

Phosphate-induced metal immobilization in a contaminated site

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“Capsule”: A mixture of H_3PO_4 and phosphate rock was effective in metal immobilization.

Abstract

To assess the efficiency of P-induced metal immobilization in soils, a pilot-scale field experiment was conducted at a metal contaminated site located in central Florida. Phosphate was applied at a P/Pb molar ratio of 4.0 with three treatments: 100% of P from H_3PO_4 , 50% of P from H_3PO_4 + 50% of P from $Ca(H_2PO_4)_2$, and 50% of P from H_3PO_4 + 5% phosphate rock in the soil. Approximately 1 year after P application, soil and plant samples were collected to determine mobility and bioavailability of selected metals (Pb, Zn, and Cu) using sequential extraction procedure and mineralogical characterization using X-ray diffraction (XRD) and scanning electron microscope-energy dispersive X-ray (SEM-EDX) analysis. Phosphorus distribution and soil pH effects were also evaluated. Phosphate was more effective in transforming soil Pb (to 53%) from the non-residual to the residual phase than soil Zn (to 15%) and soil Cu (to 13%). This was because Pb was immobilized by P via formation of an insoluble pyromorphite-like mineral in the surface and subsurface of the soil, whereas no phosphate mineral Zn or Cu was identified. While P amendment enhanced metal uptake in the roots of St. Augustine grass (*Stenotaphrum secundatum*), it significantly reduced metal translocation from root to shoot, especially Pb via formation of a pyromorphite-like mineral on the membrane surface of the root. A mixture of H_3PO_4 and phosphate rock was effective in metal immobilization, with less soil pH reduction and less soluble P. Although H_3PO_4 was effective in immobilizing Pb, its use should be limited to minimize soil pH reduction and potential eutrophication risk. Published by Elsevier Science Ltd.

Keywords: Field demonstration; Phosphate amendment; Metal immobilization; Contaminated soil

1. Introduction

Increasing awareness of the hazard that heavy metals can cause to the environment and to humans is presently pressuring society to comply with environmental regulations and develop management strategies to minimize their adverse impacts. Among available remediation technologies, in situ immobilization using metal-binding agents could be an environmentally sustainable and cost-effective alternative, especially for contaminated industrial sites. The application of P amendments to contaminated soils has been identified as a potentially efficient in situ remediation method (Cotter-Howells and Caporn, 1996; Hettiarachchi et al., 2000; Laperche et al., 1997; Ma et al., 1994). The objective is to immobilize metals primarily through the formation

of metal phosphates with reduced solubility and enhanced geochemical stability in a wide range of environmental conditions.

Phosphate has been shown to effectively immobilize Pb from contaminated soils (Boisson et al., 1999; Cotter-Howells and Caporn, 1996; Hettiarachchi et al., 2000; Laperche et al., 1996, 1997; Ma et al., 1994, 1995; Ma and Rao, 1997). It is well documented that lead phosphates are the most insoluble and stable forms of Pb in soils, and they can form rapidly in the presence of adequate Pb and P. Among all the lead phosphate minerals, chloropyromorphite has the lowest solubility, thus, it is most stable under favorable environmental conditions. Ma et al. (1993) showed that hydroxyapatite [HA , $Ca_{10}(PO_4)_6(OH)_2$] effectively immobilizes Pb in solution by formation of hydroxypyromorphite [$Pb_{10}(PO_4)_6(OH)_2$]. In addition, the potential of using phosphate rock [PR, primarily $Ca_{10}(PO_4)_5F_2$] to immobilize aqueous Pb from Pb-contaminated soils was demonstrated (Ma et al., 1995). Phosphate rock effectively

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immobilized 22–100% aqueous Pb from 13 Pb-contaminated soils. The main mechanism of Pb immobilization is via dissolution of PR and subsequent precipitation of fluoropyromorphite [$\text{Pb}_{10}(\text{PO}_4)_5\text{F}_2$]. In situ phosphate-induced formation of pyromorphite is responsible for immobilizing Pb, thereby reducing its bioavailability in soils (Hettiarachchi et al., 2000; Ruby et al., 1994).

Although P amendments have mainly been applied to remediate Pb-contaminated soil, they are also applicable to other metals such as Zn, Cu, and Cd (Xu and Schwartz, 1994). phosphate rock effectively removes Zn and Cd from aqueous solutions, but the removal mechanism is different from that of Pb. Concerning the immobilization of other metals by hydroxyapatite, several mechanisms have been proposed: (1) ion exchange processes at the surface of HA (Middelburg and Comans, 1991; Xu and Schwartz, 1994); (2) surface complexation (Xu and Schwartz, 1994); (3) precipitation of some amorphous to poorly crystalline, mixed-metal phosphates (Ma et al., 1994), and (4) substitution for Ca in HA by other metals during recrystallization (coprecipitation) (Jeanjean et al., 1994; Xu and Schwartz, 1994). The last mechanism (coprecipitation) appears more significant for Cd sorption than for Zn (Xu and Schwartz, 1994). This might be due to the fact that the ionic radius of Cd^{2+} (0.109 nm) is closer to that of Ca^{2+} (0.114 nm) than that of Zn^{2+} (0.088 nm). The isomorphic substitution by Cu^{2+} (ionic radius 0.087 nm) would be less favorable than both Cd^{2+} and Zn^{2+} . Direct evidence that Cd can occupy Ca crystallographic sites has been given using extended X-ray absorption fine structure (EXAFS) (Sery et al., 1996). It is difficult to quantitatively determine the proportions of metal removal due to specific mechanisms and it appears that the above four mechanisms more or less all work together (Xu and Schwartz, 1994). Nevertheless, the effectiveness and mechanisms of using phosphate to immobilize other metals such as Zn, Cu and Cd are not well understood.

