

**Effects of Phosphate Rock on Sequential Chemical Extraction
of Lead in Contaminated Soils**

Lena Q. Ma* and Gade N. Rao

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ABSTRACT

Lead contamination is of great concern because of its adverse effects on human health, especially children. This research evaluated the effects of phosphate rock on chemical associations of Pb in eight Pb-contaminated soils using a sequential extraction procedure. The chemical fractions are operationally defined by an extraction sequence in the order of increasing ability to dissolve Pb of lower solubilities. Additionally, more soluble forms of Pb are considered to be potentially more bioavailable than the less soluble forms. Lead in these soils was primarily associated with the carbonate and Fe-Mn oxide fractions (63–85%). Up to 21% of the Pb in these soils was associated with either the organic or the residual fraction and <11% was associated with the water-soluble and the exchangeable fractions. Phosphate rocks effectively converted Pb from the water soluble, exchangeable, carbonate, Fe-Mn oxide, and organic fractions (collectively the non-residual fraction) to the residual fraction, thus reducing Pb solubility and presumably bioavailability. Lead precipitation as a fluoropyromorphite-like mineral in these contaminated soils was suggested as the primary mechanism for reduced Pb solubility and Pb reduction in the nonresidual fraction. The effective conversion of Pb from potentially available fractions to the residual fraction suggests that phosphate rock has potential for in-situ immobilization in Pb contaminated soils.

LEAD IS A HEAVY METAL that is toxic to humans and animals. Its extensive use and widespread disposal

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in the environment have resulted in numerous Pb-contaminated soils (Turjoman and Fuller, 1987). The health concern with Pb-contaminated soils arises mostly from plant contamination by soil particles, and soil and dust ingestion by humans, especially children, and grazing animals (McBride, 1994). Therefore it is important to minimize adverse Pb impacts on the environment. Reducing Pb solubility and bioavailability in contaminated soils without removing Pb from the soil is one of such measures that could reduce Pb impacts on the environment.

The combination of containment and in-situ Pb immobilization is a promising technology to remediate Pb-contaminated soils (Czupyrna et al., 1989). The geochemical behavior of Pb indicates that phosphate, when present in sufficient amounts, reduces Pb solubility (Ma et al., 1993, 1994a,b, 1995; Nriagu, 1974; Ruby et al., 1994). Thus phosphate minerals have the potential to immobilize Pb in contaminated soils. Several insoluble Pb orthophosphate minerals may form after P reaction with Pb-contaminated soils depending on the reaction conditions, such as pH and presence of other anions and cations (Ma et al., 1993, 1994a,b, 1995). Both phosphate rocks and hydroxyapatite have been used as the primary P sources in these studies and both materials effectively reduced Pb solubility.

Ma et al. (1995) have shown that phosphate rock (primarily $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$) effectively immobilized Pb

Abbreviations: OC, Occidental Chemical Corp.; PR, phosphate rock.

from aqueous solutions, with Pb immobilization ranging from 39 to 100%. The primary mechanism of Pb immobilization is via dissolution of phosphate rock and subsequent precipitation of a fluoropyromorphite-like mineral ($Pb_{10}(PO_4)_6F_2$), although precipitation of Pb as hydrocerussite also occurred in some instances. Moreover, the potential of using Florida phosphate rock to immobilize aqueous Pb from Pb-contaminated soils was demonstrated (Ma et al., 1995). Florida phosphate rock effectively immobilized 22 to 100% aqueous Pb from 13 Pb-contaminated soils. In these studies, the effectiveness of phosphate rock to immobilize aqueous Pb was assessed based on reduction in aqueous Pb concentrations (Ma et al., 1995). Although aqueous Pb concentrations are critical for evaluating Pb bioavailability in contaminated soils, knowledge of Pb distribution in different geochemical forms will provide more detailed information on the effectiveness of Pb immobilization by phosphate rock.

