PHOSPHORUS AND MANGANESE OXIDES EFFECTS ON SOIL LEAD BIOACCESSIBILITY: PBET AND TCLP

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Abstract. Lead (Pb) is toxic to humans, especially to young children, as well as animals. Toxicity is strongly related to the bioavailability of Pb and soil Pb bioavailability can be influenced by soil amendments. This study was conducted to evaluate the effects of Mn oxides and phosphorus (P) on Pb bioaccessibility in five lead-contaminated soils or mine spoils from Kansas and Missouri, USA. Fifteen treatments were used: Brazilian (BMN) and Amonone #4 (AM#4) (commercial Mn oxides), birnessite (BIR) and cryptomalene (CRYP) (synthetic Mn oxides), phosphate rock (PR) and triple superphosphate (TSP) phosphorus sources, and combinations of each P source with the Mn oxides. A physiologically based extraction test (PBET) was used to evaluate time and treatment effects. All amendments significantly decreased Pb bioaccessibility compared with control although treatment effects differed from soil to soil. In general, TSP, PR, and BIR treatments were most effective in decreasing Pb. Some amendments reduced the toxicity characteristic leaching procedure (TCLP) concentration for Pb to below the critical value of 5 mg L^{-1}, but were not able to reduce TCLP extractable Cd to below 1 mg L^{-1}. Our results indicated that the use of P and Mn oxides for reducing soil Pb bioaccessibility in contaminated soils is promising.

Keywords: bioavailability, lead, lead bioaccessibility, manganese oxide, phosphorus

1. Introduction

Lead (Pb) contamination is a large public concern due to toxicity to animals as well as humans, especially young children. Lead-contaminated soils are widespread in the environment because of the extensive use of Pb in industrial activities (mining and smelting), urban activities (leaded gasoline and paint), and agricultural activities (pesticides) (Ma *et al.*, 1995). There are many methods employed to clean up contaminated soils and wastes, such as physical, chemical, thermal, and biological treatments. Among these methods, soil excavation is technique most accepted by the United States Environmental Protection Agency (USEPA) to clean up contaminated soils. But this method is disruptive, needs a source of clean soil and a repository for contaminated soil, and is also expensive. Moreover, soil excavation is ineffective in removing all Pb exposure or reducing bioavailability, and it is hard to restore soil productivity (Gradwohl, 1994; Ma *et al.*, 1993). Therefore, there is a need for an alternate remediation method that is less destructive and costly. *In situ*

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stabilization of Pb overcomes many of the disadvantages of excavation and other methods because it is less expensive and less disruptive. *In situ* stabilization of Pb can be accomplished either by forming insoluble Pb compounds such as pyromorphites or by adsorption of Pb on strong adsorbents like manganese (Mn) oxides, or by both processes simultaneously (Hettiarachchi *et al.*, 2000).

The formation of insoluble Pb compounds in soils can be accomplished by the addition of P as a remediation method. Pyromorphites are the most stable form of Pb under a wide range of environmental conditions. Davis *et al.* (1993) reported that pyromophites are a common weathering product of Pb compounds in mine-waste. Nriagu (1974) found pyromorphites in soils collected near roads. Ma *et al.* (1994), using X-ray diffraction, reported pyromorphite formation after the reaction of hydroxapatite and soluble Pb in the presence of NO_3^-, SO_4^{2-}, and CO_3^{2-}. Similar results were also found by Laperche *et al.* (1996). Newly formed hydroxpyromorphites were identified by X-ray diffraction after reaction of PbO and $PbCO_3$ with synthetic hydroxapatite. The formation of hydroxpyromorphites in the presence of aqueous metal cations from pH 2–7 was reported by Valsami-Jones *et al.* (1998) from work using X-ray diffraction.

Zhang and Ryan (1999a,b) studied the interaction of cerrusite, anglesite, and galena with synthetic hydroxapatite in suspension and in either 0.001 M NaCI or 0.1 M $NaNO_3$ at different pH values. They reported the formation of chloropyromorphite at pH values of 4 and 5. At lower pH values, the formation of pyromorphite was not observed because of undersaturation of the system with respect to chloropyromorphite, whereas chloropyromorphite did not form above pH 5 because of reduced dissolution of hydroxapatite. Pearson *et al.* (2000) found that there was formation of hydroxypyromorphites or a similar pyromorphite-like mineral phase by X-ray diffraction in artificial soil amended with 600 mg P kg^{-1} as KH_2PO_4. Hettiarachchi *et al.* (2000) also reported the formation of pyromorphites-like minerals in the presence of both P and Mn oxide, compared with a control soil.

The second mechanism for reducing soil Pb bioavailability is adsorption of Pb by metal oxides and hydroxides. Many researchers have studied adsorption of trace metals on oxides, particularly for iron (Fe) and aluminum (Al). Manganese oxides have received less attention despite their strong Pb adsorption ability, compared with other oxides (Nelson *et al.*, 1999). Sposito (1989) stated that Pb adsorption is mostly irreversible. Padmanabham (1983) studied sorption of Pb by Mn oxides and reported that more than 90% of adsorbed Pb would not desorb. McKenzie (1980) also found that a very large proportion of Pb adsorbed on Mn oxides was not extractable by 2.5% acetic acid, and this proportion increased upon aging. Under normal soil temperatures, the activation energies of desorption could be greater than for adsorption (McBride, 1994). For practical purposes, adsorption of Pb is not reversible or has a very weak reversibility. Furthermore, the tendency to be irreversible increases with increasing contact time between adsorbate and adsorbent (Backes *et al.*, 1995).