Accordingly, soil acidic conditions may play an important role in metal immobilization using P amendments. Under neutral soil pH environments, observed solubility of metals and phosphate remains low, causing a major limitation for the efficient metal immobilization. For example, dissolution of the initial Pb phase has been reported to be the limiting factor in the formation of hydroxypyromorphite at pH values between 5 and 8 (Laperche et al., 1996). The conversion of PbO to $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ was the most rapid at pH 5. In a similar experiment, Zhang et al. (1997) found that dissolution of anglesite (PbSO_4) and cerussite limited the rate of the formation of $\text{Pb}_5(\text{PO}_4)_3\text{OH}$. Therefore, effective metal-immobilization using P amendments requires enhanced solubility of metals by inducing acidic conditions.

In addition to soil pH, different P sources, with different solubilities, may also impact the effectiveness of metal immobilization. Our previous work (Cao et al., 2001) suggested that using soluble H_3PO_4 in combination with $\text{Ca}(\text{H}_2\text{PO}_4)_2$ or PR effectively immobilized Pb from a Pb-contaminated soil. The role of H_3PO_4 in the mixture was to solubilize cerussite and PR, thereby increasing the readily available Pb in the soil, which facilitated more precipitation of Pb phosphate compounds.

Although the immobilization of heavy metals using P amendments has been very successful in the laboratory, the implementation of this technology in the field is very limited. Thus, a field demonstration of this technology was conducted at a site heavily contaminated with Pb, Cu and Zn. The main objectives of this research were (1) to demonstrate the effectiveness of P amendments on immobilization of Pb, Cu, and Zn in the field; (2) to compare the effectiveness of different P sources on metal immobilization; and (3) to assess the effects of P amendments on metal phytoavailability.

2. Materials and methods

2.1. Site characterization and experimental plot establishment

The P-treated plots were established in a highly contaminated site in Jacksonville, Florida. Past industrial activities had contaminated this site, including a gasoline station, salvage yard, auto body shop, and recycling of lead batteries. Selected physicochemical properties of composite soil samples from different plots of the site are given in Table 1. The plots are circular with areas of approximately 4 m². phosphate amendments were applied to each plot, at a 4.0 P/Pb molar ratio based on our previous tests (Cao et al., 2001). Half of the P was applied as H_3PO_4 to all plots on 17 February 2000, by mixing with 25 l of water and uniformly spraying to each plot. The plots were then covered with plastic sheets to maintain moisture contents in the surface layers. On 27 March 2000, 41 days after the first application, the second half of the P was applied as H_3PO_4 (T1), $\text{Ca}(\text{H}_2\text{PO}_4)_2$ (T2) or 5% phosphate rock (T3). A little more phosphate (~P/Pb 4.5) was added along with the consideration of less soluble P available in phosphate rock. Amendments were mixed with soil to a depth of 10 cm. The plots without P addition were set as the control (T0). Phosphate rock consists mainly of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ with substantial CO_3^{2-} substitution in the structure (Ma et al., 1995). There was no detectable Pb in this material, but it contained some Zn (Table 1).

Table 1
Selected physicochemical properties of the soil and phosphate rock

	pH	CEC ^a (cmol kg ⁻¹)	OM ^b (%)	Sand (%)	Silt (%)	Clay (%)	P _T ^c (g kg ⁻¹)	Pb _T (g kg ⁻¹)	Cu _T (g kg ⁻¹)	Zn _T (g kg ⁻¹)
Soil	6.95±0.19	5.75±0.85	3.91±0.90	87.7±1.37	9.0±1.58	3.35±0.54	0.89±0.16	11.6±1.57	2.63±0.11	1.95±0.10
PR ^d	7.10±0.31	ND ^e	ND	ND	ND	ND	156	BDL ^f	BDL	0.054

^a Cation exchange capacity.

^b Organic matter.

^c Total concentration.

^d Phosphate rock.

^e Not determined.

^f Below detection limit (Pb = 0.25 mg kg⁻¹, Cu = 0.20 mg kg⁻¹, Zn = 0.10 mg kg⁻¹).

2.2. Soil and plant sampling

Composite soil samples were collected at six depths of 0–10, 10–20, 20–30, 30–40, 40–60, and 60–80 cm, respectively, from the three treated plots (T1, T2 and T3) and from the control plot (T0) 330 days after application of P-treatments. Sampling was triplicated for each treatment. The samples were air-dried and passed through 2-mm stainless steel sieve. St. Augustine grass (*Stenotaphrum secundatum*), a predominant grass naturally growing in the tested plots, was harvested. After being rinsed with deionized water, the grasses were separated into roots and shoots, and roots were further ultrasonified to remove adhered soil particles. Shoots and roots were oven-dried at 65 °C for 4 days and digested by USEPA Method 3050A. Plant roots used for microscopic analysis were freeze-dried.

