of 2002. Field plots in the yard study were set up using a randomized, complete-block design with three replicates. Plots measured 4 × 4 m. Amendments were surface applied and then tilled in with a tractor pulled tiller. The tailings study also used a randomized, complete-block design with three replicates. Plots measured 1 × 1 m. Amendments were hand applied to the surface of the plots and then rototilled into the soil material using a hand rototiller. Two weeks after amendment addition, plots were seeded with Bermuda grass (*Cynadon dactylon* L.).

Each set of plots included a range of soil amendments. Phosphorus was added as DAP to the yard soils at 5 g kg^{-1} P by weight and at 10 and 30 g kg^{-1} P to the tailings. In addition to DAP, a biosolids compost (compost) (224 Mg ha^{-1}); lime-stabilized biosolids (BS) (224 Mg ha^{-1}); and two drinking water treatment residuals, one Fe based (Fe) (50 Mg ha^{-1}), and one alum based (Al) (50 Mg ha^{-1}), were added singly and in combination. Rates of amendments used in the field study were based on rates of similar materials that had been effectively used in lab and field studies using similarly contaminated soil materials (Basta and McGowen, 2004; Brown et al., 2004, Brown et al., 2005). For certain treatments, amendments were combined to increase efficacy or to be effective for reducing availability for multiple endpoints. For example, in the tailings plots, biosolids were added in combination with P for some treatments. This was done with the goal of restoring a plant cover reducing Pb bioaccessibility.

Soil samples were collected before and 2 wk, 6 mo, and 18 mo after amendment addition. A composite sample of three cores per plot was collected with a stainless steel trowel. Select soil properties for both sites are presented in Table 1. All samples were analyzed for pH and electrical conductivity (EC). Total metal concentrations, texture, organic C, and total N were measured on the samples collected before amendment addition. The texture of the soils was determined by removing the organic matter using hydrogen peroxide (Gee and Bauder, 1986) fol-

Table 1. Soil properties for the yard soils and the tailings soils†

	Texture	pH	EC	N	Total C	Total Pb	Total Zn	Total Cd
			dS m^{-1}	g kg^{-1}		mg kg^{-1}		
Yard soils	Loam	6.96 ± 0.18	1.2 ± 0.3	1.23 ± 0.26	23.4 ± 5.2	623 ± 241	5308 ± 1070	25.5 ± 5.75
Tailings	Silt loam	7.96 ± 0.15	9.0 ± 2.8	0.07 ± 0.05	13.2 ± 3.6	4003 ± 2654	6830 ± 3720	28.7 ± 12.6

† Values are mean ± SD (n = 36).

lowed by the hydrometer method (Miller et al., 1997). Carbon and N were measured by dry combustion with HCl pretreatment to remove inorganic carbonates. Total metals were measured using EPA 3050 (USEPA, 1995). Bioaccessible Pb was measured according to a physiologically based extraction test described by Brown et al. (2005) for both sites for soil collected at 6 mo. It was measured on samples collected at 18 mo from the tailings site using a modified version of the Ohio State University physiologically based extraction test (Beak et al., 2006). Ammonium nitrate–extractable metals were determined following DIN Standard 19730 (Deutsch Institut fur Normung, 1995) for samples collected at 6 and 18 mo. Solution metal concentrations for the bioaccessible Pb and NH_4NO_3 extractions were measured on a flame or graphite furnace atomic adsorption spectrometer or by inductively coupled plasma optical emission spectroscopy. Noncrystalline reactive Al and Fe oxide concentrations were determined by a modified acid ammonium oxalate extraction (McKeague and Day, 1993). The solution to soil ratio of the extract was increased to 100:1 from 40:1 (Dayton and Basta, 2005ab).

Plant samples were collected in the fall at 6 mo and 18 mo. At 6 mo, percent cover was measured using a line transect. By 18 mo, a visual examination showed that almost all plots had complete plant cover. For elemental analysis, a minimum of three grab samples were cut from each plot and combined. Bermuda grass (*Cynadon dactylon* L.) was the only species collected for analysis. Plant samples were washed in sodium lauryl sulfate solution, rinsed in deionized water, dried at 70°C, ashed at 480°C for 16 h, digested with concentrated HNO_3 (15.8 *M*), and dissolved in 3M HCl (Brown et al., 2004). Samples were analyzed for Cd, Pb, and Zn using a flame atomic adsorption spectrometer. Replicate plant samples, blanks, National Institute of Standards and Technology Orchard grass standard reference material 1571, and an internal plant standard from a contaminated site were included in the analysis.

