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An inter-laboratory study to test the ability of amendments to reduce the availability of Cd, Pb, and Zn in situ

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Addition of phosphorus to Pb, Zn and Cd contaminated mine waste was able to reduce metal toxicity for a range of biological endpoints.

Abstract

An international inter-laboratory research program investigated the effectiveness of in situ remediation of soils contaminated by cadmium, lead and zinc, measuring changes in soil and soil solution chemistry, plants and soil microbiota. A common soil, from mine wastes in Jasper County MO, was used. The soil was pH 5.9, had low organic matter (1.2 g kg^{-1} C) and total Cd, Pb, and Zn concentrations of 92, 5022, and 18 532 mg kg^{-1}, respectively. Amendments included lime, phosphorus (P), red mud (RM), cyclonic ashes (CA), biosolids (BIO), and water treatment residuals (WTR). Both soil solution and NH_4NO_3 extractable metals were decreased by all treatments. Phytotoxicity of metals was reduced, with plants grown in P treatments having the highest yields and lowest metal concentration (0.5, 7.2 and 406 mg kg^{-1} Cd, Pb, and Zn). Response of soil micro-organisms was similar to plant responses. Phosphorus addition reduced the physiologically based extraction test Pb from 84% of total Pb extracted in the untreated soil to 34.1%.

Keywords: In situ remediation; Pb mine wastes; Phosphorus; Bioavailability

1. Introduction

In situ amendments to reduce the bioavailability of metals in soils offer an alternative to standard soil removal and replacement. The goal of amendment addition is the reduction in the bioavailable fraction of the metal(s). Total metal concentrations are not significantly reduced by amendment addition. Amendments are added to increase the fraction of total metal that partitions to the solid phase, either through precipitation of discrete minerals or through increased

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Abbreviations: BIO, biosolids; WTR, water treatment residuals; RM, red mud; KAD, kaolin amorphous derivatives; PBET, physiologically based extraction test; TSP, triple super phosphate; CA, cyclonic ash; CASS, cyclonic ash and steel shot.

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metal sorption. This can occur through addition of metal complexing capacity to the soil or through addition of an excess of particular elements, already present in soil, to shift equilibrium in favor of precipitation.

One emphasis of this research has been on the addition of P to Pb contaminated soils to favor precipitation of chloropyromorphite ($Pb_5(PO_4)_3Cl$). Pyromorphite is several orders of magnitude less soluble than commonly occurring soil Pb minerals including PbO and $PbCO_3$ (Ma et al., 1993). Formation of pyromorphite upon P addition to Pb acetate and Pb contaminated soils has been confirmed in laboratory studies using X-ray adsorption spectroscopy (Ryan et al., 2001). A recent field study showed a relationship between pyromorphite concentration in P amended Pb contaminated soil and decreased bioavailability as evaluated by in vivo and in vitro studies (Ryan et al., 2004).

Other amendments have been shown to decrease metal availability or extractability through increased adsorption. For example Fe oxides have been shown to decrease extractability of both Pb and As (Ford, 2002; Martinez et al., 1999; Mench et al., 1998; Trivedi et al., 2003). By-products such as red mud (bauxite processing), cyclonic ash (CA) and water treatment residuals (WTR) have shown potential to decrease metal and P extractability and phytoavailability as a result of their liming properties and high Al and/or Fe oxide concentrations (Codling et al., 2000; Geebelen et al., 2003; Gupta and Sharma, 2002; Peters and Basta, 1996; Vangronsveld et al., 1996). High Fe biosolids composts were shown to reduce in vitro and in vivo available Pb as well as phytoavailable Zn and Cd (Brown et al., 2003a, 2004).

Efficacy of amendments can vary according to the particular combination of elements at a site as well as in relation to the range of biological endpoints of concern. For example, in cases of soils co-contaminated with Pb and As, P addition to reduce Pb availability can inadvertently solubilize As (Boisson et al., 1999; Peryea and Kammereck, 1997). Addition of WTRs or other oxides to reduce metal availability may also reduce P availability sufficiently to result in P deficiencies in plant tissue (Christensen, 2002). Different amendments may be more or less suitable depending on the endpoint of concern. For example, addition of an Fe rich material and P to a Pb, Zn and Cd co-contaminated soil reduced the in vitro extractable Pb in the soil. However, plant Cd concentrations in the same treatment were increased over the untreated soil (Brown et al., 2004). Municipal biosolids have been shown to reduce Cd, Pb and Zn availability to plants and soil organisms (Brown et al., 2003b, 2005). However, biosolids addition to Pb contaminated soils does not significantly reduce in vivo bioavailability of Pb (Brown et al., 2003a,b). This suggests that direct ingestion of a Pb contaminated soil that had been amended with municipal biosolids would still pose a risk.

Even though the literature concerning in situ remediation is growing rapidly, it is difficult to draw general conclusions regarding the efficiency of soil amendments due to differences in materials and methods used by different research groups. To overcome this problem, a cooperative study was conducted to test the ability of a range of soil amendments to reduce metal availability across a range of potential receptors. The study involved four laboratories: RRES Rothamsted Research (RRES); UK, CSIRO Land and Water, Glen Osmond, South Australia; University of Washington (UW), USA; and Limburgs Universitair Centrum (LUC), Belgium. Each lab used a similar experimental design for the study. Additionally, the study was designed to address concerns of multiple receptors with measurement endpoints including changes in metal availability evaluated by plant growth and metal concentrations, soil microorganism populations and nutrient cycling capacity, metal extractability, and solubility in an in vitro procedure designed to mimic the human gastric system. Each participating lab selected a range of soils and amendments. However, all participating labs used a common soil material and common treatments. This paper will present the results from all participating labs on the common soil material.

2. Materials and methods

As part of the cooperative study, a common soil and common treatments were included in the study design for each participating laboratory. The common soil (mine waste) was collected from the US EPA Oronogo Duenweg Mining Belt Superfund (Comprehensive Environmental Response, Compensation and Liability Act) site in Jasper County, MO. The site covers 700 sq km and over 90 million Mg of waste material remain on the site including waste rock, chat and fine tailings. This area is part of the Tri-State Mining district which includes portions of Ottawa County, OK, Cherokee County, KS and Jasper and Newton counties in MO. The common soil consisted of fines, the fine fraction of mine tailings following grinding ore to extract Pb and Zn. The soil was homogenized after collection and equal portions of the soil were sent to each of the cooperating laboratories.