2.3. Sequential extraction of soil samples

Soil samples were subjected to sequential extraction using the method of Tessier et al. (1988). The extractions were carried out in 40 ml centrifuge tubes with 1 g of soil. The procedure separates metals into five operationally-defined fractions: water soluble plus exchangeable (WE), carbonate bound (CB), Fe-Mn oxides bound (FM), organic bound (OC) and residual (RS). A reference soil material SRM2710 (NIST, Gaithersburg, MD) was used to compare metal recovery based on sequential extraction with certified values. Recoveries were satisfactory for all metals, with 103±10% for Pb, 94±5.5% for Zn, and 91±4.3% for Cu.

2.4. Chemical analysis

Soil pH was measured with deionized water at a 1:1 rate of soil :solution after 24 h equilibrium. Soil organic matter was determined using the Walkley-Black procedure (Nelson and Sommers, 1982). Cation exchange capacity (CEC) was measured using the method of Rhoades (1982). Total P was measured colorimetrically with a Shimadzu 160U spectrometer using the molybdate

ascorbic acid method (Olsen and Sommers, 1982). elemental analysis was done using inductively coupled plasma spectrometry (ICP-AES) (Thermo Jarrell Ash ICP 61-E, Franklin, MA) or graphite furnace atomic absorption spectrometer (GFAAS; Perkin-Elmer SIMAA 600). Quality control samples included Standard Reference Materials of soil (2709 San Joaquin soil, 2710 Montana soil) and plant (1547 peach leaves) (NIST, Gaithersburg, MD).

2.5. Mineralogical characterization

Clay fractions of selected soil samples were separated by centrifugation and characterized using X-ray diffraction (XRD, Philips Electronic Instruments, Inc., Mahwah, NJ). Samples were scanned from 2 to 60° 2θ with CuK_α radiation on a computer-controlled diffractometer equipped with stepping motor and graphite crystal monochromator.

Selected soil clay and grass roots samples were further characterized using a scanning electron microscope (SEM, JSM-6400/TN500, JEOL, USA), equipped with energy dispersive X-ray elemental spectrometry (EDX). Vacuum-dried clay and root samples were mounted on carbon stubs using double stick tape and then coated with carbon. The analysis of roots necessitated a longer vacuum time to obtain a sufficient vacuum than that required for the soil samples.

3. Results and discussions

3.1. Soil characteristics at the contaminated site

Selected physical and chemical properties of surface soil (0–10 cm) are listed in Table 1. Organic matter (~4.0%) and soil pH (~7.0) were high compared to the average values for Florida soils, which average 2.9% and 5.04, respectively (Chen et al., 1999). Elevated organic matter mainly originated from the urban waste. Lime addition to neutralize acidity from lead battery probably resulted in the increase of soil pH (Nedwed and Clifford, 1997). Lead is the main contaminant with an average

concentration of $11,600 \text{ mg kg}^{-1}$. Also, elevated concentrations of Zn and Cu were observed (Table 1). The characteristics of metal contamination at this site have been described by Cao et al. (2001). Generally, Pb, Zn, and Cu were concentrated on the surface and their concentrations decreased with soil depth, and observed metal concentrations remained the highest in the subsurface (10–20 cm). However, a substantial amount of Pb ($> 2000 \text{ mg kg}^{-1}$) was found at depth below 30 cm. Therefore, this demonstration site was confronted with Pb contamination in both the horizontal and vertical dimension.

3.2. Effects on soil pH

As expected, soil pH was reduced in all P-treated plots due to the addition of H_3PO_4 (Fig. 1). Among all treatments, T1 promoted the greatest decrease in soil pH, while T3 promoted the least decrease. The range of pH values at the surface, varied from 6.46 in T0 to about 5.05 in T1, 5.22 in T2, and 5.71 in T3, which are in the range of typical Florida soils (Chen et al., 1999). As expected, application of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ or phosphate rock combined with H_3PO_4 maintained soil pH slightly higher than H_3PO_4 alone. Soil pH in all plots increased with the depth up to 40 cm, after which it decreased with depth, with soil pH being the highest at soil depth of 20–30 cm. Reduction of soil pH was mostly limited to the top 40 cm and was less than 1.5 units.

Although application of H_3PO_4 caused a decrease in soil pH, it was necessary to reduce soil pH to near 5–6 for efficient metal immobilization in this demonstrate site. As shown in Fig. 2, lead in this site was mainly associated with carbonate (T0). Therefore, it was essential to add H_3PO_4 to the soil to dissolve carbonate-associated Pb for the subsequent precipitation of insoluble pyromorphite-like mineral. Concerning the precipitation of the pyromorphite-like mineral, at a given lead and phosphate concentration, more pyromorphite-like mineral was formed at pH 5 than at pH 6 or 7 (Laperche et al., 1996).

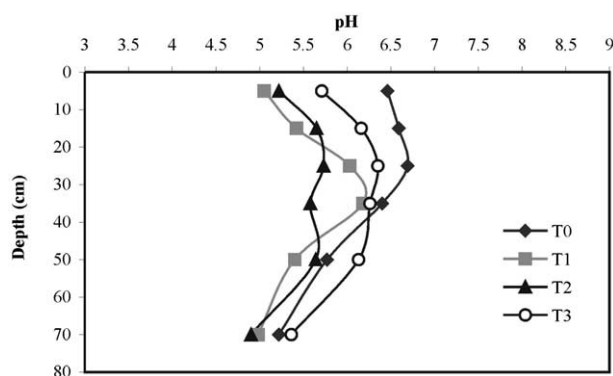


Fig. 1. pH values in the soil profile of the control (T0) and P-treated (T1, T2, and T3) plots. T1, 100% of P from H_3PO_4 ; T2, 50% of P from H_3PO_4 + 50% of P from $\text{Ca}(\text{H}_2\text{PO}_4)_2$; and T3, 50% of P from H_3PO_4 + 5% phosphate rock in the soil.

