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FIELD APPLICATION OF PHOSPHATE ROCK FOR REMEDIATION OF METAL-CONTAMINATED SOILS

FINAL REPORT

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FIELD APPLICATION OF PHOSPHATE ROCK FOR REMEDIATION OF METAL-CONTAMINATED SOILS

FINAL REPORT

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PERSPECTIVE

Environmental regulatory agencies are always interested in the development of technology that will offer low-cost, effective means to remediate contaminated sites. Sites contaminated with lead have been of particular interest since they are perhaps the most commonly found heavy metal-contaminated sites in the nation. Dr. Ma's work is an effort to develop a treatment technique that would provide a rapid, simple, low-cost, and effective methodology to achieve the goal of reducing the bioavailability of lead in soils and waters.

G. Michael Lloyd, Jr.
Research Director, Chemical Processing

ABSTRACT

This research project focused on the long-term feasibility of phosphate-induced Pb immobilization in the field. The selected site is located at urban area of Northwest Jacksonville and was contaminated with Pb primarily due to past battery recycling activities. Based on our laboratory results, a pilot-scale field demonstration was initiated in 2000. Phosphate amendment was employed at a P/Pb molar ratio of 4. Half of the P amendment was first applied as H_3PO_4 to all plots, and six weeks later the other half was applied as H_3PO_4 in Treatment 1 (T1), $Ca(H_2PO_4)_2$ in Treatment 2 (T2) and 5% phosphate rock in Treatment 3 (T3).

For this study, soil samples were collected on 8/27/2005, 4.5 years after the initial P application, and were analyzed for pH and total Pb, Ca and P concentrations. In addition, Pb concentrations extracted using the toxicity characteristic leaching procedure (TCLP), synthetic precipitation leaching procedure (SPLP), and physiologically based extraction test (PBET) in the soil samples were determined. No water was available for sampling during the trip, therefore no data will be presented.

After 4.5 years of phosphate application, the acidification effects of phosphoric acid were only observed in Treatment T1 at the top 30 cm, with a pH reduction of 1 unit compared to the control. In all treatments, the highest Pb concentrations were observed at 20-40 cm, ranging from 296 to 36,300 mg kg^{-1}. The total Pb concentration in the control was much lower than those in P-treated soils, which makes it difficult to evaluate the effects of P application in the soil. As expected, P concentrations in all three treatments were elevated, especially at the surface soil and with Treatment T3. As far as P leaching is concerned, Treatment T2 was the most efficient, with the least amount of P being migrated down the soil profile. Though it may have added more risk for P leaching down to the groundwater, the fact that phosphate rock migrated down the soil profile implied that Pb immobilization at subsurface soil is possible by adding phosphate rock to surface soil. This may be significant in terms of soil remediation since phosphate-induced Pb immobilization has been limited to surface soil only.

Due to the heterogeneity of soil Pb distribution and lower Pb concentrations in the control sample, evaluation of phosphate-induced Pb immobilization was based on normalized data, i.e. ratios of TCLP-Pb, SPLP-Pb, and PBET-Pb to total Pb were used. Among the three treatments, all three treatments were effective in reducing TCLP-Pb (43-50%) and PBET-Pb (19-75%), with Treatment T3 being most effective partially because phosphate rock remained in the soil even after 4.5 years. On the other hand, Treatment T1 was effective in reducing SPLP-Pb (42-62%) in the soil. Among the three treatments, the PBET (2.85-100% of total Pb) was the strongest in extracting soil Pb, followed by TCLP (0.34-7.43% of total Pb) and SPLP (0.21 to 4.88% of total Pb).

Our research further suggests that P amendments can be a cost-effective and environmental-friendly alternative to treat Pb-contaminated soils. However, caution should excised to maximize lead immobilization and minimize potential adverse impacts

caused by application of phosphate amendments to soils. It is recommended to reverse the phases of P application, i.e., to add calcium phosphate and phosphate rock first and apply phosphoric acid second, or add them all simultaneously. This would lead to the dissolution of cerussite and more insoluble P amendments at the same time, favoring lead immobilization and minimizing potential P and Pb leaching.

ACKNOWLEDGMENTS

This research was sponsored in part by the Florida Institute of Phosphate Research. The authors would like to express sincere appreciation to Mr. G. Michael Lloyd, Jr. of the Florida Institute of Phosphate Research for his vision and leadership provided to this project, and for his assistance and support throughout this research project.

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MATERIALS AND METHODS

INTRODUCTION

Many anthropogenic activities generate wastes and tailings that have contributed to the elevation of heavy metals in the environment. Heavy metals are toxic to animals, humans and aquatic life. The ubiquitous nature of heavy metals, their toxicity even in trace quantities, and their tendency to bioaccumulate in the food chain have led to stricter environmental regulations in heavy metal discharges. Therefore, it is necessary to develop schemes to remove heavy metals from both waste waters and landfill leachates and to remediate metal contaminated sites (Ma and others 1993). Among heavy metals, lead (Pb) is of most environmental concern to USEPA and Florida Department of Environmental Protection (FDEP).

There are thousands of Pb-contaminated sites nationwide. A total of 1,208 contaminated sites are currently listed on the EPA National Priority List waiting to be remedied. In Florida alone, there are 52 such sites on the list. The presence of hazardous levels of Pb in soils collected in Tampa is evidence of Pb pollution in the urban environment, which requires remedial actions to adequately protect public health, especially that of children.

Considerable attention is now being paid to develop cost-effective technologies to remedy contaminated sites with the primary goal of reducing human metal exposure via drinking water, direct ingestion and dust inhalation (Cotter-Howells and Thornton 1991). Among the remediation technologies available for contaminated sites, *in situ* metal immobilization is an economically realistic and cost-effective alternative, especially for vast industrial sites. *In situ* immobilization refers to *in situ* reduction of metal bioavailability and leachability in contaminated soils using environmentally friendly amendments, i.e. adding substance(s) to soils to immobilize a contaminant in a form whose geochemical stability and water solubility reduce leachate concentrations to acceptable levels (Czupyrna and others 1989). The application of phosphate amendments has been identified as a potentially efficient *in situ* remediation technology. The principal objective of this technique is to form new mineral phases of metal phosphate with reduced solubility and increased geochemical stability in a wide range of environmental conditions.

Phosphate has been shown to effectively immobilize Pb from various contaminated soils (Boisson and others 1999; Cotter-Howells and Caporn 1996; Hettiarachchi and others 2000; Laperche and others 1996, 1997; Ma and others 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 lead and phosphate. Among all the lead phosphate minerals, chloropyromorphite has the lowest solubility; thus, it is the most stable under favorable environmental conditions. Ma (1993) showed that hydroxyapatite ($Ca_5(PO_4)_3OH$) has the potential to immobilize Pb in solution by the formation of hydroxypyromorphite.

Phosphate rock [primarily $Ca_{10}(PO_4)_5F_2$] effectively immobilized Pb from aqueous solutions, with immobilization ranging from 39% to 100%. The main mechanism of Pb immobilization is via dissolution of phosphate rock and subsequent precipitation of a fluoropyromorphite-like mineral [$Pb_{10}(PO_4)_5F_2$]. Moreover, the potential of using phosphate rock to immobilize aqueous Pb from Pb-contaminated soil was demonstrated (Ma and others 1995). Phosphate rock could effectively immobilize 22% to 100% of the aqueous Pb from 13 Pb-contaminated soils. In these studies, the effectiveness of phosphate rock to immobilize Pb was based on the formation of insoluble lead phosphate. Formation of pyromorphite upon the addition of apatite or soluble inorganic P amendments has been observed in Pb-contaminated soils (Cotter-Howells 1996; Laperche and others 1997). The formation of lead phosphates in contaminated soils may be responsible for immobilizing Pb and thereby reducing its bioavailability (Hettiarachchi and others 2000; Ruby and others 1994).

Laperche and others (1996) reacted hydroxyapatite with litharge/massicot (PbO), cerussite ($PbCO_3$), and they are successful in isolating Pb-enriched fractions from contaminated soil at pH values of between 5 and 8. Dissolution of the initial Pb phase appeared to limit the rate of hydroxypyromorphite ($Pb_5(PO_4)_3OH$) formation. Conversion to $Pb_5(PO_4)_3OH$ was fastest at pH=5. Similarly, Zhang and others (1997) found that the dissolution of anglesite ($PbSO_4$) and cerussite ($PbCO_3$) limited their rate of conversion to $Pb_5(PO_4)_3OH$. Thus, the acidity of the soil plays an important role in the immobilization of metal using phosphate amendment. The mechanism of metal immobilization after phosphate amendment could be considered as the dissolution of metal compounds in soils, followed by the precipitation of insoluble metal phosphates. Under existing soil environments, the observed solubility of Pb compounds and phosphate minerals remained limited, a major limitation for their effective and efficient immobilization. For example, lead carbonate (cerrusite) has been identified as a major mineral in many contaminated soils, particularly in battery recycling sites (Nedwed and Clifford 1997; Royer and others 1992). Therefore, effective Pb immobilization using phosphate amendments requires inducing acidic conditions that will promote the solubility of Pb minerals as well as lead phosphate formation. In addition, different phosphorus sources, due to their own different solubilities, may also affect metal immobilization.

A comparison for various metal-remedial technologies shows that one cubic yard of soil remediation cost about \$170, \$470, \$25, \$85, and \$40, respectively, for phytoremediation, electrokinetics, phosphate mixing, cement solidification, and dig and haul technology. Therefore, phosphate treatment is the most cost-effective (www.pimsnw.com). Although much knowledge has been acquired about the mechanisms and requirements involved in the immobilization of heavy metals using phosphate amendments, and laboratory experiments using phosphate treatment have been successful, to our knowledge, the implementation of this technology remains a very limited test *in situ* in the field.

