THE USE OF PHOSPHORUS AND OTHER SOIL AMENDMENTS FOR *IN SITU* STABILIZATION OF SOIL LEAD

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ABSTRACT

This study was conducted to evaluate the effects of P, Mn oxide, and time on bioavailable Pb in five metal-contaminated soils or mine spoils in the absence or the presence of plants, and to evaluate the effect of those treatments on phytoavailability of Pb, Cd, and Zn. The addition of P or Mn oxide reduced bioavailable Pb compared to control, as measured by a modified physiologically based extraction procedure (PBET). The maximum reduction in bioavailable Pb was always observed with the addition of P and manganese oxides together. X-ray diffractometry analyses support the PBET results, indicating that more "pyromorphite-like minerals" may have formed in the presence of both P and Mn oxides. Synergistic effects from the presence of Mn oxide with P in reducing Pb bioavailability were still evident after extensive cropping of the soils. Several mechanisms, alone or in combination, may have been responsible for this synergistic effect. The concentrations of Pb, Cd, and Zn in sudax and Swiss chard plant tissues were reduced in the presence of soluble P, and soluble P or insoluble P with Mn oxides. This new improved *in situ* technique to remediate Pb-contaminated soil and mine wastes has advantages over standard methods.

Key words: *in situ stabilization, bioavailable PB, soil remediation*

INTRODUCTION

Lead-contaminated soil is a primary source of Pb exposure to young children. Remediation procedures used today for Pb-contaminated soils are costly, disruptive, and not sustainable. *In situ* remediation techniques overcome many of these disadvantages. It has been suggested that the formation of Pb phosphates in soils contaminated with both Pb and P is responsible for immobilizing Pb, thereby reducing the bioavailability of Pb (Ruby et al., 1994). Lead phosphates, and in particular pyromorphites, are some of the most stable forms of Pb in soils under a wide range of environmental conditions (Nriagu, 1973). Experimental evidence supports the hypothesis that lead phosphates can form rapidly in the presence of adequate lead and phosphate in aqueous systems (Ma et al., 1993; Zhang and Ryan, 1999) and in Pb-contaminated soils (Laperche et al., 1996; Zhang et al., 1998). In addition to the formation of insoluble Pb compounds as a means of reducing Pb bioavailability, adsorption of Pb represents another potentially important process for reducing Pb bioavailability. McKenzie (1980) demonstrated that Pb adsorbs more or less irreversibly to manganese (IV) (hydr)oxides over iron oxides by a factor of 40, suggesting that manganese oxides can be used as a strong adsorbent or scavenger for Pb. Two incubation studies were conducted to evaluate the effects of (I) P source, level of P, and time and (II) P and/or Mn oxide on bioavailable Pb in five metal-contaminated soils or mine spoils. A greenhouse experiment was conducted to evaluate the effect of a presence of plants on bioavailable Pb in *in situ*-treated (P or/and Mn oxide), Pb-contaminated soils, and to evaluate the effect of those treatments on phytoavailability of Pb, Cd, and Zn.

MATERIALS AND METHODS

Five contaminated soils/mine waste materials (TCR, AR, Joplin, Dearing, and Galena) were collected from the tri-state mining area. Total metal concentrations ranged from 1200 to 9100 mg Pb/kg, 30 to 190 mg Cd/kg, and 4500 to 42600 mg Zn/kg. Selected physical and chemical properties of the materials are given in Table 1.

Incubation Study I

Seven treatments were used as follows: zero P (control); 2500 mg P/kg as triple superphosphate (TSP2500); phosphate rock (PR2500); phosphoric acid (PA2500) or preacidification to pH 5.0 with acetic acid followed by TSP (acetic); and 5000 mg of TSP (TSP5000). Predetermined amounts of CaO were added for all samples, except for the control and PR, 24 hrs after P treatment to increase the soil pH to 7.0 to 7.5. Triplicate samples were incubated for five different sampling times (3, 28, 84, 252, and 365 days) at 20% gravimetric moisture content and 25°C. Air-dried samples were analyzed for soil pH, plant available P (Bray-1 extractable P), and bioavailable Pb by a modified *in vitro bioaccessibility* test (physiologically based extraction test- PBET) (Ruby et al., 1996). The concentration of Pb in PBET extracts was analyzed using ICP-AES. X-ray diffraction data was collected for the <10 :m size fraction separated by using an ATM sonic sifter.