Zhang and Ryan (1999) studied the formation of pyromorphite from a combination of different Pb solids and apatite suspensions under varying pH conditions. They found that the dissolution of apatite and Pb bearing solids was the rate-limiting step of the reaction involving formation of pyromorphite.

3.3. Mineralogical characterization of soil samples

XRD patterns of the P-treated and control soils are shown in Fig. 2. A distinctive peak at 2.96 \AA in the P-treated soil samples (T1, T2 and T3) suggested in situ formation of a pyromorphite-like mineral 330 days after P application. Similarly, Cotter-Howells and Thornton (1991) and Laperche et al. (1996) observed a peak at 2.96 \AA upon P addition to a Pb-contaminated soil. Thermodynamics predict that Pb phosphate minerals are the most stable among Pb compounds (Lindsay, 1979). Thus, they can be readily formed in the presence of adequate Pb and P. Ruby et al. (1994) demonstrated that weathering of galena (PbSO_4) to insoluble lead phosphates occurred in soils at a port facility historically used for shipment of phosphate ore. Cotter-Howells (1996) reported the presence of substantial amount of pyromorphite in contaminated garden, and urban and motorway roadsides. Two additional weak peaks, which occurred at 2.87 and 3.19 \AA were identified, which may represent mixed Ca–Pb phosphates (Laperche et al., 1997). However, further research is needed to identify these unknown minerals. Discrete association of Pb with P in P-treated soils was further documented by SEM elemental dot maps of particles from a surface soil sample taken from T2 (Fig. 3a). The close association of Ca with P suggests that Pb precipitation occurred on the surface of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ particle.

The main mechanism of Pb immobilization is via dissolution of P or meta-stable Pb compounds and subsequent precipitation of a pyromorphite-like mineral. However, immobilization mechanisms for other metals may be different from that of Pb. Ion exchange has been proposed as an important mechanism in the removal of Zn from solution (Suzuki et al., 1981). In addition, Xu and Schwartz (1994) suggested that the dominant sorption process involving Zn interaction with hydroxyapatite was surface complexation of Zn with functional groups such as P–OH and coprecipitation of Zn with Ca into the apatite structure. The coprecipitation mechanism is probably more important for Zn sorption than for Pb since its ionic radius is closer to Ca than that of Pb (0.133 nm).

The intensities of 2.97 \AA peaks in soil samples of T3 were greater than those of T1 and T2. Increased peak intensity of the pyromorphite-like mineral in the T3 soil samples could indicate continued formation of the mineral in soil due to long-term supply of continuous source of PO_4^{3-} from PR after P application.

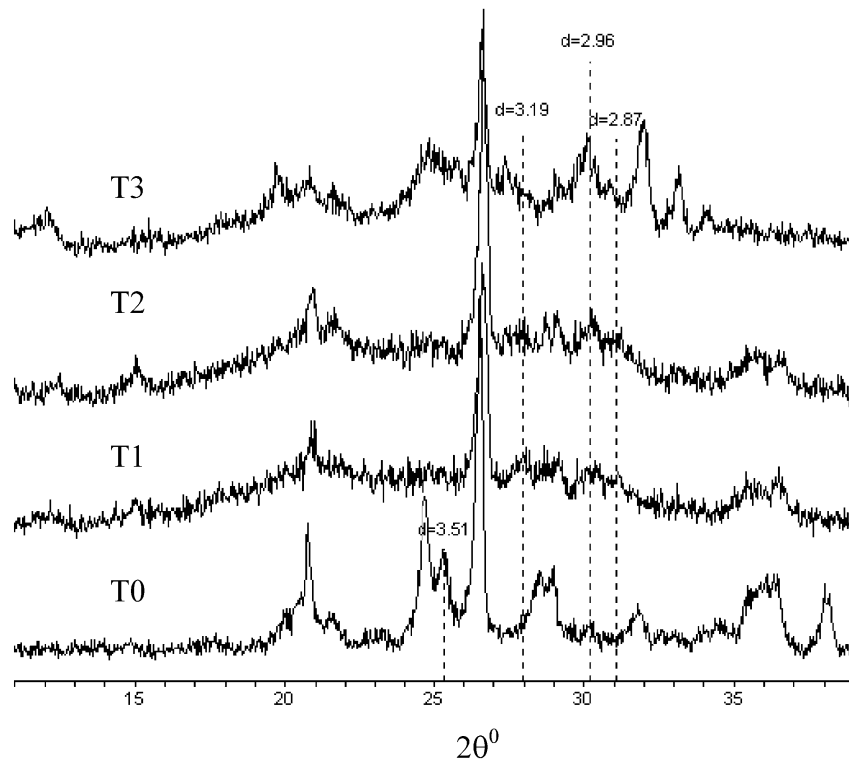


Fig. 2. X-ray diffraction patterns of surface soils (0–10cm) taken from the control (T0) and P-treated (T1, T2, and T3) plots. T1, 100% of P from H_3PO_4 ; T2, 50% of P from H_3PO_4 + 50% of P from $Ca(H_2PO_4)_2$; and T3, 50% of P from H_3PO_4 + 5% phosphate rock in the soil.