In addition to the common soil, the group agreed to include a P treatment in their experimental design. Both RRES and CSIRO labs added P as monocalcium phosphate (fertilizer grade Triple Super Phosphate) at a 2% weight by weight (w/w) basis using the P concentration of the TSP to determine the weight of TSP added. The LUC group added P as reagent grade rock phosphate ($Ca_5(PO_4)_3F$), also on a 2% w/w basis. The UW added P in liquid form as H_3PO_4, then waited 1 week after P addition before adding lime. The phosphoric acid was added at a 1.25 M ratio to the total Pb, Zn and Cd in the soil. This approach was used based on results from a field study conducted using a range of P amendments on a smelter contaminated site in Jasper County (Brown et al., 2004). For all labs, the rate of P addition was based on total P concentration rather than the formula weight of the compound used.

In addition to the common amendments, the other amendments tested by individual labs included a range of compounds. At LUC, both cyclonic ash (5%) (CA) and steel shots (SS) (1%) in combination with cyclonic ashes (CASS) were tested (Mench et al., 2000). Red mud was included by both CSIRO and RRES. RRES used two red muds, one from Hungary (RMH) and one from the UK (RMUK). The RMUK had previously shown potential to reduce metal solubility and toxicity (Lombi et al., 2001). CSIRO added red mud from Australia (RMA) in combination with municipal biosolids. Red mud was added at RRES at a 2% w/w rate of addition. At CSIRO, the red mud and biosolids were each added at a 1% rate for a total amendment addition rate of 2% w/w. Water treatment residuals were included at RRES (WTRA, WTRB), CSIRO (BWTS, and BWTSNA) and UW (WTR). At RRES, the WTR were added at a standard 2%w/w ratio. At CSIRO, the WTR were added in combination with municipal biosolids, each at 1% w/w for a 2% total rate of amendment addition. At UW WTR were added at a 2.5% w/w rate. Biosolids (BIO) were also used at UW, both singly at 10% w/w, and in combination with WTR (WTR+BIO) with each amendment in this treatment added at 2.5%. RRES also included a red gypsum, a by-product from titanium processing. This is similar to the Fe-rich material that has previously shown potential to reduce metal availability (Berti and Cunningham, 1997; Brown et al., 2004). Finally, CSIRO included an amendment consisting of kaolin amorphous derivatives (1% w/w) and biosolids (1% w/w) (KAD+BIO). The KAD used has a very high cation exchange capacity (232 cmol_c kg^{-1} as well as a high surface area (207 m^2/g).

Chemical characterization of the soil and amendments was carried out by RRES. Particle size distribution in the soil was determined using the pipette method after destruction of organic material by H_2O_2 (Gee and Bauder, 1986). Soil pH and electrical conductivity (EC) were determined in a water suspension of soil using a 1:5 soil/solution ratio. Total soil carbon (C) was determined using a LECO CR-12 furnace at 1200 °C and soil cation-exchange capacity was measured using a NH_4Cl leaching procedure (Rayment and Higginson, 1992). The amounts of crystallinity of the Fe, Al and Mn oxides were estimated using sodium citrate dithionite and ammonium oxalate extractions (Iyengar et al., 1981). Total metal concentrations were determined by aqua regia digestion and analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Soil and amendment characteristics are presented in Table 1. The common soil had a CEC of 0.3 cmol_c kg^{-1} and was 76% sand, 22% silt and 2% clay. The total C

Table 1
Total metal concentrations and other characteristics of soil amendments

Research group	Amendment	pH	EC (mS cm^{-1})	Oxides (Na-dithionite) (mg kg^{-1})		Oxides (NH_4 oxalate) (mg kg^{-1})		As (mg kg^{-1})	Cd (mg kg^{-1})	Cu (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})
				Al	Fe	Al	Fe					
Jasper County	Common soil	5.9	0.14	97	5916	116	3234	4	92	64	5022	18532
RRES	TSP	8.0	2.54	11253	14292	4526	7569	5	5	527	40	652
	Red gypsum (RG)	6.3	0.36	81672	6187	19120	3398	79	4	79	8	46
	WTRA	13.2	10.2	6952	2020	1061	5688	9	3	38	23	20
	WTRB	6.4	21.1	46	53533	5	44763	77	0	1264	96	12
	RMH	12.6	24.9	4143	5738	1320	8987	9	12	12	6	138
	RMUK	10.8	3.81	20510	2052	3751	17833	36	6	4	58	36
UW	BIO	6.4	3.80	2696	5801	1603	7375	14	12	432	108	642
	WTR	10.9	2.12	58620	1202	40765	1702	0	12	92	2	106
LUC	CA	7.5	0.69	89547	942	12745	878	3	10	130	6	32
	SS	9.4	5.44	93307	802	21503	1405	3	10	120	0	50
CSIRO	TSP	2.6	28.7	2422	2391	877	3280	10	24	40	4	342
	RMA	7.1	3.14	4215	81365	4799	246000	4	0	0	76	460
	KAD	6.3	0.24	1263	160000	702	106000	20	1	34	149	335
	WTR	10.7	3.69	55944	466	13189	251000	131	2	72	152	142
	WTRNA	13.2	14.0	18764	996	5966	336000	173	0	48	184	158

concentration of the soil was 1.2 g kg^{-1} and total N was 0.1 g kg^{-1}.

At all labs, the remediation treatments were added to the soils in a randomized block design with three replicates. Following incorporation of the remediation treatments into the soil the moisture content of the soil was raised to field capacity and the soils were allowed to incubate in a controlled environment (glasshouse or growth chamber) for a period of 4 weeks. Rhizon® soil moisture samplers (Rhizon Research Products, Wageningen, The Netherlands) were inserted into the soil to allow sampling of soil pore water during the experiment.

After soils were put into the pots, 12–14 seeds of the rye grass (*Lolium mutiflorum* and *Lolium perenne*) were placed directly below the soil surface. During the first planting, the rye grass was harvested after 50 d, allowed to re-grow and then harvested again at 40 d. Plants were fertilized using liquid nutrient solutions through the course of the study. To avoid precipitation two stock solutions were prepared; one with all nutrients but K and P and another containing K and P. Nutrient solutions were added to the pots bi-weekly while plants were growing.