Statistical analysis was conducted on the two sets of plots using SPSS SPSS version 11.04 for Macintosh (SPSS, Inc., 2005). The significance of main effect (including time and treatment) means for all variables was tested using ANOVA. When main effect means were significant, values for individual treatments were separated using the Waller-Duncan *t* test with a significance level of $p < 0.05$. Means ± SD are presented in the text and figures. Mine wastes are highly heterogeneous materials; therefore, total metal concentrations and other properties can vary over small distances. Standard deviations for many variables reported in the study are high, presumably as a result of the variable soil matrix.

Results and Discussion

Soils

Total Pb was much higher in the tailings material (4003 ± 2654 mg kg^{-1}) than in the yard soils (623 ± 241 mg kg^{-1}) and was more variable (Table 1). Soil Cd was similar for both sites, with total Cd in the yard study (25.5 ± 5.75 mg kg^{-1}) not significantly lower than total Cd in the tailings study (28.7 ± 12.6 mg kg^{-1}). Soil Zn at both sites was also similar: 6830 ± 3720 mg kg^{-1} tailings compared with 5308 ± 1070 mg kg^{-1} yard. Based on EC, pH, organic C, and total N content, the tailings material seems to be less like a functional soil than the yard soils. Organic C in the yard soils averaged 23.4 ± 5.2 g kg^{-1} with C in the tailings 13.2 ± 3.6 g kg^{-1}.

Differences in total N between the two sites were more pronounced, with N in the yard soils equal to 1.23 ± 0.26 g kg^{-1} and N in the tailings equal to 0.07 ± 0.05 g kg^{-1}. Texture in the tailings was also coarser, with the soils falling into a Silt Loam or Sandy Loam textural class. Soils in the yard experiment were all classified as Loam. Soil EC was high enough in the tailings to be detrimental to most plant species (9.0 ± 2.8 dS m^{-1}). Soil pH was at or above 7 for both sites before amendment addition.

Electrical Conductivity

Samples collected at 6 and 18 mo show a dramatic decrease in EC from year 1 to year 2 of the study (Table 2). The annual precipitation for Picher, Oklahoma is 110 cm yr^{-1} and is sufficient to remove excess salts from soil profile providing there is adequate drainage. Electrical conductivity in the tailings fell from 3.1 ± 2.15 in 2002 to 0.98 ± 0.44 dS m^{-1} in 2003. Electrical conductivity in the yard soils decreased from 1.19 ± 0.96 to 0.36 ± 0.14 dS m^{-1}. In the tailings, those treatments that included DAP at 30 g kg^{-1} had generally higher EC than other

Table 2. Soil pH and electrical conductivity (EC) for the tailings study and the yard study. Soil pH results are the average for 2002–2003. Electrical conductivity is presented for 2002 and 2003.

Treatment	pH	EC 2002	EC 2003
		dS m^{-1}	
Tailings†			
Control	7.32e‡	2.21a	1.29de
DAP(1%)	6.18abc	4.45a	1.51e
DAP(3%)	6.26abc	7.41b	1.44de
BS	7.5e	1.95a	1.06bcde
DAP(1%)+BS	6.86cde	2.78a	0.64abc
DAP(3%)+BS	5.92ab	3.93a	0.93abcde
Compost	6.92cde	1.64a	0.44a
DAP(1%)+Compost	5.54ab	1.95a	0.65abc
DAP(3%)+Compost	5.52a	3.93a	0.90abcd
Fe+DAP(1%)	6.33bcd	4.49a	1.16cde
Fe+BS	7.5e	1.81a	0.98abcde
Fe+DAP(1%)+BS	7.1de	2.15a	0.52ab
Yard			
Control	7.11de	0.29a	0.18a
DAP	6.18ab	2.98b	0.38abcd
DAP+BS	7.12de	1.30a	0.38abcd
DAP+Compost	5.75a	1.23a	0.32abc
BS	7.51ef	0.83a	0.40bcd
Compost	6.74cd	0.77a	0.22ab
BS+Al	7.51ef	0.83a	0.32abc
Compost+Al	6.92d	0.33a	0.27ab
DAP+Al	6.36bc	2.63b	0.41de
DAP/BS/Al	6.86cd	1.10a	0.57d
Fe+BS	7.64f	0.99a	0.42bcd
DAP/Compost/Al	6.14ab	1.03a	0.35abc

† BS, biosolids; DAP, diammonium phosphate.

‡ Values followed by the same letter are not significantly different ($p < 0.05$).

Table 3. Bioaccessible (PBET) Pb and NH_4NO_3–extractable Cd and Zn for the Tailings study and the yard study. Results are for soil samples collected in 2003 except for PBET in tailings (average of samples collected at 6 and 18 mo).