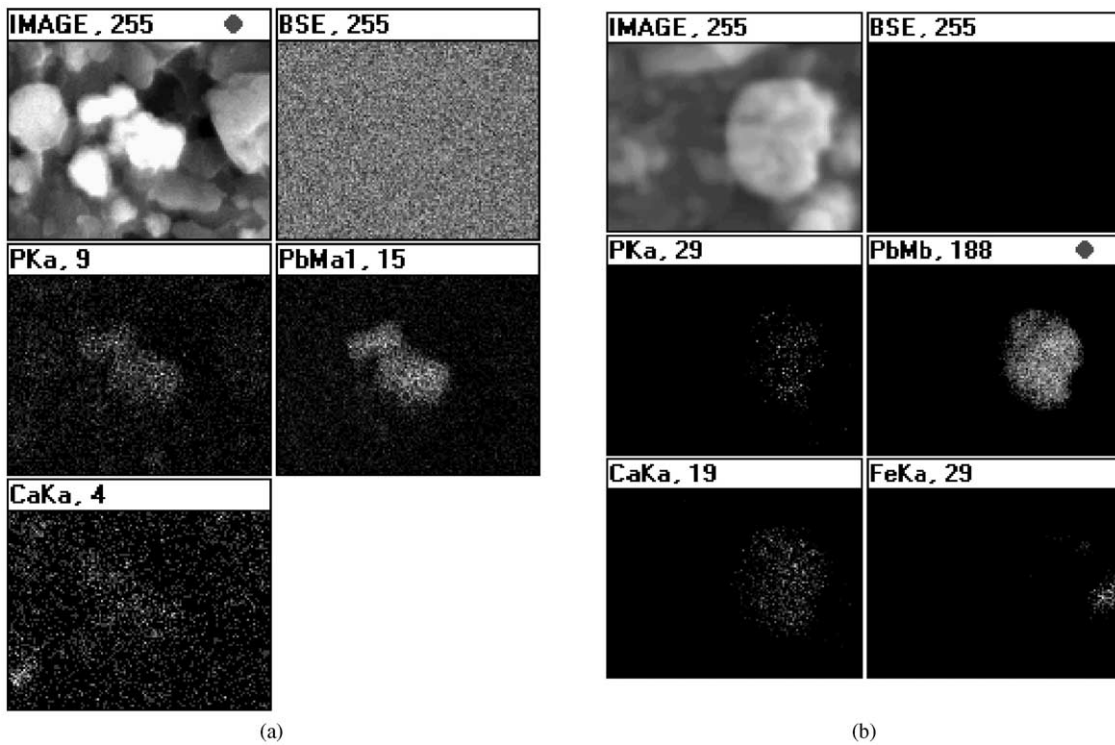


Fig. 3. Elemental distribution map of a T2 soil sample taken from (a) surface (0–10 cm), and (b) subsurface (30–40 cm). T2, 50% of P from H_3PO_4 + 50% of P from $Ca(H_2PO_4)_2$.

3.4. Metal distribution in soils

Chemical fractionation has been extensively used to assess the mobility and bioavailability of heavy metals in soils. Assuming the non-residual metal (associated with exchangeable, carbonate, Fe–Mn oxides, and organic fraction) is more bioavailable than the residual metal, then the effectiveness of in situ remediation of metal contaminated soils can be assessed using a fractionation scheme (Ma and Rao, 1997). The more effective treatments convert greater amounts of metal from the non-residual to the residual fraction.

Fig. 4 shows the distribution of Pb, Zn and Cu in the surface soils of the control (T0) and the P-treated plots (T1, T2 and T3). In the control soil, Pb was primarily associated with the carbonate fraction (43%). This was consistent with the XRD data (Fig. 2), which showed the presence of cerussite (3.51 Å). On the other hand, Zn and Cu were mainly associated with Fe–Mn oxide fractions (51% for Zn and 32% for Cu).

For surface soil, all P treatments were able to modify the partitioning of Pb from the non-residual/potentially available phase to the residual/less available phase (Fig. 4). In this respect, the major transformation was a reduction in the carbonate bound Pb (up to about 36%), while the residual phase was increased to 53%, which is consistent with our hypothesis of dissolving cerussite with phosphoric acid, followed by the precipitation of geochemically stable pyromorphite (Ma et al., 1995). In addition, Fe–Mn oxides bound Pb also decreased by about 5–18% (Fig. 4). This reduction can be attributed to the desorption of Pb from oxide surfaces, as a consequence of reduced pH, a result of phosphoric acid additions (Fig. 1). Among the three P treatments, phosphate rock (T3) was the most effective in converting Pb from the non-residual to the residual fraction, while the H₃PO₄ treatment (T1) was the least effective. This can be attributed to the fact that more P was available for formation of Pb phosphate from T3 (PR) than from T1 (H₃PO₄) treatment since some of the P from T1 was lost via leaching (Table 2) and substantially more P was added in T3 as PR (5%) than T1 or T2. Hettiarachchi et al. (2001) reported that PR was more effective than triple superphosphate or phosphoric acid in reducing Pb bioavailability for Zn–Pb contaminated soils.