Nelson *et al.* (1999) also studied Pb adsorption on Mn oxides and reported that Pb adsorption ranged from 2.94–43.6 μmol m^{-2}, depending on the oxide. In natural soil environments, mineral surfaces are always modified to some extent by amorphous phases, organic matter, and inorganic ions. McKenzie (1980) studied Pb adsorption by Mn oxides and reported that adsorption of Pb without P was 10 μmol m^{-2} on birnessite and 5 μmol/m^2 on cryptomelane. Weesner and Bleam (1998), using electrophoretic mobility and X-ray absorption spectroscopy, reported adsorbed Pb as an inner-sphere complex on pristine geothite, with no evidence of inner-sphere adsorption on pristine boehmite surfaces. They also found that sulfate and phosphate increased Pb adsorption on boehmite in the pH range from 5–7, but had no significant effect on goethite. Wang (2000) studied Pb adsorption on Mn oxide surfaces modified with P and found that the amount of Pb adsorbed was 32–40 μmol m^{-2}. He also reported that there was no effect of phosphate modification on Pb adsorption by birnessite.

Adsorption of Pb and precipitation of insoluble Pb complexes might take place at the same time, and both act to reduce soil Pb bioavailability. Hettiarachchi *et al.* (2000) studied in situ stabilization of soil Pb with cryptomelane and P. They found that treatment with cryptomelane and P decreased Pb bioavailability more than did cryptomelane or P treatment alone. They reported that adsorption of Pb and coprecipitation of Pb with P might take place and reduce soil Pb bioavailability. Unfortunately, there are no studies in the literature on the effectiveness of various Mn oxides on Pb bioavailability except Hetttiarachchi *et al.* (2000), and they used a synthetic Mn oxide (cryptomelane). The effectiveness of other synthetic Mn oxides and of commercially available Mn oxides is unknown. The use of commercially available Mn oxides is an important practical issue because they would likely be much less expensive than synthetic Mn oxides.

The objectives of this study were to evaluate the influence of P and different Mn oxides on soil Pb bioaccessibility over time and to compare the effectiveness of commercial and synthetic Mn oxides in reducing soil Pb bioaccessibility.

2. Materials and Methods

2.1. MATERIALS

Five contaminated soil materials from 5 different locations in the Tri-state Mining Region in the United States were collected from a depth of 0–20 cm. Two materials were mine spoils, chat and Dearing. Chat is a by-product of the initial processing of Zn/Pb ores at the mine site and was collected near the city of Galena, Kansas. Dearing is a smelter waste and was collected at an abandoned smelter near the city of Dearing, Kansas. Three contaminated soils were designated as active repository (AR), time-critical repository (TCR), and Joplin. The AR and TCR samples were collected from repositories used to store contaminated soils removed from residential areas in Joplin, Missouri during soil excavation. The Joplin sample was collected from a vacant lot in Joplin, Missouri, close to an abandoned Zn/Pb smelter. These contaminated soil materials were sieved through a stainless steel 2-mm screen, air dried, and stored in plastic containers at room temperature. Selected chemical and physical properties of these contaminated soil materials are presented in Table I.

2.2. PREPARATION OF MANGANESE OXIDES

Birnessite (BIR) and cryptomelane (CRYP) were used in this study as synthetic Mn oxides. Reagent-grade chemicals were used to prepare both synthetic Mn oxides without further purification. The BIR was prepared by following the methods described by McKenzie (1971). One mole of $KMnO_4$ was dissolved in 2.5 L of water and the solution was brought to boiling, then two moles of concentrated HCl were added dropwise over ten minutes with vigorous stirring. After cooling, the precipitate was recovered by centrifugation and then washed with 0.05 M $HClO_4$, followed by several washings with deionized water. Excess anions and cations were removed from the system by the washing process. The washing was stopped when the pH was neutral. The BIR was air dried and ground to pass through a 250-μm sieve before use. The surface area of birnessite was 50 m^2g^{-1} as measured by the BET method.

The CRYP was prepared according to the methods described by McKenzie (1980). A solution composed of 0.35 mole of $KMnO_4$ in 800 mL of water was prepared, heated to 60 °C, and poured into a solution of 0.5 mole of $MnSO_4$ in one liter of 2 M acetic acid. The mixture was heated to 80 °C and stirred for five minutes. The precipitate was washed with deionized water and dried at 45 °C. The CRYP was ground to pass through a 250-μm sieve before use. The surface area of fine-grained CRYP was measured as 111 m^2g^{-1} by the BET method. There was sufficient CRYP in the lab from previous studies to use in this study. Therefore, CRYP was not freshly prepared.

Brazilian (BMN) and Amonone #4 (AM#4) commercial Mn oxides were obtained from American Minerals (New Castle, Delaware, USA). The BMN had coarse particles and was passed through a 2-mm sieve before use. The AM#4 had fine particles and was passed through a 250-μm sieve before use. Surface areas of the BMN and AM#4 were measured as 17 and 18 m^2g^{-1}, respectively, by the BET method.