The lack of field demonstration of this relatively new technology has greatly hindered its acceptance and application as cost-effective method to remedy heavy metal-contaminated soils. Thus, a field demonstration of this technology, at a site heavily contaminated with Pb and other heavy metals, was conducted in a previous study (Cao and others 2003). A mixture of H_3PO_4 and $Ca(H_2PO_4)_2$ as well as phosphate rock was used as the source of P. Soluble P ensures rapid Pb immobilization, whereas phosphate rock provides long-term Pb immobilization by P.

The objective of this research is to continue monitoring the long-term effectiveness of the field application of P amendments on metal mobility, solubility and availability using chemical, biological and mineralogical methods. The field application of P amendments in this project started in the year 2000; so far, we have collected soil and water data for two years (2001 and 2002). For a remediation technology to be successfully applied in the field, it is critical to know its long-term effectiveness, i.e. 5-10 years after its application. Specifically, we would like to (1) demonstrate the feasibility and effectiveness of phosphate amendments on immobilization of Pb in a contaminated site; and (2) assess the mobility and bioavailability of Pb in contaminated soil after the application of P treatments.

EXPERIMENTAL SITE CHARACTERIZATION

The lead-contaminated site is located in an urban area of northwest Jacksonville, Florida. It consists of a vacant, fenced rectangular area (4,100 m^2), and is covered by vegetation (mainly grasses). Past industrial activities, which included a gasoline station, salvage yard, auto body shop, and the recycling of lead batteries, have all contributed to the contamination of this site. The total lead concentrations in the soil ranged from 36 to 21,074 mg kg^{-1}. Lead concentration decreased with soil depth, with the majority of the Pb present near the soil surface (0-20 cm). Mineralogical characterization of the site by x-ray diffraction (XRD) reveals that $PbCO_3$ (cerussite) is the predominant Pb mineral on the site (Cao and others 2002).

EXPERIMENTAL PLOT INFORMATION

Four test plots for P treatment were established on the north-central ("hotspot") zone of the selected Jacksonville site. These plots had a Pb concentration of >2,000 mg Pb kg^{-1}. Selected soil properties at the test plots were given in the previous report (Cao and others 2002). Each plot consisted of an area of 4 m^2 that was isolated by a high-density polyethylene geomembrane liner 2.5 mm thick to prevent flooding out of or into the plots. The plots were separated 1.5 m in distance from each other to avoid possible inter-plot contamination (Figure 1).

Phosphate amendments were applied to three plots (T1, T2, and T3) at a molar ratio of P to Pb of 4, except for Treatment T3 (Cao and others 2002). The mean Pb concentration in the soil was used, e.g., 5,085 mg kg^{-1}. The total amount of P added was calculated for the surface soil of 0-20 cm depth. It was applied at a rate of 3,040 mg P

kg^{-1} soil for Treatments T1 and T2, and 10,840 mg P kg^{-1} soil for Treatment T3 (Chen and others 2003).

To pre-acidify the soil, half of the P was first applied to the three plots on 02/17/2000 as $CaCl_2$+H_3PO_4 by mixing it with 25 L of water (liquid to solid ratio = 0.03) and spraying it uniformly in each area. The plots were then covered with plastic sheets to maintain the moisture content of the surface layers and to prevent leaching from rainfall. The addition of $CaCl_2$ was to provide adequate Cl^- needed for the formation of the least soluble lead phosphate, chloropyromorphite ($Pb_5(PO_4)Cl_2$).

On 03/27/2000, 40 days after the first application, the second half of the P amendments was applied as H_3PO_4 in Treatment T1, $Ca(H_2PO_4)_2$ in Treatment T2 and 5% phosphate rock (PR) in Treatment T3 by uniformly mixing them with a shovel to a depth of 20 cm. This is a passive mixing approach with minimum site disturbance compared to a large-scale field operation using machinery such as plus mills. The plot without P treatment was set as the control (T0). After the second P application, the plots were exposed to rainfall. St. Augustine grass (*Stenotaphrum secundatum*) was predominantly and naturally growing at the tested site. After P application, aboveground biomass regenerated from the roots.

Monitoring wells (MW1, MW2, and MW3) were installed in the centers of the T1, T2, and T3 plots, respectively. The wells consisted of PVC with a 1.9 cm internal diameter, and 2 m long screens, which were installed 1.7 m above and 2 m below groundwater level. Well installations were performed using a geoprobe, with points hydraulically driven to the required depth with minimum disturbance of the test zone.

The phosphate rock used in this research was obtained from Occidental Corp. (White Springs, FL). It consisted mainly of $Ca_{10}(PO_4)_6F_2$, with substantial CO_3^{2-} substitution in the structure (Ma and others 1995). In our study, low concentrations of Pb and other metals were detected in the phosphate rock.

Figure 1. Application of P at the Jacksonville Demonstration Site.

SAMPLING PROCEDURE

Triplicate composite soil samples were collected from each plot at six depths of 0-10, 10-20, 20-30, 30-40, 40-60, and 60-80 cm, respectively, on August 27, 2005, approximately 4.5 years (1,610 days) after the first P application. This resulted in a total of 72 soil samples. Control samples were taken from three randomly chosen places outside of the treated areas. One of the limitations of this experimental plot is the absence of a designated control area. The samples were air-dried and passed through a 2 mm sieve. Unfortunately, there was no water available for sampling during the trip, therefore no data will be presented.

CHARACTERIZATION OF SOIL SAMPLES

Chemical Analyses

The soil samples were analyzed for total Pb and Ca via flame atomic absorption spectroscopy after being digested using the hot-block digestion procedure (USEPA Method 3050a). The samples were analyzed with a Varian 220 Flame AA, using a SIPS sample introduction system and an air-acetylene flame. Calibration was checked using a second source reference solution to +/- 15% recovery. Quality control samples included Standard Reference Materials of soil (2709 San Joaquin Soil, 2710 Montana Soil) (U.S.

Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899).

Soil pH was measured with deionized water at a 2:1 soil:solution ratio after 24 h of equilibrium. Approximately 8g of soil was weighed into a 20mL vial. Twice the weight of the soil aliquot was added to the vial, which was then capped and shaken to mix the sample thoroughly, and allowed to sit for 24 hours before analysis. Total phosphorus was measured colorimetrically with a Shimadzu 160U spectrometer using the molybdate ascorbic acid method (Olsen and Sommers 1982).

In Vitro Pb Bioavailability Assay

Lead bioavailability of the soil samples was determined using an *in vitro* method (Ruby and others 1993). The *in vitro* test, which is also referred to as a physiologically based extraction test (PBET), was developed to evaluate the relative bioavailability of ingested metals from different mine wastes in the gastrointestinal tracts of animals and humans. This method uses a laboratory digestion procedure to reproduce gastrointestinal tract chemistry and function, and provides a screening-level estimate of the relative dissolution of metals from different mine wastes. This is especially important for Pb, since inhalation and ingestion are the two major pathways for human exposure in Pb-contaminated soils.

Toxicity Characteristic Leaching Procedure for Pb

The toxicity characteristic leaching procedure (TCLP) is designed to evaluate the potential of hazardous constituent migration through vadose zone soils to the water table under landfill conditions. Higher Pb concentration in TCLP extracts means higher Pb mobility in a soil. The modified TCLP method was conducted on soil samples to determine the effectiveness of P-induced Pb immobilization in the soil.

Synthetic Precipitation Leaching Procedure for Pb

A synthetic precipitation leaching procedure (SPLP) was used to determine leachable Pb concentrations in the soils. It was done using extraction fluid No. 1 (pH 4.20), which simulates unbuffered acid rain for sites east of the Mississippi. The SPLP Pb concentration was determined following the procedure of USEPA Method 1311 at a solid to liquid ratio of 1:20 (USEPA 1994). This procedure is used to determine the mobility of inorganic elements present in soils.

DATA ANALYSIS AND QUALITY CONTROL

All results are expressed as an average of the triplicate samples with standard deviation. Standard soil reference materials (2709 San Joaquin soil and 2710 Montana soil) from the National Institute of Science and Technology were carried through the digestion and analyzed as a part of the quality assurance-quality control protocol (within 100 ± 20%). Reagent blanks and internal standards were used where appropriate to ensure accuracy and precision in the lead analysis. Differences among different means were determined by analysis of variance.

RESULTS AND DISCUSSION

SOIL pH

It is expected that the application of phosphoric acid to a soil will reduce soil pH, which was observed in the soil samples collected up to 480 days after P application (Cao and others 2003). Even after 1,610 days (4.5 years) of P application, the effects of acidification are still visible, especially in the phosphoric acid treatment (T1) area (Table 1 and Figure 2).

Table 1. Changes in Soil pH at Different Depths 4.5 Years After P Treatment at the Surface 20 cm.

Depth (cm)	Control	T1	T2	T3
0-10	5.89+/-0.26	4.88+/-0.26	5.82+/-0.37	5.72+/-0.27
10-20	6.04+/-0.22	5.31+/-0.35	5.52+/-0.19	5.75+/-0.31
20-30	6.17+/-0.33	5.47+/-0.30	5.78+/-0.38	5.90+/-0.21
30-40	6.16+/-0.42	5.59+/-0.29	5.20+/-0.87	6.01+/-0.24
40-60	5.92+/-0.25	5.58+/-0.42	5.04+/-0.71	6.08+/-0.38
60-80	5.67+/-0.12	5.57+/-0.32	5.12+/-0.61	6.00+/-0.29