Geochemical forms of trace metals in soil affect their solubilities, therefore directly influence their potential bioavailability (Xian, 1987, 1989). Thus, assessing environmental impacts of trace metals in soils by aqueous concentrations of trace metals is incomplete. In particular, it may be helpful to obtain information on the degree of bioavailability of trace metals (Scokart et al., 1987). Sequential extraction using various leaching agents is commonly used to help assess bioavailability of trace metals in soils. Numerous schemes for soils and sediments have been described (Gupta and Chen, 1975; Miller and McFee, 1983; Tessier and Campbell, 1988; Tessier et al., 1979; Welte et al., 1983). The extraction scheme is based on operationally defined fractions: water soluble, exchangeable, carbonate, Fe-Mn oxides, organic, and residual fractions (Tessier et al., 1979). It must be borne in mind that the extractions are not entirely specific and there will be overlap between the fractions. Despite these uncertainties, extraction procedures provide semiquantitative evidence regarding the forms of trace metals, and indirectly their bioavailability (Harrison and Wilson, 1982).

A major pathway for Pb exposure by small children is via direct soil ingestion, and an important question is the bioavailability of Pb from various sources. Lead in soil is present in different chemical or physical forms and thus its bioavailability may vary (Freeman et al., 1992). Epidemiological studies of children residing in communities contaminated by Pb from smelter or urban sources frequently have higher blood levels than children living in areas contaminated with Pb from mining wastes, even when soil Pb concentrations are similar

(Steele et al., 1990). It seems that differences in Pb source and thus Pb species rather than the total amount of Pb may help to account for the discrepancy. In this case, sequential extraction may be useful to indirectly assess Pb bioavailability in soils.

Assuming the nonresidual Pb (sum of water soluble, exchangeable, carbonate, Fe-Mn oxides, and organic fractions) is more bioavailable than the residual Pb, then the effectiveness of in-situ remediation of Pb-contaminated soils can be assessed using a fractionation scheme, with more effective treatment converting greater amounts of Pb from the nonresidual to the residual fraction or from more to less bioavailable forms, i.e., from the water soluble and exchangeable to carbonate, Fe-Mn oxide, or organic fractions. The scheme of Tessier et al. (1979), one of the most widely used, was selected to evaluate the efficacy of decontamination treatments (Pardo et al., 1990; Raret et al., 1988; Spevackova and Kucera, 1989).

The objectives of this study were to use sequential extraction to determine Pb distribution in eight Pb-contaminated soils and to evaluate the effectiveness of using phosphate rocks to immobilize Pb from Pb-contaminated soils.

MATERIALS AND METHOD

Materials

Eight Pb-contaminated soils were collected from various U.S. locations. The soil samples were passed 1-mm screen and their properties are shown in Tables 1 and 2. These soils reflect two sources of Pb contamination: agricultural activities, such as application of the pesticide $PbHAsO_4$; and industrial activities, such as smelting. Phosphate rock from Occidental Chemical Corp. (OC), one of the most effective phosphate rocks to immobilize Pb (Ma et al., 1995), was used in this study. It was ground to fine powder using a disk mill. It has a specific surface area of $18200 \text{ m}^2 \text{ kg}^{-1}$, as measured by N_2 -BET adsorption using a Micromeritics Flowsorb 2300 surface area analyzer.

Experimental Procedure

Phosphate rock of 0, 0.125, or 0.25 g and 1 g of each soil were reacted with 15 mL deionized for 2 h in a 40-mL polycarbonate centrifuge tube at room temperature, and the following fractions were obtained: the water soluble, exchangeable, carbonate, Fe-Mn oxides, organic, and residual, using the procedure of Tessier et al. (1979).

Water Soluble. Soil sample extracted with 15 mL of deionized water for 2 h.

Exchangeable. The residue from water soluble fraction is extracted with 8 mL of 1 M MgCl_2 (pH 7.0) for 1 h.

Carbonate-Bound. The residue from exchangeable fraction

Table 1. Properties of the eight Pb-contaminated soils used in this study.

