Field demonstration of in situ immobilization of soil Pb using P amendments[☆]

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Abstract

A long-term field-scale demonstration project on the feasibility of using P to immobilize Pb in a Pb-contaminated urban soil was conducted. Phosphate was applied at an average rate of 3040 mg P/kg soil based on a P/Pb molar ration of 4.0, with four treatments: T_0, no P application; T_1, H_3PO_4 only; T_2, 1/2 H_3PO_4 + 1/2 CaH_2PO_4; and T_3, 1/2 H_3PO_4 + 1/2 phosphate rock. Soil samples were collected and analyzed 220 days after the P applications. For all P treatments, toxicity characteristic leaching procedure (TCLP) extractable Pb levels in surface soils (0–10 cm) were reduced to below 5.0 mg Pb/l, with T_2 also effective in reducing the TCLP Pb level in subsurface soils (10–30 cm, <4.63 mg/l). Sequential extraction analysis indicates that P was effective in transforming soil Pb from non-residual fractions to a residual fraction. Such a transformation was mainly through dissolution of Pb associated with carbonate fraction and precipitation of pyromorphite-like minerals, which were confirmed using X-ray diffraction (XRD). Among these three treatments, T_3 was the most effective in reducing Pb mobility and minimizing P and Pb leaching in the soil. Our research clearly demonstrates that P amendments were effective in immobilizing Pb in contaminated soil.
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1. Introduction

The Agency for Toxic Substances and Disease Registry (ATSDR) and the US Environmental Protection Agency (US EPA) rank Pb as the second-priority hazardous substance in the US (ATSDR, 1999). Incidental ingestion of Pb-contaminated soil has been proposed as a primary exposure pathway for elevated blood Pb levels in young children (Chaney et al., 2000). Lead-contaminated soils are found in both urban and rural settings. House paint, leaded gasoline, shooting ranges and Pb smelters, including secondary Pb smelters such as battery recycling, are common sources of Pb contamination (Chaney et al., 2000).

The US EPA has established a soil screening level of 400 mg/kg as a preliminary remediation goal (US EPA, 1996). When Pb concentrations are elevated, the toxicity characteristic leaching procedure (TCLP) can be used to assess Pb toxicity and mobility (US EPA, 1995). The TCLP regulatory limit is currently set at 5 mg Pb/l for hazardous wastes (US EPA, 1998). If untreated waste contains >5.0 mg Pb/l, it is considered as hazardous waste.

The primary objective of in situ immobilization of Pb-contaminated soil is to reduce Pb bioavailability to environmentally acceptable levels (Ma and Rao, 1999). Soil excavation has been used as the primary remediation strategy, which is both disruptive and costly (Rabinowitz, 1993). In addition, total removal of all Pb-contaminated soils for disposal elsewhere is not always feasible, as they may exceed existing landfill space. Other treatments are either too costly or only partially effective. An alternative approach to remediate Pb-contaminated soils has been developed, which uses P-rich materials, such as P fertilizers, phosphate rock, biosolids and manures, to immobilize Pb in soils (Chaney et al., 2000). This technique is of particular interest because of its cost-effectiveness and less disruptive nature (Ma et al., 1993; Ma and Rao, 1999; Berti and Cunningham, 1997). For example, excavation and off-site disposal of contaminated soil (top 60 cm) costs $282–1080 /mg soil, while in situ stabilization of Pb-contaminated soil using P amendments costs as little as $9–55 /mg soil (Berti and Cunningham, 1997; Ma and Rao, 1999).

Phosphorus reacts with many heavy metals, metalloids and radionuclides to form secondary phosphate precipitates that are stable over a wide range of environmental conditions. Geochemical modeling indicates that addition of P amendments to Pb-contaminated soil can result in the formation of Pb phosphate with an estimated solubility of 0.1 μg Pb/l (Ruby et al., 1994). Laboratory-scale studies have examined the mechanisms and effectiveness of Pb immobilization using various P amendments in Pb-contaminated soils (Ruby et al., 1994; Ma et al., 1995; Laperche et al., 1996; Zhang and Ryan, 1998). Experimental evidence supports the hypothesis that Pb phosphates, including hydroxypyromorphite [HP; $Pb_5(PO_4)_3OH$], chloropyromorphite [CP; $Pb_5(PO_4)_3Cl$] or fluoropyromorphite [FP; $Pb_5(PO_4)_3F$], depending on the concentrations of Cl^-, F^- and OH^- ions, can rapidly form when adequate Pb and P are present (Ma et al., 1993, 1994). Reduction in aqueous Pb was primarily through the dissolution of apatite or rock phosphate, and subsequent precipitation of pyromorphite-like minerals (Ma et al., 1995; Chen et al., 1997). The formation of Pb phosphates has thus been proposed to be responsible for immobilizing Pb, thereby reducing its bioavailability (Ruby et al., 1994; Hettiarachchi et al., 2000).