Soil water samples were collected from the Rhizon samplers at six points during the experiment. Soil water was sampled immediately before seeding and harvests for both rye and lettuce. In most cases suction was maintained for 2–3 h and 25–35 ml of solution were collected. In order to decrease adsorption of metals the samples were acidified with HCl immediately after collection. Extractable metals were also measured after the study using a 1 M NH_4NO_3 extraction. The NH_4NO_3-extractable metals were determined following DIN Standard 19730 (Deutsch Institut fur Normung, 1995). Briefly, 10 g of soil were added to 25 ml of 1.0 M NH_4NO_3 solution, shaken on a reciprocal shaker for 2 h, and filtered through a 0.45-μm pore size syringe filter. The resultant filtrate was analyzed by ICP spectrometry to determine trace element concentrations.

Soil pH and EC was determined after every plant harvest. A small aliquot of soil was removed from the top 5 cm of each pot. Soils were mixed with deionized water at a soil/water ratio of 1:5, allowed to incubate, with intermittent stirring, for 1 h in order to reach equilibrium. Following pH readings, the solutions were analyzed for EC.

2.1. Plant analysis

For all crops, it was necessary to harvest some plants early because they showed signs of phytotoxicity before the planned harvest date. Above ground, living tissue was harvested, washed in a mild sodium lauryl sulfate solution, double rinsed in deionized water, and dried for 48 h at 70 °C. Foliar metal analysis was completed in accordance with standard procedures in each laboratory. The filtered extracts were analyzed for metal concentrations via ICP spectrometry. Duplicate samples, blanks, and internal as well as National Institute of Standards and Technology (NIST) plant samples were routinely included in plant analysis for data quality control.

2.2. Microbial endpoints

A relevant microbially driven soil function, N transformation, and a measure of the total soil microbial biomass were chosen as microbial endpoints. The N transformation test was performed in accordance with OECD Technical Guideline 216 (Organization for Economic Co-operation and Development, 2000). This N transformation test is designed to measure nitrate formation in soils after addition of an organic substrate. Nitrate will be formed if microorganisms are able to degrade the C–N bonds in the organic substrate. This indicates that the soils are capable of degrading organic matter and recycling nutrients. For this test, soil samples (8 g) were pre-incubated at 40% water holding capacity for a period of 7 days at 20 °C. Powdered plant meal (homogenized bean crop samples provided to all laboratories by RRES) was added to the soil samples at a rate of addition equivalent to 5 g of plant meal per kg soil. One duplicate sample was extracted with 0.1 M KCl (35 mL) immediately following addition of plant meal. The suspension was shaken for 60 min at 150 rpm on an end-over-end shaker. Samples were then centrifuged at 2500 rpm for 5 min at 15 °C. Aliquots of the supernatants were stored at −15 °C prior to analysis for nitrate-N and ammonium-N by ion chromatography. Replicate samples were extracted following incubation at 20 °C for a period of 28 days.

Biomass C was used to measure the microbial population of a soil, following the method of Wu et al. (1990). This procedure was carried out as follows: Six replicate 15 g samples of oven dry soil (<2 mm) were brought to 40% water holding capacity. Three replicate soil samples were transferred to a dessicator housing NaOH, chloroform and anti-bumping granules. The dessicator was evacuated by use of a water pump and allowed to fumigate during 24 h at a constant temperature of 25 °C. Following fumigation any remaining NaOH and chloroform was removed and the dessicator was again evacuated to rid the system of any remaining chloroform. Fumigated and non-fumigated soil samples were extracted with 0.5 M K_2SO_4 (60 mL) by shaking on an end-over-end shaker at 200 rpm for 30 min. Extracts were filtered prior to storage at −15 °C until analysis of dissolved organic carbon.

2.3. PBET

The potential bioavailability of lead to humans was assessed using the physical based extraction technique developed by Ruby et al. (1999). Soil was sieved to <250 μm and mixed with a 0.4 M glycine ($C_2H_5NO_2$) solution at pH 2.2 at a 1:100 ratio. The mixture was shaken for 1 h at 37 °C in a modified toxic characteristic leaching procedure (TCLP) extractor that turned sample bottles end-over-end to mimic the stomach environment. After 1 h, the extraction was filtered through 0.45 μm syringe filters, and the pH was tested to assure that the pH had not strayed from 2.2 by more than 0.5 log units. Samples were then analyzed using by ICP spectrometry and compared to the total Pb concentration of the <250 μm fraction, which was determined by X-ray fluorescence (XRF) at CSIRO. The NIST soil standard SRM 2711, a moderately contaminated soil from Montana, was routinely included in PBET analysis.

3. Results and discussion

3.1. Soil

Both soil pH and electrical conductivity (EC) were affected by treatment addition (Table 2). The pH in the untreated soil ranged from 6.31 (UW) to 6.78 (CSIRO). Rock phosphate (LUC) addition had no effect on soil pH. At UW, RES and CSIRO, in order to compensate for the reduction in pH following TSP or H_3PO_4 addition, lime was added to the soil to bring the pH to >5.5 This was also done when H_3PO_4 was tested in field plots (Ryan et al., 2004). For the elements of concern in this study, Pb, Cd, and Zn metal solubility decreases as soil pH increases across the range of pH values commonly found in agronomic soils. For this reason it is not clear if the ability of certain amendments to reduce metal availability is based on their lime equivalence or on other factors. To test this, a lime only treatment was included in three of the four labs that participated in the study. However, there were still differences in pH across treated soils, making it difficult to determine if the liming effect accounted for the observed reductions in metal extractability (Table 3). For the P treatment, it is possible that soil pH was not as important as for other treatments. This would be the case as the purpose of P addition is precipitation of a new discrete Pb mineral phase that is stable across the pH values typically found in arable soils. A similar mechanism could also occur for Cd and Zn. Hamon et al. (2002) used an isotopic dilution technique to assess the effect of pH on the lability of Cd and Zn upon application of P. Their work was conducted using the same soil used in this work. They reported that the size of the labile pool of Cd and Zn increased with acidification to pH 5.6 and pH 6.0, respectively, at which point there was no further increase in the labile pool. This suggests that a new solid phase containing Cd and Zn is formed when P is added to a soil and that these phases may be stable under acidic conditions.