2.3. INCUBATION STUDY

One incubation study was conducted to assess the efficacy of various combinations of the four Mn oxides and phosphate rock (PR) or triple superphosphate (TSP) for reducing Pb bioaccessibility with each soil or mine waste. When P or Mn oxide was used as a soil amendment, they were added to provide 5000 mg P or Mn oxide kg^{-1}.

TABLE I

Selected chemical and physical properties of soil materials ($<250\ \mu$m fraction) prior to treatment applications

Soil material	Sand (%)	Silt (%)	Clay (%)	OM (g kg^{-1})	CEC (cmol$_c$ kg^{-1})	Cd$_T$[a] (mg kg^{-1})	Pb$_T$ (mg kg^{-1})	Zn$_T$ (mg kg^{-1})	BAF$_s$[b] (%)	P$_T$ (mg kg^{-1})	Ca (mg kg^{-1})	K (mg kg^{-1})	Mg (mg kg^{-1})	Na (mg kg^{-1})
AR	38	52	10	80	12	45	1615	6926	17	1664	2769	174	141	6
Chat	44	46	10	17	4	99	2069	46027	28	538	802	37	57	3
Dearing	56	38	6	244	48	372	16273	76274	11	517	1675	137	132	99
Joplin	28	64	8	92	18	42	6560	5830	37	564	3182	108	149	13
TCR	22	66	12	60	14	14	1747	2216	28	1498	2706	76	156	23

[a] Total elemental analysis by 4 M HNO_3 digestion.

[b] Bioavailability factor (BAF$_s$) is calculated as soluble Pb in the stomach phase of the PBET divided by total soil Pb in the $<250\ \mu$m particle size fraction, multiplied by 100.

A total of 15 treatments were used as follows: control, PR, TSP, CRYP, BIR, BMN, AM# 4, PR+CRYP, PR+BIR, PR+BMN, PR+AM# 4, TSP+CRYP, TSP+BIR, TSP+BMN, and TSP+AM# 4. A 400 g quantity of soil or mine waste was weighed into a plastic cup. Treatments were applied to the soil and then mixed thoroughly. Deionized water was used to adjust the gravimetric moisture content to 200 g kg^{-1}, then soils were mixed again. Three days after treatment application, a predetermined amount of CaO was added to the soil mixtures having a pH of <7 to increase the soil pH to approximately 7. Plastic cups were covered with parafilm 'M' and incubated at 200 g kg^{-1} gravimetric moisture content at 25 °C. Subsamples were collected at 7 days, 1 month, 3 months, and 6 months after initiation of the study.

Once a month, the moisture content of soils was adjusted back to 200 g kg^{-1} with deionized water if necessary. At each sampling time, 100 g of soil was taken and air dried, and a subsample was analyzed for pH. Bioaccessible Pb was determined by a modified Physiologically Based Extraction Test (PBET) after sieving the soils through a 250-μm stainless steel sieve. The experimental design was a split plot with three replications. The main plot factor was treatment combination and the subplot factor was time.

2.4. PBET PROCEDURE

A PBET method described by Ruby *et al.* (1996) was used to evaluate Pb bioaccessibility. This test is modeled after the human digestion system, and uses gastric and intestinal solutions at the appropriate pH, and all extractions are performed at 37 °C. Several studies have noted either poor reproducibility or limited utility of the intestinal phase and, therefore, data from this portion of the procedure were not used in this study (Ruby *et al.*, 1996; Hettiarachchi *et al.*, 2000). For the stomach phase, the gastric solution was prepared by adding 2 g of anhydrous citric acid, 2 g of DL- malic acid, 5 g of pepsin (activity of 800–2500 units mg^{-1}), and 2 mL of glacial acetic acid to a 4 L flask and making to volume with deionized water. One g of soil (<250 μm) was weighed in a 125-mL HDPE bottle, 100 mL of gastric solution added, and the bottle was covered with a cap with a rubber septa. A predetermined amount of trace-metal-grade concentrated hydrochloric acid was used to adjust the pH of the mixture to 2.0. After the cap was tightened, the headspace of the bottle was replaced with Ar gas. The bottle was shaken for 1 h at 37 °C. After 1 h, 10 mL was removed by using a cellulose-acetate membrane filter with a 10-mL disposable syringe. This aliquot represented bioacccessible Pb in the gastric phase. Gastric phase samples were stored in 20-mL scintillation vials at 4 °C. A drop of concentrated trace-metal-grade HNO_3 acid was added to each vial. Samples were analyzed by using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Bioaccessible Pb is expressed as the percentage of Pb extracted in the PBET procedure relative to the control sample. Duplicate, blank, and check samples were run with each extraction for quality control.