Treatment	PBET Pb	Cd	Zn
	%	mg kg^{-1}	
Tailings†			
Control	92.1e‡	3.72c	48.1cd
DAP(1%)	49bc	0.67b	81d
DAP(3%)	22.5a	0.071a	11.1b
BS	87.4e	0.084a	17.8bc
DAP(1%)+BS	60.2cd	0.039a	3.24a
DAP(3%)+BS	14.5a	0.084a	13.8ab
Compost	59.3cd	0.172ab	11.3b
DAP(1%)+Compost	42b	0.141ab	26.9bcd
DAP(3%)+Compost	37.6b	0.04ab	25.2bcd
Fe+DAP(1%)	66d	0.146ab	25.4bcd
Fe+BS	62.4cd	0.152ab	15.3bc
Fe+DAP(1%)+BS	52.1bc	0.038a	9.57ab
Yard			
Control	84b	0.4bc	29.3cd
DAP	55a	0.51c	174e
DAP+BS	51a	0.033a	2.38ab
DAP+Compost	51a	0.12a	29.9cd
BS	52a	0.048a	3.7ab
Compost	49a	0.056a	3.65ab
BS+Al	55a	0.065a	3.2ab
Compost+Al	36a	0.025a	2.23ab
DAP+Al	55a	0.33b	94.9de
DAP/BS/Al	50a	0.02a	1.16a
Fe+BS	49a	0.032a	2.34ab
DAP/Compost/Al	55a	0.14a	47.4bc

† BS, biosolids; DAP, diammonium phosphate.

‡ Means followed by the same letter are not significantly different ($p < 0.05$).

treatments. For example, EC in the DAP 30 g kg^{-1} soil averaged 3.7 dS m^{-1} over both years, whereas EC in the BS treatment averaged 1.5 dS m^{-1}. The same pattern was observed in the yard soils, with EC in the DAP 5 g kg^{-1} treatment equal to 1.7 dS m^{-1} compared with 0.23 dS m^{-1} in the unamended soil.

Soil pH

Soil pH in the unamended soil in the yard and tailings study was near neutral (7.11 and 7.32, respectively) (Table 2). Several of the amendments decreased soil pH. In general, addition of DAP, alone and in combination with other amendments, decreased soil pH in both experiments. However, soil pH of the10 g kg^{-1} DAP+Biosolids treatment was comparable to the control soil (Table 3). Lime-stabilized BS offset the acidity produced from DAP sufficiently for the 10 g kg^{-1} DAP treatment but not for the 30 g kg^{-1} DAP+BS treatment. In the yard soils, all DAP amendments except those that included BS reduced soil pH to between 5.75 (DAP+compost) and 6.36 (DAP+Al).

Although addition of high rates of biosolids has been associated with reductions in soil pH, the biosolids used in the study were lime stabilized and contained sufficient calcium carbonate equivalent to maintain soil pH at levels similar to the control soil. In the tailings study, the combination of higher rates of DAP and a coarser texture resulted in a more substantial decrease in soil pH. In the amendments that contained DAP in the tailings study, soil pH ranged from 5.52 (DAP 3% + compost) to 6.33 (DAP 1%+Fe). All of the biosolids treatments, excluding the DAP3%+BS treatment (pH 5.92) had pH similar to the unamended soil. Oxidation of ammonium in DAP produces significant acidity. Therefore, DAP has to be used at moderate rates (≤10 g kg^{-1}) or in combination with an alkaline material. Alkaline biosolids offer the benefits of alkalinity, nutrients, and other properties important to vegetative growth. Therefore, an organic amendment such as alkaline biosolids may be preferable to offset DAP acidity in a blend than using inorganic amendments such as limestone.