Soil EC was increased as a result of treatment addition for a number of the treatments tested. There were also differences between labs with EC in the common treatments varying by lab. Electrical conductivity in the control treatment ranged from 0.22 mS cm^{-1}(CSIRO, UW) to 3.87 mS cm^{-1} (RRES). Specific measurement methods or frequency of measures may have contributed to this observed difference. Elevated EC may have been responsible for the lack of germination observed in some of the treatments that were among the most effective at reducing extractable Cd, Pb and Zn. For example, the KP treatment included at CSIRO was as effective as TSP in reducing extractable metals and PBET Pb. However,

Table 2
pH and electrical conductivity (EC) of the soil from Jasper County

CSIRO		RRES		LUC		UW	
	pH		pH		pH		pH
Control	6.78 c	Control	6.64 a	Control	6.59 a	Control	6.31 a
Lime	7.86 e	RG	6.85 b	Lime	7.62 b	Lime	7.04 c
P (TSP)	5.63 a	P (TSP)	6.43 a	P (Rock P)	6.5 a	P (H_3PO_4)	7.04 c
P (KP)	7.15 d	RMH	7.59 d	CA	7.6 b	Bio	6.62 b
KAD+BIO	7.25 c	RMUK	7.34 c	CASS	7.63 b	WTR	6.93 c
WTRBNA	6.55 b	WTRA	6.49 a			WTR+BIO	6.92 b
WTRB	6.43 b	WTRB	6.47 a				
	EC (mS cm^{-1})		EC (mS cm^{-1})		EC (mS cm^{-1})		EC (mS cm^{-1})
Control	0.27 a	Control	3.88 ab	Control	1.3 a	Control	0.2 a
Lime	0.68 c	RG	6.6 cd	Lime	2.14 b	Lime	0.45 a
P (TSP)	0.62 bc	P (TSP)	2.29 a	P (Rock P)	1.3 a	P (H_3PO_4)	0.57 a
P (KP)	1.18 d	RMH	9.6 e	CA	1.8 ab	Bio	0.55 a
KAD+BIO	0.61 bc	RMUK	7.7 de	CASS	1.6 ab	WTR	0.31 a
WTRBNA	0.27 a	WTRA	3.0 ab			WTR+BIO	0.39 a
WTRB	0.2 a	WTRB	5.0 bc				

Means followed by a different letter within laboratories are significantly different using the Duncan Waller procedure.

Table 3
Ammonium nitrate extractable Zn and soil water Zn as measured in the common soil used by all laboratories

CSIRO		RRES		LUC		UW	
Treatment	NH_4NO_3 Zn (mg kg^{-1})	Treatment	NH_4NO_3 Zn (mg kg^{-1})	Treatment	NH_4NO_3 Zn (mg kg^{-1})	Treatment	NH_4NO_3 Zn (mg kg^{-1})
Control	428 g	Control	405 d	Control	271 d	Control	237 d
Lime	65.7 b	RG	320 c	Lime	44 a	Lime	96 c
P (TSP)	7.0 a	P (TSP)	12.3 a	P (Rock P)	238 c	P (H_3PO_4)	0.4 a
KP	0.3 a	RMH	83.7 b	CA	60.3 b	BIO	64 b
KAD+BIO	86.5 c	RMUK	140 b	CASS	51.3 ab	WTR	62 b
WTRBNA	173 e	WTRA	483 e			WTR+BIO	95 c
WTRB	254 f	WTRB	584 f				
Treatment	Water Zn (mg kg^{-1})	Treatment	Water Zn (mg kg^{-1})	Treatment	Water Zn (mg kg^{-1})	Treatment	Water Zn (mg kg^{-1})
Control	416 d	Control	147 b	Control	215 c	Control	145 c
Lime	8.9 ab	RG	233 b	Lime	6.9 a	Lime	9.7 a
P (TSP)	23 ab	P (TSP)	1.6 a	P (Rock P)	74 bc	P (H_3PO_4)	2.6 a
KP	0.8 a	RMH	5.5 a	CA	0.9 a	BIO	23 b
KAD+BIO	5.1 ab	RMUK	31 a	CASS	0.6 a	WTR	8.7 a
WTRBNA	37 b	WTRA	170 b			WTR+BIO	9 a
WTRB	132 c	WTRB	379 c				

The ammonium nitrate extractable Zn was measured 1× while the soil water Zn was measured at multiple intervals ($n > 4$) through the course of the pot study. Means within each lab followed by the same letter are not significantly different (Duncan Waller procedure).

there was no germination in this treatment. The EC in this treatment was 1.18 mS cm^{-1} compared to 0.62 mS cm^{-1} in the TSP treatment. The red gypsum and red muds tested at RRES had the highest EC of any of the treatments tested, ranging from 6.59 mS cm^{-1} (RG) to 9.59 mS cm^{-1} (RMH). These treatments also had lower plant yield than the P treatment (2.29 mS cm^{-1}) at the same lab. The high EC values suggest that additional leaching of soils amended with these treatments would be useful before planting.

3.2. Plant response-rye grass

Rye grass yield was highest at RRES with average yield across all treatments and harvests equal to 1.2 g per pot. Yield at other locations ranged from 0.19 g per pot (LUC) to 0.66 g per pot (UW). Use of different grass species and cultivars may partially explain the differences in yield between participating laboratories. Harvest was also a factor in plant yield with yield decreasing from the first harvest (0.77 ± 0.16) to the second (0.52 ± 0.13). A third harvest was collected at UW and yield for this harvest showed further reduction (0.38 ± 0.1). Overall, the treatment with the highest yield was P added as TSP or as H_3PO_4 with an average yield across all labs and harvests of 2.64 g per pot. The second highest yield was observed in the BIO+WTR treatment at UW with average yield across three harvests equal to 1.85 g per pot. Most other treatments had yields similar to the control soil > 0.34 g per pot. Exceptions were BIO alone 0.76 g per pot and a WTR at RRES 0.7 g per pot.

The highest yields over all (6.2 g per pot) were observed in the TSP treatment at RRES. The same treatment at CSIRO yielded 1.8 g per pot, with the H_3PO_4 treatment at UW yielding 0.8 g per pot. Yield in the rock phosphate treatment used at LUC was 0.1 g per pot. Yield in the P and control treatments, as well as highest yield treatment in each lab are presented in Fig. 1.