2.5. ADSORPTION EXPERIMENT

For each Mn oxide, a concentrated mineral suspension (125 m^2L^{-1}) was prepared. Lead nitrate was used to prepare a solution of 10 mmol Pb L^{-1} at pH 4.0. Five mL of a concentrated mineral suspension was put in to a 50-mL centrifuge tube, and the volume was made up to 25 mL by adding 0.01 M $NaNO_3$. Thus, the adsorption experiments were performed in a suspension with mineral surface area concentrations of 25 m^2L^{-1} and a total surface area of 0.625 m^2. The pH of the suspension was adjusted to 6 with 0.01 M NaOH or 0.1 M HNO_3. Concentrated Pb-nitrate solution was added such that the initial Pb concentration in the suspension was 0.25, 0.5, 1.0, or 1.5 mmol L^{-1}. After a 16-hour equilibration period, samples were centrifuged at 2000 G for 10 min. The pH of the supernatant was measured with a combination glass-reference pH electrode, and the supernatant was analyzed for Pb by using ICP. The amount of Pb adsorbed was calculated by the change in Pb concentration in the equilibrium solution.

2.6. MODIFIED TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP) TEST

This test was performed for sampling times at 7 days and 6 months for the Dearing and TCR samples in the incubation study. The extraction solution was prepared by adding 5.7 mL of glacial acetic acid into a 1 L volumetric flask and then making to volume with deionized water as described for extraction solution No. 2 of the TCLP test (US EPA, 1991). The extraction solution pH was 2.9. One gram of soil was put in a glass bottle, and 20 mL of extracting solution was added. The cap of the bottle was tightened and the bottle was placed on an end-to-end shaker at 180 excursions min^{-1} for 18 hours at 23 °C. An aliquot was filtered by using Whatman No. 42 filter paper and was analyzed for Pb and Cd by using ICP-AES.

2.7. MINERALOGICAL ANALYSES

The $<250\ \mu m$ fraction of all soil samples from the first incubation study at two sampling times (7 days and 6 months) were analyzed with a Philips X-ray diffractometer (Philips Electronic Instruments, Inc., Mahwah, NJ) as random powder mounts with Cu Kα radiation of 1.54050 Å wavelength at 35 kV and 20 mA. A continuous scanning technique from 2 to $66^\circ 2\theta$ was used for measurements.

2.8. DATA ANALYSES

Statistical analyses were done with SAS for Windows version 6.12 (SAS Institute, 1987). A protected least significant difference (LSD) test was used to separate the means.

3. Results and Discussion

The total Pb concentration in soil materials ranged from 1,615–16,273 mg kg^{-1}, and the Pb bioavailability factor (BAF_s) before treatment applications ranged from 11–37% (Table I). Dearing had the highest total Pb concentration (16,273 mg kg^{-1}) and also the lowest Pb BAF_s (11%). Our results support conclusions of others who reported that total Pb concentration does not provide reliable information about Pb bioavailability. Hettiarachchi *et al.* (2000) reported similar results in that their smelter slag had the highest Pb concentration and the least Pb bioavailability.

Before treatment applications, all soil samples were analyzed by XRD. There was no evidence of cerussite, pyromorphites, or apatites as common Pb and P minerals. It is possible that these minerals were present, but at concentrations below the detection limit of 10–20 g kg^{-1} (Ma *et al.*, 1994). All four Mn oxides minerals were also analyzed by XRD. There was no evidence of crytalline materials in BIR or the commercial Mn oxides. Birnessite typically exhibits peaks at 7.09, 3.56, 2.51, or 2.42 Å, and the peaks may have been absent because the BIR was freshly prepared. Cryptomelane exhibits characteristic peaks at 2.39, 3.10, 4.91, or 6.94 Å (JCPDS International Center, 1987). The three most prominent peaks of CRYP were found at 2.39, 3.10, and 6.94 Å.

There was no significant time-by-treatment interaction for Pb bioaccessibility for the stomach phase extractions for any soils or mine wastes in the incubation study (Table II). Therefore, data were averaged over time. When added alone, both P sources significantly decreased Pb bioaccessibility compared with the control except for the Dearing smelter slag. When CRYP or BIR were added alone, significant reductions in soil Pb bioaccessibility compared to the control were found for AR, chat and TCR but not for Dearing or Joplin. Of the two commercial Mn oxides, the only significant reduction compared to the control was AM#4 for the AR soil. For the Dearing smelter slag, only the combined treatments of PR or TSP plus one of the Mn oxides statistically decreased Pb bioaccessibility compared with any other treatments. In general, TSP, PR, and BIR treatments were more effective in decreasing Pb bioaccessibility.

For the amendments of the Joplin and Dearing materials that contained both P and Mn oxides, there were generally no significant differences in soil Pb bioaccessibility when comparing Mn sources within each of the P sources (Table II). The exceptions were that PR+BMN was significantly higher than PR+AM#4 for Dearing, and that TSP+BIR was significantly lower than TSP+CRYP for Joplin. This suggests that commercially available Mn oxides were as effective as synthetic Mn oxides for these two soils. Because these commercially available Mn oxides are cheap and available in large quantities, compared with synthetic materials, they could be cost-effective alternatives to synthetic Mn oxides.

The reduction of Pb bioaccessibility by treatments might be attributed the interactions between Pb solids, Mn oxides, P, and soil constituents, resulting in the formation of insoluble Pb compounds, adsorption of Pb, or both processes simultaneously.