Phosphate amendment also modified Zn and Cu distribution in soil, with an increase in residual Zn and Cu (Fig. 4). The main transformation for Cu was the reduction of carbonate and Fe–Mn oxide fractions, and for Zn was the reduction in exchangeable, carbonate and organic fractions. Phosphate treatment increased residual Zn by 6–16% and Cu by 3–14% across the treatment. Obviously, P amendment was less effective for immobilization of Zn and Cu than for Pb as previously reported (Ma et al., 1994). In a system with

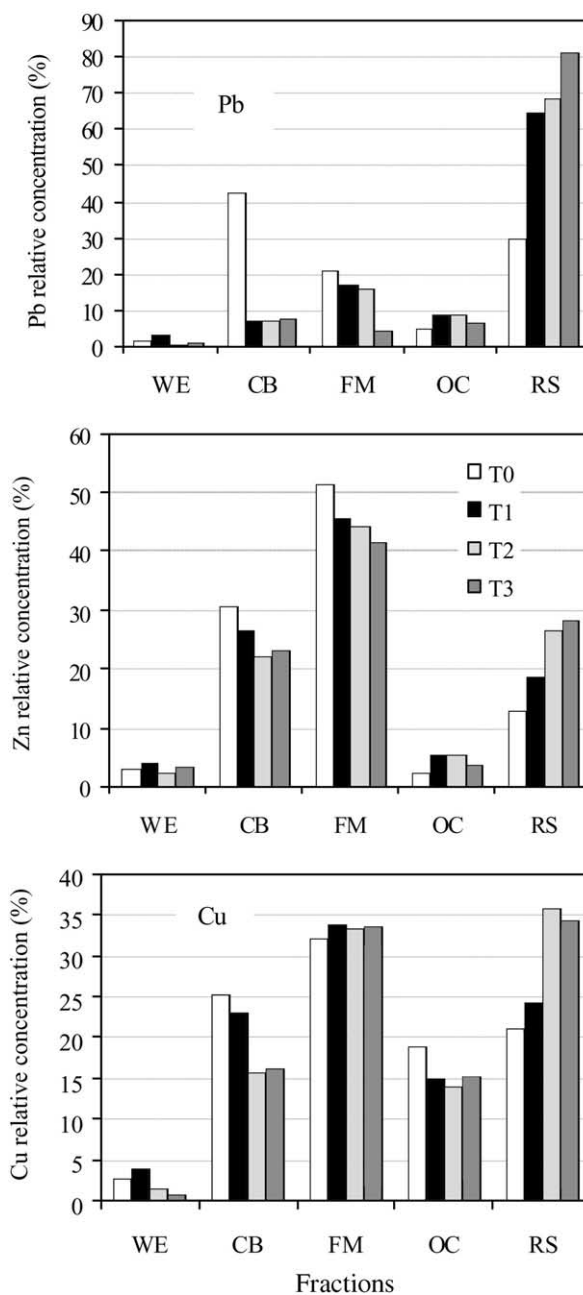


Fig. 4. Relative concentrations of Pb, Zn, and Cu in each fraction of surface soils (0–10 cm) from the control (T0) and P treated (T1, T2, and T3) plots. T1, 100% of P from H₃PO₄; T2, 50% of P from H₃PO₄+50% of P from Ca(H₂PO₄)₂; and T3, 50% of P from H₃PO₄+5% phosphate rock in the soil. WE, Water soluble and exchangeable; CB, Carbonate; FM, Fe–Mn oxide; OC, Organic matter; RS, Residual.

multiple metals, minerals with lower solubility form first. Solubility products of zinc and copper phosphate are much greater than that of lead phosphate (Lindsay, 1979), and more soluble Pb was available for the precipitation formation than Zn and Cu (data not shown). Therefore, lead phosphate was probably formed prior to copper and zinc. Cotter-Howells (1996) treated Zn-contaminated soil with soluble phosphate and detected

Zn phosphate by XRD. However, hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) is much more soluble than pyromorphite, so Zn phosphate may not control Zn solubility in this case. The reduction in extractable Zn by phosphate can be due to sorption to the phosphate mineral rather than precipitation of hopeite (Xu and Schwartz, 1994).

phosphate was not only effective in modifying Pb distribution in surface soil, but also in the subsurface soil to 40 cm (Fig. 5). Generally, P was effective in converting Pb from non-residual to residual fractions throughout the soil profile except at depth 60–80 cm. It is possible by the time the P traveled to that depth, little was left to react with soil Pb (Table 2). At the 30–40 cm depth, the percentage of Pb in the residue fraction increased from 4% to 10–25% in P-treated soils compared to the control. The effectiveness of P in immobilizing Pb in subsurface soil was also demonstrated by the close association of Pb with P as shown in Fig. 3b. the SEM elemental dot map was conducted using a soil sample taken at the depth of 30–40 cm in T2, suggesting the presence of pyromorphite after P application (Fig. 3b). However, Cu and Zn were not associated with P. In situ formation of pyromorphite in subsurface soil demonstrate the effectiveness of P-induced Pb immobilization beyond surface soils.