Many of the treatments were very effective at reducing plant Cd, Pb and Zn (Table 4). Plant Cd in the untreated soil ranged from 6.2 (UW) to 23.4 mg kg^{-1} at RRES. Phosphorus (TSP or H_3PO_4) addition was the most effective treatment and reduced plant Cd concentrations to 0.49 ± 0.02. Other treatments used at individual labs that were statistically similar (Duncan

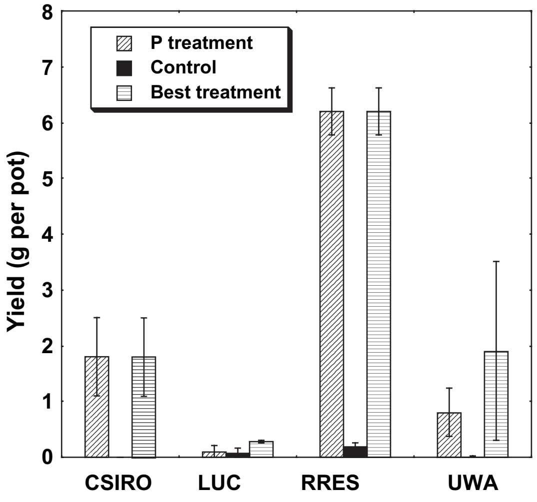

Fig. 1. Rye grass (*Lolium mutiflorum* and *Lolium perenne*) yield (g per pot) for the untreated, P, and best yielding treatments for all laboratories. For RRES and CSIRO, the P treatment was also the treatment with the highest yield.

Table 4
Rye grass Cd (a), Pb (b) and Zn (c) for plants grown in the common Jasper County soil, treated with a range of amendments

CSIRO		RRES		LUC		UW	
Treatment	Plant Cd (mg kg^{-1})	Treatment	Plant Cd (mg kg^{-1})	Treatment	Plant Cd (mg kg^{-1})	Treatment	Plant Cd (mg kg^{-1})
Control	No yield (ny)	Control	23.4 b	Control	8 c	Control	6.2 b
Lime	12.6 c	RG	27.5 b	Lime	1.35 a	Lime	9.6 c
P (TSP)	0.53 a	P (TSP)	0.47 a	P (Rock P)	2.1 a	P (H_3PO_4)	0.47 a
KP	ny	RMH	4 a	CA	2.75 b	Bio	1.37 a
KAD+BIO	8.83 b	RMUK	6.5 a	CASS	1.85 a	WTR	8.5 c
WTRBNA	15.9 d	WTRA	5.1 a			WTR+BIO	4.3 b
WTRB	25.1 e	WTRB	35.1 c				
Treatment	Plant Pb (mg kg^{-1})	Treatment	Plant Pb (mg kg^{-1})	Treatment	Plant Pb (mg kg^{-1})	Treatment	Plant Pb (mg kg^{-1})
Control	ny	Control	83.2 cd	Control	14.9 a	Control	82.7 b
Lime	410 c	RG	72.6 c	Lime	65.9 c	Lime	293 c
P (TSP)	12.9 a	P (TSP)	2.3 a	P (Rock P)	49.6 bc	P (H_3PO_4)	6.4 a
KP	Ny	RMH	98.3 d	CA	51.2 bc	Bio	15.6 a
KAD+BIO	358 bc	RMUK	122 e	CASS	47.5 b	WTR	344 c
WTRBNA	328 bc	WTRA	66.8 bc			WTR+BIO	126 b
WTRB	235 b	WTRB	51.4 b				
Treatment	Plant Zn (mg kg^{-1})	Treatment	Plant Zn (mg kg^{-1})	Treatment	Plant Zn (mg kg^{-1})	Treatment	Plant Zn (mg kg^{-1})
Control	ny	Control	4956 bc	Control	2967 d	Control	2273 b
Lime	1415 c	RG	6176 c	Lime	1166 b	Lime	2965 b
P (TSP)	639 a	P (TSP)	208 a	P (Rock P)	2429 c	P (H_3PO_4)	371 a
KP	Ny	RMH	471 a	CA	595 a	Bio	3778 c
KAD+BIO	1021 b	RMUK	681 a	CASS	549 a	WTR	3246 c
WTRBNA	2007 d	WTRA	3786 b			WTR+BIO	3260 c
WTRB	4000 e	WTRB	14024 d				

Means are averaged across two cuttings of the rye grass. Values followed by different letters within each lab are significantly different using the Duncan Waller means separation procedure.

Waller means separation on untransformed data) to P included the two RM treatments and one WTR treatment at RRES and the BIO treatment at UW. The second WTR treatment tested at RRES actually increased plant Cd over the untreated soil. The less effective WTR is a Fe based material with high concentrations of both Na-dithionite (53 533 mg kg^{-1}) and NH_4 oxalate (44 763 mg kg^{-1}) extractable Fe (Table 1). However, the WTR tested at UW and at CSIRO had the highest plant Cd of all treatments tested and these materials do not have consistent characteristics that might explain the increase in plant available Cd. Additionally, while NH_4NO_3 extractable Cd was highest in the RRES WTR with high plant Cd, the WTRs used at UW and CSIRO reduced extractable Cd over the control soil. At LUC, all of the treatments reduced plant Cd concentration over the untreated soil (8.0 mg kg^{-1}), The most effective treatment was lime.

Phosphorus was also the most effective amendment at reducing plant Pb. Plant Pb was reduced from 83 mg kg^{-1} (RRES and UW) to 7.2±3.1 mg kg^{-1} (CSIRO, RRES, UW). The only other amendment tested that decreased Pb and was statistically similar to P across all labs was BIO at UW. All other amendments were similar to or actually increased plant Pb over the unamended soil. All of the amendments tested at LUC increased plant Pb. Both the WTR and WTR+BIO treatments at UW also increased plant Pb over the unamended soil. At UW, this increase in plant Pb was concurrent with a decrease in plant P concentration in the WTR treatment with average plant P in this treatment equal to 930±83 mg kg^{-1}. Average plant P in the unamended soil at UW was 4800±267 mg kg^{-1}.