Sample name	Abbreviation	Locations	Source of contamination
Burch	BU	Washington	$PbHAsO_4$
Twin	TW	Washington	$PbHAsO_4$
East Field 1	EF1	Montana	smelter
East Field 2	EF2	Montana	smelter
PTC	PT	Oklahoma	smelter
BPS	BP	Pennsylvania	battery breaking site
AEC 1-1	DA	Connecticut	incineration ash
Area 40	DU	Washington	building demolition

Table 2. Total elemental concentrations, organic matter content, and suspension pH of the 8 Pb-contaminated soils.

Sample	pH [†]	SOM [‡]	Al	Fe	Ca	Mg	P	Pb	Mn	Ba	Zn	Cu	Ni	Cd
mg kg ⁻¹								mg kg ⁻¹						
BU	5.85	25	87.1	38.5	21.1	88	10	2680	762	594	154	48.4	29	14
TW	7.28	23	90.9	26.4	24.6	7.7	08	705	551	763	115	20.5	9.3	41
EF1	6.78	21	68.8	35.0	15.5	8.5	14	5 970	673	751	2 430	1 260	19	158
EF2	6.80	22	73.4	35.1	15.2	8.7	13	4480	664	748	1310	639	19	93
PT	7.51	61	30.5	35.4	15.3	2.1	1.0	1300	544	486	574	241	98	41
BP	6.14	15	57.1	33.4	31.8	5.2	05	40 100	642	384	86	120	20	62
DA	7.51	19	48.5	35	3.90	2.9	03	12500	1520	518	782	1010	29	41
DU	5.53	120	54.1	120	17.6	9.6	09	7 640	1 060	2 630	5 680	2 620	21	6.4

[†] Measured in 1:2 soil/water suspensions after 24 h.

[‡] Soil organic content.

is extracted with 8 mL of 1 M NaOAc (adjusted to pH 5.0 with HOAc) for 5 h.

Fe-Mn Oxides-Bound. The residue from carbonate fraction is extracted with 0.04 M NH₂OH.HCl in 25% (v/v) HOAc at 96°C with occasional agitation for 6 h.

Organic-Bound. The residue from Fe-Mn oxide fraction is extracted with 3 mL of 0.02 M HNO₃ and 5 mL of 30% H₂O₂ (adjusted to pH 2 with HNO₃). The mixture is heated to 85°C for 2 h, with occasional agitation. A second 3 mL aliquot of 30% H₂O₂ (pH 2 with HNO₃) is added and the mixture heated again to 85°C for 3 h with intermittent agitation. After cooling, 5 mL of 3.2 M NH₄OAc in 20% (v/v) HNO₃ is added and the samples diluted to 20 mL and agitated continuously for 30 min.

Residual. The residues from organic fraction are digested using a HF-HCl/HNO₃ dissolution procedure in a Parr 4745 acid digestion Bomb (Bernas, 1968). A standard Reference Material (2711 Montana Soil), obtained from National Insti-

tute of Standards and Technology (Gaithersburg, MD 20899), was used to verify the acid digestion method used in this study. The recovery for all trace metals in the standard was within 100 ± 10%.

After each successive extraction, separation was done by centrifuging (Beckman Model J2-21) at 14K rpm (15400 × g) for 30 min. The supernatants were removed with a pipette, filtered with 0.2-µm Nucleopore polycarbonate membrane filters, and analyzed for metals. The residue was washed with 8 mL of deionized water followed by vigorous hand shaking, and then followed by 30 min of centrifugation before the next extraction.

Analytical Methods

All extractions were conducted in triplicate in acid-washed (5% HNO₃) polycarbonate labware. All chemicals used in this