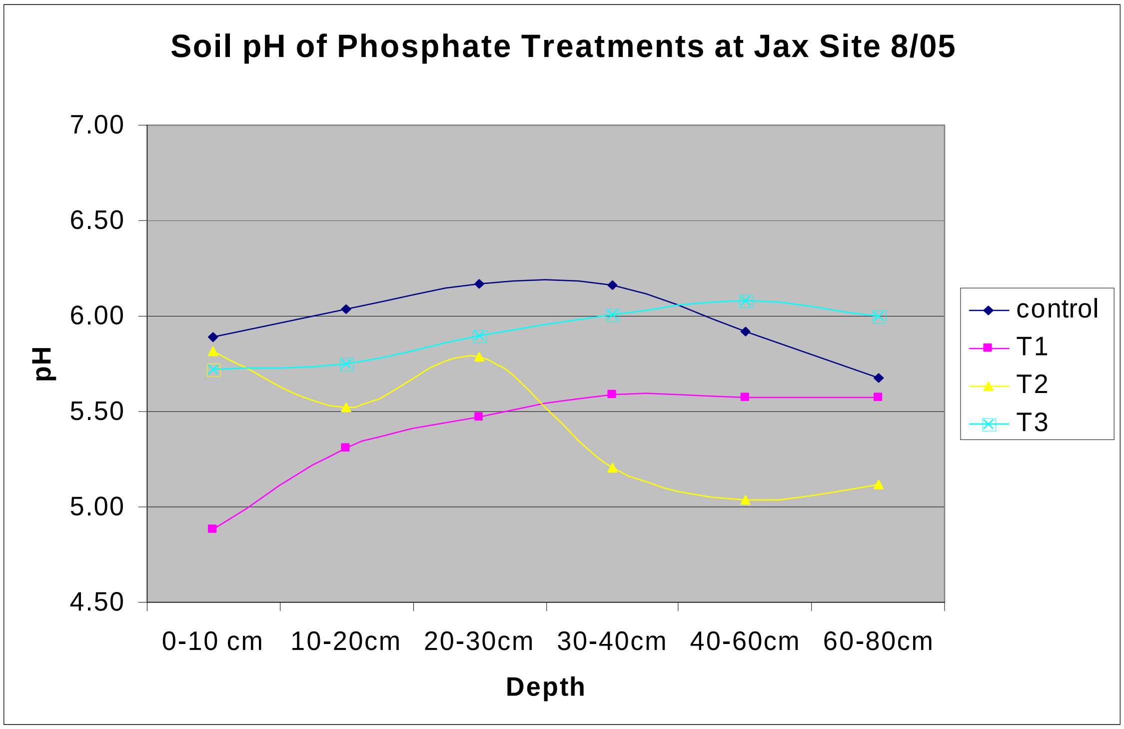

Figure 2. Changes in Soil pH with Soil Depth 4.5 Years After P Treatment at the Surface 20 cm.

In the control treatment, the soil pH at the surface was 5.89, varying from a range of 5.67 to 6.17 with soil depth. In Treatment T1, the soil pH at the surface was 4.88, which was one unit lower than the control. This reduction in pH was observed up to the 20-30 cm depth, after which the pH effect was limited. Compared to Treatment T1, the pH effect in Treatments T2 and T3 was limited. This was especially true for Treatment T3, which showed little change in soil pH at all depths. However, though no change in pH was observed up to 30 cm, lower pHs were observed at lower depths in Treatment T2. It is not clear as to why this happened.

Though soil pH changed with soil depths, no consistent trend was observed. Soil pH in the control and in Treatment T2 were lower at a lower depth, whereas those in Treatments T1 and T3 were lower at the surface. This makes it complicated to determine the P-induced effects on soil pH. The fact that the soil was unable to return to its original pH even after 4.5 years clearly demonstrated the importance of controlling the use of phosphoric acid to minimize the reduction in soil pH.

TOTAL Pb CONCENTRATIONS IN THE SOIL

In Soil Samples Collected 4.5 Years After P Application (This Study)

The site is very heterogeneous, as can be seen from the large standard deviations in the total Pb data (Table 2). Moreover, half of the samples were digested and analyzed twice due to what we felt were unacceptable variations in the digestion of the triplicate samples as compared to the initial digestion. NIST SRM 2710 (Montana Soil) was analyzed in duplicate, with each batch of samples having a recovery of 89 ± 2%. Two blanks and 10% of the triplicate samples were digested with each digestion batch. Due to the large variability in total Pb concentrations and the difficulty in trying to pick an appropriate spike target relative to the calibration range of the instrument, it is difficult to interpretate the data. All blanks were below the detection limit.

The heterogeneity in total Pb concentrations in the soil was obvious with soil depth as well as in different locations (Table 2). In the control treatment, Pb contamination was mostly limited to the top 40 cm of soil, ranging from 4,290 at the surface to 5,260 mg kg^{-1} at the 30-40 cm depth. The total Pb concentrations were greatly reduced after a depth of 40 cm, ranging from 296 to 620 mg kg^{-1}. It is interesting to note that the highest Pb concentration in the control soil was observed not at the surface, but rather at the subsurface at a depth of 20-30 cm. It is possible that over the years, some of the Pb from the surface may have migrated down the soil profile.

Table 2. Total Pb Concentrations in Soil Samples at Different Depths Collected 4.5 Years After Receiving P Treatment at the Surface (mg kg^{-1}).

Depth (cm)	Control	T1	T2	T3
0-10 cm	4290±226	7560±1780	16620±10000	5130±1400
10-20 cm	6490±5420	9210±2970	36300±2260	6940±679
20-30 cm	8390±6230	10800±566	29100±3120	18800±3480
30-40 cm	5260±7110	27200±10500	3800±1680	11800±4280
40-60 cm	620±355	5200±1700	4740±2960	5020±2800
60-80 cm	296±154	5110±6190	4110±3060	1400±503
SRM 2710*	4950±1051			

*: This represents the average of 6 trials of SRM 2710. True Value = 5532 mg/kg.

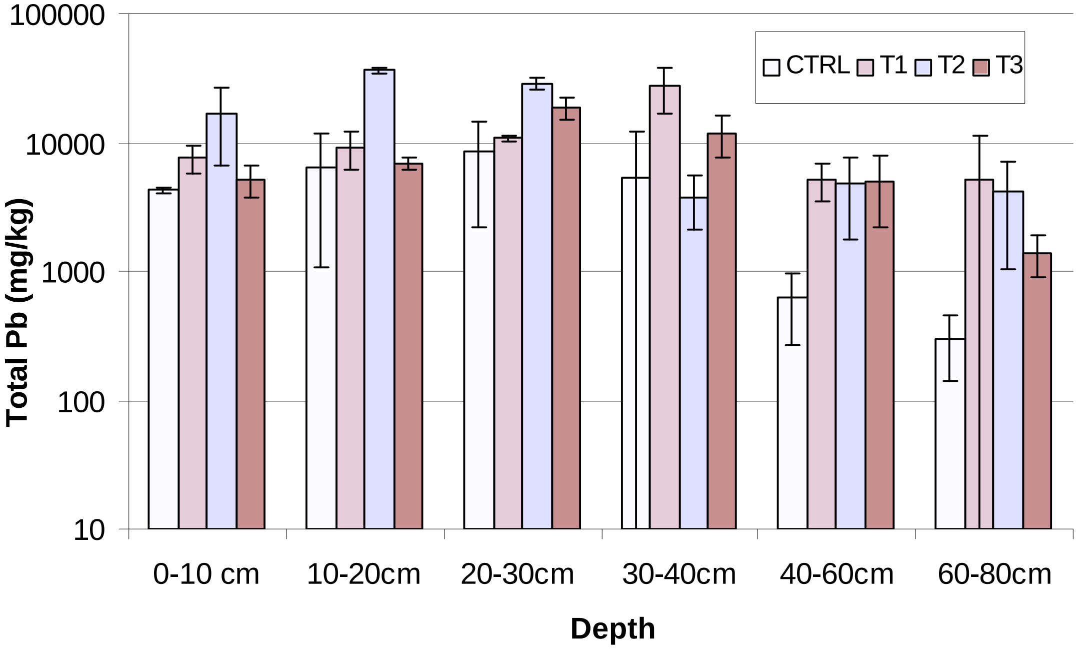

Figure 3. Changes in Total Pb Concentrations with Soil Depth 4.5 Years After P Treatment at the Surface 20 cm.

Unlike the control, in Treatment T1 elevated Pb concentrations were observed up to a depth of 80 cm, i.e., throughout the whole soil profile. It is possible that some of the Pb from the surface may have migrated down the soil profile. The addition of phosphoric acid may have facilitated the Pb migration. The highest Pb concentrations in Treatment T1 were observed at 30-40 cm, followed by 20-30 cm. Again, the lowest Pb concentrations were observed at the lowest depth.

Consistently in all four treatments, the highest Pb concentrations were observed at 20-40 cm, with none at the surface. Elevated Pb concentrations in the 40-80 cm range in Treatments T2 and T3 may support the hypothesis that the addition of P may have induced Pb mobilization from surface soil to subsurface soil. This is a very important consideration when applying phosphoric acid to a Pb-contaminated soil.

Again, given the large variations among the duplicate samples, caution needs to be exercised when using the data. In addition, it is also important to consider the inherited heterogeneity of Pb concentrations in contaminated soils. It is not possible to mix the soil to make it homogeneous, so extra care needs to be taken when dealing with such data.

Compared to Soil Samples Collected 220 Days After P Application (Chen and others 2003)

Due to the heterogeneity of soil Pb distribution, total Pb concentrations in soil samples collected previously (Chen and others 2003) were quite different from those in this study. One significant difference was that the total Pb concentration in the control in this study was much lower than that in the previous study. For example, the total Pb in this study was 4,290 mg kg^{-1} at the 0-10 cm depth compared to 11,595 mg kg^{-1} in the previous study, which is almost three times lower (Figures 3 and 4). In fact, the total Pb concentration in the control was the lowest among the four treatments in this study (Figure 3). The total Pb concentrations in Treatments T1, T2 and T3 were 7,560, 16,600, and 5,130 mg kg^{-1}, respectively, which were 1.8, 3.9 and 1.2 times greater than those in the control at the 0-10 cm depth (Figure 3).

In the previous study, total Pb concentrations at depths of up to 30 cm were comparable among the four treatments (Figure 4). At depths greater than 30 cm, the total Pb concentrations in the control were generally lower than those in the P-treated soils. However, this was not the case in this study. Throughout the soil profile, total Pb concentrations in the control were the lowest among the four treatments (Figure 3), with the differences being greater in the top 40 cm. The lower Pb concentration in the control compared to the soils that received P application made it difficult to compare the treatment effect of P application.