Under most soil environments, solubility of both Pb and P remains low, limiting the effectiveness of P-induced Pb immobilization (Laperche et al., 1996; Zhang and Ryan, 1998). For example, dissolution of the initial Pb phase has been reported to be the limiting factor in the formation of HP at pH 5–8, and the conversion of PbO to HP is found to be most rapid at pH 5 (Laperche et al., 1996). Therefore, effective in situ Pb-immobilization requires enhanced solubility of

Pb by inducing acidic conditions, making it necessary to acidify soil prior to P addition by adding H_3PO_4 or other acids. Reduced soil pH would facilitate dissolution of soil Pb and P to enhance the formation of pyromorphite (Hettiarachchi et al., 2001; Yang et al., 2001).

The rate of phosphorus application for effective Pb-immobilization is another important issue. Application of hydroxyapatite to aqueous Pb or Pb-contaminated soils at a P/Pb molar ratio of 3:5 has been suggested for transforming soil Pb into pyromorphite based on the molar ratio in CP (Ma et al., 1993; Laperche et al., 1996). However, since soluble P may not react with insoluble Pb, higher P/Pb molar ratios (up to 11.2) have been used (Zhang and Ryan, 1998; Basta et al., 2001; Hettiarachchi et al., 2001).

Successful in situ immobilization treatments for Pb-contaminated soils should provide long-term reduction in Pb bioavailability by modifying Pb geochemistry (Berti and Cunningham, 1997). Direct identification of mineralogical changes resulting from P addition using X-ray diffraction (XRD) helps to evaluate the long-term stability or permanency for site remediation (Ma et al., 1994). Another alternate approach to evaluate the effectiveness of in situ Pb immobilization products is to use TCLP (Berti and Cunningham, 1997; Hettiarachchi et al., 2000), sequential extraction (SE) (Berti and Cunningham, 1997; Ma and Rao, 1997) or a physiologically based extraction procedure that simulates metal ingestion and gastrointestinal bioavailability to humans (Basta et al., 2001).

Effective Pb immobilization by the formation of pyromorphite has been reported upon addition of apatite (e.g. Ma et al., 1993; Chen et al., 1997; Zhang and Ryan, 1998), phosphate rock (e.g. Ma et al., 1995; Basta et al., 2001; Hettiarachchi et al., 2000), phosphatic clay (Singh et al., 2001) or soluble P (e.g. Berti and Cunningham, 1997; Hettiarachchi et al., 2001) on Pb-contaminated soils at laboratory bench scale. Phosphoric acid has also been suggested as a cost-effective remedial amendment for in situ Pb immobilization (Yang et al., 2001). However, lack of field demonstration and site-specific field characterization has hindered the acceptance and application of in situ Pb immobilization technology on a wider scale. Other major limitations for the adoption of this technology include limited solubility of Pb minerals present in the existing soil environment (Singh et al., 2001) and the potential adverse effects of P addition on the environment (Chen et al., 2001).

The purpose of this study was to (i) determine the effects of different phosphate amendments on the in situ immobilization of Pb in a contaminated soil; and (ii) document chemical fractionation and leaching characteristics of soil Pb, as well as Pb mineral transformation, upon P applications in field conditions. Quantifying these parameters will help to develop effective remedi-

Table 1
Selected chemical and physical properties of the soil at the demonstration site for the top 10-cm profile prior to treatment applications

Plot	pH	Organic C (%)	Clay (%)	CEC (cmol/kg)	Total P (mg/kg)	Total Pb (mg/kg)	TCLP Pb (mg/l)
T_0	7.1	3.0	2.8	4.7	692	10 907	144.3
T_1	6.8	3.6	3.6	6.1	390	5965	54.1
T_2	7.0	4.1	4.1	5.5	478	15 919	162.5
T_3	7.0	5.1	3.7	6.7	925	9100	66.7

T_0, no P application; T_1, H_3PO_4 only; T_2, $1/2$ $H_3PO_4 + 1/2$ CaH_2PO_4; T_3, $1/2$ $H_3PO_4 + 5\%$ rock phosphate. CEC, cation exchange capacity.

ation strategies for Pb-contaminated soils on a field scale.

2. Materials and methods

2.1. Site description and soil characterization

A fenced-in Pb-contaminated site of approximately 0.405 ha in Jacksonville, Florida was selected to test this remediation technology. Past industrial activities included a gasoline station, a salvage yard and an auto body shop that disposed batteries, waste oil and organic contaminants on the site. Our preliminary investigation

indicated that the priority contaminants included Pb (110–396 mg/l TCLP Pb) (Table 1; Singh et al., 2000).