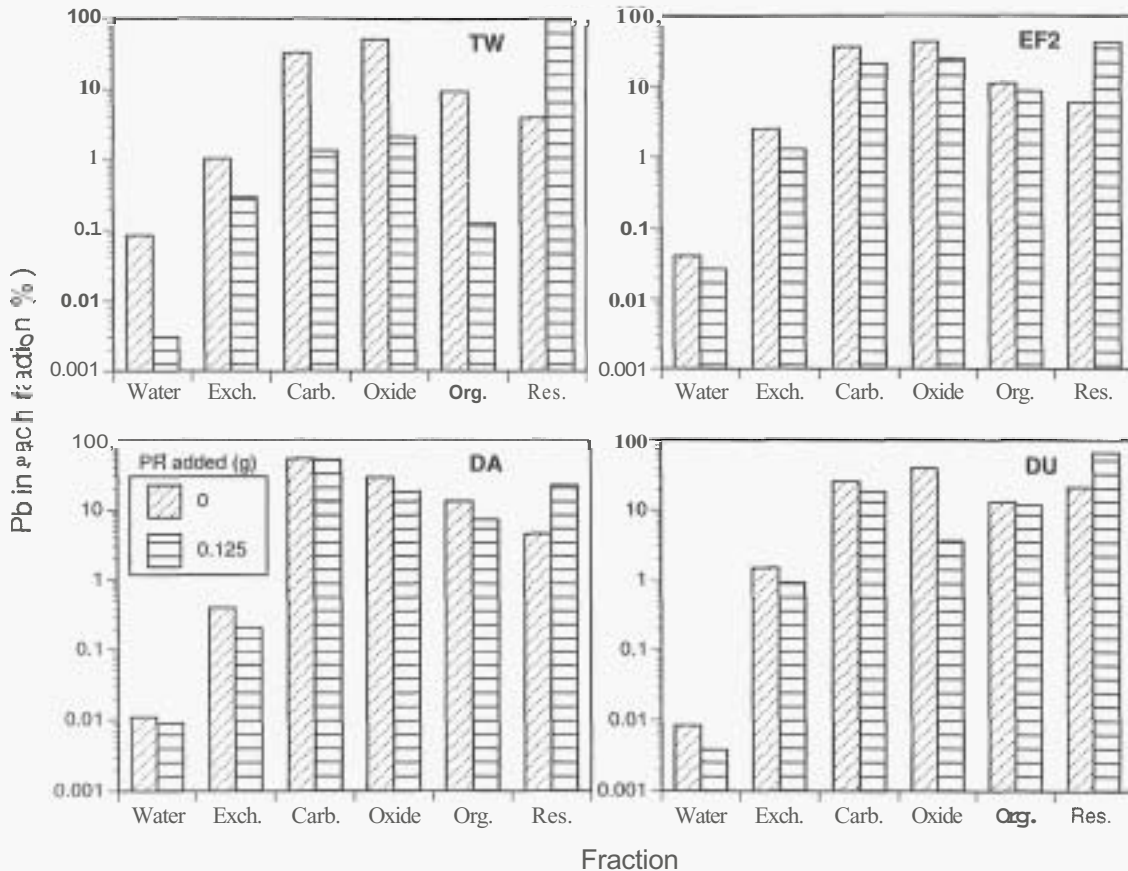


Fig. 1. Lead distribution in different fractions of four Pb-contaminated soils in the presence of 0.125 g of OC phosphate rock (PR).

study were of analytical grade or better. Double deionized water was used.

Total Pb concentrations of the supernatants from each step were analyzed by atomic absorption spectrophotometer (Perkin-Elmer 2380) equipped with a graphite furnace atomizer. Flame atomic absorption was used to analyze Pb concentrations $>1 \text{ mg L}^{-1}$ and a graphite furnace atomizer was used to measure Pb concentrations $<1 \text{ mg L}^{-1}$. Multilevel standards (Fisher Scientific) for Ca and Pb were prepared for each extraction step in the same matrix as the extracting reagents to minimize matrix effects. Blanks were used for background correction and other sources of error. At least one duplicate and one spike sample were run every 20 samples and the spike recovery was found to be within $100 \pm 10\%$.