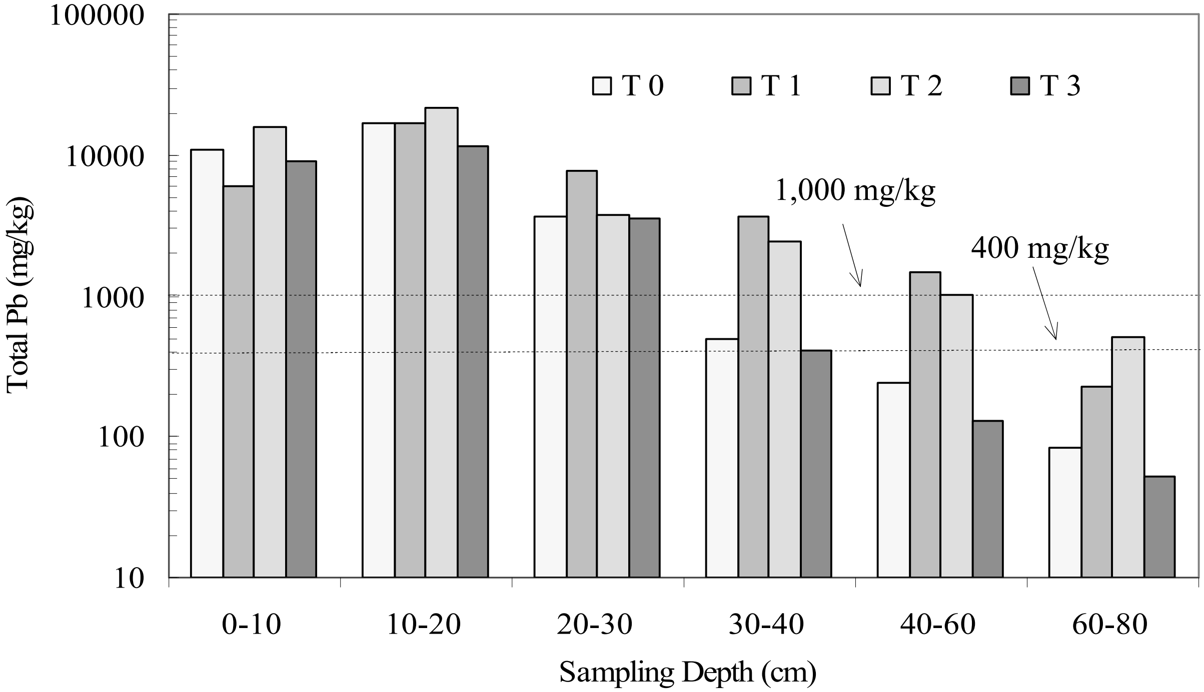

Figure 4. Changes in Total Pb Concentrations with Soil Depth 220 Days After P Treatment at the Surface 20 cm (from Chen and others 2003).

TOTAL P CONCENTRATIONS IN THE SOIL

Total P in Soil Samples Collected 4.5 Years After P Application (This Study)

The amount of P applied to the soil was based on the molar ratio of P/Pb of 4. Half of the P was applied as phosphoric acid plus $CaCl_2$ and the other half as phosphoric acid (T1), $Ca(H_2PO_4)_2$ (T2), and phosphate rock (T3). The total P/Pb molar ratio for Treatments T1 and T2 was 4, but not for T3 since 5% of the phosphate rock was added instead of a 2 molar ratio of P/Pb. The P was applied at a rate of 3,040 mg P kg^{-1} soil for Treatments T1 and T2, and 8,670 mg P kg^{-1} soil for Treatment T3. So, in terms of the total P applied among the three treatments, Treatment T3 had the highest, which was 3.6 times greater than those of treatments T1 and T2. On the other hand, in terms of total soluble P, TreatmentsT1 and T2 were higher than Treatment T3.

As expected, P concentrations in all three treatments were elevated, especially at the surface soil and with treatment T3 (Figure 5). Total P in the control was less than 1 g kg^{-1} regardless of the soil depth. However, P concentrations in the three treatments varied greatly with treatment and soil depth. Among the three treatments, T3 had the greatest P throughout the soil profile, while Treatments T1 and T2 were similar.

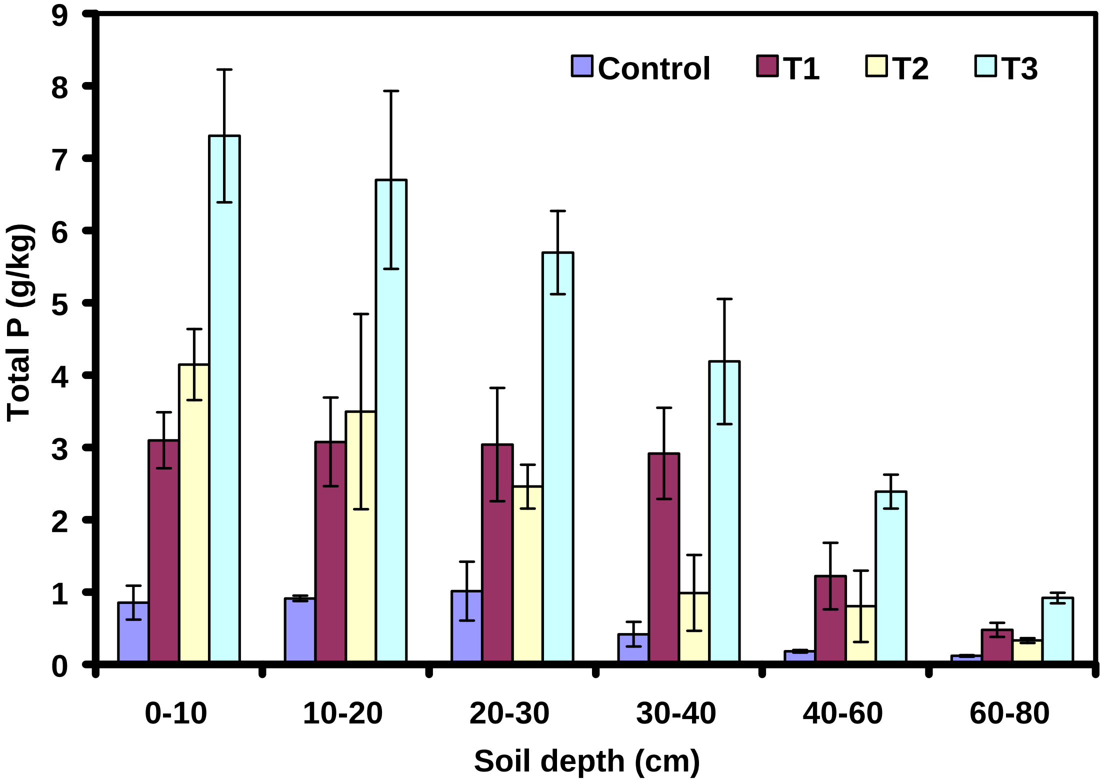

Figure 5. Changes in Total P Concentrations with Soil Depth 4.5 years After P Treatment at the Surface 20 cm.

Since the P was applied to the surface soil (top 20 cm), it is expected that most of the P was present at the surface for all three treatments. For Treatment T1, P concentrations at depths of 0-10, 10-20, and 20-30 cm were similar, with that at the depth of 30-40 cm being slightly lower and that at 60-80 cm being the lowest. For Treatments T2 and T3, similar trends were observed, i.e., greater P concentration in the top 30 cm, with 60-80 cm being the lowest.

Though the phosphoric acid was applied to the top 20 cm, it had migrated down to the soil profile up to 60 cm. A similar trend was observed in Treatment T3. Though not soluble, it is possible that phosphate rock powders traveled down the soil profile with rain water. Compared to Treatments T1 and T3, P migration in Treatment T2 was less obvious. In Treatment T2, P migrated only to a depth of 20-30 cm. As far as P leaching is concerned, Treatment T2 was the most efficient, with the least amount of P being migrated down the soil profile.

Phosphate Retention in Soil Samples Collected 4.5 Years After P Application (This Study)

The P was applied to the top 20 cm soil at a rate of 3,040 mg P kg^{-1} soil for Treatments T1 and T2, and 8,760 mg P kg^{-1} soil for Treatment T3. The P concentrations in the control soil at different depths were 855, 914, 1013, 417, 182, and 119 mg kg^{-1}, respectively (Figure 5). Based on the fact that the P was applied only to the top 20 cm and counting the existing P concentrations in the soil, the amounts of P retained by the soil were calculated (Table 3).

It was expected that some of the added P would be leached out of the soil profile. In the study of Cao and others (2003), approximately 86.3, 88.5 and 94.2% of the P was retained in the soil profile in Treatments T1, T2, and T3, respectively, which were collected 330 days after P application (Table 4). However, 4.5 years after P application, the amounts of P retained in all three treatments were greater than 100%, which doesn't make sense. To make comparison easier, the data were normalized to 100% for each treatment (Table 3). Due to the large variations, the P data were analyzed twice; still, the data make little sense.

Table 3. Percentage Retention of P at Different Soil Depths in P-Amended Soils.

Depth (cm)	T1*	T2	T3
	%†		
0-10	36.9	54.1	37.2
10-20	35.6	42.5	33.4
20-30	33.3	23.8	27.0
30-40	41.1	9.4	21.7
40-60	17.1	10.2	12.7
60-80	5.9	3.5	4.6
Total	170	144	137
	Normalized to 100% for Each Treatment		
	T1*	T2	T3
0-10	21.7	37.6	27.2
10-20	20.9	29.5	24.3
20-30	19.6	16.5	19.7
30-40	24.2	6.52	15.9
40-60	10.1	7.11	9.30
60-80	3.47	2.42	3.36
Total	100	100	100

* H_3PO_4 alone, T1; ½ H_3PO_4+½$Ca(H_2PO_4)_2$, T2; and ½ H_3PO_4+5% phosphate rock, T3.