Incubation Study II

Nine treatments were used as follows: zero P (control); 5000 mg P/kg as triple super phosphate (TSP) or phosphate rock (PR); 2500 mg of MnO_2/kg (X); 5000 mg of MnO_2/kg (2X); PR (PR5000); 2500 mg of MnO_2 + 5000 mg of P as TSP (TSP+X) or PR (PR+X); and 5000 mg of MnO_2 + 5000 mg of P as TSP (TSP+2X) or PR (PR+2X). Predetermined amounts of CaO were added for all samples, except for the control and PR, 24 hrs after P treatment to increase the soil pH. Triplicate samples were incubated for three different sampling times (4, 12, and 24 weeks) at 20% gravimetric moisture content and 25°C. Air-dried samples were analyzed for soil pH and bioavailable Pb. X-ray diffraction data was collected as described before.

Table 1. Selected chemical and physical properties of soil materials (#2 mm fraction) prior to treatment applications.

Soil Material	Sand	Silt	Clay	CEC	Total P	pH	Organic Carbon
	%			cmol/kg	mg/kg		g/kg
TCR	38	42	20	18.3	998	7.0	26.1
AR	44	40	16	18.1	855	7.0	26.6
Joplin	56	30	14	38.0	750	6.7	36.5
Chat	78	16	6	2.9	293	7.2	5.8
Dearing	76	20	4	45.6	360	6.0	37.1

Greenhouse Study

Sudax [*Sorghum vulgare* (L.) Moench] and Swiss chard variety Fordhook giant [*Beta vulgaris* (L.) Koch] were used. Eight treatments in triplicate were evaluated as follows: no P (control); 2500 mg P/kg soil as TSP fertilizer (TSP2500); 5000 mg P/kg soil as TSP (TSP5000) or PR (PR5000); 5000 mg of MnO_2 /kg soil (2X); 2500 mg P as triple superphosphate fertilizer plus 5000 mg of MnO_2/kg of soil (TSP2500+2X); 5000 mg P as TSP plus 5000 mg of MnO_2/kg of soil (TSP5000+2X); and 5000 mg P as PR plus 5000 mg of MnO_2/kg of soil (PR5000+2X). After the fourth cutting of sudax, soil samples were collected, air dried, and analyzed for bioavailable Pb. Plant tissue Pb, Cd, Zn, and P concentrations were also measured.

RESULTS AND DISCUSSION

Incubation Study I

The acetic, PA2500, and TSP5000 treatments reduced soil pH to 5.2"0.3 in all materials except chat (data not shown). The addition of TSP2500 reduced soil pH to 5.7"0.2 in all materials, whereas PR had no effect on soil pH even at the highest level. Calcium oxide additions increased soil pH to near 7.0 in most samples. The samples that received TSP5000 had the lowest pH of all materials tested, indicating that the CaO added was not sufficient to neutralize the acidity created by the dissolution of TSP.

Plant-available P in soils can be estimated by one of several methods depending on soil characteristics (Kuo, 1996). Bray-1 extractable P is generally used for acidic to near-neutral soils. Soils treated with TSP (TSP2500, TSP5000, and acetic) and PA2500 had levels of Bray-1 P well above those required for normal plant growth (Table 2). However, PR2500 and PR5000 did not change Bray 1-P levels significantly, indicating the relative insolubility of PR compared to the other P sources. Although excessive levels of plant-

Table 2. Bray-1 extractable P in soil materials at two sampling times.