To determine Pb distribution in the soil, 61 topsoil (0–10 cm) cores were collected from 25 rectangular grids (14.8 m×11.5 m) using a soil auger. Additional soil samples were taken from each of the four trial plots (near location A, Fig. 1) at 0–10-, 10–20-, 20–30-, 30–40-, 40–60- and 60–80-cm increments for detailed soil characterization prior to P applications.

2.2. P application to demonstration plots

Demonstration plots were established in the most heavily contaminated section of the site (total Pb con-
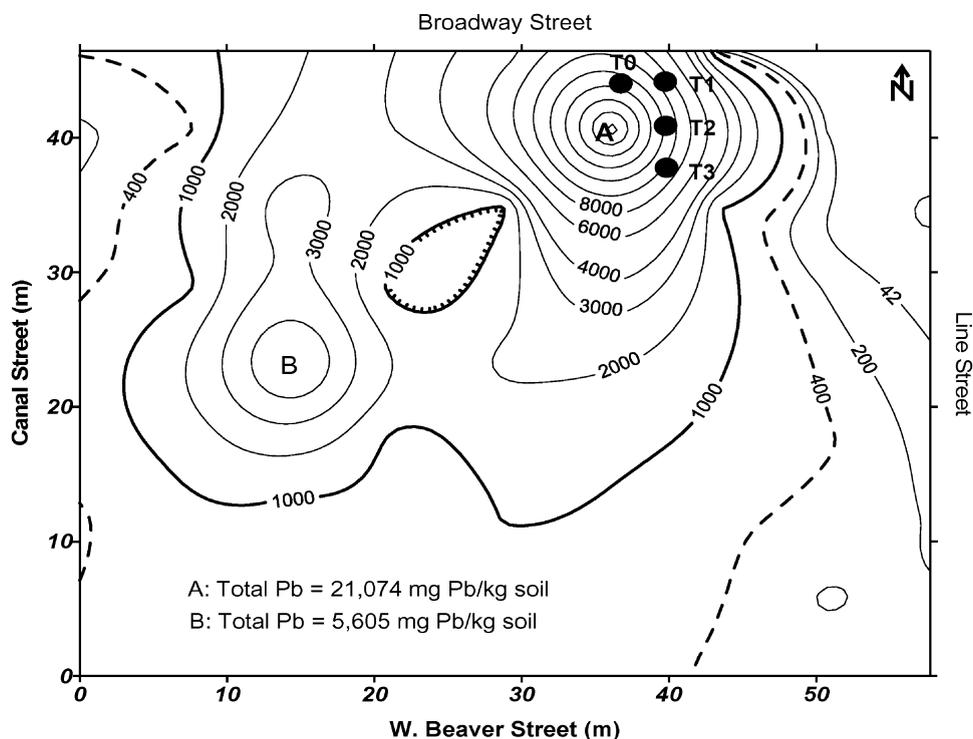

Fig. 1. Distribution of total Pb (mg/kg) in the contaminated soil at depth of 0–10 cm in the field demonstration site. Circles show location of the four demonstration plots with: T_0, no P application; T_1, H_3PO_4 only; T_2, $1/2$ $H_3PO_4 + 1/2$ CaH_2PO_4; and T_3, $1/2$ $H_3PO_4 + 5\%$ rock phosphate.

centration 21 074 mg/kg; Fig. 1). Each circular plot (1.5 m apart), approximately 4 m^2 in size, was circled by high-density polyethylene geomembrane liner to prevent possible inter-plot contamination. Four P treatments, T_0 (no P application), T_1 (H_3PO_4 only), T_2 (1/2 H_3PO_4 + 1/2 $CaHPO_4$) and T_3 (1/2 H_3PO_4 + 1/2 rock phosphate), were used at a P application rate equivalent to 3040 mg P/kg soil and P/Pb molar ratio of 4.0, except for T_3 (Singh et al., 2000). To pre-acidify soils, half of the P was applied as $CaCl_2 + H_3PO_4$ on 17 February 2000, using 25 l of water. The aqueous P was sprayed on and mixed uniformly with the top 10 cm of soils, and covered with a plastic sheet to prevent leaching by rainfall. The addition of $CaCl_2$ was to facilitate the formation of stable CP. The remaining P was applied using either H_3PO_4 (T_1), $CaHPO_4$ (T_2) or rock phosphate (T_3) by mixing it with the top 10 cm of soil on 27 March 2000. Phosphate rock used in this study was obtained from the Occidental Chemical Corp, White Spring, FL. It contained 156 g/kg of P mainly as $Ca_5(PO_4)_3F$, with substantial CO_3^{2-} substitution in the structure, and was previously shown to be effective in immobilizing Pb from various Pb-contaminated soils (Ma et al., 1995).