3.5. Phosphorus distribution in the soil profile

Attempts were made in this study to determine the total and soluble P distribution based on the amount of P added and the amount of P left in the soil 330 days after P application. This was an important task for the field test from the viewpoint of potential secondary

Table 2
Total and soluble P at different soil depths in the P-amended plots

Depth (cm)	T1 ^a		T2		T3	
	Total P ^b	Soluble P ^c	Total P	Soluble P	Total P	Soluble P
0–10	45.1	222	54.3	462	73.0	209
10–20	16.6	195	17.7	110	11.7	48.0
20–30	15.7	21.1	7.61	50.0	6.70	7.05
30–40	4.47	11.2	6.30	38.0	2.21	15.3
40–60	3.45	30.0	1.31	27.0	0.21	1.05
60–80	1.00	9.30	0.82	6.01	0.11	0.00
Total	86.3	488	88.5	693	94.2	280

^a 100% of P from H_3PO_4 alone, T1; 50% of P from H_3PO_4 + 50% of P from $\text{Ca}(\text{H}_2\text{PO}_4)_2$, T2; and 50% of P from H_3PO_4 + 5% phosphate rock in the soil, T3.

^b Expressed as percent (%) of total added phosphorus.

^c Soluble P was extracted with NaHCO_3 solution (Olsen and Sommers, 1982), and expressed as mg kg^{-1} dried soil.

contamination of P and for evaluating P utilization efficiency.

Total phosphorus added to the soil was mainly present in the surface soil layer in all treatments, ranging from 45.1% for T1, 54.3% for T2, and 73% for T3, with an overall P retention of 86–94% in the soil profile (0–80 cm, Table 2). As expected, downward migration of P was observed in this soil with low buffer capacity, which was consistent with the fact that P immobilization occurred in the subsurface soil (Figs. 3 and 5). Similarly, soluble P showed greatest in the surface soil and declined sharply with depth (Table 2). T3 had least soluble P in the surface and profile soil compared with T1 and T2 treatment. Thus, T3 posed the least eutrophication risk among the three treatments.

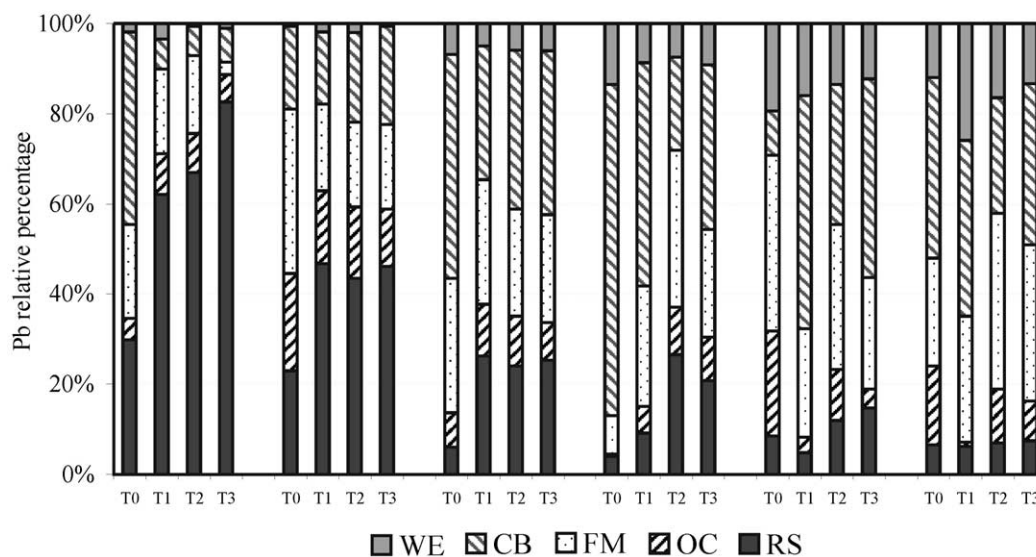


Fig. 5. Relative concentrations of Pb in each fraction of soil profile from the control (T0) and P treated (T1, T2, and T3) plots. T1, 100% of P from H_3PO_4 ; T2, 50% of P from H_3PO_4 + 50% of P from $\text{Ca}(\text{H}_2\text{PO}_4)_2$; and T3, 50% of P from H_3PO_4 + 5% phosphate rock in the soil. WE, Water soluble and exchangeable; CB, Carbonate; FM, Fe–Mn oxide; OC, Organic matter; RS, Residual.

3.6. Metal phytoavailability

In this study, P amendment was applied at a molar ratio of 4.0 P/Pb. A considerable amount of phosphate was added to the soil, resulting in more P taken up by *St. augustine grass* (*Stenotaphrum secundatum*) (Table 3), which grew naturally in the site. Phosphate concentrations were significantly elevated in the grass (root and shoot) in P-treated soils. In addition to P, elevated concentrations of Pb, Zn, Cu and Ca were also observed in plant roots in P-treated plots as compared to the control. However, metal concentrations in plant shoots were considerably lower in the P-treated plots than those of the control, except for Cu. More Pb accumulation in the roots after P addition was also observed by Laperche et al. (1997) they reported that for treatments with high quantities of P added, the content of Pb in the plant roots was the same or higher than for the unamended soil. Higher P uptake may have enhanced metal uptake due to improved plant nutrition. In addition, H_3PO_4 application possibly resulted in a temporary increase in metal availability. Among the three treatments, less Pb was accumulated in grass roots grown in T3 than T1 and T2, again demonstrating the effective of PR in immobilizing soil Pb.

