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FIELD DEMONSTRATION OF METAL IMMOBILIZATION IN CONTAMINATED SOILS USING PHOSPHATE AMENDMENTS

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FIELD DEMONSTRATION OF METAL IMMOBILIZATION IN CONTAMINATED SOILS USING PHOSPHATE AMENDMENTS

FINAL REPORT

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DISCLAIMER

PERSPECTIVE

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

The adverse health effects from lead in the environment have received a great amount of attention and are a cause for much concern. While many contaminated sites have been identified, the vast majority of such sites have not been subjected to remediation due in large part to the high cost of treating the soil using presently recognized best treatment technology.

While it is possible to remove all the soil from a lead-contaminated site and to store it elsewhere, this approach also has drawbacks. Methods have been proposed for removing lead from soil by chemical extraction but this procedure is even more costly and time-consuming. In essence, all of the accepted treatment methods have not proven to offer a simple, uncomplicated solution to the problem.

A number of years ago, FIPR funded a laboratory study to use phosphates to react with the lead and form insoluble, biologically inactive compounds that would make the lead unavailable to both plants and animals. By utilizing this technology it would be possible to remove the lead from both soil and water and eliminate the concerns relative to adverse health effects.

The next step in this program was to demonstrate that it was possible to apply the principles developed in the laboratory to address a real-life contamination problem. The site reported on in this report was selected to demonstrate the effectiveness of this technology and a number of treatment variations are being tested there. The results to date are quite encouraging and the site will be monitored for an additional number of years to define the long-term results of these treatment practices.

While this test program is still ongoing, the results are encouraging enough that it is being considered for application to other sites.

ABSTRACT

Lab tests and a field demonstration were conducted to evaluate the feasibility and effectiveness of immobilizing metals in contaminated soils using phosphate. Phosphate was more effective for Pb immobilization than for Zn, Cu, and Cd. The formation of insoluble pyromorphite-like minerals was responsible for Pb immobilization, whereas Zn, Cu, and Cd immobilization may be attributed to the coprecipitation and surface complexation mechanisms. The most efficient formation of pyromorphite-like minerals was found at pH 3 and at an application rate of 4 P/Pb. Soil acidification was necessary to dissolve soil Pb carbonates and to make them readily available for the formation of pyromorphite-like minerals. Therefore, a two-step phosphate amendment was applied at a contaminated site in which the soil was first acidified with H_3PO_4, and $Ca(H_2PO_4)_2$ or phosphate rock was then added. Phosphate effectively induced transformation of soil Pb from the non-residual to the residual fraction, with residual Pb increase by up to 55%. Modeling indicated that lead phosphate minerals controlled Pb^{2+} activities in the P-treated soils. Phosphate treatments significantly reduced Pb uptake by *Stenotaphrum secundatum.* A mixture of H_3PO_4 and phosphate rock yielded the best overall results for *in situ* Pb immobilization, with less soil pH change and less phosphorus leaching.

ACKNOWLEDGMENTS

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LIST OF ABBREVIATIONS AND ACRONYMS

XRD:	X-ray Diffraction
SEM-EDS:	Scanning Electron Microscopy-Energy Dispersive X-ray Elemental Spectroscopy
ICP-AES:	Inductively Coupled Plasma Atomic Emission Spectrometry
SMR:	Stoichiometric Molar Ratio
GFAAS:	Graphite Furnace Atomic Absorption Spectroscopy
FAAS:	Flame Atomic Absorption Spectroscopy
QA/QC:	Quality Assurance/Quality Control
CEC:	Cation Exchangeable Capacity
OM:	Organic Matter
TCLP:	Toxicity Characteristic Leaching Procedure
EPA:	Environmental Protection Agency
FDEP:	Florida Department of Environmental Protection

EXECUTIVE SUMMARY

This research project focused on the field demonstration of metal immobilization in contaminated soils using P amendments. The selected site is located at urban area of Northwest Jacksonville and was contaminated with Pb primarily due to past battery recycling activities. The soil is characterized by alkaline pH and high concentration of organic matter and sand. Both lab test and field demonstration has been conducted in this project research.