	Soil Material									
	TCR		AR		Joplin		Chat		Dearing	
Treatment	3 d	365 d	3 d	365 d	3 d	365 d	3 d	365 d	3 d	365 d
	---------------------------------------mg/kg---------------------------------------									
Control	124 d†	123 e	132 e	136 c	109 e	103 e	14 d	17 e	4 e	12 e
TSP2500	1705 b	1728 c	1796 c	1336 b	1759 c	1565 c	1479 b	1092 c	862 b	685 b
TSP5000	2864 a	2876 a	3061 a	2140 a	2841 a	2527 a	2737 a	2181 a	1488 a	1133 a
acetic	1427 c	1407 d	1148 d	1191 b	1507 d	1419 d	732 c	859 d	746 c	561 c
PR2500	146 d	142 e	158 e	160 c	132 e	121 e	32 d	48 e	11 e	15 e
PR5000	159 d	162 e	176 e	203 c	162 e	155 e	44 d	79 e	20 e	22 e
PA2500	1855 b	1846 b	2239 b	1988 a	1935 b	1809 b	1375 b	1316 b	487 d	437 d

† Means with the same letter within a column are not significantly different at P<0.05.

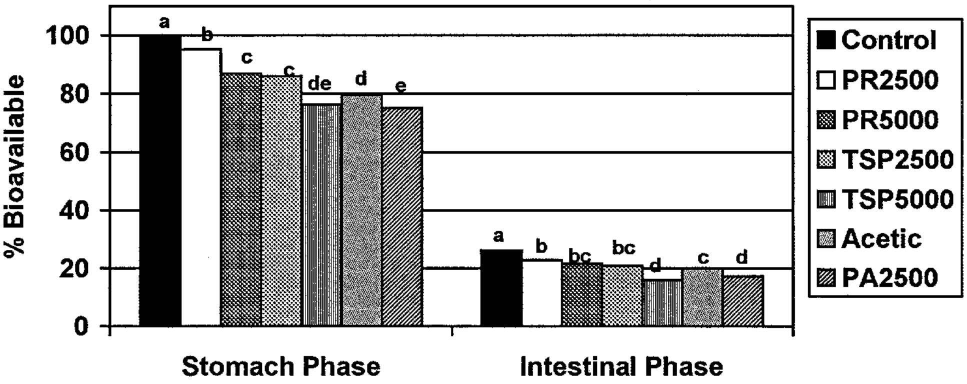

Figure 1. Bioavailable Pb by PBET for the Dearing material. Bioavailable Pb is expressed as a percentage of bioavailable Pb in the control sample. Means with the same letter within a phase are not significantly different at P<0.05.

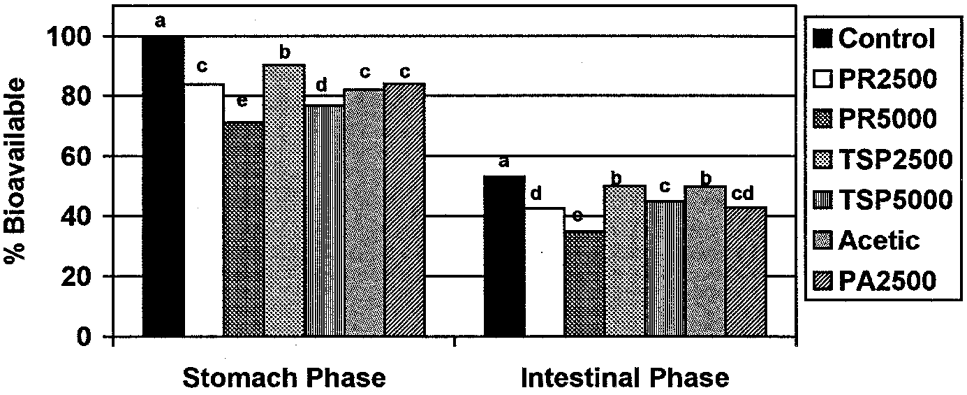

Figure 2. Bioavailable Pb by PBET for the Dearing material. Bioavailable Pb is expressed as a percentage of bioavailable Pb in the control sample. Means with the same letter within a phase are not significantly different at P<0.05.

available P are not harmful to plants, they have been correlated with higher P losses in runoff. Thus, PR may present less of an environmental risk from enhanced eutrophication compared to the other P sources.

In general, the reproducibility of bioavailable Pb values was higher in the stomach phase than in the intestinal phase. Average coefficients of variability were 6"3% for the stomach phase and 14"6 % for the intestinal phase.