TABLE II

Treatment effects on soil Pb bioaccessibility

	Sample				
Treatment[@]	AR (%)	Chat (%)	Dearing (%)	Joplin (%)	TCR (%)
Control	100a[a]	100 a	100 a	100 ab	100 a
PR	57 cde	56 de	84 abcd	70 def	46 def
TSP	64 c	67 c	88 abc	75 de	58 cde
CRYP	82 b	78 b	95 ab	95 abc	75 bc
BIR	50 ef	19 h	88 abc	85 bcd	50 def
BMN	94 a	101 a	102 a	110 a	106 a
AM#4	82 b	93 a	97 ab	100 ab	88 ab
PR+CRYP	32 g	35 g	77 bcde	62 ef	36 efg
PR+BIR	22 h	10 h	72 cde	58 f	18 g
PR+BMN	54 def	47 ef	86 abc	67 def	49 def
PR+AM#4	49 f	42 fg	70 de	63 ef	46 def
TSP+CRYP	48 f	40 fg	63 e	78 cde	61 cd
TSP+BIR	28 h	10 h	65 e	56 f	25 fg
TSP+BMN	61 cd	59 cd	67 e	71 def	60 cde
TSP+AM#4	54 def	57 cde	77 bcde	70 def	67 bcd

[a] Means with the same letter within a column are not significantly different by LSD at $P = 0.05$.
[@] PR = phosphate rock, TSP = triple superphosphate, CRYP = cryptomelane, BIR = birnessite, BMN = Brazilian commercial Mn oxide, AM#4 = Amonone #4 commercial Mn oxide.

These interactions could involve the dissolution of Pb-bearing solids, desorption of Pb from organic and inorganic constituents, and the formation of different Pb solids and complexes (Hettiarachchi *et al.*, 2000).

Most treatments significantly decreased soil Pb bioaccessibility, compared with the control, but the magnitude of this effect was different from soil to soil. The greatest reduction in Pb bioaccessibility was with the chat sample whereas the least reduction occurred with Dearing smelter slag (Table II). Lead bioaccessibility is influenced by geochemical factors including Pb mineralogy, dissolution kinetics, the degree of encapsulation, and rinding by precipitation products (Schoof *et al.*, 1995; Ruby *et al.*, 1994, 1996; Medlin, 1997). Total concentrations of metals do not correlate with bioaccessibility of metals, metal solubility, or free metal activity (Hare and Tessier, 1996; Singh *et al.*, 2001). Soil properties influence bioaccessibility of metals by controlling the retention, mobility, and transformation of metals in soils. These properties include pH, redox potential, cation exchange capacity, organic matter, mineralogy of soil, and amount of metal (Calace *et al.*, 2002). Mineralogy and pH may play an important role in variation for Pb bioccessibility among the soils. Although XRD did not show differences in mineralogy among soil materials, there may be differences in mineralogy that we could not detect. Hettiarachchi *et al.*

(2000) reported that the chat material contained free carbonates, and the ambient pH of chat is very high. A Pb carbonate placed into the acidic conditions of the PBET procedure would dissolve readily, whereas other Pb solids may not. Chat also had the least organic matter content (1.7 g kg^{-1}) and CEC (4 cmol$_c$ kg^{-1}) among all soil materials used in this study, whereas Dearing smelter slag had the lowest pH, the highest organic matter content (24.4 g kg^{-1}), and CEC (47.7 cmol$_c$ kg^{-1}). It has been reported that naturally occurring compounds with reductant characteristics can dissolve Mn oxides and release adsorbed metals (Godtfrodsen and Stone, 1994). Hettiarachchi *et al.* (2000) reported that the reason for the lesser reduction in Pb bioavailability in chat might be the lower OM content. Moreover, chat may adsorb less Pb, compared with other soil materials, and allow more Pb in solution to react with P and MnO_2.

3.1. ADSORPTION EXPERIMENT

The greatest amounts of Pb adsorbed by BIR, CRYP, BMN, and AM#4 were 33, 24, 1.0, and 1.9 μmol m^{-2}, respectively (Figure 1). The synthetic MnO_2 materials adsorbed more Pb than did the commercial Mn oxide materials by at least an order of magnitude. The specific surface areas of BIR and CRYP were 50 and 111 m^{2}g^{-1}, respectively and 18 and 17 m^{2}g^{-1} for AM#4 and BMN, respectively. The large surface areas of synthetic MnO_2 materials contribute to their greater adsorption ability, compared with the commercial materials, and may be the reason the synthetic materials were more effective in reducing soil Pb bioaccessibility

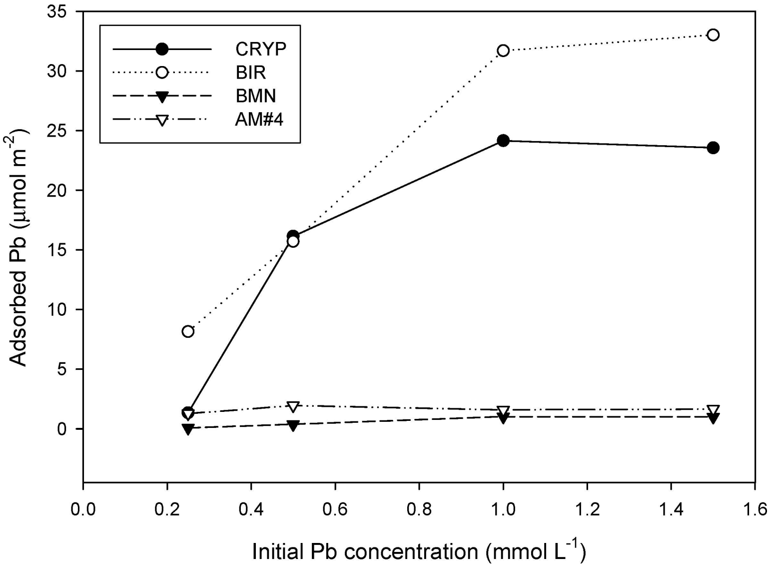

Figure 1. Adsorption of Pb on manganese oxides.