Lab research activities included screening of phosphorous sources, optimization of their application rates and design parameters for the field demonstration of heavy metal immobilization using P amendments. Leachability of metals in treated soil was measured by using a combination of batch and column tests to evaluate the immobilization capability of applied treatments. Among various phosphate amendments evaluated, a mixture of $Ca(H_2PO_4)_2$, $CaCl_2$ and H_3PO_4 at a application 4 P/Pb rate was the most effective in immobilizing Pb. For efficient immobilization, pH reduction with H_3PO_4 became necessary to dissolve carbonate-bound metals and make them readily available for the geochemically stable metal phosphate formation.

The effectiveness of phosphatic clay for immobilizing heavy metals (Pb, Cd, and Zn) from aqueous solutions was also investigated. The amounts of metals sorbed onto phosphatic clay decreased in the order Pb > Cd > Zn. The Langmuir model effectively described metal sorption behavior, but sorption mechanisms varied among studied metals. Desorption data also confirmed that metal sorption onto phosphatic clay is highly hysteric. Only 8.1–23.1 % of Pb, 8.4-45 % of Cd and 21.9-73.9 % of Zn sorbed on phosphatic clay were remobilized by EPA toxicity characteristic leaching procedure solutions (TCLP, pH 3-5). Formation of fluoropyromorphite after reaction of aqueous Pb with phosphatic clay confirmed that precipitation is the dominant mechanism for Pb removal from aqueous solution. There was no observed evidence of crystalline phase formation during reaction of aqueous Cd and Zn with phosphatic clay. Possible sorption mechanisms for Cd and Zn may include coprecipitation, complexation, and ion exchange. Results suggest that phosphatic clay could be an effective amendment for the *in situ* remediation of contaminated soils.

Another laboratory experiment was designed to evaluate the dissolution and immobilization kinetics of Pb in contaminated soils at fixed pHs varying from 7 to 3 using soluble phosphorous. Following descending dissolution order of PbO > $PbCO_3$ > $PbSO_4$ was observed and it remained pH dependent process for most studied Pb solid phases. Natural contaminated soils showed Pb dissolution and immobilization behavior similar to cerussite ($PbCO_3$) spiked soils. Also, X-ray diffraction patterns confirmed that the highest transformation of chloro-pyromorphite from different Pb-solid phases in contaminated soil occurred at the pH 3 compared to other studied pHs.

Based on the above laboratory results, a pilot-scale field experiment was conducted at a site highly contaminated with heavy metals to assess the efficiency of phosphate amendments on Pb immobilization. Phosphate amendment was employed at a 4 P/Pb molar ratio. 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). The results showed that T1 significantly declined soil pH in each soil depth, while T3 changed it little. Soil pH values in P treated plots were recovered with time. P treatments showed most effective immobilization for lead with the partitioning modification of soil Pb from the non-residual phase to the residual phase. In the surface soil, the major transformation was a up to about 36% decrease in the carbonate-bound Pb over time, while the residual phase was increased by up to 53%. T3 showed the most transformation among three treatments. As a consequence, Pb concentration in TCLP extracts was decreased by over 95% compared to the control. Four months after P treatment, TCLP-Pb was reduced to below regulatory level of 5 mg/l. XRD and SEM-EDX analysis showed that insoluble pyromorphite-like mineral was formed *in situ* in all P-treated plots after phosphate application, which is the first field evidence of P-induced formation of pyromorphite. Lead phosphate mineral showed a long-term stability. The efficacy of P treatments to immobilize Pb continued further to subsurface soils. At 30-40cm of P-treated soils, pyromorphite-like mineral was still detected by SEM-EDX in P-treated plots. T3 treatment showed least soluble P in the soil than other two treatments, indicating that T3 treatment pose less risk of secondary contamination with P release as runoff.