2.3. Sample and data analyses

Composite soil samples, each comprising three sub-samples, were taken on 25 September 2000, 220 days after the P application, at the following depths: 0–10; 10–20; 20–30; 30–40; 40–60; and 60–80 cm. Soil samples were air-dried, crushed and passed through a 2-mm sieve. Soil pH was measured with a glass electrode in a 1:2 solid/water suspension after 24 h of equilibrium. Organic C was estimated by the Walkley–Black method (Jackson, 1958). Particle size fractionation was performed by the pipette method (Gee and Bauder, 1986) and cation exchange capacity (CEC) was determined by the method of Rhoades (1982).

For total Pb contents, soil samples were digested using US EPA Method 3051a, a microwave-assisted HNO_3–HCl (3:1 v/v) digestion method (US EPA, 1997). TCLP tests were performed using a modified US EPA Method 1311 (US EPA, 1995). This procedure uses a 5.7-ml aliquot of glacial acetic acid (pH 4.93) in 500 ml of deionized water and 64.3 ml of 1 N NaOH, diluting to a volume of 1 l. A 100-ml aliquot of this solution was used to extract Pb from the soil samples, each weighing 5 g (US EPA, 1995). Soil sequential extraction was carried out on selected soil samples based on Tessier et al. (1979). This procedure separates soil Pb into six operationally defined fractions, including water-soluble, exchangeable, carbonate, Fe–Mn oxide, organic and residual Pb fractions. Lead concentrations >1.0 mg/l were analyzed using a flame atomic absorption spectrometer (Perkin Elmer 3030,

Norwalk, CT) and <1.0 mg/l using an atomic absorption spectrophotometer (Perkin Elmer SAMMA 6000, Norwalk, CT). Iso-contour maps of soil Pb concentrations were generated using Surfer® 7 (Golden Software Inc, Golden, CO).

Total P concentrations were analyzed using a multi-channel inductively coupled plasma spectrophotometer (Thermo Jarrell Ash ICAP 61-E, Franklin, MA). Standard soil reference materials from the National Institute of Science and Technology (NIST, Gaithersburg, MD) were used to assess method accuracy and precision. The amount of P remaining in the 0–80-cm profile was calculated by the difference between P contents in the profile before P application and 220 days after P application.

Crystalline Pb components in soils were investigated using an X-ray diffractometer (Philips Electronic Instruments Inc, Mahwah, NJ) using CuK_α radiation at 35 kV and 20 mA. Measurements were made using continuous scanning techniques, and XRD patterns were obtained from 2 to 60° 2θ at a scan speed of 2°/min.

3. Results and discussion

3.1. General site characteristics

Initial soil analyses confirmed that a substantial portion of the site was significantly contaminated with Pb (Fig. 1). Total Pb in the top 10-cm depth was highly variable across the site, ranging from 45.0 to 21 074 mg/kg, with a standard deviation of 3393 mg/kg. Over 80% of the area sampled exceeded the 400 mg/kg critical level specified by the EPA as a preliminary remediation goal for residential soils, and over 40% of the sampled area exceeded the 1000 mg/kg critical level for industrial soils (US EPA, 1996). The extreme heterogeneity of Pb distribution in the contaminated site makes it impossible to select areas with similar Pb concentrations unless the soil was disturbed, which is undesirable. Thus, Pb concentrations in the four plots were different (Fig. 1 and Table 1).

According to the USDA soil taxonomy, the soil at the demonstration site is classified as a sandy, siliceous, thermic, ultic Alguod that was subsequently replaced with construction fill materials, leading to severe disturbance of the original soil structure. These soils are very sandy, with neutral pH (Table 1). Organic C contents at the site ranged from 3.0 to 5.1%, while the cation exchange capacity (CEC) values ranged from 4.7 to 6.7 cmol/kg. Total soil P at the site ranged from 390 to 925 mg/kg.