Available Zinc and Cadmium

Available Cd and Zn, as measured by a 1 *M* ammonium nitrate extraction, were generally reduced by amendment addition in both studies (Table 3). Available Pb was low in these soils (<5 mg kg^{-1}). There was no effect on extractable Pb in either study (data not shown). In the yard soils, all treatments reduced extractable Cd in comparison to the unamended soils, except for the DAP and DAP+Al treatments (Table 3). The DAP amendment increased extractable Zn in comparison with the unamended soil (174 mg kg^{-1} and 29.3 mg kg^{-1}, respectively). The DAP+Al amendment also increased extractable Zn (94.9 mg kg^{-1}). These observed increases were likely the result of a decrease in soil pH. Although other studies have shown that P addition is able to increase soil binding of Cd and Zn even at low soil pH, it seems that pH may have been a more significant factor in this case (Hamon et al., 2002: Brown et al., 2004). McGowen et al. (2001) reported large reductions in solubility and transport of Pb, Cd, and Zn after treatment of highly contaminated Zn smelter tailings with DAP. DAP treatment decreased the transport of soluble Pb, Cd, and Zn by more than 94% compared with the untreated smelter soil. This soil had been treated with coarse limestone before DAP application. Levi-Minzi and Petruzzelli (1984) reported that DAP decreased Cd solubility in soil cadmium suspensions, whereas Pierzynski and Schwab (1993) found that DAP increased metal solubility due to the acidification from nitrification. The ability of soluble phosphorus-containing treatments to reduce Zn availability depends on their effect on soil pH and the type of Zn contaminant (i.e., solid phase species of Zn). The amendments that resulted in the largest decrease in extractable Zn included the DAP+BS+AL treatment (1.16 mg kg^{-1}), the Fe+BS treatment (2.34 mg kg^{-1}) and the BS treatment (3.7 mg kg^{-1}). Because the pH in these treatments was similar to that in the unamended soil, it is likely that the observed decrease in extractable Zn was the result of increased soil-binding capacity after amendment addition. Increased binding capacity is potentially the result of adsorptive surfaces of amorphous oxide minerals, increased reactive organic matter, or a combination of both factors (Basta et al., 2005).

In the tailings study, all treatments reduced extractable Cd in comparison to the unamended soil (3.72 mg kg^{-1}) (Table 3). The least effective amendment was DAP 10 g kg^{-1} (0.67 mg kg^{-1}), and the most effective amendments included DAP+BS treatments (0.04 [10 g kg^{-1} DAP] and 0.8 [30 g kg^{-1} DAP] mg kg^{-1}), the

DAP 30 g kg^{-1} (0.07 mg kg^{-1}), and the BS (0.084 mg kg^{-1}) treatment. Extractable Zn in the unamended tailings soil was 48.1 mg kg^{-1}. The amendments that reduced extractable Zn most effectively included the DAP(10 g kg^{-1})+BS treatment (3.24 mg kg^{-1}) and the Fe+DAP(10 g kg^{-1})+BS treatment (9.57 mg kg^{-1}). For the BS treatment and the Fe+BS treatments, adding DAP resulted in a decrease in extractable Zn. As in the yard study, the DAP 10 g kg^{-1} treatment increased extractable Zn compared with the unamended soil (81 mg kg^{-1} versus 48.1 mg kg^{-1}). Amendments containing BS or compost increased the binding capacity of soil for Zn by increasing the soil organic C content (Table 4). Treatments containing Fe water treatment residuals (WTR) increased reactive Fe in soil (Table 4). When extractable Zn and Cd from the yard and the tailings study are plotted against pH, there is no statistical relationship between these variables indicating that factors other than pH-affected metal extractability. For this study, those factors may have included increased organic matter in the soils, precipitation of P-Zn phases, and increased binding to metal oxide surfaces (Hettiarachchi et al., 2006).

Bioaccessible Lead

For the yard soils, a large fraction (84%) of the total Pb was bioaccessible (Table 3). All of the amendments tested were able to reduce bioaccessible Pb. Reductions ranged from 57% in the compost+Al residual treatment to 35% in the DAP treatment and in the DAP+Al residual treatments. Due to high variation across replicates, the differences between these treatments were not significant. One of the goals of this study was to test a range of amendments in combination to see if mixtures of different amendments could increase the binding capacity of the soil, thus reducing Pb solubility. It seems that adding Al WTR residual to the compost had some success in this portion of the study. Addition of Al residual to compost increased reactive Al (Table 4). However, the increase was not the highest observed across all amendments, and other increases were not related to decreases in bioaccessible Pb. Bioaccessible Pb was 49% of total Pb in the compost alone treatment and 36% in the compost+Al residual treatment (Table 3). Generally, however, there was no benefit gained by combining different amendments.

For the tailings soils, treatment ($F = 79.3$) and extraction ($F = 23.8$) were highly significant for bioaccessible Pb. The average accessible Pb across all treatments decreased from 66 ± 23.8% for samples collected at 6 mo to 41.2 ± 25.4% for samples collected at 18 mo. This change may have been the result of the different extraction ratios used or changes in availability over time. Because there was not a significant interaction between extract and treatment, results have been averaged across both extractions (Table 3). The bioaccessible Pb in the tailings soil of 92.1% was similar to the yard soils. Addition of P as DAP alone decreased bioaccessible Pb. Addition of DAP at 10 and 30 g kg^{-1} reduced bioaccessible Pb 47% and 76%, respectively. Biosolids alone did not decrease bioaccessible Pb. This is similar to results observed in lab studies (Brown et al., 2003, 2005). However, addition of DAP or Fe WTR to Biosolids decreased bioaccessible Pb. Although compost alone decreased extractable P, as was observed with BS, addition of P to compost resulted in further reductions in bioaccessible Pb. For the tailings soils, DAP alone at either rate of addition or DAP 1%+BS were the most effective amendments for reducing bioaccessible Pb.