In addition to transformation of Pb from more available (non-residual) to least available (residual) form and reduction in TCLP-Pb, P treatment significantly reduced Pb contents in shoots of St. Augustine (*Stenotaphrum secundatum*), which grows on the site. Formation of pyromorphite in the rhizosphere of roots grown in P-treated soil was also detected by SEM-EDX. Groundwater analysis showed that Pb concentrations were reduced in P-treated monitoring wells.

On the basis of the laboratory results and field data, we concluded that P amendments are effective in Pb immobilization and it shows a long-term stability. A mixture of H_3PO_4 and phosphate rock has relatively excellent efficiencies for metal immobilization, with less soil pH change and less P release as runoff. 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. Although H_3PO_4 is needed to catalyze the dissolution of 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 invert the phases 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 formation of pyromorphite-like minerals and minimizing potential P and Pb leaching.

INTRODUCTION

Contamination of ground and surface water by heavy metals from previously abandoned disposal sites and some currently operating sites has caused much environmental concern (Vasuki 1987). Heavy metals are toxic to animals, humans and aquatic life. The ubiquitous nature of heavy metals, their toxicity even in trace quantities, their tendency to bioaccumulate in the food chain, as well as the stricter environmental regulations related to heavy metal discharges make it necessary to develop schemes to remove heavy metals from both waste waters and landfill leachates and to remediate these metal contaminated sites (Viraraghavan and Rao 1991). Among heavy metals, lead is of most environmental concern to USEPA and Florida Department of Environmental Protection (FDEP).

There are tens of thousands of lead-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 Sapp Battery Salvage site, located in Northwest Florida, is one such an example. The site was contaminated from cracking used automotive batteries during 1970-1980, resulting in contamination of 23 acres of soils (Trnovsky and others 1988; 1989). The upper soil horizon contained total Pb concentrations up to 135,000 mg/kg and the surface water and sediments contained up to 140 mg/l and 37,700 mg/kg Pb, respectively (Trnovsky and others 1989). The estimated cost to remedy the site ranged from 3 to 26 million dollars. As a result of a prohibitively high remediation cost, the site is still not remedied after more than 20 years of investigation and litigation. Soil contamination occurs in industrial areas as well as in urban areas. A recent survey found Pb concentrations in soils adjacent to homes and near expressways in Tampa, Florida as high as 2,000 mg/kg (Brinkmann 1994). 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, especially 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 (Moore 1986). 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 environment-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, 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 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 formation of hydroxypyromorphite. Phosphate rock (primarily $Ca_{10}(PO_4)_5F_2$) effectively immobilized Pb from aqueous solution 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% aqueous Pb from 13 Pb contaminated soils. In these studies, the effectiveness of phosphate rock to immobilize Pb was based on formation of insoluble lead phosphate. Formation of pyromorphite upon addition of apatite or soluble inorganic P amendments has been observed in Pb-contaminate soils (Cotter-Howells 1996; Laperche and others 1997). The formation of Pb phosphates in contaminated soils may be responsible for immobilizing Pb and thereby reducing its bioavailability (Hettiarachchi and others 2000; Ruby and others 1994).

Although research into the use of phosphate as a soils amendment has focused mainly on Pb remediation, several publications centered on the application of phosphate to other metals. It is reported that Zn and Cd are removed from aqueous solutions by phosphate rock, but the removal mechanism is different from that Pb. Concerning the immobilization of other metals by hydroxyapatite (HA), 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 and others 1994), and (4) substitution of Ca in HA by other metals during recrystallization (coprecipitation) (Jeanjean and others 1994; Xu and Schwartz 1994). The last mechanism (coprecipitation) appears more significant for Cd sorption than for Zn sorption (Xu and Schwartz 1994). This might be due to the fact that the ionic radius of Cd^{2+} (0.097 nm) is closer to the one of Ca^{2+} (0.094 nm) than the radius of Zn^{2+} (0.074 nm) so that isomorphic substitution of Ca^{2+} by Cd^{2+} is more favorable. The isomorphic substitution by Cu^{2+} (ionic radius 0.069 nm) would be less favorable than both Cd^{2+} and Zn^{2+}. Direct evidence that Cd can occupy Ca crystallographic sites has been given by means of Extended X-ray Absorption Fine Structure (EXAFS) (Sery and others 1996). It seems difficult to quantitatively estimate the amount of metal removal due to any specific mechanism and it appears that the different mechanisms all work more or less together (Xu and Schwartz 1994). Nevertheless, the effects of phosphate on immobilization and bioavailabilities of other metals such as Zn and Cd are still not well understood.