† Expressed as percent (%) of total added phosphorus. It was calculated based on the fact that the P was applied only to the top 20 cm at a rate of 3,040 mg P kg^{-1} soil for Treatments T1 and T2, and 8,670 mg P kg^{-1} soil for Treatment T3. The calculation also counted for the existing P concentrations in the soil at different depths, which were 855, 914, 1013, 417, 182, and 119 mg kg^{-1}.

Table 4. Percentage Retention of P at Different Soil Depths in P-Amended Plots (Cao and Others 2003).

Depth (cm)	T1*	T2	T3
	%†		
0-10	45.1	54.3	73.0
10-20	16.6	17.7	11.7
20-30	15.7	7.61	6.70
30-40	4.47	6.30	2.21
40-60	3.45	1.31	0.21
60-80	1.00	0.82	0.11
Total	86.3	88.5	94.2

* H_3PO_4 alone, T1; ½ H_3PO_4+½$Ca(H_2PO_4)_2$, T2; and ½ H_3PO_4+5% phosphate rock, T3.
† Expressed as percent (%) of total added phosphorus.

Phosphate migration down the soil profile was also obvious by the relative distribution of P in the soil profile. In the study of Cao and others (2003), most of the P was retained in the surface soil 330 days after P application. For example, 54.3 and 73% of the P was retained in the top 10 cm. In the current study, much less P remained in the top 10 cm, i.e., 21.7-37.6% (normalized data). When phosphate rock was selected as a P source, it was expected that it would stay in the soil on a long-term basis since it was applied as powders and is relatively insoluble. It is possible that phosphate rock particles migrated down the soil profile in this sandy soil.

In the previous study (Table 4), there was significant reduction in P concentrations from 0-10 cm to 10-20 cm, i.e. 45.1%, 54.3% and 73.0% to 16.6%, 17.7%, and 11.7% for Treatments T1, T2, and T3. This is because all the P was applied to the top 20 cm, with 50% of the P sprayed on the surface as a liquid. This was not observed in this study, i.e., little change was observed from depths 0-30 cm, and even at 30-40 cm, a substantial amount of P was observed (Table 3). It is suspected that some of the surface soil (with high P) might have fallen down the soil profile during soil sampling, i.e., the elevated P at the subsurface may have been caused by artifact. For each sampling trip, three separate samples were collected for each depth for each treatment. Over the years, there must have been at least 15 samples collected over an area of 1 m^2. As such, unintended physical mixing of soil samples was not unreasonable.

A comparison of P concentrations during three sampling periods was compiled in Figure 6. The decrease in soil P with depth was obvious for the sampling dates in 2001 and 2002, but not in 2005.

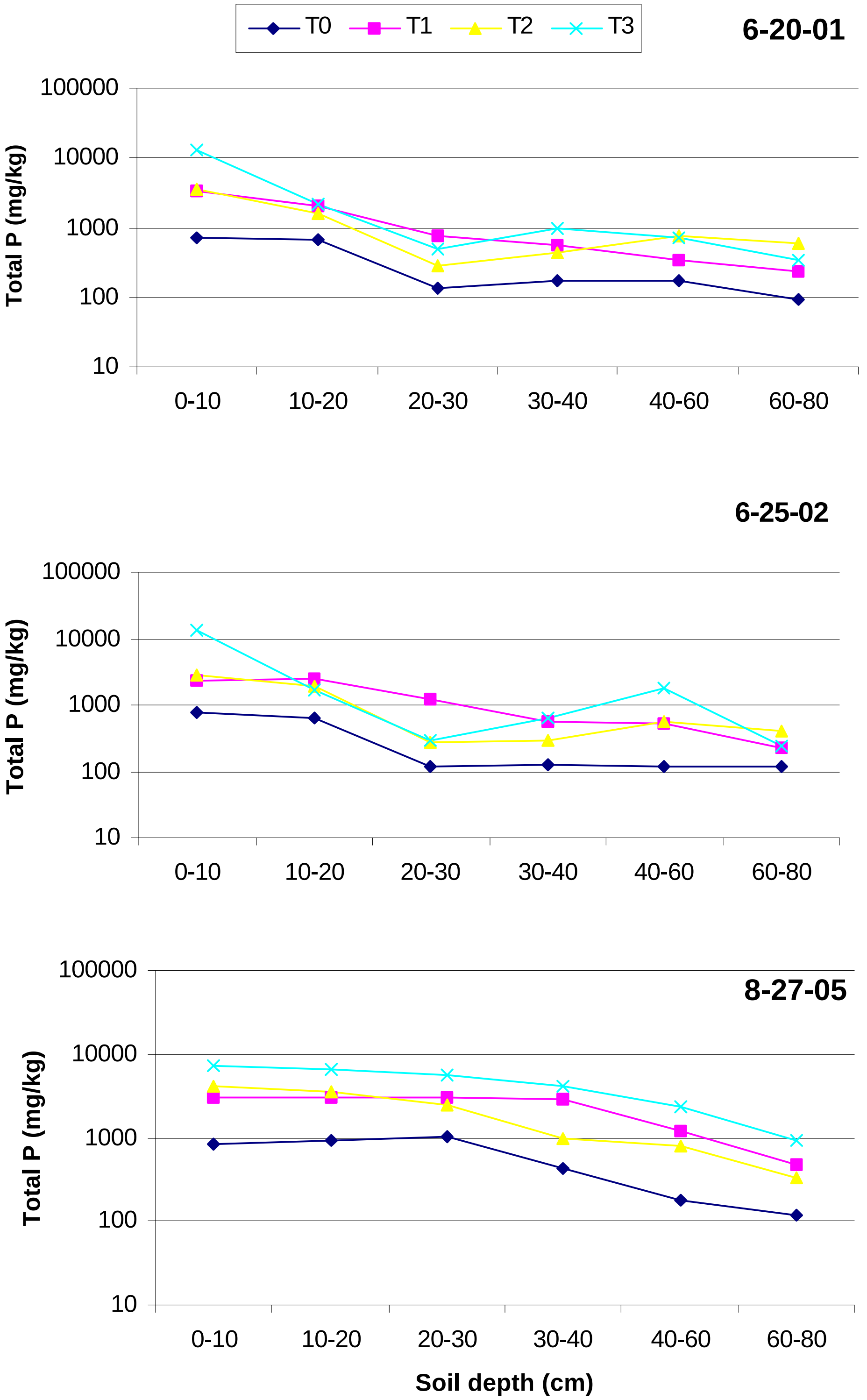

Figure 6. Comparison of P Concentrations at Different Depths Over the 4.5 Years After P Treatment at the Surface 20 cm.

TOTAL Ca CONCENTRATIONS IN THE SOIL

Total Ca in Soil Samples Collected 4.5 Years After P Application

In addition to total P concentrations, total Ca concentrations were also determined in the soil samples (Figure 7). The amounts of calcium applied to the soil were different among the three treatments. Half of the P was applied as phosphoric acid plus $CaCl_2$ and the other half as phosphoric acid (T1), $Ca(H_2PO_4)_2$ (T2), and phosphate rock (T3). The total P/Pb molar ratio for Treatments T1 and T2 was 4, but not for T3 since 5% phosphate rock was added instead of a 2 molar ratio of P/Pb. So, in terms of the total Ca applied among the three treatments, Treatment T3 had the highest Ca followed by treatment T2, with treatment T1 having the lowest Ca. Since $CaCl_2$ was applied in all treatments, it was not considered in Ca mass balance, presumably it has been all leached out from the soil profile.

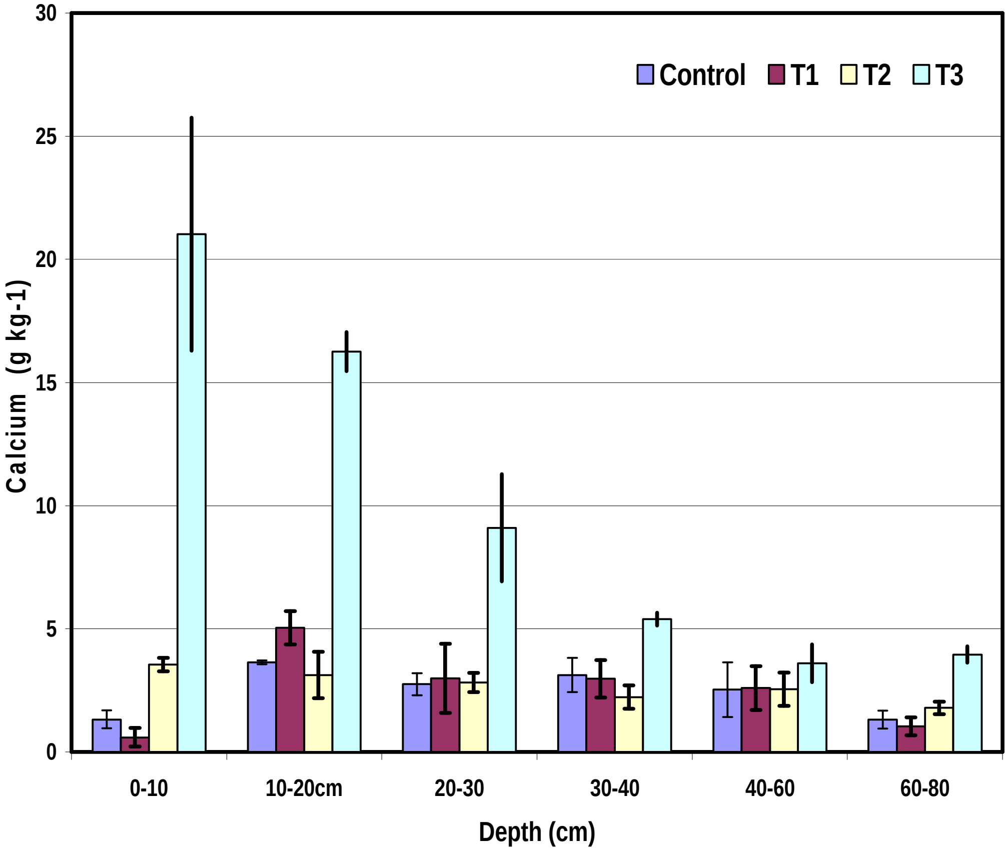

Figure 7. Changes in Total Ca Concentrations with Soil Depth 4.5 Years After P Treatment at the Surface 20 cm.