RESULTS AND DISCUSSION

Lead Distribution in Lead-Contaminated Soils

Lead in these soils was primarily associated with the Fe-Mn oxide fraction (44–55%), except BP and DU soils in which Pb was mainly associated with the carbonate fraction (53–57%) (Fig. 1 and 2). There is no apparent reason why Pb-carbonate was the primary fraction in the BP and DU, since their pHs (6.14 and 5.53) were too low for the presence of carbonates. This may imply poor selectivity of the fractionation scheme for carbon-

ate. Others have also found Pb to be associated with Fe and Mn oxides (Chlopecka, 1993; Jordao and Nickless, 1989; Ramos et al., 1994). The sum of Fe-Mn oxide and carbonate fractions accounted for 63 to 85% of the Pb in these contaminated soils, which is consistent with the report that Pb was predominantly associated with these two fractions (Harrison and Wilson, 1982). Zimdahl and Skogerboe (1977) reported a strong correlation between Pb and organic C in the soils they studied, implying the importance of organic C to fix Pb in the soils. However, these results were based on soils spiked with $\text{Pb}(\text{NO}_3)_2$ instead of natural Pb-contaminated soils, which may explain the difference. The next most abundant fractions in the eight Pb-contaminated soils were the organic and residual fractions, ranging from 0.9 to 19% and 4 to 21%, respectively (Fig. 1 and 2). Gibson and Farmer (1986) reported that 13% of the Pb in six soils containing Pb concentration of $>400 \text{ mg kg}^{-1}$ was associated with the residual fraction, which is consistent with our results. The sum of Pb associated with exchangeable and carbonate fractions in our study accounted for 27 to 68% of the total Pb, which indicates that Pb in these soils may be highly available for plants. Xian (1989) found that the sum of the exchangeable and the carbonate-bound forms were strongly correlated with Pb uptake by