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 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 dissolution of anglesite ($PbSO_4$) and cerussite ($PbCO_3$) limited their rate of conversion to $Pb_5(PO_4)_3OH$. Thus, acidity of 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 and followed by the precipitation of insoluble metal phosphates. Under existing soil environments, observed solubility of Pb compounds and phosphate minerals remained limited, a major limitation for their effective and efficient immobilization. For example, lead carbonate (cerussite) 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 enhanced solubility of Pb minerals by inducing acidic conditions that will promote their solubility 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 soil remediation cost about \$170, \$470, \$25, \$85, and \$40 for phytoremediation, electrokinetics, phosphate mixing, cement solidification and dig & haul technology, respectively. 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 has been successful, to our knowledge, the implementation of this technology remains a very limited test *in situ* in the field. 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 the present study. A mixture of H_3PO_4 and $Ca(H_2PO_4)_2$ as well as phosphate rock was used as P source. Soluble P ensures rapid Pb immobilization, whereas phosphate rock provides long term Pb immobilization by P. The main objectives of this research are (1) to demonstrate the feasibility and effectiveness of phosphate amendments on the *in situ* immobilization of Pb, Cu and Zn in a contaminated site; (2) to assess mobility and bioavailability of Pb, Zn and Cu in contaminated soil after application of phosphate treatments, and ultimately (3) to verify if the lab test is consistent with the field application.

SELECTION AND CHARACTERIZATION OF A HEAVY METAL-CONTAMINATED SITE

SITE CHARACTERIZATION

Much effort was made to identify the most suitable site for this demonstration project. A lead contaminated site located at urban area of Northwest Jacksonville, meets our selection criteria and was selected. To use this site to demonstrate metal immobilization using P amendments, we obtained permission from a representative from FDEP as well as the site owner.

The selected experimental site is a vacant, fenced lot of rectangular shape (71.4 m by 57.3 m) occupying approximately one acre. The site is covered by vegetation mainly as grasses (Figure 1). We observed vegetation stress in patches. This site is situated in a topographically flat area at an elevation of approximately 23 feet above sea level and is characterized by slight topographic relief with surface runoff flowing in a west to southwesterly direction.

Figure 1. View of the Selected Jacksonville Demonstration Site.

According to previous site assessment reports, this site housed several facilities, which may have caused environmental threat to the site and its neighborhood. Gasoline service station was located in southeast corner of the property in 1930s. In 1940-50, central part of this site was used as a salvage yard. Boarder between two properties has visual evidence of surface discharge of waste oil and other organic contaminants. Two excavation pits, resulted by the removal of underground storage tank (UST), were also present in the north central and northwest part of this property. Contaminated soils were excavated and disposed off in 1992. In the past six years, two environmental assessments were performed on this site by two different consultants. These assessment results showed elevated level of both total and Toxicity Characteristic Leaching Procedure (TCLP) lead concentrations, which were above the State Soil Cleanup Levels. Therefore, remedial action is required not only to clean up lead-contaminated site, but also to allow use of both soil and site as a part of new rehabilitation strategy.