Similarly, shoot P concentrations were elevated in grass growing in P-treated plots (Table 3), while shoot tissue Pb contents decreased significantly in these samples. Possibly P limited Pb translocation in the plant root, most likely by formation of pyromorphite. The SEM-EDX data were consistent with this hypothesis, i.e. that P was associated with Pb on the membrane surface of the plant root (Fig. 6). As a result of Pb association with P, translocation of Pb from root to shoot significantly decreased. Compared to the control (T0), addition of P reduced shoot Pb by 41–66%. Laperche et al. (1997) reported that the addition of HA to Pb polluted soils led

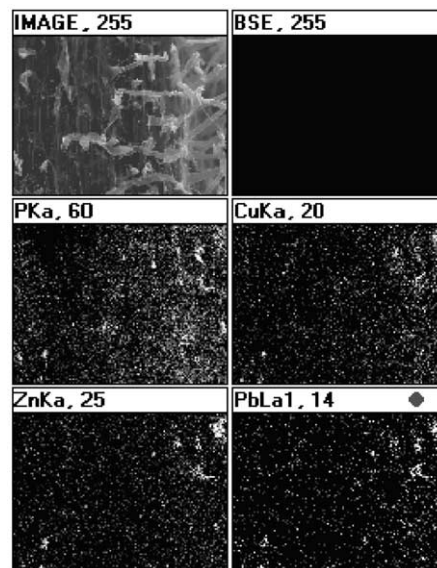


Fig. 6. Elemental distribution map of metal phosphate mineral on the membrane surface of the grass root (*Stenotaphrum secundatum*) grown in T2 soil. T2, 50% of P from H_3PO_4 + 50% of P from $Ca(H_2PO_4)_2$.

to a decrease of the Pb concentrations in shoots of sudax (*Sorghum bicolor* L. Moench). Therefore, formation of pyromorphite in the soil and association of P with Pb in the roots appear to be responsible for the reduction of Pb contents in plant shoots.

Zinc concentrations in plant tissues showed similar trends as Pb concentrations, i.e., root Zn increased with P addition, while shoot Zn decreased (Table 3). However, phosphate had a less effect on Zn uptake. After P application, root Pb concentration increased by 2–25 times, whereas root Zn increased by only 1–1.7 times relative to the control. In the shoots, Pb decreased by 43–52%, whereas Zn decreased by 26–35%. Like Pb, Zn was also associated with P (Fig. 6). Thus, Zn may be sorbed on, or co-precipitated with, pyromorphite (Ma et al., 1994; Nriagu, 1984). Zinc coprecipitation with pyromorphite would reduce its bioavailability and translocation from root to shoot, leading to the decrease of Zn concentrations in shoots. Unlike Pb and Zn, Cu concentration in the grass shoot was not affected by P amendment, though Cu was also associated with P (Fig. 6). There was no significant difference between the control and P treatments (Table 3). It is unclear why P was not effective in reducing Cu translocation from root to shoot.

Though addition of P amendments increased Ca content in the roots, Ca content in the shoots were reduced. Thus, high Ca availability in the soil, especially T2 ($Ca(H_2PO_4)_2$) and T3 (PR), didn't increase Ca translocation to plant shoots, which was similar to Pb uptake and translocation. Laperche et al. (1997) found that particles adhering to root surfaces in Pb contaminated soils showed co-association of Pb, P and Ca. They

Table 3
P and metal concentrations in the roots and shoots of *St. Augustine grass* (*Stenotaphrum secundatum*)

	P (mg kg ⁻¹ DW)	Pb (mg kg ⁻¹ DW)	Zn (mg kg ⁻¹ DW)	Cu (mg kg ⁻¹ DW)	Ca (mg kg ⁻¹ DW)
<i>Root</i>					
T0	910c	140c	208c	144c	6400c
T1	2150a	444b	355a	934a	6753c
T2	1251b	600a	312b	244b	8320b
T3	1080c	110c	216c	109d	12,780a
<i>Shoot</i>					
T0	970c	59.1a	195a	14.1a	17,640a
T1	1448b	20.2c	128c	13.4a	9990c
T2	1546b	35.0b	145b	15.9a	11,820c
T3	1842a	30.3b	131c	15.4a	13,420b

Means with the same letter within a column are not significantly different at $P < 0.05$, Student-*t* test.

hypothesized that precipitates form in the root can be formed. The increasing P concentration in the root upon P addition could therefore lead to an increase of Ca precipitates in the roots. In the present study, Ca association with P was observed in the soil and inside the roots (Figs. 3 and 6).

4. Conclusions

This pilot-scale field study indicates that P amendments are efficient in transforming lead from non-residual into residual forms. The effective immobilization of lead is attributed to the in situ formation of insoluble pyromorphite-like minerals after application of P amendment. Phosphate amendment is effective for Pb immobilization, but less for Zn and Cu. Although P amendment enhanced the accumulation of Pb, Zn, and Cu in the roots of *Stenotaphrum secundatum*, it significantly reduced metal translocation from roots to shoots (except for Cu) via formation or co-precipitation of insoluble metal phosphate in the roots. A mixture of H_3PO_4 and rock phosphate efficiently immobilized metals, with less impact on soil pH and less leaching of soluble P than H_3PO_4 alone and $H_3PO_4 + Ca(H_2PO_4)_2$. In addition, because this in situ technology does not change the total concentration in soil, it is important to investigate the long-term effects of P on soil Pb as well as Zn and Cu immobilization, which is particularly helpful for assessing the feasibility of P amendment in the field.

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