Among the three treatments, elevated Ca concentrations in the soil profile were observed only in Treatment T3, which was consistent with the P data (Figure 5). In other words, both P and Ca data suggested that phosphate rock indeed had migrated down the soil profile. The highest Ca concentration was observed at the depth of 0-10 cm, and decreased with soil depth. Even at the depth of 60-80 cm, the total Ca concentration in Treatment T3 was two times greater than that in the control. This was the first time we observed migration of phosphate rock in the soil. Without looking at the data, one would have expected that the Ca in Treatment T2 would have been more mobile since it is more soluble than that in Treatment T3. It is possible that the large quantity of phosphate rock applied may also have facilitated its migration down the soil profile.

Though it may have added more risk for P leaching down to the groundwater, the new finding implied that Pb immobilization in subsurface soil is possible by adding phosphate rock to surface soil. This may be significant in terms of soil remediation, since phosphate-induced Pb immobilization has been limited to surface soil only. With the migration of phosphate rock, we may be able to utilize this new observation to more effectively immobilize Pb in contaminated soils.

Calcium Retention in Soil Samples 4.5 Years After P Application

Due to the heterogeneity of soil Ca concentrations, such a comparison is just a rough estimate of Ca retention in soils. The amount of Ca added in all treatments as $CaCl_2$ was negligible, amounting to only 16.7 mg kg^{-1}, so it was not considered during Ca mass balance. The amounts of Ca added in Treatments T2 and T3 was 1.96 g kg^{-1} as $Ca(H_2PO_4)_2$ and 34.4 g kg^{-1} as phosphate rock in the top 20 cm of the soil.

Though up to 30% of the Ca was retained for Treatment T2, most of it came from one depth at 60-80 cm (Table 6). It is possible that this is real, i.e., the added Ca was not completely leached from the soil. However, given conditions in Florida, all soluble Ca should have been leached out of the soil after 4.5 years. For Treatment T3, however, almost all the Ca was retained in the soil since Ca was applied as concentrated phosphate rock in powder form. As discussed earlier, phosphate rock was mobile, since Ca was found in all soil depths up to 60-80 cm. The majority of the Ca (87%), however, stayed at the surface 30 cm, with only limited migration of phosphate rock occurring during the 4.5 years after its application.

The Ca retention at depths of 30-40, 40-60 and 60-80 cm were 5.10%, 2.40% and 5.94%, respectively, and 2.27, 1.07 and 2.65 g kg^{-1}, respectively (Table 5, Figure 6). The phosphate rock contains 15.6% P and 34.3% Ca and a total of 34.4 g kg^{-1} was added to the surface 20 cm. Based on the total P added as phosphate rock, the remaining P from phosphate rock would then be 1033, 487, and 1206 mg kg^{-1}. These figures were much lower than those determined in the soil (Figure 5).

This calculation was supported by the strong correlation between total Ca and total P in the soil samples, with $r^2 = 0.82$. The strong correlation may also indicate that Ca and P were leached out of the soil at a similar rate.

Table 5. Percentage Retention of Ca at Different Soil Depths in P-Amended Plots (This Study).

Depth (cm)	T1*	T2	T3
	%†		
0-10	--	0.0	44.2
10-20	--	0.0	28.3
20-30	--	3.68	14.2
30-40	--	0.0	5.10
40-60	--	1.34	2.40
60-80	--	24.6	5.94
Total	--	30	100

* H_3PO_4 alone, T1; ½ H_3PO_4+½$Ca(H_2PO_4)_2$, T2; and ½ H_3PO_4+5% phosphate rock, T3.

† Expressed as percent (%) of total added Ca. It was calculated based on the fact that the Ca was applied only to the top 20 cm at a rate of 1960 mg kg^{-1} soil for Treatment T2, and 3440 mg kg^{-1} soil for Treatment T3. The calculation also counted for the existing Ca concentrations in the soil at different depths, which were 1320, 3640, 2750, 3120, 2530 and 1310 mg kg^{-1}.

TCLP Pb CONCENTRATIONS IN THE SOIL

TCLP Pb in Soil Samples

The toxicity characteristic leaching procedure (TCLP) is designed to evaluate the potential of hazardous constituent migration through the vadose zone soils to the water table under landfill conditions. Higher Pb concentrations in TCLP extracts mean higher Pb mobility in a soil. Except for one anomaly for Treatment T1 at 30-40 cm, all TCLP Pb concentrations were below 20 mg L^{-1}, including the control (Figure 8). As discussed earlier, due to the low Pb concentration in the control, and different Pb concentrations among the treatments, it is difficult to compare TCLP Pb among the treatments.

For the surface soil (0-10 cm), all three treatments were effective in reducing TCLP Pb from 9.4 to below 5 mg L^{-1} (Figure 8). Among the three treatments, T3 was the most effective, partially because phosphate rock still remained in the soil profile after 4.5 years of leaching. This is consistent with our original objective of using phosphate rock for long-term stability of Pb in the soil. There was no significant difference in TCLP Pb between T1 and T2.

Comparison of TCLP Pb in Soil Samples

TCLP Pb data have not been shown much in the past, due partially to the randomness of the collected soil samples. To illustrate the random changes in TCLP Pb, a comparison of TCLP Pb was made across five sampling dates (Table 6). Based on TCLP Pb in the control (T0), it is clear that TCLP Pb changed randomly with no trend to follow, either with sampling date or soil depth. It all depended where the samples were collected. Since total Pb concentrations in the soil changed both vertically and horizontally (Table 2), it will be impossible to evaluate the treatment effects. Besides T0, changes in TCLP Pb in the other three treatments were also random, indicating little effect from P application.

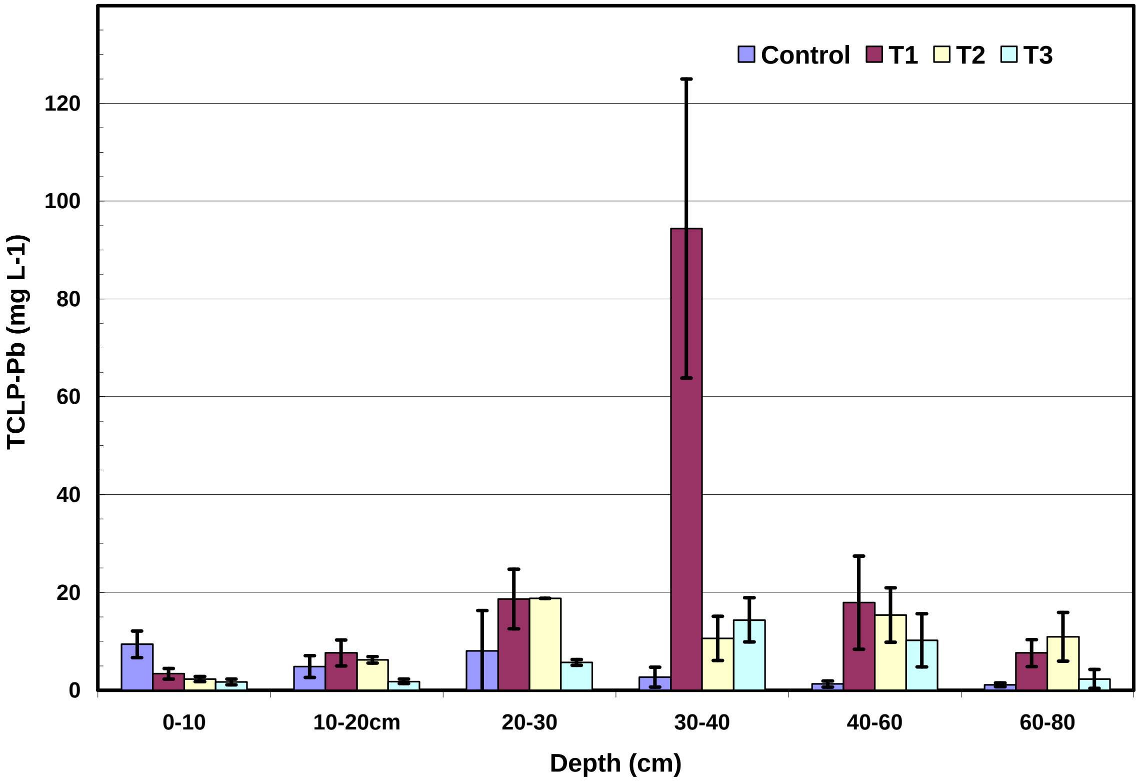

Figure 8. Changes in TCLP Pb Concentrations with Soil Depth 4.5 Years After P Treatment at the Surface 20 cm.

Table 6. Changes in TCLP Pb Concentrations in Soil Samples Collected Over 4.5-Year Period.

Depth (cm)	06-25-2000			
	T0[#]	T1	T2	T3
0-10	5.29	4.07	**7.19**	2.09
10-20	**15.8***[*]	**101**	**15.5**	**9.56**
20-30	1.02	**16.5**	**8.19**	3.54
30-40	0.39	**8.51**	3.27	1.99
40-60	0.18	2.10	2.57	0.48
60-80	2.20	**10.8**	3.24	0.60
Depth (cm)	09-26-2000			
	T0	T1	T2	T3
0-10	1.72	1.68	1.93	1.72
10-20	**35.9**	3.97	**87.7**	**35.9**
20-30	**16.5**	2.4	**19.3**	**16.5**
30-40	2.92	2.84	1.84	2.92
40-60	1.11	3.54	0.28	1.11
60-80	0.34	1.74	0.09	0.34
Depth (cm)	01-17-2001			
	T0	T1	T2	T3
0-10	**30.7**	1.58	1.41	1.24
10-20	**47.2**	**10.7**	**7.98**	**12.1**
20-30	**12.0**	**44.4**	3.46	**13.3**
30-40	3.58	2.60	3.59	0.76
40-60	0.10	0.34	4.09	0.87
60-80	0.25	0.74	**7.99**	0.41
Depth (cm)	06-20-2001			
	T0	T1	T2	T3
0-10	**166**	1.82	1.70	1.52
10-20	**76.0**	**23.2**	**32.6**	**14.1**
20-30	**5.77**	**21.5**	**10.8**	2.26
30-40	**24.7**	3.93	**5.75**	1.31
40-60	**18.3**	1.85	3.15	1.19
60-80	2.71	0.35	**6.03**	0.44
Depth (cm)	08-27-2005			
	T0	T1	T2	T3
0-10	**9.40**	3.38	2.30	1.69
10-20	4.85	7.63	**6.19**	1.80
20-30	**8.06**	**18.7**	**18.7**	**5.69**
30-40	2.69	**94.4**	**10.6**	**14.4**
40-60	1.30	**17.9**	**15.4**	**10.2**
60-80	1.10	**7.61**	**10.9**	2.30

* TCLP Pb >5 mg L^{-1} is presented in bold type.