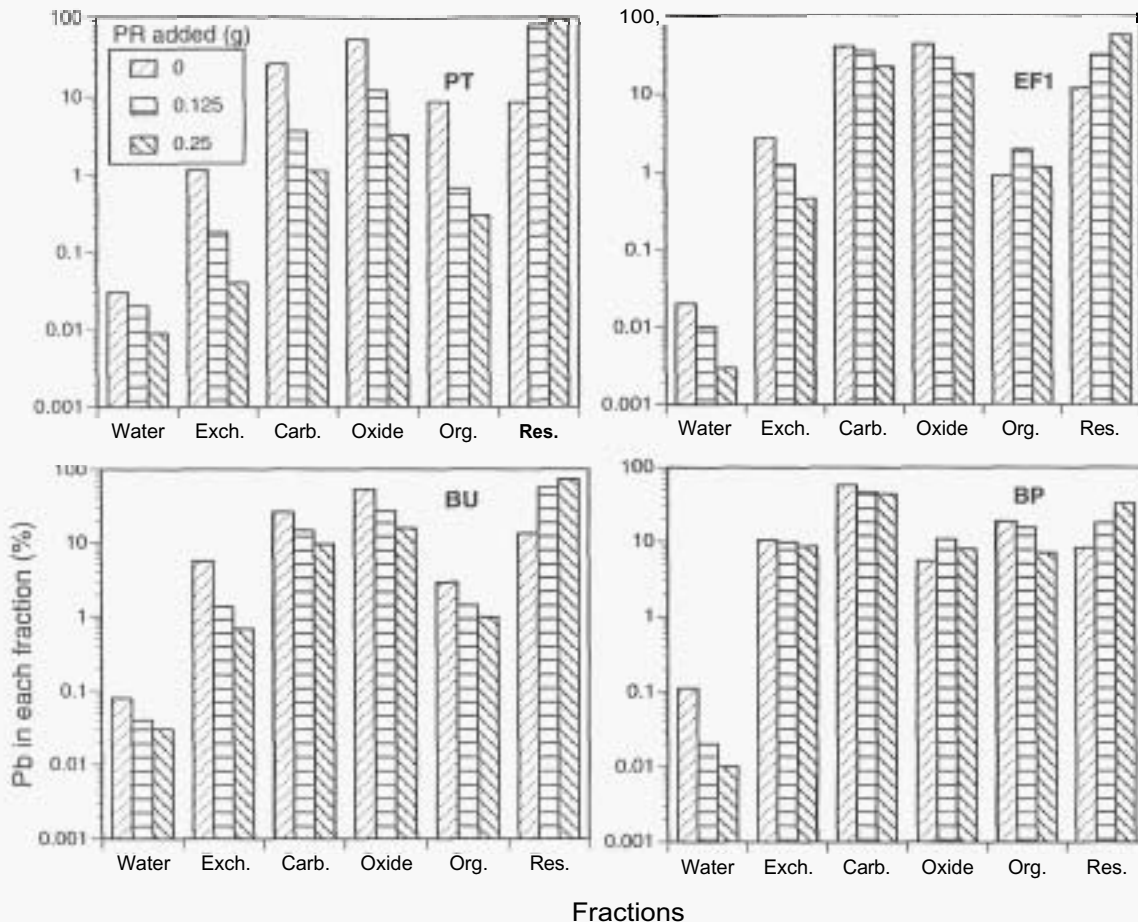


Fig. 2. Lead distribution in different fractions in four Pb-contaminated soils in the presence of different amount of OC phosphate rock (PR).

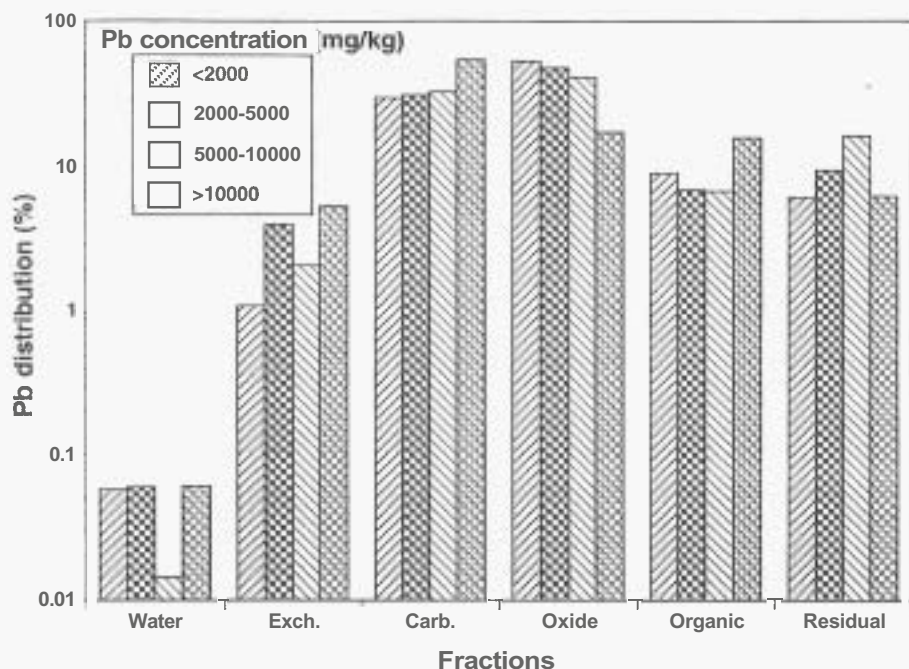


Fig. 3. The effect of total Pb concentrations on Pb distribution in different chemical fractions.

cabbage [*Brassica oleracea* (Capita Group)] and kidney bean plants (*Phaseolus vulgaris* L.). The sum of the water soluble and exchangeable Pb only represented 0.4 to 11% of the total Pb; nevertheless, they are the most bioavailable form of Pb. It is clear that a major portion of Pb in all the soils tested was associated with potentially available fractions, which indicates that Pb in these soils may be highly bioavailable.

Lead distribution in these soils varies greatly, depending on the source of Pb contamination as well as soil properties (Forstner, 1984). For example, the percentage of Pb associated with the organic and Fe-Mn oxide fractions was independent of the organic matter, and total Fe and Mn contents in the soils, respectively ($r < 0.13$) (Table 1, Fig. 1 and 2). In this case, source of Pb contamination and other soil properties (influenced by soil formation factors) may play a more important role than soil organic matter and total Fe and Mn contents. Furthermore, based on the contamination source, EF1, EF2, and PT soils, and TW and BU soils should have similar Pb distribution patterns (Table 1). However, Pb distribution in EF2, PT, and TW soils followed the same order: Fe-Mn oxide > carbonate > organic > residual > exchangeable > water soluble, whereas those in BU and EF1 followed the order: Fe-Mn oxide > carbonate > residual > exchangeable > organic > water soluble (Fig. 1 and 2). Lead distribution in the other three soils followed entirely different orders. In general, Pb associations in these soils were in the order: Fe-Mn oxide, carbonate > organic, residual > exchangeable > water soluble. In the study by Xian (1989), most of the Pb, in the seven soils from former smelter sites, was associated with the Fe-Mn oxide and organic fractions, accounting for >61 to 78% of the total Pb. This differed from our smelter site soils