The treatment-by-time interaction was not significant and, therefore, data are reported as averaged over time. Without exception, all soil amendments reduced bioavailable Pb in both the stomach and intestinal phases, compared to the control (only Dearing and Joplin data are shown; Figures 1 and 2).

For the Dearing material, the PA2500 treatment produced the greatest reduction in bioavailable Pb and PR2500, the least for both the stomach and intestinal phases (Figure 1). Preacidification with acetic acid produced significantly lower bioavailable Pb compared to the same amount of P from TSP or PR in this sample, but not in the others (Figures 1 and 2).

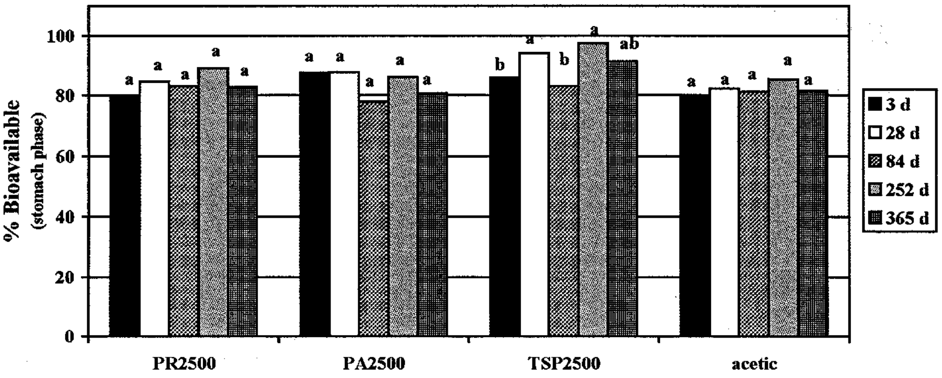

Figure 3. Effect of time on bioavailable Pb by PBET for the Joplin material. Means with the same letter within a treatment are not significantly different at P<0.05.

A slag is a vitrified glass by-product formed by the smelting process and generally is composed of Fe_2O_3, CaO, and SiO_2 (Medlin, 1997). The pH of ~6.0 for the Dearing smelter slag material indicates that it did not contain any CaO. However, Pb solids in this material may have Fe and Si oxide rinds, and dissolution of these rinds during preacidification could have promoted the reaction between the Pb solids and P.

For all materials except Dearing, PR was equally or more effective than TSP or H_3PO_4 in reducing bioavailable Pb. The dissolution of PR and subsequent formation of pyromorphite can be expressed as follows:

$$Ca_5(PO_4)_3X(s) + 6H^+(aq) \Leftrightarrow 5Ca^{2+}(aq) + 3H_2PO_4^-(aq) + X^-(aq) \quad (1)$$

$$5Pb^{2+}(aq) + 3H_2PO_4^-(aq) + X^-(aq) \Leftrightarrow Pb_5(PO_4)_3X(s) + 6H^+(aq) \quad (2)$$

where X= F^-, OH^-, or Cl^-. The addition of P as PR had little or no effect on soil pH (data not shown). Because the dissolution of apatite requires free H^+ ions, PR applied to a near-neutral soil material would not undergo dissolution to a great extent. This unreacted P could then dissolve in the stomach phase of the PBET, resulting in more Pb immobilization compared to any of the soluble P sources.

In this study, Pb bioavailability was influenced little by time, and results were similar for all materials. Data for the Joplin soil are shown as an example (Figure 3). The lack of a time effect suggests that either the reactions between soil Pb and P occurred within the first three days of the incubation and changed little thereafter, or that the reactions between soil Pb and P in the stomach-phase solution were not influenced by the contact time for soil Pb and P.