Table 4. Effect of treatments on soil properties important in sequestration of Cd, Zn, and Pb for tailings and yard soil.

Treatment	Total C	Al Oxides	Fe Oxides
	g kg^{-1}	mg kg^{-1}	
Tailings†			
Control	8.52ef‡	174e	4966c
DAP 1%	8.86ef	1099de	6864c
DAP 3%	5.46f	2509abc	7257c
BS	27.5abc	1607bcd	6663c
BS+DAP (1%)	17.1bcdef	1581bcd	6103c
BS+DAP (3%)	17.0bcdef	2800ab	7378c
Compost	35.4a	1557cd	4161c
Compost+DAP (1%)	22.8bcd	3117a	6049c
Compost+DAP (3%)	16.1cdef	3117a	6116c
Fe+DAP+Al	12.7def	1416cd	23 009a
BS+Fe	29.3ab	1633bcd	16 039b
BS+Fe+DAP	19.1bcde	1637bcd	18 624b
Yard soil			
Control		769c	3253g
DAP		1965bc	4527efg
DAP+BS		2578bc	6912cd
DAP+Compost		3261abc	5200def
BS		3038abc	7608c
Compost		2725bc	4477efg
BS+Al		3883abc	6170def
Compost+Al		4985abc	4727efg
DAP+Al		4334abc	4878efg
DAP/BS/Al		5835ab	9813b
Fe+BS		3185abc	13 218a
DAP/Compost/Al		7282a	3877fg

† BS, biosolids; DAP, diammonium phosphate.

‡ Means followed by the same letter are not significantly different ($p < 0.05$).

Plant Growth and Cadmium and Zinc Bioaccumulation

Growth

Plant cover in the yard soils was affected by treatment for the 6 mo harvest with very little growth in all treatments that included DAP; the highest cover occurred in the BS alone treatment. Plots treated with DAP alone, DAP+BS, DAP+compost, and DAP+Al all had less than 5% cover. Cover in the BS alone treatment was 73.3 ± 12.6 with cover in the control treatment equal to 56.7 ± 5.8%. By the second sampling, all plots had close to 100% cover indicating that treatment effects on plant growth were short term.

In the tailings study, a combination of poor physical properties, excessive salinity of 9.0 dS m^{-1}, and elevated metal concentrations suggested a higher potential for phytotoxic conditions in the unamended soil. The rates of DAP used here were 10 g kg^{-1} and 30 g kg^{-1} P in comparison to 5 g kg^{-1} P in the yard soils. All treatments that included DAP, excluding the DAP 1%+Fe treatment, had no plant growth for the first year of the study. In contrast, the compost treatment and the Fe+BS treatments each supported 100% vegetative cover. The cover consisted of Bermuda grass and

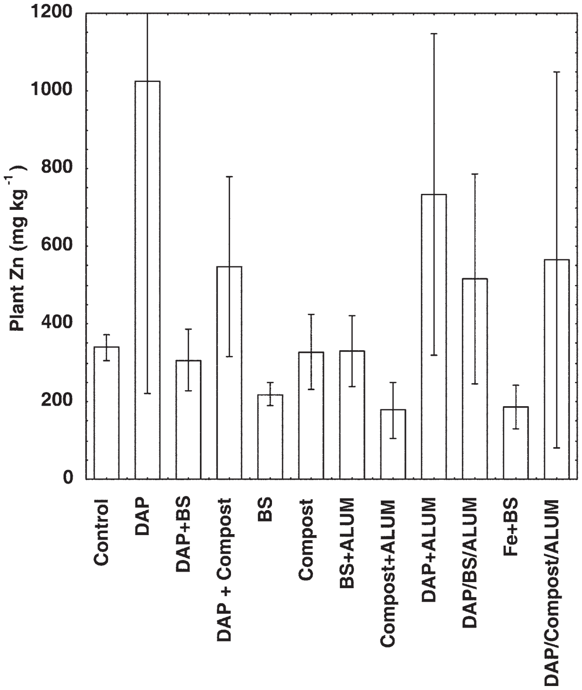

Fig. 1. Bermuda grass (*Cynadon dactylon* L.) Zn concentrations (mg kg^{-1}) for plant samples collected from the yard study in 2002–2003. Means and SD are shown.

volunteer species. For comparison, these same treatments in the yard soils supported 62 ± 27.5% and 53 ± 30% cover, respectively. The other amendments that supported some vegetative cover in 2002 were the BS alone and DAP 1%+Fe treatments. Cover in the unamended soils averaged 53%. By 2003, all plots supported plant growth, with no significant differences in percent cover. Significant decreases in soil salinity for DAP treatments from 2002 to 2003 were observed with levels similar to the control soil by the second growing may have been responsible for increased cover in the second year (Table 2). It was also apparent in 2003 that volunteer species had colonized the plots, with at least one tree and a range of different grasses growing in the plot area.