(EF1, EF2, and PT), in which the two fractions accounted for 45 to 64% of the total Pb, because 26 to 41% of the Pb in our soils was associated with the carbonate fraction (Fig. 1 and 2). Please note that differences in fractionation schemes used by different researchers will also affect metal distribution in soils.

An attempt was made to determine the effect of total Pb content in soils on Pb distribution in various chemical fractions. Lead fractions in the water soluble, exchangeable, and organic fractions were independent of the total Pb in soils (Fig. 3). However, there was a slight decrease of Pb in the Fe-Mn oxide fraction and a slight increase of Pb in the carbonate fraction as total Pb increased. In a different study, Gibson and Farmer (1986) reported that Pb concentrations in the exchangeable, organic, and residual fractions increased and those in the carbonate and Fe-Mn fractions were unchanged as total Pb concentrations increased from <99 to >400 mg kg⁻¹. The extent of Pb contamination in the soils of this study (>705 mg kg⁻¹) were much more severe than those in Gibson and Farmer's study (<705 mg kg⁻¹), which may account for the difference in Pb distribution patterns as total Pb concentrations increased. These results again suggest that many factors affect Pb distribution in these soils.

Effect of OC Phosphate Rock on Lead Distribution

Phosphate rock was present in the soil samples throughout the extractions; thus, Pb immobilization occurred in each of the six extraction steps. Our results show that most of the Pb in these soils was concentrated in the potentially bioavailable fractions (79-96%, the nonresidual fraction; Fig. 1 and 2). The presence of

Table 3. Lead distribution in eight contaminated soils in the presence of different amounts of OC phosphate rock (OCPR).

OCPR added (g)	BU			EF1				
	0	0.125	0.25	0	0.125	0.25		
Residual Pb, %	13	56	73	12	32	57		
Nonresidual Pb, %	87	44	27	88	68	42		
Decrease in nonresidual Pb, %		50	69		23	52		
Sum of all fractions	2920 ± 58	2850 ± 44	2660 ± 87	6310 ± 190	6190 ± 421	6380 ± 438		
Total via single digestion	2680 ± 80			5970 ± 226				
OCPR added (g)	BP			PT				
	0	0.125	0.25	0	0.125	0.25		
Residual Pb, %	8.0	18	32	9.0	83	95		
Nonresidual Pb, %	92	82	68	91	17	5.0		
Decrease in nonresidual Pb, %		10	26		82	95		
Sum of all fractions	41100 ± 669	47700 ± 1050	37900 ± 730	662 ± 37	847 ± 72	736 ± 66		
Total via single digestion	40100 ± 800			1300 ± 85				
OCPR added (g)	TW		EF2		DA		DU	
	0	0.125	0	0.125	0	0.125	0	0.125
Residual Pb, %	4.0	96	6.0	43	4.0	20	21	66
Nonresidual Pb, %	96	4.0	94	57	96	78	79	35
Decrease in nonresidual Pb, %		96		40		19		56
Sum of all fractions	768 ± 48	874 ± 62	4920 ± 170	4985 ± 310	10600 ± 790	9550 ± 740	8330 ± 550	7800 ± 474
Total via single digestion	705 ± 50		4480 ± 250		12500 ± 710		7640 ± 510	

phosphate rock significantly reduced extractable Pb in the nonresidual fraction, and increased Pb concentration in the residual fraction of all eight soils (Table 3). The percentage of Pb reduction in the nonresidual fraction ranged from 10 to 96% in the presence of OC phosphate rock, indicating the effectiveness of phosphate rock to reduce Pb solubility in the presence of these reagents. Lead reduction from the nonresidual fraction was mainly from the carbonate and Fe–Mn oxide fractions, which accounted for 63 to 85% of total Pb in the soils (Fig. 1 and 2). This demonstrated the effectiveness of phosphate rock to convert Pb associated with the exchangeable, carbonate, Fe–Mn oxide, and organic to the more stable residual fraction. In general, the effectiveness of phosphate rock in converting Pb from the nonresidual fractions was increased by increasing OC phosphate rock (Fig. 1 and 2).