Control, T0; H_3PO_4 alone, T1; ½ H_3PO_4+½$Ca(H_2PO_4)_2$, T2; and ½ H_3PO_4+5% phosphate rock, T3.

Ratios of TCLP Pb to Total Pb in Soil Samples

To better evaluate the effect of P application on TCLP Pb, the ratio of Pb extracted by TCLP solution to total Pb was calculated (Table 7). It is clear that only a small fraction of the total Pb was extracted by TCLP, ranging from 0.34-7.43%, with an average of 3.19%. There was no significant difference in the ratios of TCLP Pb to total Pb in Treatments T0, T1 and T2, with the average ranging from 3.41 to 3.80. However, the average for Treatment T3, which was 1.93, was significantly lower compared to the other three treatments. Since only Treatment T3 retained significant amounts of P in the soil profile (the highest among the three treatments), it makes sense that much less Pb was extracted from Treatment T3. To further support this hypothesis, another correlation was calculated, i.e., the ratio of TCLP Pb/total Pb and total P ($r^2 = -0.56$), which indicates that P was effective in reducing TCLP Pb in the soil profile (Table 8).

Correlation Between Different Variables in Soil Samples

To better evaluate the effects of P application on Pb immobilization in the soil, the correlation coefficient (r^2) between the total Pb and TCLP Pb in samples collected in this study was calculated. The correlation coefficient of 0.48 (Table 8) indicates that the two variables were correlated with greater total Pb, resulting in greater TCLP Pb.

Since P was added to the soil for the purpose of immobilization, the correlation coefficient between TCLP Pb and total P in the soil samples was also calculated and was determined to be 0.006. This indicates that the P in the soil had little impact on TCLP Pb. This may be because the strong correlation between TCLP Pb and total Pb may override the relationship between the TCLP Pb and total P, which in theory should be strongly correlated. The fact that total Pb and total P were correlated ($r^2 = 0.32$) indicates that the two were associated to some extent, i.e., the Pb in the soil helped to retain the added P in the soil profile (Table 8).

Table 7. Percentage Pb Extracted by TCLP Solution in the Soil Samples Collected 4.5 Years After Phosphate Application.

Depth (cm)	T0*	T1	T2	T3
	%			
0-10	4.38	0.89	2.77	0.66
10-20	1.49	1.66	0.34	0.52
20-30	1.92	3.46	1.29	0.61
30-40	1.02	6.94	5.58	2.44
40-60	4.19	6.88	6.50	4.06
60-80	7.43	2.98	5.30	3.29
Average	3.41	3.80	3.63	1.93

* Control, T0; H_3PO_4 alone, T1; ½ H_3PO_4+½$Ca(H_2PO_4)_2$, T2; and ½ H_3PO_4+5% phosphate rock, T3.

Table 8. Correlation Coefficients among Different Variables in the Soil Samples Collected 4.5 Years After Phosphate Application.

Variables	TCLP Pb	TCLP Pb	Total Pb	TCLP Pb/Total Pb
	Total Pb	Total P	Total P	Total P
r^2	0.48	0.006	0.32	-0.56
Variables	SPLP Pb	SPLP Pb	TCLP Pb	SPLP Pb/Total Pb
	Total Pb	Total P	SPLP-Pb	Total P
r^2	0.69	0.53	0.27	0.02
Variables	PBET Pb	PBET Pb	TCLP Pb	PBET Pb/Total Pb
	Total Pb	Total P	PBET-Pb	Total P
r^2	0.84	-0.42	0.45	-0.42

SPLP Pb CONCENTRATIONS IN THE SOIL

SPLP Pb in Soil Samples

The synthetic precipitation leaching procedure (SPLP) has often been used to assess the risk of groundwater contamination posed by contaminated soils. The concentrations of pollutants in SPLP leachate can be measured and compared to groundwater quality criteria to determine if groundwater contamination is likely.

This was the first time that we determined SPLP Pb in this soil (Figure 9), so no comparison can be made with previous data. The effects of P application were not apparent from the SPLP Pb. If anything, it seemed that P application increased SPLP Pb in the soil.

Ratios of SPLP Pb to Total Pb in Soil Samples

Similar to TCLP Pb, assessment of the effects of P application on SPLP Pb will be difficult due to the differences in total Pb concentrations in different soil samples. As a result, the percentage of Pb extracted with SPLP to total Pb was calculated (Table 9).

The amount of Pb extracted by the SPLP solution was low, ranging from 0.21 to 4.88%, lower than that extracted by the TCLP solution. This was expected because the pH in the SPLP solution (4-5) was higher than that of the TCLP solution (~2-4). Among the three treatments, only Treatment T1 showed lower Pb extraction (0.69%) compared to the other three treatments (1.18-1.82%). This is different from TCLP, since Treatment T3 was more effective.

Correlation Between Different Variables

To better evaluate the effects of P application on Pb immobilization in the soil, the correlation coefficient (r^2) between total Pb and SPLP Pb in samples collected in this study was calculated. The result was 0.69 (Table 8), indicating that the two variables were correlated, with greater total Pb resulting in greater SPLP Pb. The correlation between SPLP Pb and total Pb was stronger than that between SPLP Pb (0.69) and total Pb (0.48).

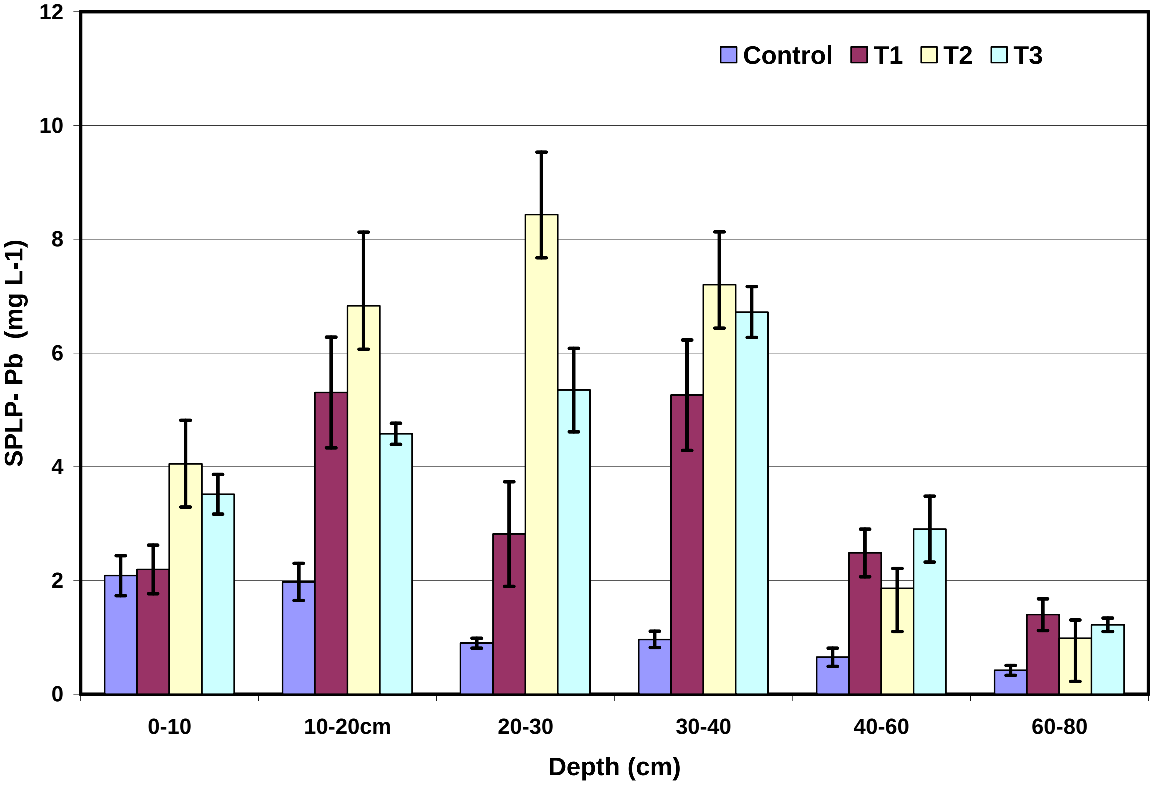

Figure 9. Changes in SPLP Pb Concentrations with Soil Depth 4.5 Years After Phosphate Treatment at the Surface 20 cm.

Table 9. Percentage Pb Extracted by SPLP Solution in the Soil Samples Collected 4.5 Years After P Application.

Depth (cm)	T0*	T1	T2	T3
	%			
0-10	0.97	0.58	4.88	1.37
10-20	0.61	1.15	0.38	1.32
20-30	0.21	0.52	0.58	0.57
30-40	0.37	0.39	3.79	1.14
40-60	2.09	0.95	0.79	1.16
60-80	2.83	0.55	0.48	1.74
Average	1.18	0.69	1.82	1.22

*Control, T0; H_3PO_4 alone, T1; ½ H_3PO_4+½$Ca(H_2PO_4)_2$, T2; and ½ H_3PO_4+5% phosphate rock, T3.