Plant Zn concentrations were similar to plant Cd and Pb with respect to the greatest observed decreases occurring in the TSP and H_3PO_4 treatments. Plant Zn decreased from 3400±270 mg kg^{-1} (RRES, LUC, UW) to 406±41 mg kg^{-1} (CSIRO, RRES, UW) in these treatments. Similarly effective treatments included both RM (RRES) and the CA and CASS treatments (LUC). Although the reductions in plant Zn were significant and were generally accompanied by the highest observed yields, these concentrations are potentially at or near what is often considered toxic levels (Chaney, 1993). In addition, the second highest yielding treatment overall, the WTR+BIO treatment at UW, had plant Zn concentrations that were higher than the untreated soil (3260 mg kg^{-1}) and clearly above previously defined toxicity thresholds. It is not clear why the grass in this treatment was able to survive, and it is less clear why the yield was high. High plant Zn (3778 mg kg^{-1}) was also observed in the BIO treatment at UW. In this treatment yield remained high for three harvests and was actually higher than yield in the P treatment for the final harvest (1.02±0.46 versus 0.38±0.02 g per pot).

The overall assessment of these results is that P treatments, with the exception of rock phosphate, were the most efficient in enhancing plant growth and decreasing metal concentrations in plants. This effect may be attributed to both the capacity of P to form sparingly soluble metal phosphates in soils and the enhanced P availability that in the tested soil may represent a limiting factor to plant and microbial growth. The lack of performance of rock phosphate may be due to the poor solubility of P at pH 6.5 (pH of the amended soil). Biosolids, alone or in combinations with other materials, were the second best treatment in terms of plant growth. However, although they decreased Pb and Cd concentrations to levels that were statistically similar to P, BIO addition did not reduce plant Zn concentrations. In contrast, lime and other materials decreased metal solubility (see below) but this did not result in a positive effect in terms of plant growth or metal content. Some of these materials, such as the WTR have high P binding capacities. This, in combination with the potential for P to be a limiting factor for plant growth in this soil may explain the low yields in these treatments.

3.3. Extractions

The two extracts used as a surrogate measures of metal availability, soil pore water as obtained by Rhizon soil moisture samplers, and NH_4NO_3 extractable trace metals (Deutsch Institut fur Normung, 1995) are non-aggressive extracts developed to measure what is in soil solution and what is readily labile in soils. These are potentially more suitable for measures of plant available metals in contaminated soils than more aggressive extracts that were developed for use in potentially nutrient deficient soils (Hall et al., 1998; Knight et al., 1998; McLaughlin et al., 2000; O'Connor, 1988; Zhang et al., 2001). The Jasper County soil, as evidenced by the phytotoxic conditions in the untreated soil is at the extreme end of a contaminated soil. It is more accurately described as mine waste rather than soil. Yield responses were observed in only a few of the treatments tested, suggesting that the phytotoxicity was not reduced by the majority of the soil amendments tested. However, extractable metal concentrations were reduced by amendment addition. These results suggest that in cases of extreme contamination, soil extracts may not be an adequate predictor of plant response.

Across all labs, NH_4NO_3 extractable Cd in the untreated soil ranged from 0.95 mg kg^{-1} (UW) to 2.17 mg kg^{-1} (CSIRO). The NH_4NO_3 extractable Cd was significantly reduced over the untreated soil for all amendments used by CSIRO and UW and all excluding one WTR for RRES. The magnitude of the reduction varied with the greatest reductions observed for the P treatments (<0.03 mg Cd kg^{-1} for all P treatments excluding rock phosphate) and the biosolids treatment

(0.08 mg Cd kg^{-1}). These treatments also had the highest yield for rye grass. All of the treatments tested at CSIRO, LUC, and UW reduced soil water Cd concentrations in comparison to the untreated soil. Soil water Cd ranged from 2.28 at CSIRO to 0.78 at UW. Phosphorus addition reduced this to <0.01 mg kg^{-1}.

Extractable Zn (NH_4NO_3) was also reduced by a range of treatments, with P being the most effective. Results are presented for NH_4NO_3 and Rhizon extractable Zn in Table 3. Reductions in the extractable concentration of Zn were similar to those observed for Cd and Pb. Extractable Zn concentrations in the unamended soil was similar in all labs (254 ± 12 mg kg^{-1}) with the exception of CSIRO (584 mg kg^{-1}). In the P amended soils, NH_4NO_3 extractable Zn was reduced to <12 mg kg^{-1} for all forms of P added excluding rock phosphate (237 mg kg^{-1}). The variation in soil water Zn in the unamended soils was wider ranging from 416 (CSIRO) to 147 (RRES, UW) mg kg^{-1}.

All treatments (excluding rock phosphate) also reduced the NH_4NO_3 extractable Pb concentration over the unamended soil with P (TSP or H_3PO_4) being the most effective. For soil water Pb, Pb concentration in the untreated soil was consistent across labs ranging from 3.08 (LUC) to 1.9 (CSIRO) mg kg^{-1}. Concentrations remained stable across sampling times for all labs.

NH_4NO_3 extractable Zn and Cd was related to rye grass metal concentration with an *R* value of 0.76 for Zn and 0.66 for Cd (Fig. 2). The relationship with soil water extractable Zn and Cd was less defined with an *R* value of 0.38 for Cd and 0.60 for Zn (Fig. 3). The relationship between extractable or soluble Zn and Cd and plant concentrations of these elements may have been compromised by the very low yield in some treatments and the absence of yield in others. There was no relationship between NH_4NO_3 or soil solution extractable Pb and plant Pb (Fig. 4) indicating that these measures may not reflect the plant available pool of total soil Pb or that other factors are involved in plant uptake of Pb. These results are consistent with those observed for relationships between extractable Cd, Pb, and Zn and plant uptake of these elements from amended contaminated soils from the same mining district (Basta et al., 2001; Brown et al., 2004; Hettiarachchi and Pierzynski, 2002).

3.4. PBET

Lead availability as measured by the PBET extract was similar across the unamended soils for all laboratories (Table 5). The percent of the total Pb that was extracted using this measure ranged from 79.5% at RRES to 85% at LUC. Across all labs and all treatments used, P added as either TSP, KP, or H_3PO_4 was the most effective amendment at reducing Pb extractability with 31.6 and 30.9% of the total Pb extracted in the TSP amended soils in CSIRO and RRES, respectively. Potassium phosphate addition reduced Pb extractability to 34.1% versus 84.9% in the untreated CSIRO soil. Phosphoric acid addition reduced Pb extractability with 39.9% of the total Pb extracted in this treatment. Rock phosphate was significantly less effective than the other P amendments tested with 66.3% of the total Pb extractable in the rock phosphate treated soil.