Zinc and Cadmium Uptake

In the yard soils, plant Cd and Pb concentrations were similar for both harvests. Average Cd across all treatments was equal to 2.98 ± 2.51 mg kg^{-1} in 2002 and 3.15 ± 1.57 mg kg^{-1} in 2003. The mean concentration for plant Pb across all treatments was 4.12 ± 2.01 mg kg^{-1} in 2002 and 4.94 ± 1.86 mg kg^{-1} in 2003. Plant Zn concentrations generally increased in 2003, with the mean concentration in 2002 equal to 302 ± 116 mg kg^{-1} and in 2003 equal to 480 ± 415 mg kg^{-1}. Amendment addition did not have any significant effect on plant Cd or Pb concentrations. Averaged across both years, plant Cd ranged from 1.82 ± 0.61 mg kg^{-1} in the compost treatment to 4.93 ± 3.55 mg kg $^{-1}$ in the DAP/BS/Al treatment with Cd concentration in plants from the control treatment of 4.35 ± 1.92 mg kg^{-1}. Plant Pb ranged from 3.55 ± 1.11 mg kg^{-1} in the DAP+compost treatment to 6.28 ± 4.59 mg kg^{-1} in the DAP treatment with concentration in the control treatment of 4.45 ± 1.33 mg kg^{-1}.

Plant Zn was affected by amendment addition with some amendments increasing plant Zn concentration over the control and others decreasing Zn concentrations (Fig. 1).

The highest plant Zn (1024 ± 803 mg kg^{-1}) was observed in the 5 g kg^{-1} DAP–amended plots. Plants growing in the unamended soil had average plant Zn concentrations of 339 ± 34 mg kg^{-1}. All the treatments that included DAP had plant Zn concentrations that were similar or higher to the untreated soil. Two of the DAP treatments, DAP alone and DAP+Al WTR increased available Zn and plant Zn (Table 3). This may be the result of the decreased soil pH in the some of the DAP treatments. The BS+DAP treatment, which had the smallest effect on soil pH of all DAP treatments, did not significantly reduce plant Zn even though it decreased available Zn by an order of magnitude (Table 3).

The only amendments that reduced plant Zn concentrations in comparison to the control in the yard soils were the compost+Al residuals and Fe+BS treatments. Plant Zn in these treatments averaged 179 ± 72 and 186 ± 55 mg kg^{-1}, respectively. It seems that for the compost and the BS treatments, addition of additional adsorptive capacity in the form of Fe for BS and Al for the compost was sufficient to limit the phytoavailability of plant Zn (Table 4). The effect on phytoavailable Zn and bioaccessible Pb was more pronounced for the compost treatment even though measures of total Al oxides in the compost and compost+Al treatments were statistically similar. Plants grown in compost alone had average plant Zn concentrations of 328 ± 96 mg kg^{-1}. In the BS alone treatment, plant Zn was similar to both of the lowest treatments, averaging 218 ± 30 mg kg^{-1}.

In the tailings soils, there was no plant growth in the 10 g kg^{-1} or 30 g kg^{-1} DAP treatments in 2002 (Fig. 2). Yield in treatments that included DAP in combination with other residuals was generally minimal, with harvestable plant material present in only one or two of the replicates. Because no harvestable plant material was present in the majority of the treatments in 2002, plant metal concentrations have not been averaged over years. However, it is helpful to look at some general trends in plant uptake. Overall plant Pb was similar in 2002–2003, averaging 14.5 ± 14.5 mg kg^{-1} in 2002 and 12.7 ± 8.0 mg kg^{-1} in 2003. There were increases in plant Cd and Zn from 2002 to 2003, and variability across treatments was also high. Plant Cd averaged 1.89 ± 1.35 mg kg^{-1} in 2002 and 3.54 ± 4.17 mg kg^{-1} in 2003. Plant Zn averaged 322 ± 121 mg kg^{-1} in 2002 and 554 ± 255 mg kg^{-1} in 2003. This increase occurred in all treatments that had plant growth for both years and therefore is not the result of high Zn concentrations in the DAP amended plots that only supported vegetation in 2003.