X-ray diffraction patterns for selected treatments of Dearing soil are shown in Figure 4. Of the three most prominent peaks of hydroxypyromorphite ($Pb_5(PO_4)_3OH$, HP), two can be seen without interference from quartz (2.85 and 2.97 Å, JCPDF 24-586). Both of these peaks also were present in the control, indicating that the materials contained pyromorphite prior to P amendment. The addition of P from the soluble P sources increased the intensity of the 2.85 Å peak, indicating that more "pyromorphite-like minerals" formed after P

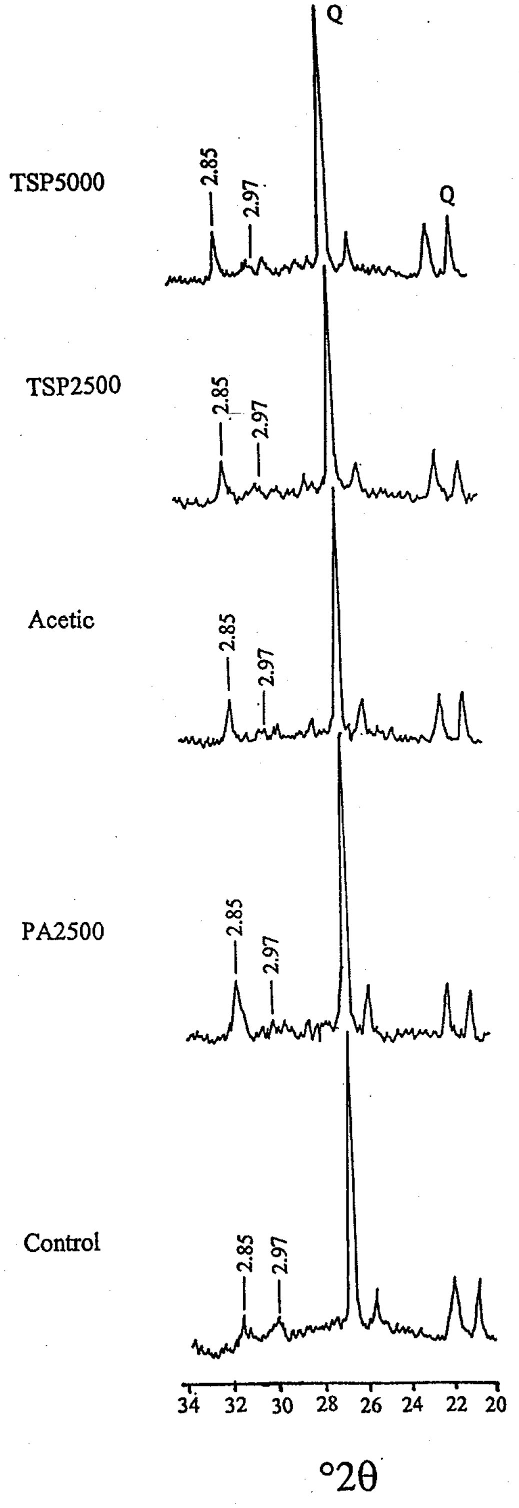

Figure 4. XRD patterns for selected treatments for the # 10-:m particle size fraction of the Dearing material.

addition. The phosphoric acid-treated samples (PA2500) had the most intense pyromorphite peak and showed the greatest reduction in bioavailable Pb by PBET (Figure 1). Two peaks at 2.85 and 2.97 Å, attributed to HP, were also present in the PR-treated Dearing sample, although the intensities were not different than the control (data not shown).

Incubation Study II

The treatment by time interaction was not significant and, therefore, data are presented as averaged over time (Figures 5 and 6). The use of either P or Mn oxide significantly reduced bioavailable Pb as measured by PBET in all five soils compared to the control. Increasing the amount of Mn oxide added further reduced bioavailable Pb. The greatest reduction in Pb bioavailability was observed when soils were treated with P and Mn oxides together. Several mechanisms, alone or in combination, may have been responsible for this synergistic effect. Those include enhanced sorption of Pb onto phosphate-sorbed Mn oxide surfaces; formation of insoluble pyromorphite-like minerals on the surfaces of Mn oxides; and reductive dissolution of Mn oxide in the acidic stomach phase of PBET test, along with P and Pb solids followed by reprecipitation of Pb and P, or Pb-Mn and P as stable compounds. Reduced soluble Mn in the stomach phase of PBET extractions of both Mn oxide and P-treated soils were observed in support of these hypotheses.