SOIL CHARACTERIZATION

Soil samples were air-dried, sieved (2-mm), and digested using the hot-block digestion procedure (USEPA Method 3050). Soil organic matter was determined using the Walkley-Black procedure (Nelson and Sommers 1982). Cation exchange capacity (CEC) was determined using the method of Rhoades (1982). Total phosphorus was measured colorimetrically with a Shimadzu 160U spectrometer using the molybdate ascorbic acid method (Olsen and Sommers 1982). Selected physical and chemical properties of surface soil (0-10 cm) were listed in Table 1. Organic matter (~4.0%) and soil pH (~7.0) were high compared to other Florida soils (Chen and others 1999). Elevated organic matter was mainly originated from the urban waste. Lime addition probably resulted in the increase of soil pH.

Table 1. Selected Physicochemical Properties of the Soil.

pH	CECξ	OM¶	Sand	Silt	Clay	$P_{T\S}$	Pb_T	Cu_T	Zn_T
	cmol kg^{-1}	%				mg kg^{-1}			
6.95 ±0.19	5.75 ±0.85	3.91 ±0.90	87.7 ±1.37	9.0 ±1.58	3.35 ±0.54	891 ±162	1,1634 ±1574	2,635 ±106	1,952 ±83

ξ Cation exchange capacity; ¶ Organic matter; § Total concentration

LEAD SPATIAL DISTRIBUTION OF THE SITE

Lead is the main contaminant with the total concentration of 11,634 mg kg^{-1}. To identify and quantify lead present at the site, iso-concentrations of total Pb were plotted using the total lead data obtained from the intensive grid-soil-sampling at different depths. The selected plots were established on the zone with the Pb concentration more than 2,000 mg Pb kg^{-1} soil. The site was divided into 4 different concentration zones (e.g. < 500, 500-1,000, 1,000-2,000 and > 2,000 mg kg^{-1} Pb) for detailed site characterization. A contamination hot spot was centered in the north central part of the site (Figure 2). Such information is useful for optimizing P application rates by avoiding either underdoses or overdoses.

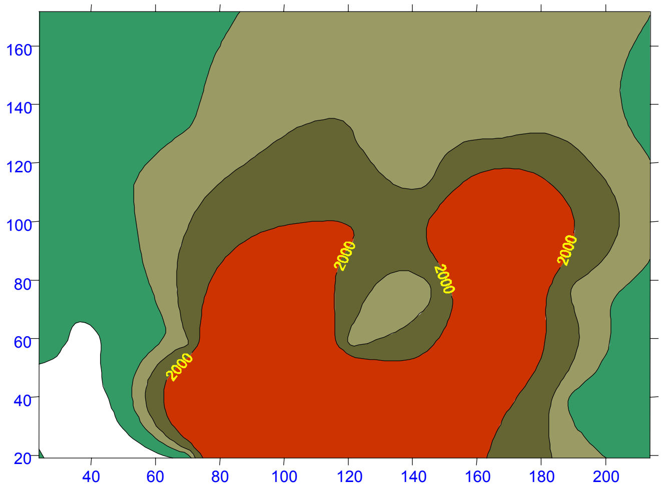


Figure 2. Iso-Contour Map of Total Pb in the Top 10-cm Soil in the Jacksonville Site.

Lead concentration decreased as the soil depth increase, with the exception of higher concentration in the second layer relative to the surface layer (Figure 3). Lead contamination was mainly concentrated on the surface and near surface soil. However, there is still a substantial amount of lead found in the deep soil. For example, more than 2,000 mg kg^{-1} of lead was detected in 30-40cm deep soil. Therefore, this demonstration site was confronted with Pb contamination from both spatial and vertical dimension. Overall, lead contamination was considered one of the primary environmental problem. In addition, it could be seen from Fig. 2-3 that a higher heterogeneity for Pb distribution occurred in this site, which may limit the effective assessment of P treatment. However, this limitation could be overcome by using the same molar ratios of Pb/P during P application.