Generally, Pb recovery from the sequential extraction analysis in the absence of OC phosphate rock was within $100 \pm 10\%$ of the total Pb concentrations via single digestion, except for the PT soil, which was 49% (Table 3). It was unclear why only half of the Pb was recovered during the sequential extraction in this soil. Thus, except PT soil, errors from sequential extraction procedure were negligible and the results could indicate Pb redistribution in the soils. Total Pb obtained by adding all fractions generally decreased with increasing OC phosphate rock with some exceptions. For example, total Pb concentration of all fractions in BU soil was 2920 mg kg^{-1} , and it reduced to 2660 mg kg^{-1} as OC phosphate rock increased to 0.25 kg/kg of soil (Table 3).

The behavior of various Pb–phosphates in the presence of different extractants of this sequential scheme was investigated. It is difficult to obtain pure fluoropyromorphite sample; hence, hydroxypyromorphite $[\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2]$, which is similar to fluoropyromorphite in terms of both structure and properties, was tested. In our experiment, it was found that 99.9% of the Pb in hydroxypyromorphite was associated with the residual

fraction, demonstrating the ineffectiveness of all the nonresidual extractants to dissolve Pb from hydroxypyromorphite and the stability of hydroxypyromorphite in the presence of these extractants (data not shown). We can thus infer that fluoropyromorphite will behave similarly to hydroxypyromorphite and cannot be extracted by the nonresidual extractants. Little Pb ($<0.5\%$) was extracted by the nonresidual extractants from other pure Pb–phosphates $[\text{Pb}_3(\text{PO}_4)_2]$ and PbHPO_4 (data not shown). We have previously demonstrated that Pb immobilization by phosphate rock from aqueous solution was through phosphate rock dissolution and precipitation of fluoropyromorphite-like mineral (Ma et al., 1995). Similarly, we can hypothesize that the primary mechanism for Pb reduction in the nonresidual fractions by phosphate rocks, and reduced total Pb recovery via fractionation in the presence of phosphate rock was through formation of fluoropyromorphite-like mineral. Lead phosphates are the most stable of all Pb minerals (Nriagu, 1974), thus they are extremely insoluble and were not totally dissolved even in strong acids.

Although the sequential extraction procedure employed in this study cannot identify the actual Pb forms, it appears to be useful for classifying Pb within several general geochemical fractions. The Fe–Mn oxide and carbonate fractions proved to be the most important for these Pb-contaminated soils, whereas organic fractions were less important. In all the soils studied, most of the Pb was associated with potentially available fractions, i.e., the nonresidual fraction. The OC phosphate rock effectively immobilized Pb in these fractions. The extremely low solubility of pyromorphite may contribute to the stability of Pb in the presence of phosphate rock in these soils (Nriagu, 1974). The fact that phosphate rock effectively immobilized Pb in the presence of various reagents strongly demonstrated its potential for remediating Pb-contaminated soil materials. However, the quantity of phosphate rock used in this study can

be uneconomically high to treat Pb-contaminated soils. Hence, more soluble P sources would have to be mixed with phosphate rock for field application to increase the effectiveness of Pb immobilization in contaminated soils. More soluble P sources could quickly reduce aqueous Pb to below acceptable level, while phosphate rock would supply a constant P source in soil to react with Pb for long-term Pb immobilization, especially in an environment where P may be removed by plants or microbes. While addition of phosphate rock may reduce the adverse Pb-impacts in contaminated soils, one needs also to consider the potential adverse effects of excessive P on the environment.

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