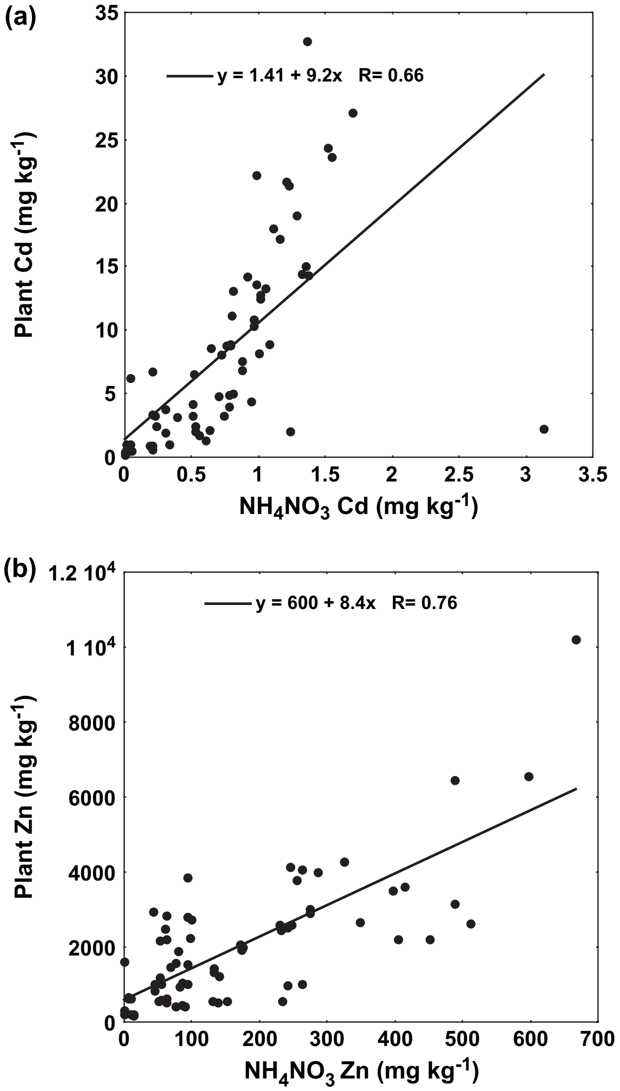

Fig. 2. Ammonium nitrate extractable Cd (a) and Zn,(b) for soil collected from a mine waste site in Jasper County, MO in relation to rye grass (*Lolium mutiflorum* and *Lolium perenne*) Cd and Zn in untreated and amended soils. Data points include measured available metal concentrations from untreated and amended soils and plant metal concentrations from two cuttings of rye grass.

The other treatments tested were much less effective than P addition in reducing Pb availability. Of the water treatment residuals tested, all except for one were statistically similar to the untreated soil. The reduction showed by one of the WTR tested at RRES showed a 9% decrease in extractable Pb. The other treatment

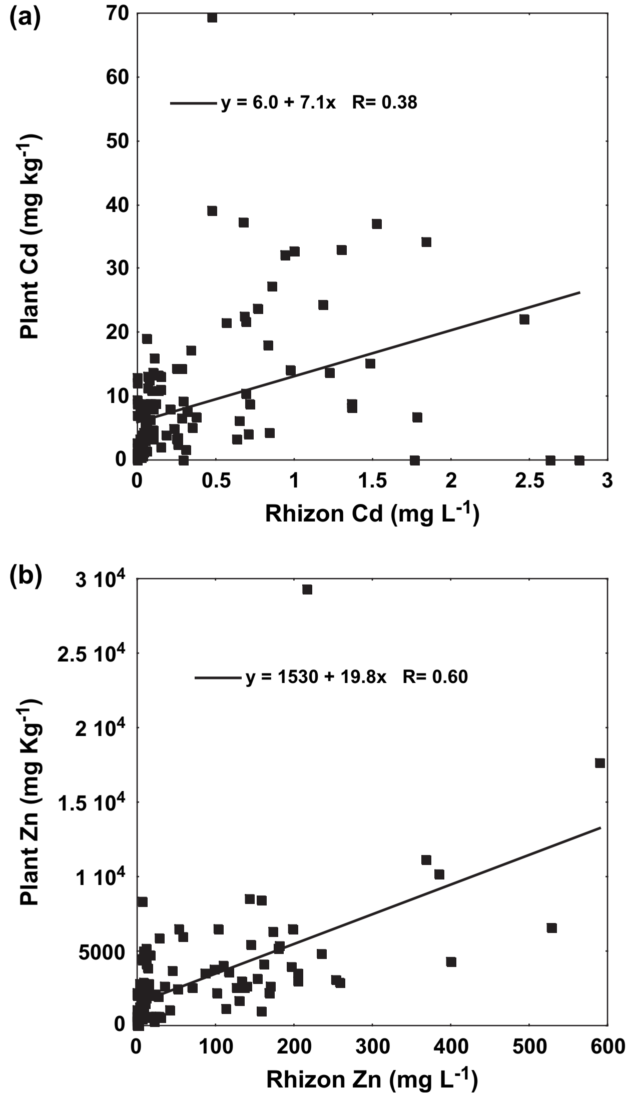

Fig. 3. Rhizon® soil water extractable Cd (a) and Zn (b) for soil collected from a mine waste site in Jasper County, MO in relation to rye grass (*Lolium mutiflorum* and *Lolium perenne*) Cd and Zn in untreated and amended soils. Data from two harvests of rye grass are included.

that showed some reduction over the untreated soil was the CASS amendment tested at LUC where reduction was similar to that observed for phosphate rock.

3.5. Microbial biomass

Results from the fumigation assay were too variable at LUC and UW for any conclusions to be drawn. However, results from both CSIRO and RRES showed less variability and response to treatments was consistent over both labs. Biomass C in the P treatment measured 147.7 (UW) and 157 mg C kg^{-1} (RRES). For the untreated soil, values ranged from 34.1 (RRES) to 72.3 mg C kg^{-1} (CSIRO). At both CSIRO and RRES, P was the only amendment that increased soil microbial biomass as measured by this assay. It should be noted that the microbial biomass measures in the untreated soil were extremely low and are indicative of a soil with little to no native microbial activity. Even though biomass increased by 94 mg kg^{-1} on average with the most effective amendment, total soil microbial biomass was still well below what would be expected for an uncontaminated soil.