3.2. Effect of P amendments on soil pH

It has been reported that effective P-induced Pb-immobilization requires enhanced solubility of Pb and
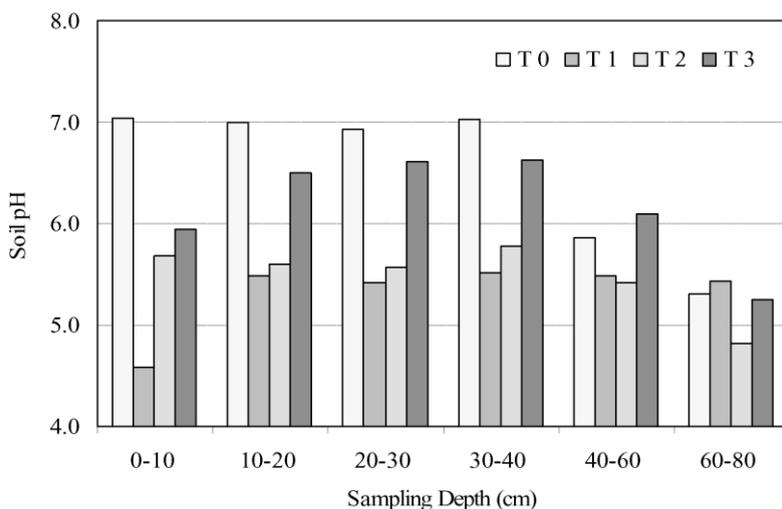
Fig. 2. Effects of different P amendments (T_0, T_1, T_2 and T_3, as in Fig. 1) on soil pH values measured 220 days after P application.

P, which can be accomplished by lowing soil pH (Ma et al., 1993, 1995; Chen et al., 1997). In a preliminary batch test using samples from the demonstration site, Singh et al. (2000) found that a reduction in soil pH to 5.0–5.5 provided optimum conditions for Pb immobilization.

In P-treated plots, soil pH in the top 10 cm was reduced by the addition of H_3PO_4, and the reduction followed the order of $T_1 > T_2 > T_3$ (Fig. 2). Similar reductions in soil pH were observed in the subsurface samples for T_1 and T_2. However, no obvious pH reduction was observed for T_3. This is consistent with other studies in which the use of H_3PO_4 was effective in

reducing soil pH, but not rock phosphate (Basta et al., 2001; Hettiarachchi et al., 2001).

3.3. Effect on TCLP-extractable Pb

The results of TCLP tests (Table 1) showed that the untreated topsoil (0–10 cm) exceeded the 5 mg/l critical level and would be characterized as hazardous waste (US EPA, 1995). Similar to total Pb, the highest TCLP-extractable Pb was observed at 10–20 cm in T_0 (Fig. 3). The TCLP value for the 20–30-cm depth also exceeded the 5 mg Pb/l critical level. This is probably because most of the Pb is bound to carbonate (Fig. 4),
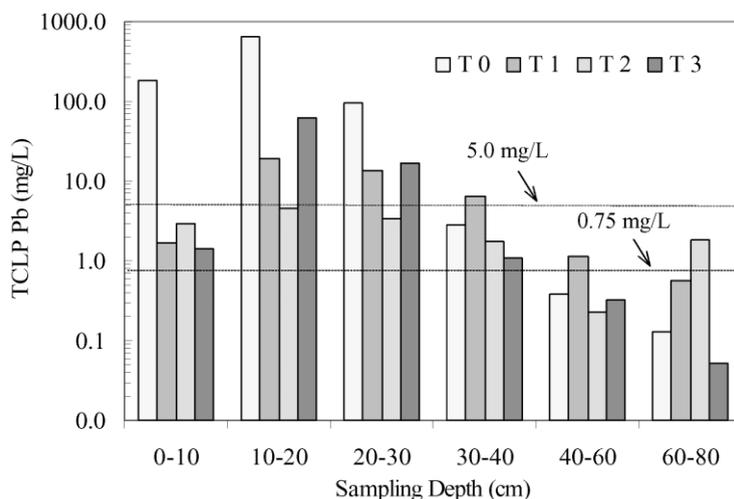

Fig. 3. Effects of different P amendments (T_0, T_1, T_2 and T_3, as in Fig. 1) on TCLP Pb concentrations measured 220 days after P application.
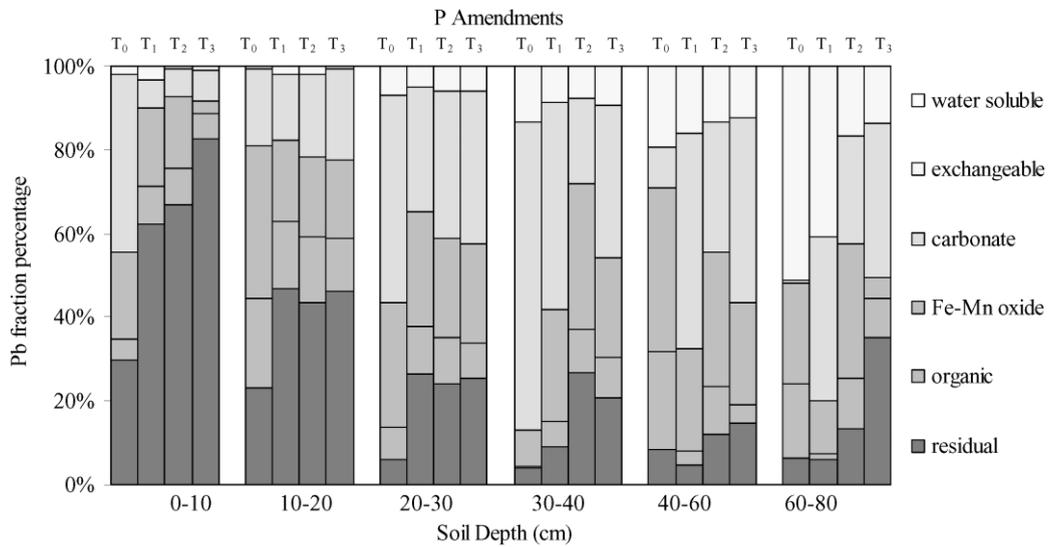
Fig. 4. Effects of different P amendments ((T_0, T_1, T_2 and T_3, as in Fig. 1) on chemical fractions of soil Pb at different depths, measured 220 days after P addition.