As observed in the previous incubation study, HP peaks (2.97 and 2.85 D) were present in the control indicating that HP was present in the Dearing material prior to P

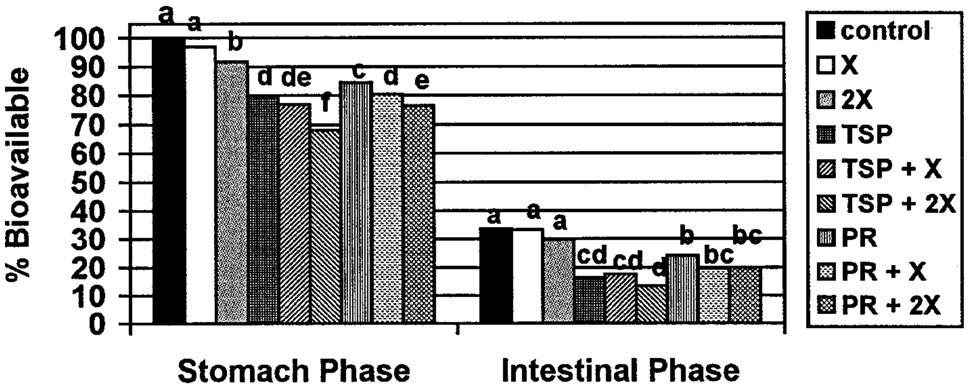

Figure 5. Bioavailable Pb by PBET for the Dearing material. Bioavailable Pb is expressed as a percentage of bioavailable Pb in the control sample. Means with the same letter within a phase are not significantly different at $P<0.05$.

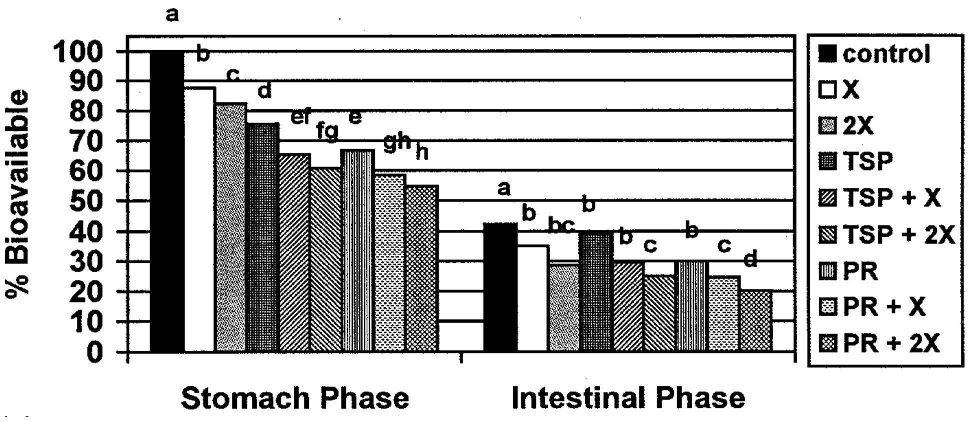

Figure 6. Bioavailable Pb by PBET for the Joplin material. Bioavailable Pb is expressed as a percentage of bioavailable Pb in the control sample. Means with the same letter within a phase are not significantly different at $P<0.05$.

addition. Also, the addition of P as TSP increased the intensity of 2.85 D peak of HP, indicating that more "pyromorphite-like minerals" formed in the presence of P (data not shown).

Flouroapatite (FA) is the major component of the PR used in these studies. The three most intense peaks of FA were at 2.80, 2.77, and 2.70 D (JCPDF 15-876). Figure 7 shows those FA peaks in the samples that received PR. However, the intensity of those peaks was reduced and the symmetry was changed compared to the pure PR material (data not shown).

Only the most intense Mn oxide (cryptomelane) peak at 2.39 D was observed in the 2X-treated soil samples at four weeks (Figure 7). A complete disappearance of cryptomelane peaks was observed when cryptomelane was added with TSP (data not shown) or PR (Figure 7). Sorption of Pb onto oxides could be responsible for the disappearance of X-ray lines.