(Table II). A contribution of surface area to adsorption capacity of minerals is important, but that is not the only factor determining adsorption ability of minerals. Our data indicated that the BIR had greater Pb adsorption capacity than did CRYP, although the surface area of BIR is lower than CRYP. McKenzie (1980) reported that Pb adsorption was 10 μmol m^{-2} on BIR, and 5 μmol m^{-2} on CRYP. The greater adsorption capacity of BIR, compared with CRYP, could be caused by differences in their mineral structures. Cryptomelane has a frame structure preventing ions from entering the crystal structure whereas BIR has a layer structure, allowing ions to pass to interlayer positions (McKenzie, 1980).

3.2. TCLP EXTRACTABLE METALS

The TCLP test is used in the United States to determine whether contaminated soils or solid wastes are to be classified as hazardous wastes. There are critical values for select elements and organic compounds. The critical values are expressed as a concentration in the extracting solution and the critical values are 5 and 1 mg L^{-1} for Pb and Cd, respectively (Stanforth and Chawdhury, 1993).

There was no time-by-treatment interaction for extractable Cd and Pb for either the Dearing smelter slag or TCR. Time did not have a significant effect on extractable Cd and Pb, except for extractable Pb in the Dearing smelter slag. Extractable Cd and Pb for the Dearing sample exceeded the critical values (Figures 2 and 3). Hettiarachchi *et al.* (2000) reported that extractable Cd and Pb in the Dearing smelter slag were greater than the critical values. All treatments significantly decreased extractable Cd and Pb in the Dearing sample, except for AM#4 and BMN. The TSP

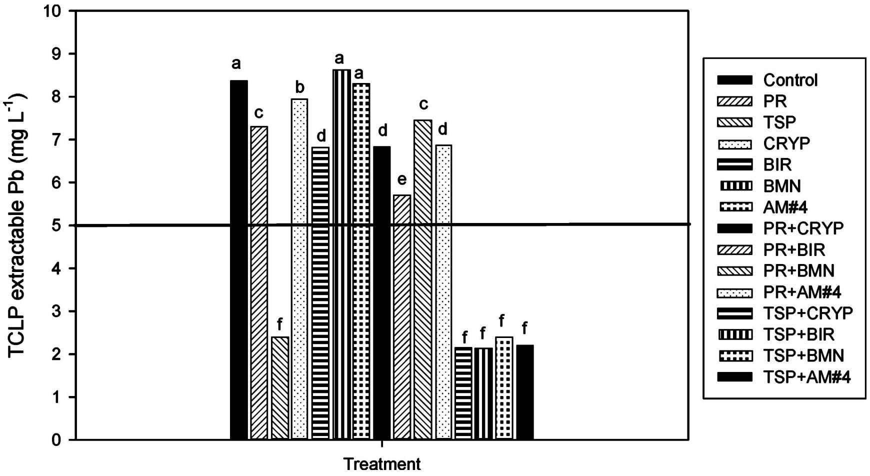

Figure 2. Modified toxicity characteristic leaching procedure (TCLP) test results for Pb in the Dearing material. The horizontal line denotes the critical value for hazardous waste. Means with the same letter are not significantly different at $P < 0.05$.

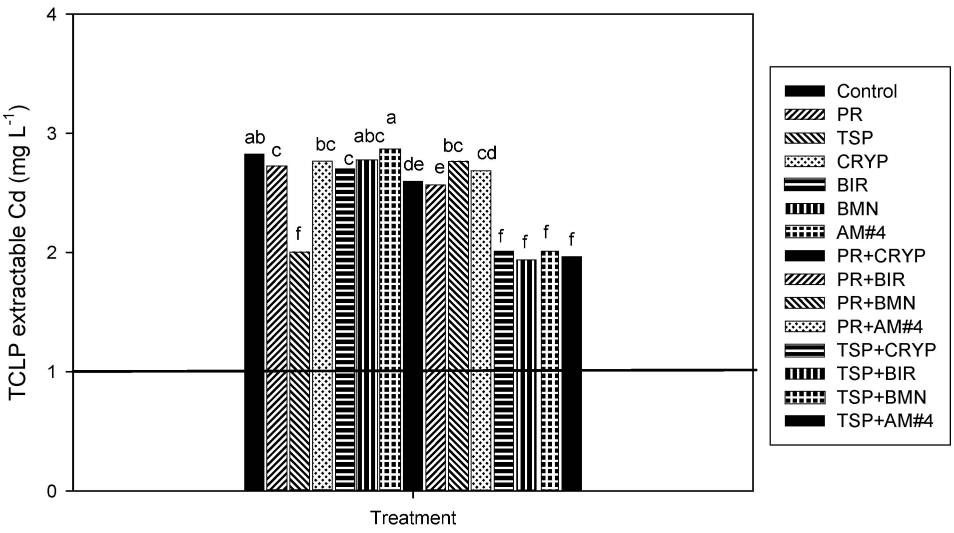

Figure 3. Modified toxicity characteristic leaching procedure (TCLP) test results for Cd in the Dearing material. The horizontal line denotes the critical value for hazardous waste. Means with the same letter are not significantly different at $P < 0.05$.