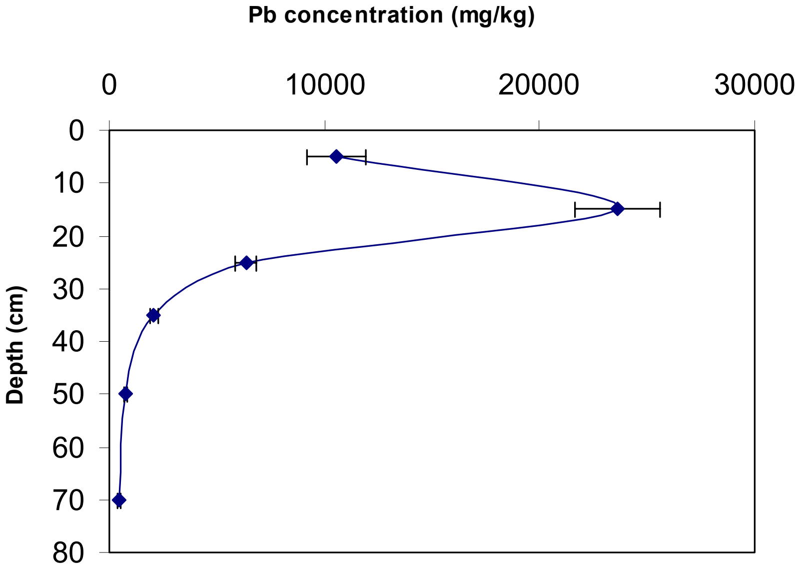


Figure 3. Distribution of Heavy Metals in the Plot Soil Profile.

Detailed mineralogical characterization was conducted on particle size and magnetic fractions using x-ray diffraction (XRD) and scanning electron microscope (SEM). Cerussite ($PbCO_3$) was identified using the 3.51Å peak from the XRD pattern (Figure 4). The presence of $PbCO_3$ is consistent with the slightly alkaline soil conditions, which may be attributed to lime addition or formation of lead carbonate. Figure 5 shows SEM image and relative element concentration. $PbCO_3$ is present in association with Cu, Zn, and Sn.

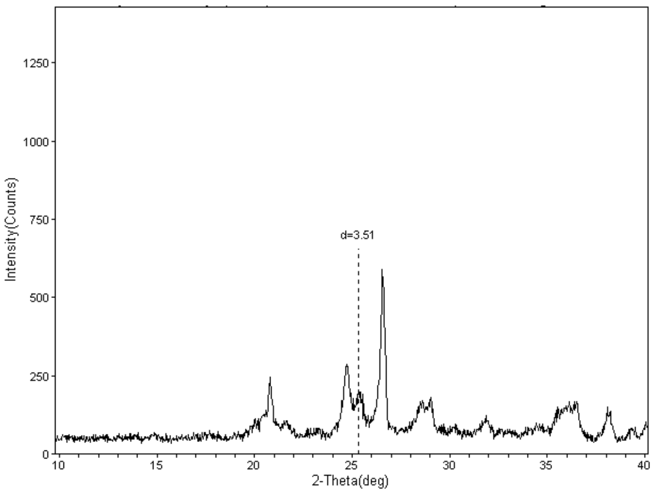


Figure 4. X-Ray Diffraction Pattern of Soil in Demonstration Site.