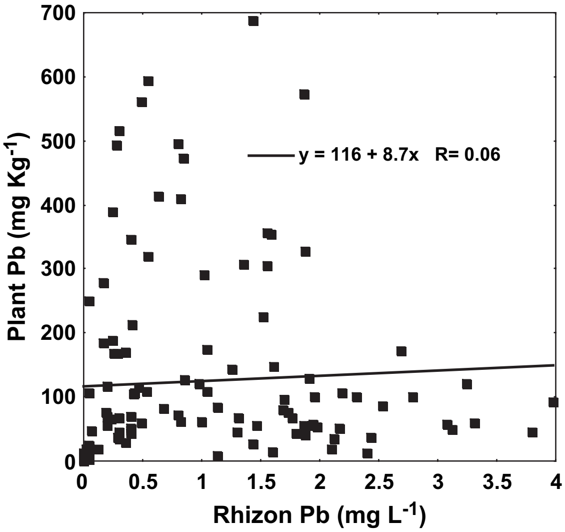

Fig. 4. Rhizon® soil water extractable Pb for soil collected from a mine waste site in Jasper County, MO in relation to rye grass (*Lolium mutiflorum* and *Lolium perenne*) Cd and Zn in untreated and amended soils. Data from two harvests of rye grass are included.

3.6. Nitrogen transformation

Results from this assay were not consistent across the different labs. This is likely the result of when this incubation/extraction was carried out. At UW, the extract was done following the initial soil incubation but before planting or fertilizing the soil. Total NO_3^- in the untreated soil was below 2 mg kg^{-1} NO_3^--N for the duration of the study. The P treatment increased the fraction of N added as plant biomass that was microbially transformed to NO_3^-. At the initiation of the incubation total NO_3^- in this treatment was 4 mg kg^{-1} NO_3^--N. This increased to 17 mg kg^{-1} NO_3^--N after 28 days. The biosolids treatment also showed higher N than the control. Here at time 0, NO_3^--N concentration was 212 mg kg^{-1}. This stayed relatively consistent through the incubation. However, it is likely that this observed increase was related to the high N content of the biosolids. A similar trend was observed at CSIRO with NO_3^--N in the untreated soil significantly lower at day 28 than in the P treatment (86.7 versus 98.9 mg kg^{-1} NO_3^--N). Results from RRES showed the most pronounced differences, however, results followed an opposite pattern from those at UW and CSIRO. At RRES, the extract was run on the soils after the plants

Table 5
Physiologically based extraction test (PBET) extractable Pb (% extractable of total Pb) for the Jasper County soil

CSIRO		RRES		LUC		UW	
Treatment	Extractable Pb (% of total)	Treatment	Extractable Pb (% of total)	Treatment	Extractable Pb (% of total)	Treatment	Extractable Pb (% of total)
Control	84.9 c	Control	79.5 c	Control	85 b	Control	82.5 c
Lime	82.5 c	RG	77.8 c	Lime	70 ab	Lime	79.7 bc
P (TSP)	31.6 a	P (TSP)	30.9 a	P (Rock P)	66 a	P (H_3PO_4)	39.9 a
KP	34.1 a	RMH	77.8 c	CA	74 ab	BIO	77.1 b
KAD+BIO	54.1 b	RMUK	78.4 c	CASS	59 a	WTR	77.7 bc
WTRBNA	79.6 c	WTRA	70.6 b			WTR+BIO	82 c
WTRB	83.3 c	WTRB	77.8 c				

Values followed by different letters within each laboratory are significantly different ($p<0.05$).

had been harvested. The differences in results are likely the result of residual N being present in the soil following extensive fertilization. With this in mind, the results from RRES are consistent with the results from the other labs. The NO_3^--N concentration was highest in the untreated throughout the incubation (274 mg kg^{-1} NO_3^--N). This suggests that there was no active microbial community in the control soil to use the N that had been added for plant fertilizer. The lowest NO_3^- concentration (57 mg kg^{-1} NO_3^--N) was observed in the P treatment. This suggests that microbial activity had been restored to this soil and that the microbes utilized the added N. In addition, this treatment had the highest plant yield, suggesting that plant uptake of the added N was also a factor. RRES was also the only lab that measured NH_4-N. Here, concentrations of NH_4-N remained relatively consistent across the incubation period for the unamended soil, averaging 72.5 mg kg^{-1} NH_4-N. However, concentrations of NH_4-N increased over time in the P treatment going from 26.3 at T 0 d to 62 at T 28 d. This indicates that the microbial community was actively decomposing the plant material that had been added at the beginning of this assay.

4. Conclusions

Results from this study indicate that it is possible to reduce the availability of Pb, Cd, and Zn in a highly contaminated soil with the use of soil amendments. Of the amendments tested by the participating labs, P added as either TSP or H_3PO_4 appeared to be the most effective. Phosphorus addition to the soil resulted in increased plant growth, reduced metal concentration in plant tissue, reduced soil solution and extractable metals, reduced bioavailability of soil Pb, and increased microbial activity based on two measures. Although P addition resulted in marked improvement in the soil's ability to support plant growth and microbial activity, it should be noted that the amendment was not sufficient to sufficiently reduce the bioavailability of soil Cd, Pb, and Zn to restore this highly contaminated soil to what would be considered normal function.

Many of the amendments tested, including P added as rock phosphate (probably due to the low solubility of this form of P), limestone, a range of WTR residuals, cyclonic ashes, steel shots and red muds showed no improvement over the unamended soil by all indices except for soil extractions. This suggests that soil extracts, even extracts designed to measure metal availability in cases of potential toxicity, may not be a sufficient measure to evaluate in situ soil amendments. Results from this study indicate that it is much more straightforward to reduce extractable metals in a contaminated system than to restore normal function including plant growth and microbial activity. Finally results from this study demonstrate that it is important to recognize that there are significant differences in efficacy within categories of amendments. For example, the acid forming forms of P used in the study were much more effective than rock phosphate in restoring function to the common soil. In addition, there were large differences in response to the specific WTR used. It is not possible to generalize about the response to a general category of amendments based on the response to a single type of WTR.

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