which readily dissolves in acidic conditions such as that of the TCLP solution (Berti and Cunningham, 1997).

All P amendment reduced TCLP-extractable Pb in the top 10-cm profile to below the critical level of 5 mg/l, with T_3 being the most and T_2 the least effective (Fig. 3). At a depth of 10–30 cm, however, the greatest reductions in TCLP-extractable Pb were obtained with T_2. Although T_1 and T_3 treatments reduced TCLP-extractable Pb in the 10–30-cm profile, it was still

greater than the critical level of 5 mg/l. This is consistent with the results of Berti and Cunningham (1997), who reported that P addition at 0.5% as KH_2PO_4 reduced TCLP-extractable Pb to <35 mg/l in three soils with total Pb concentrations ranging from 1200 to 3500 mg/kg. Hettiarachchi et al. (2000) reported that addition of 2500–5000 P mg/kg with triple super phosphate significantly reduced TCLP-extractable Pb in five soils with high total Pb (1179–12 414 mg/kg),
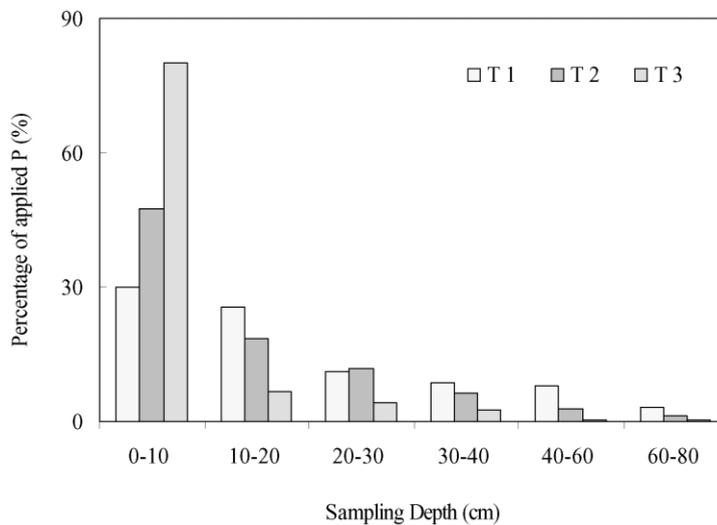

Fig. 5. Distribution of applied P (%) in soil profiles of P-treated plots (T_0, T_1, T_2 and T_3, as in Fig. 1), measured 220 days after P application.

while addition of rock phosphate alone was less effective. It is possible that most of the P stayed in the surface soil, as shown in Fig. 5, and thus there was less P available to react with Pb in the subsurface.

3.4. Distribution of Pb in different fractions

Although metal fractionation by sequential extraction is only operationally defined and a certain degree of overlap between the forms is inevitable, it is useful for understanding Pb transformation among different geochemical fractions (Tessier et al., 1979). Soils with a large proportion of Pb in water-soluble and exchangeable fractions are potentially of greater hazard when compared to soils where Pb primarily resides in the residual fractions (Berti and Cunningham, 1997).

The sequential extraction analysis of the untreated soil (T_0) at the site showed that Pb was primarily associated with the carbonate fraction, except at depths of 10–20 and 60–80 cm, where Fe–Mn oxide and exchangeable Pb were the predominant fractions (Fig. 4). Soil Pb in the residual fraction was <30% at a depth of 0–20 cm, which decreased with the depth. This vertical distribution pattern of Pb partitioning reflects the Pb–pH relationship in the soil profile. When soil pH was high (>7.0), as for the 0–40-cm depth (Fig. 2), carbonated-associated Pb became more important, ranging from 18.3 to 73.4% (Fig. 4). Conversely, when the pH value decreased to <6, as for the 40–80-cm depth, $PbCO_3$ was dissolved, contributing Pb to the water-soluble and exchangeable fractions. However, because of high total Pb (2705–28 953 mg/kg), the exchangeable Pb in the surface layers (0–30 cm) was also high (176–191 mg/kg). This relatively large pool of Pb in the exchangeable fraction suggests that the soil presents a potential hazard to human health and the environment through direct soil ingestion and leaching to groundwater (Berti and Cunningham, 1997).