Our initial intention for this field trial was to test amendments singly and in combination in an attempt to increase metal adsorption capacity in the soils and reduce availability as measured by plant uptake and in vitro extractions. Plant uptake results from the tailings portion of the study illustrate that this effort was generally unsuccessful and that amendments added singly were generally as effective as those added in combination. There were significant reductions in plant Cd and Zn in certain treatments. Plant Cd and Zn concentrations for amendments added singly are shown in Fig. 3. Addition of BS or DAP 30 g kg^{-1} lowered plant Zn concentration over those found for the unamended soil. Plant Cd concentration was also reduced in the plots amended with BS. However, some combined treatments did achieve increased efficacy when multiple endpoints are considered. For example, biosolids+1% DAP or BS+1% DAP+Fe decreased plant Cd and Zn over DAP added singly and bioaccessible Pb over biosolids added singly. However, reductions for either endpoint were less pronounced when amendments were combined.

Plant Zn and Cd concentrations for all treatments that included DAP are shown in Fig. 3. Combining the DAP with other amendments, including BS, compost, and Fe, had mixed results. Two amendments containing DAP showed significant reductions in plant Cd: DAP(10 g kg^{-1})+BS and BS+10 g kg^{-1} DAP+Fe. DAP alone did not decrease plant Cd. Plant Cd in the DAP 10 g kg^{-1} treatment was 5.4 ± 0.2 mg kg^{-1}versus 9.27 ± 13 mg kg^{-1} in the untreated soil. Including BS with the DAP reduced plant Cd concentrations to 1.39 ± 0.64 mg kg^{-1}. This decrease may have been the result of increased soil pH (pH in DAP 1% was 6.18; in the DAP 1%+BS soil pH was 6.86). Compost+DAP had no effect on plant Cd. Mixing BS with the DAP amendment at 30 g kg^{-1} had no effect on plant Cd concentrations; plant Cd in the DAP 30 g kg^{-1} treatment was 4.4 ± 2.4 mg kg^{-1} and was 5.0 ± 0.9 mg kg^{-1} in the DAP(30 g kg^{-1})+BS treatment. The pH in both of these treatments was similar. Mixing Fe with DAP 10 g kg^{-1} resulted in no decrease in plant Cd.

Plant Zn concentrations in the DAP 10 g kg^{-1} amendment (623 ± 93 mg kg^{-1}) were similar to the unamended soil (912 ± 144 mg kg^{-1}). At the 10 g kg^{-1} DAP rate, mixing BS or BS+Fe (only one sample over the 2-yr harvest) with the DAP decreased plant Zn (272 ± 113 and 303 mg kg^{-1}, respectively), but DAP+compost (608 mg kg^{-1}) and DAP+Fe addition (787 ± 421 mg kg^{-1}) did not. While including BS increased soil pH in the 10 g kg^{-1} DAP amended soils, compost and Fe did not. At the 30 g kg^{-1} DAP application rate (430 ± 64 mg kg^{-1}), neither the BS (692 ± 337 mg kg^{-1}) or the compost (387 ± 80 mg kg^{-1}) reduced Zn phytoavailability. Plant Zn and Cd concentrations were similar in both DAP treatments. The largest reduction in plant Zn was seen in the DAP(10 g kg^{-1})+BS treatment where plant Zn in 2003 was 272 ± 113 mg kg^{-1}. It may be that, in addition to increasing soil pH, the biosolids provided additional fertility that may have been related to reduced plant uptake of Zn and Cd.

For the amendments that included BS and no DAP, plant data were collected for both years. Biosolids alone significantly reduced plant Zn and Cd concentrations over the unamended soil (Fig. 2). In 2003, plant Cd and Zn in the unamended soil was 9.27 ± 13 and 912 ± 144 mg kg^{-1}, respectively. In the BS treatment, plant Cd and Zn were 1.16 ± 0.47 and 338 ± 22 mg kg^{-1}, respectively. Adding Fe to the BS did not result in a decrease in plant Cd and Zn concentrations compared with the BS alone treatment (data not shown). Mixing DAP with the biosolids did not decrease plant uptake at the 10 g kg^{-1}rate (2003 plant Cd in the BS treatment was 1.16 ± 0.33 mg kg^{-1} and was 1.39 ± 0.64 mg kg^{-1} in the DAP 1%+BS treatment). When 30 g kg^{-1} DAP was mixed with BS, plant Zn (692 ± 337 mg kg^{-1}) and Cd (5 ± 0.93 mg kg^{-1}) concentrations were increased over the BS-alone treatment and were similar to the unamended soil. This may have been due to the pH decrease when 30 g kg^{-1} DAP was added to the soil. The lime in the biosolids was not sufficient to bring pH in the 30 g kg^{-1} DAP treatments back to neutral. Potential risks of food chain transfer as a result of in situ restoration have been discussed elsewhere (Brown et al., 2005). Because only one type of grass was tested for this site, it is beyond the scope of this paper to determine the potential for negative effects as a result of grazing on restored sites.