Since P was added to the soil to immobilize Pb, the correlation coefficient between SPLP Pb and total P in the soil samples was calculated, which was 0.53 (Table 8). This indicates that P application may have increased SPLP Pb in the soil. This hypothesis is supported by SPLP Pb data (Figure 9) and the low correlation coefficient between SPLP Pb/total Pb and total P. It is interesting to note that TCLP Pb and SPLP Pb were not highly correlated, with an r^2 of 0.27 (Table 8). This may indicate that the two solutions extracted different pools of lead from the soil.

PBET Pb CONCENTRATIONS IN THE SOIL

PBET Pb in Soil Samples

A Physiologically Based Extraction Test (PBET) was used to estimate Pb bioavailability (*in vivo*), which simulates Pb dissolution under gastrointestinal conditions based on chemical extraction (Yang and others 2001). Lead bioavailability in contaminated soils has been shown to vary with its mineralogical forms (Davis and others 1993). *In vivo* and *in vitro* assays have indicated that the mammalian gastrointestinal availability of Pb is controlled by the form and relative solubility of Pb solids (Ruby and others 1996). PBET has been used to assess the Pb bioavailability in a contaminated soil after receiving P (Hettiarachchi and others 2000).

Similar to TCLP Pb, all three treatments were effective in reducing PBET Pb in the surface soil (0-10 cm) (Figure 10). For the subsurface soils, Treatments T1 and T2 were not effective in reducing PBET Pb. However, T3 was effective in reducing PBET Pb at all depths. Thus, in terms of PBET Pb, Treatment T3 was the most effective.

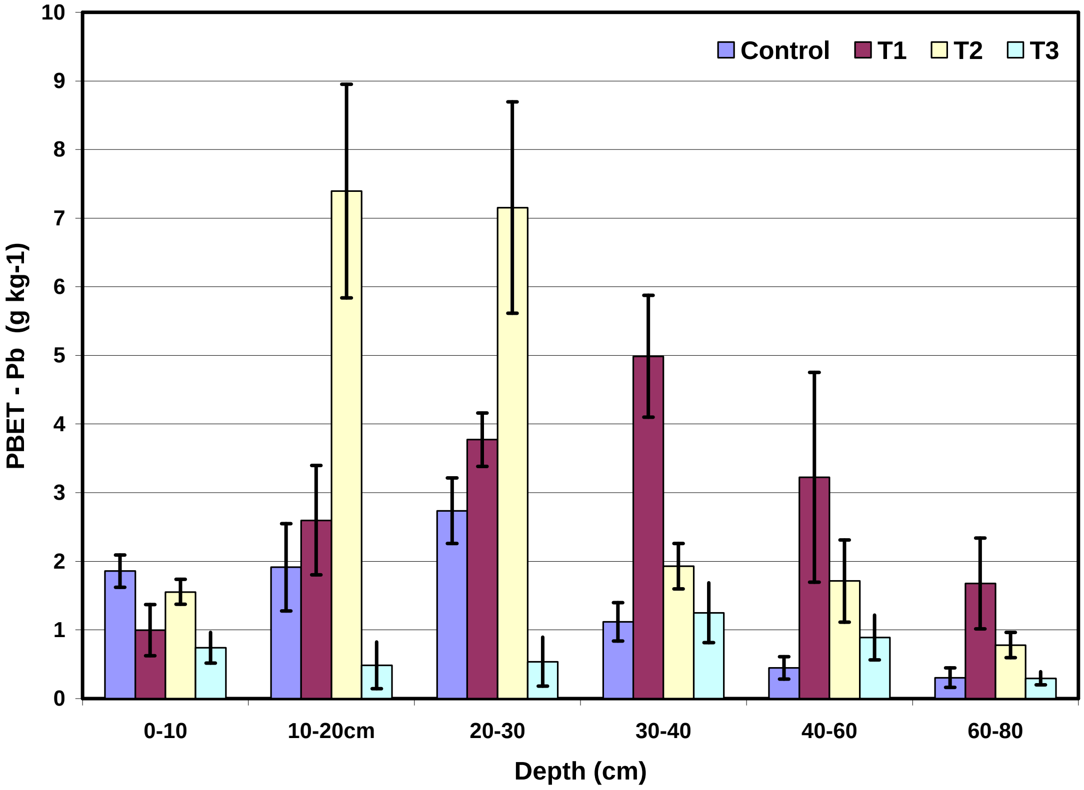

Figure 10. Changes in PBET Pb Concentrations with Soil Depth 4.5 Years After P Treatment at the Surface 20 cm.

Ratios of PBET Pb to Total Pb in Soil Samples

To correct for the effect of different total Pb concentrations, the ratios of PBET Pb to total Pb in the soil samples were calculated (Table 10). The amounts of Pb extracted by PBET were much greater than those of SPLP (by an average factor of 27) and TCLP (by an average factor of 11). This indicates that PBET is a much stronger method of extracting Pb than either SPLP or TCLP.

Among the four treatments, the ratio of PBET Pb to total Pb was the highest in the control, followed by Treatments T2, T1 and T3 in descending order. Based on the ratio, Treatment T3 was the most effective and Treatment T2 was the least effective.

Table 10. Amounts of Pb Extracted by PBET (%) in the Soil Samples Collected 4.5 Years After P Application.

Depth (cm)	T0*	T1	T2	T3
	%			
0-10	43.3	13.2	93.6	14.4
10-20	29.5	28.2	20.4	6.98
20-30	32.6	34.9	24.6	2.85
30-40	21.2	18.3	50.7	10.6
40-60	71.9	62.0	36.1	17.7
60-80	102	32.8	19.0	21.0
Average	50.1	31.6	40.7	12.3

* Control, T0; H_3PO_4 alone, T1; ½ H_3PO_4+½$Ca(H_2PO_4)_2$, T2; and ½ H_3PO_4+5% phosphate rock, T3.

Correlation Between Different Variables

PBET Pb and total Pb were highly correlated, with an r^2 of 0.84 (Table 8), whereas PBET Pb and total P were negatively correlated ($r^2 = -0.42$). This means that P application was effective in reducing PBET Pb in the soil samples. The fact that PBET Pb and TCLP Pb were correlated ($r^2 = 0.45$) means they both extracted substantial amount of similar pools of Pb from the soil.

CONCLUSIONS

We have reported the results of a pilot-scale field experiment on long-term efficiency of P amendments to immobilize Pb. Among the three treatments, Treatment T3 (phosphoric acid plus phosphate rock) was the most effective in reducing TCLP Pb (Pb mobility) and PBET Pb (Pb bioavailability), whereas Treatment T1 (phosphoric acid) was effective in reducing SPLP Pb (Pb leaching) in the soils collected 4.5 years after P application. Overall, a mixture of H_3PO_4 and rock phosphate yielded the best results in Pb immobilization, with the least impact on soil pH and the least risk of potential eutrophication.

Based on our field data, we conclude that phosphate amendments can be effectively used to immobilize Pb in contaminated soils, thus offering an alternative to the current phosphate remediation technology for the contaminated soil. However, caution should be exercised to maximize lead immobilization and minimize potential adverse impacts caused by the application of phosphate amendments to soils. Although H_3PO_4 is needed to catalyze the dissolution of a metal-stable solid, making it available for further immobilization reactions, its use should be taken with care. Phosphoric acid may decrease soil pH, especially in low buffering sandy soils, and consequently may cause leaching of P and other metals. Another possible strategy, which could work better, would be to reverse the sequence of P application, i.e., to add calcium phosphate and phosphate rock at the first phase and apply the phosphoric acid in the second phase, or add calcium phosphate or phosphate rock and phosphoric acid simultaneously. Thus, it would lead to the dissolution of cerussite and more insoluble P amendments at the same time, favoring Pb immobilization and minimizing potential P and Pb leaching.

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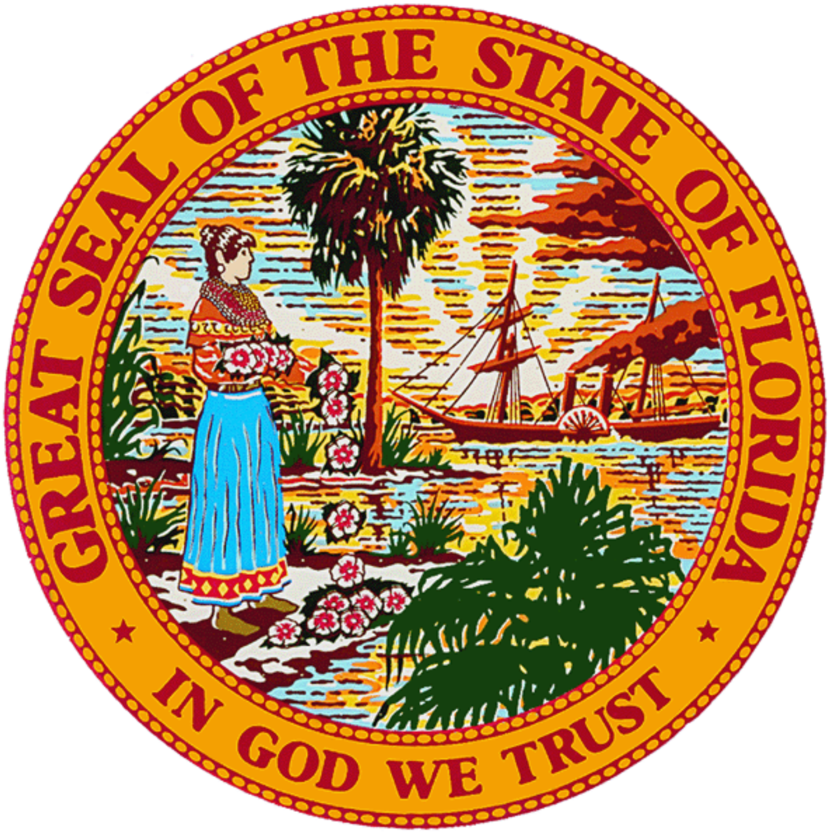
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