treatments produced the greatest reduction in extractable Cd and Pb, however, with no significant differences among them. This reduction was great enough to bring the extractable Pb under the critical value, but this was not true for extractable Cd. Similar results were found by Hettiarachchi *et al.* (2000). Chen *et al.* (1997) found a reduction in TCLP extractable Pb and Cd upon addition of mineral apatite. That reduction for Pb was attributed to the precipitation of a wide array of pyromorphites, whereas sorption of Cd, ion exchange, or the precipitation of Cd as octavite ($CdCO_3$) were more pronounced than the formation of Cd phosphates.

In the untreated TCR soil material, extractable Cd and Pb were already present at less than the critical values for toxic waste (data not shown). All treatments significantly reduced extractable Cd in the TCR soil material compared with the control. The TSP treatments had the greatest reduction in extractable Cd and Pb, with no significant differences among them. The PR+BIR treatment was also as effective as the TSP treatments. Extractable Pb in TCR was decreased significantly by all treatments except BMN. The greatest reduction occurred with TSP+BIR and TSP+CRYP, but reductions from these treatments did not significantly differ from those of TSP+AM#4. The commercially available Mn oxides alone were not as effective as synthetic ones in reducing the extractable Pb in TCR and Dearing.

4. Conclusions

In general, soil Pb bioaccessibility was reduced by using PR, TSP, or synthetic Mn oxides alone, and commercially available Mn oxides were less effective as a sole amendment. Combining PR or TSP with synthetic Mn oxides was more effective in reducing Pb bioaccessibility, compared with using either of the materials alone. Enhanced sorption of Pb onto P-affected Mn oxide surfaces, plus the formation of insoluble Pb compounds such as pyromorphites, likely contributed to this effect. In general, the PBET results showed that Pb bioaccessibility in treated samples decreased with time.

Commercially available Mn oxides were as effective as synthetic ones for some soils when combined with P, and could be a cost-effective alternative to synthetic Mn oxides under some circumstances. The effectiveness of the treatments differed from soil to soil. The maximum reduction in Pb bioaccessibility was in the chat material, whereas the least reduction was in the Dearing smelter slag. The synthetic Mn oxides adsorbed more Pb than did commercial ones. Between the synthetic Mn oxides, BIR had a greater Pb adsorption, although it has a less surface area than CRYP does. The layer structure of the BIR might explain its greater adsorption capacity compared with CRYP.

Triple superphosphate produced the greatest reduction in TCLP-extractable Pb and Cd. For Pb in the Dearing sample, the reduction was sufficient to reduce extractable Pb below the critical value for hazardous waste.

References

Backes, C. A., McLaren, R. G., Rate, A. W. and Swift, R. S.: 1995, 'Kinetics of cadmium and cobalt desorption from iron and manganese oxides', *Soil Sci. Soc. Am. J.* **59**, 778–785.

Calace, N., Petronio, B. M., Picciolo, M. and Pietroletti, M.: 2002, 'Heavy metal uptake by barley growing in polluted soils: Relationship with heavy metal speciation in soils', *Commun. Soil Sci. Plant. Anal.* **33**, 103–115.

Chen, X., Wright, J. V., Conca, J. L. and Peurrung, L. M.: 1997, 'Evaluation of heavy metal remediation using mineral apatite', *Water Air Soil Pollut* **98**, 57–78.

Davis, A., Drexler, J. W., Ruby, M. W. and Nicholson, A.: 1993, 'Micromineralogy of mine wastes in relation to lead bioavailability, Butte, Montana', *Environ. Sci. Technol.* **27**, 1415–1425.

Godtfrodsen, K. L. and Stone, A. T.: 1994, 'Solubilization of manganese dioxide-bound copper by naturally occurring organic compounds', *Environ. Sci. Technol.* **28**, 1450–1458.

Gradwohl, R.: 1994, 'Heavy metal bioavailability of contaminated soils, remediation methods and long term stability', Master's Thesis. Oklahoma State University, Stillwater, Oklahoma.

Hare, L. and Tessier, A.: 1996, 'Predicting animal cadmium concentrations in lakes', *Nature* **360**, 430–432.

Hettiarachchi, G. M., Pierzynski, G. M. and Ransom, M.: 2001, '*In situ* stabilization of soil lead using phosphorus', *J. Environ. Qual.* **30**, 1214–1221.

Hettiarachchi, G. M., Pierzynski, G. M. and Ransom, M.: 2000, '*In situ* stabilization of soil lead using phosphorus and manganese oxide', *Environ. Sci. Technol.* **34**, 4614–4619.

Joint Committee on Powder Diffraction Standards International Center for Diffraction Data: 1987, Powder diffraction file. Alphabetical index/ inorganic phases. Swarthmore, PA, USA.

Laperche, V., Traina, S. J., Gaddam, P. and Logan, T. J.: 1996, 'Chemical and mineralogical characterizations of Pb in a contaminated soil: Reactions with synthetic apatite', *Environ. Sci. Technol.* **30**, 3321–3326.