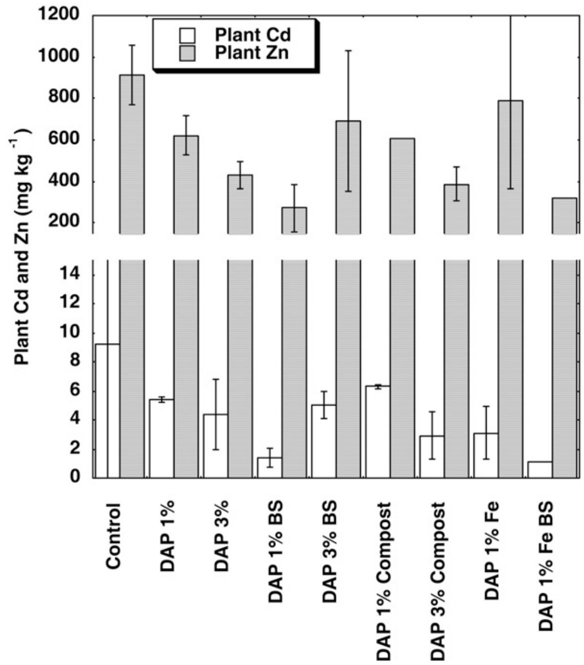

Fig. 2. Bermuda grass (*Cynadon dactylon* L.) Zn and Cd concentrations (mg kg^{-1}) for plant samples collected from the tailings study in 2002–2003. Plant uptake results are presented for amendments that included DAP added at 1% and 3% P. Means and SD are shown.

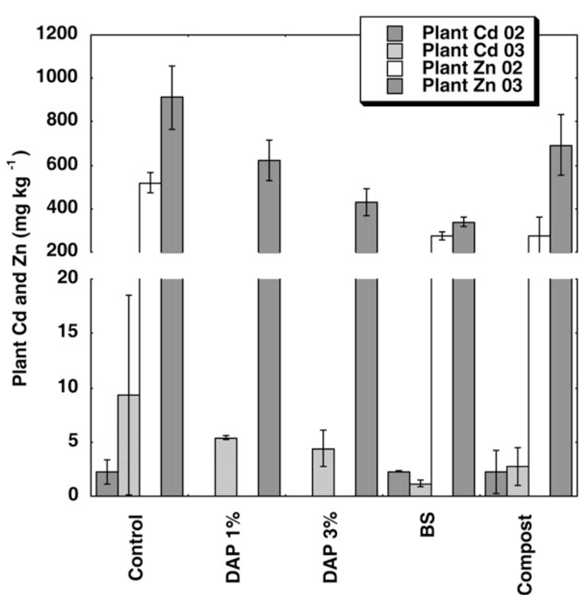

Fig. 3. Bermuda grass (*Cynadon dactylon* L.) Zn and Cd concentrations (mg kg^{-1}) for plant samples collected from the tailings study in 2002–2003. Plant uptake results are presented for amendments added singly. Means and SD are shown.

Conclusions

Results from the yard soil study and the tailings study suggest that several soil amendments can be used at the Tar Creek site to restore a plant cover and reduce Pb availability. For the yard soils, all amendments tested reduced the bioaccessible Pb, with the lowest available fraction in the compost+Al treatment. This amendment also had a healthy plant cover with low Zn concentrations. Although P addition is equally effective at reducing in vitro Pb, it was detrimental for plant growth during the first growing season, with reduced soil pH and elevated plant Zn. These results suggest that if DAP alone is used in home gardens, it is necessary to lime soils after amendment addition. It might also be necessary to cover the soils with a landscape fabric for an initial period until the amended soils are able to support a plant cover.

For the tailings soils, the primary concerns for remediation relate to the establishment of a plant cover on the mine wastes. This would serve multiple purposes: the visual reminders of mining would be removed, and the mine waste would still be available for commercial use. The plant cover would increase habitat, reduce fugitive dust and erosive potential, and limit utility of the areas for dirt bikes. The amendments that were most effective at supporting plant growth, reducing extractable metal concentration, and reducing plant concentration of Zn and Cd were the biosolids and biosolids+1% DAP treatments. The biosolids+1% DAP treatment also reduced bioaccessible Pb and would reduce Pb exposure associated with incidental ingestion of soil. Alkaline biosolids in combination with DAP may prove to be useful at the Tar Creek, Oklahoma site. This study suggests that a range of soil amendments offers a low-cost alternative to standard remedial practices for yard soils and mine waste piles at this site.

Acknowledgments

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