Phosphate addition significantly changed Pb distribution among different fractions (Fig. 4). Lead associated with the carbonate fraction in the topsoil (0–10 cm) was reduced from 42.6 to 6.7–7.5%, whereas that in the residual fraction increased from 29.8 to 62.2–83.5%. Similar trends were evident at lower depths (10–40 cm). This agrees with the results of Berti and Cunningham (1997), who reported a significant reduction in soil Pb in the exchangeable fraction and increases in residual fractions upon P addition. This transformation of Pb fractions at the site became more evident at the subsurface (>30 cm). This was especially true for the T_3 treated soil, reflecting the effectiveness of phosphate rock in reducing Pb mobility and bioavailability (Basta et al., 2001). However, there is no apparent reason why Pb–carbonate became more predominant at greater depths (40–80 cm) upon P application, since the pH values (4.8–6.1) were low for the presence of

carbonates, which may imply poor selectivity of the fractionation scheme for carbonate (Ma and Rao, 1997). Lead associated with Fe–Mn oxide was reduced to between 2.1 and 18% in the top 30 cm upon P addition. This reduction may be attributed to desorption of Pb from oxide surfaces, resulting from the pH reduction following H_3PO_4 addition and precipitation of P with soluble Pb (Zhang et al., 1997).

Ma and Rao (1997) reported that phosphate rock converted Pb associated with non-residual (the water soluble, exchangeable, carbonate, Fe–Mn oxide and organic Pb fractions) to the residual fraction. In this investigation, T_3, P applied at an average rate of 3040 mg P/kg, with 1/2 H_3PO_4 + 1/2 phosphate rock, was most effective among the three P treatments in converting Pb from the non-residual to residual fractions in the top 10 cm of soil (Fig. 4). This is consistent with the results of Hettiarachchi et al. (2001), who reported that phosphate rock was equally or more effective than triple super phosphate or H_3PO_4 in reducing bioavailable Pb in five metal-contaminated soils and mine wastes, at application rates of 2500–5000 mg P/kg soil.

3.5. Distribution of applied P in soils

Soil P enrichment and potential leaching can be an environmental concern for in situ Pb immobilization using P amendments. In this study, P was primarily concentrated in the top 20 cm of the soil, which accounted for 86.3, 88.5 and 94.2% of the total applied P for T_1, T_2 and T_3, respectively (Fig. 5). Total P declined rapidly with depth, following the order of $T_3 >$ $T_2 > T_1$. The percentages of applied P recovered in the top 10-cm profile were 31% (T_1), 48% (T_2) and 80% (T_3) (Fig. 5). The remainder of the P probably moved downward. Phosphorus enrichment and its downward migration could potentially result in increased P loss to water. Clearly, this aspect of the in situ Pb immobilization technology requires further research.

3.6. Changes in Pb mineralogy upon P additions

Mineralogical analyses using XRD indicated that in the top (0–10 cm) untreated contaminated soils (T_0) crystalline forms of the soil Pb existed primarily as cerussite (Fig. 6). This is consistent with the results of Nedwed and Clifford (1997), who reported that cerrusite was the major mineral in Pb-contaminated soils from battery recycling sites. It has been reported that cerussite is formed in an environment of high dissolved Pb, high carbonate ions and relatively low pH, while hydrocerussite is common under conditions of high dissolved Pb, high pH and low carbonate (Chen et al., 1997). Stumm and Morgan (1970) pointed out that the boundary between a predominance of cerussite vs. hydrocerussite occurred at pH 7.3. Since soil pH in the top 10 cm of
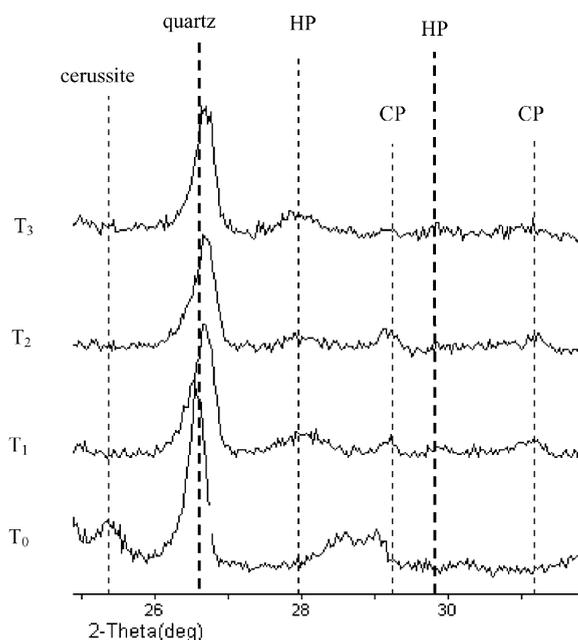
Fig. 6. X-Ray diffraction patterns for the top 10 cm of soil under different P amendments after 220 days (T_0, T_1, T_2 and T_3, as in Fig. 1); CP, chloropyromorphite; HP, hydroxypyromorphite.