Ma, Q. Y., Logan, T. J. and Traina, S. J.: 1995, ‘Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks’, *Environ. Sci. Technol.* **29**, 1118–1126.

Ma, Q. Y., Logan, T. J., Traina, S. J. and Ryan, J. A.: 1994, ‘Effects of NO_3^-, Cl^-, F^-, SO_4^{-2}, and CO_3^{-2} on Pb^{+2} immobilization by hydroxyapatite’, *Environ. Sci. Technol.* **28**, 408–418.

Ma, Q. Y., Traina, S. J. and Logan, T. J.: 1993, ‘*In situ* lead immobilization by apatite’, *Environ. Sci. Technol.* **27**, 1803–1810.

McBride, M. B.: 1994, *Environmental Chemistry of Soils*. Oxford University Press, Inc. NY, 406 pp.

McKenzie, R. M.: 1971, ‘The synthesis of birnessite, cryptomelane, and some other oxides and hydroxides of manganese’, *Mineralogical Magazine* **38**, 493–502.

McKenzie, R. M.: 1980, ‘The adsorption of lead and other heavy metals on oxides of manganese and iron’, *Aust. J. Soil Res.* **18**, 61–73.

Medlin, E. A.: 1997, ‘An in vitro method for estimating the relative bioavailability of lead in humans’, Master’s Thesis, Department of Geological Sciences, University of Colorado, Boulder, CO, USA.

Nelson, Y. M., Lion, L. W., Ghiorse, W. C. and Shuler, M. L.: 1999, ‘Production of biogenic Mn oxides by Leptothrix discophors SS-1 in a chemically defined growth medium and evaluation of their Pb adsorption characteristics’, *Appl. Environ. Microb.* **65**, 175–180.

Nriagu, J. O.: 1974, ‘Lead orthophosphates-IV. Formation and stability in the environment’, *Geochimica et Cosmochimica Acta* **38**, 887–898.

Padmanabham, D.: 1983, ‘Comparative study of the adsorption-desorption behavior of copper(II), zinc(II), cobolt(II), and lead(II) at the geothite-solution interface’, *Aust. J. Soil Res.* **21**, 515–525.

Pearson, M. S., Maenpaa, K., Pierzynski, G. M. and Lydy, M. J.: 2000, ‘Effects of soil amendments on earthworm bioavailability in metal contaminated artificial soils’, *J. Environ. Qual.* **29**, 1611–1617.

Ruby, M. V., Davis, A. and Nicholson, A.: 1994, ‘*In situ* formation of lead phosphates in soils as a method to immobilize lead’, *Environ. Sci. Technol.* **28**, 646–654.

Ruby, M. V., Davis, A., Schoof, R., Eberle, S. and Sellstone, C. M.: 1996, ‘Estimation of bioavailability using a physiologically based extraction test’, *Environ. Sci. Technol.* **30**, 422–430.

SAS institute Inc., 1987, SAS user’s guide: Statistics, version 6 edition. Cary, N.C.

Schoof, R. A., Butcher, M. K., Sellstone, C., Ball, R. W., Fricke, J. R., Keller, V. and Keehn, B.: 1995, ‘An assessment of lead absorption from soil affected by smelter emissions’, *Environ. Geochem. and Health* **17**, 189–199.

Singh, S. P., Ma, L. Q. and Harris, W. G.: 2001. ‘Heavy metal interactions with phosphoric clay: Sorption and desorption behaviour’, *J. Environ. Qual.* **30**, 1961–1968.

Sposito, G.: 1989, *The Chemistry of Soils*. Oxford Univ. Press. Inc., New York, NY, 277 pp.

Stanforth, R. R. and Chowdhury, A. K.: 1993, ‘*In situ* method for decreasing heavy metal leaching from soil or waste’, US patent 5, 202, 033. Date issued April 13.

United States Environmental Protection Agency: 1991, Test methods for evaluating solid wastes. Physical/Chemical Methods, Method 1311. EPA/530/SW-846.

Valsami-Jones, E., Ragnarsdottir, K. V., Putnis, A., Bosbach, D., Kemp, A. J. and Cressey, G.: 1998, ‘The dissolution of apatite in the presence of aqueous metal cations at pH 2–7’, *Chemical Geology* **151**, 215–233.

Wang, H.: 2000, ‘Lead adsorption on Mn oxide surfaces modified with phosphate’, MS Thesis, Department of Agronomy, Kansas State University, Manhattan, KS, USA.

Weesner, F. J. and Bleam, W. F.: 1998, ‘Binding characteristics of Pb2+ on anion-modifed and pristine hydrous oxide surfaces studied by electrophoretic mobility and X-ray absorption spectroscopy’, *J. Colloid and Interface Sci.* **205**, 380–389.

Zhang, P. and Ryan, J. A.: 1999a, ‘Formation of chloropyromorphite from galena (PbS) in the presence of hydroxyapatite’, *Environ. Sci. Technol.* **33**, 618–624.

Zhang, P. and Ryan, J. A.: 1999b, ‘Transformation of Pb (II) from cerrusite to chloropyromorphite in the presence of hydroxyapatite under varying conditions of pH’, *Environ. Sci. Technol.* **33**, 625–630.