Greenhouse Study

The addition of P and/or Mn oxide significantly reduced bioavailable Pb compared to the

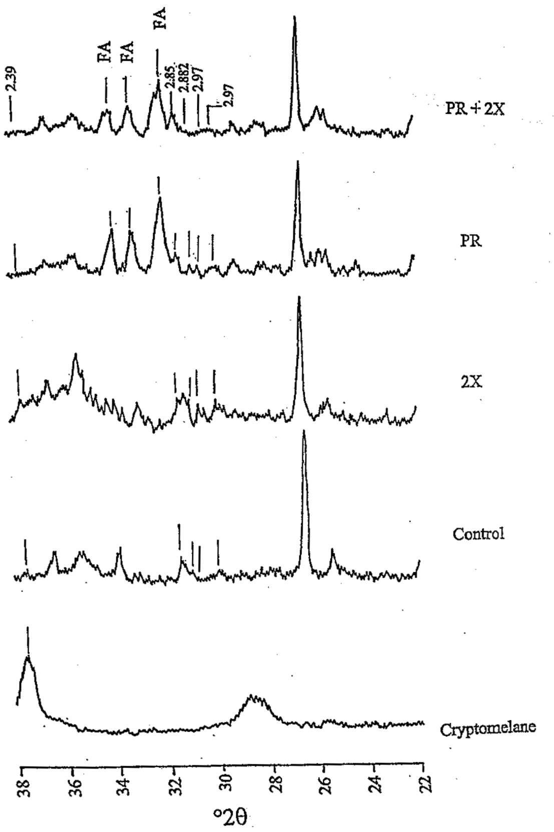

Figure 7. XRD patterns for cryptomelane and control, 2X, PR, and PR+2X treatments at four weeks for the Dearing material.

control, even after extensive cropping of the soils (Figure 8). The greatest reduction in soil bioavailable Pb was still observed in samples treated with a combination of P and Mn oxide in all materials tested. The addition of TSP2500 did not produce reductions in bioavailable Pb, suggesting that removal of P in the TSP-amended soils by plants could reverse the beneficial effect of P on bioavailable Pb, unless there is sufficient soluble P present (TSP2500 vs TSP5000) or soluble P is combined with Mn oxides (TSP2500 vsTSP2500+2X).

The concentrations of Pb, Cd, and Zn in shoot tissue of both sudax and Swiss chard were reduced upon soluble P addition (data not shown). The addition of cryptomelane also reduced tissue Pb concentrations in sudax. The addition of PR alone did not change plant tissue metal concentrations. The addition of PR and Mn oxide reduced plant tissue Pb concentrations, and to lesser extent Cd and Zn. Enhanced sorption of metals by P-sorbed Mn oxide surfaces could be the reason for this observation.

ACKNOWLEDGMENTS

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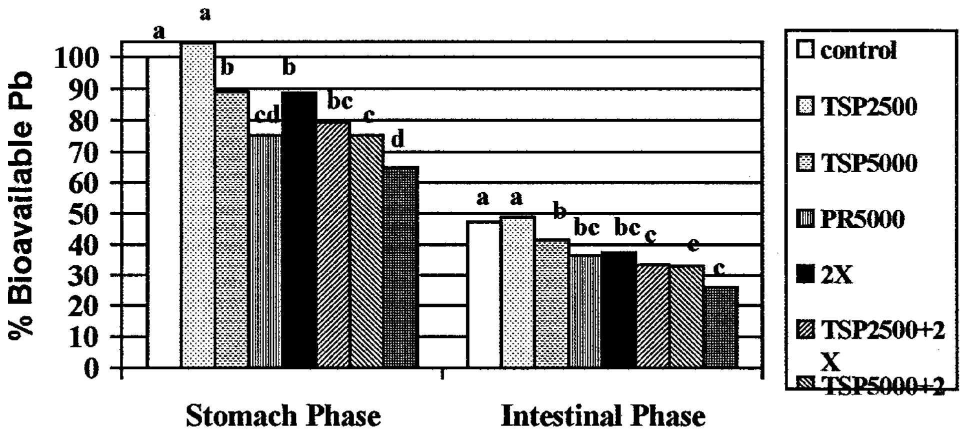

Figure 8. Bioavailable Pb by PBET for the Joplin soil after four cuttings of sudax. Bioavailable Pb is expressed as a percentage of bioavailable Pb in the control sample. Means with the same letter within a phase are not significantly different at $P<0.05$.

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