soil was 7.1 (T_0), cerussite was the predominate mineral in the soil.

Hydroxypyromorphite was identified in the top 10 cm of soil in the P-treated soil, while CP was identified only in soils treated with soluble P (T_1 and T_2) (Fig. 6). This observation may suggest that HP instead of CP may be the primary Pb phosphate form upon P application as rock phosphate. In previous studies, Ma et al. (1995) suggested formation of FP in Pb-contaminated soils upon P addition as phosphate rock. However, HP was identified in phosphate rock-treated Pb-contaminated soils, although the major component in the phosphate rock was identified as fluoroapatite (Hettiarachchi et al., 2001). One possible explanation for this is that T_3 treated soil had the highest pH among the three P treatments (Fig. 2) and the availability of free Cl^- provided by $CaCl_2$. Chloropyromorphite was formed at low pH (T_1 and T_2) with free Cl^-, while HP was formed at relatively high pH (T_3) with free OH^-. Chen et al. (1997) reported that in alkaline solutions the activity of OH^- was much higher than that of F^-, resulting in the formation of HP and reducing crystallinity of CP. Nevertheless, the disappearance of cerussite peaks and the appearance of HP and CP peaks after P addition confirm that P amendments enhanced immobilization of Pb by changing the Pb chemistry.

Since cerrusite was the major Pb mineral in the untreated soil and fluoroapatite was the major P component in phosphate rock, dissolution of Pb and P minerals and the subsequent formation of HP or CP could be the dominant mechanisms for Pb immobilization in the soil. Theoretically, dissolution of phosphate rock increases Ca, P and OH^- concentrations in solution. It is therefore expected that higher pH reduces the effectiveness of Pb immobilization by phosphate rock due to low P solubility (Ma and Rao, 1999). However, interaction of P with metals tends to decrease soil pH, especially when reaction time and P application rates are increased (Singh et al., 2001). This in turn could be a significant factor in transformation of the less stable HP to the more stable CP (Chen et al., 1997; Badawy et al., 2002). Similarly, acidification (pH <6) of the phosphate rock-treated Pb-contaminated soil decreased gastrointestinal-available Pb (Basta et al., 2001). This suggests that soil treatment with phosphate rock can reduce Pb extractability.

In most laboratory-scale batch studies, soil acidification enhances Pb immobilization (Zhang and Ryan, 1998; Basta et al., 2001; Yang et al., 2001). In such a closed equilibrium system, Pb immobilization is instantaneous due to chemical precipitation (Melamed et al., 2000). In this investigation of an open and non-equilibrium system, downward movement of P (Fig. 4) occurs within or possibly outside the soil profile, due to the coarse-textured nature of this soil (Table 1) and reduced soil pH.

4. Summary and conclusions

All P treatments (T_1, T_2 and T_3), applied at a rate of 3040 mg P/kg soil, reduced TCLP-extractable Pb levels to below the 5 mg/l critical level in the top 10 cm of soil. T_2 was also effective in reducing TCLP-Pb levels in the subsurface soils (10–30 cm). The fractionation data suggest that T_3 was most efficient in transforming Pb from the non-residual to the residual fractions. The XRD analyses indicate that the dissolution of cerussite and subsequent formation of HP or CP could be the dominant mechanisms for Pb immobilization by T_1 and T_2, while the formation of HP was the dominant mechanism in T_3.

Our results demonstrate that acidification (with H_3PO_4) prior to P application may catalyze the dissolution of Pb and phosphate rock, and thus increase the effectiveness of Pb immobilization in Pb-contaminated urban soils. However, soil acidification using soluble P sources may promote leaching of P, Pb and other metals, and could increase the risk of groundwater contamination. Further investigations incorporating groundwater monitoring data are therefore necessary to optimize P application rates and the ratio between phosphate rock

and soluble P sources, in order to develop an environmentally sound in situ Pb remediation technology.

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