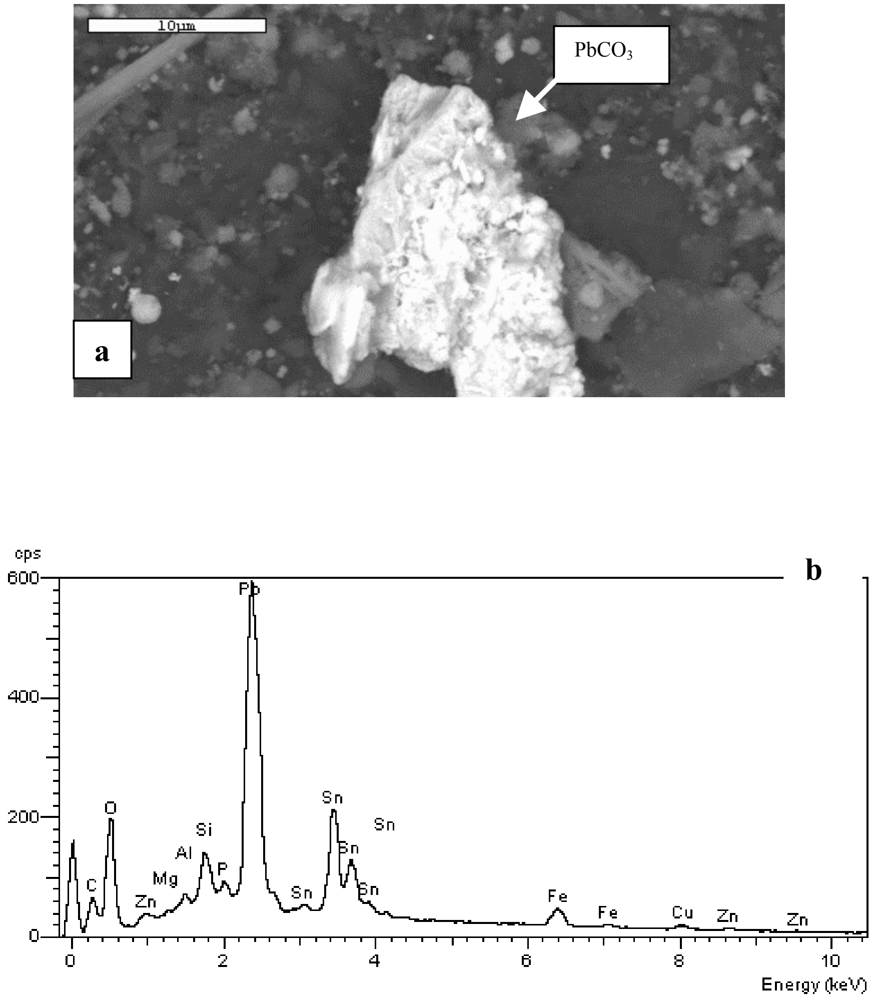


Figure 5. (a) Scanning Electron Microscope (SEM) Image, and (b) Relative Elemental Concentration of a Lead-Rich Soil Particle in the Pb-Contaminated Site.

OPTIMIZATION OF P TREATMENT RATES AND CONDITIONS USING BATCH AND COLUMN TESTS

BACKGROUND

Phosphate is known to react with many heavy metals, metalloids and radionuclides to form secondary phosphate precipitates that are stable over a wide range of geochemical conditions (Nriagu 1974, Wright and others 1987). Thus, it has been used to immobilize metals in contaminated soils (Ma and others 1993; 1995; Laperche and others 1996). Metal immobilization using phosphate amendments offers a potential *in situ* remediation technique to reduce both the mobility and bioavailability of heavy metals in contaminated soils and sediments, which has received much attention recently. During last several years, research results have successfully demonstrated the reduction of aqueous Pb in soils by mixing phosphate minerals with Pb-contaminated soils (Ma and others 1993; 1994; Cotter-Howells 1996). Cost effectiveness and environmental friendliness have made the application of phosphate minerals to Pb-contaminated soils a promising in situ technology to remediate Pb-contaminated soils. In recent years, extensive knowledge has been gained in the field of metal immobilization in contaminated soils using phosphorus amendments at bench scales (Ma and Rao 1999).

However, successful application of innovative *in situ* treatment technologies requires a comprehensive understanding of both treatment technology as well as site specific soil characteristics. The metal of concern must be dissolved and available for the precipitation with P for its successful immobilization. Under existing soil environments, observed solubility of Pb and phosphate minerals remained limited, a major limitation for their effective and efficient immobilization. For example, lead carbonate (cerussite) has been identified as a major Pb mineral in many contaminated soils, particularly from battery recycling sites (Nedwed and Clifford 1997; Royer and others 1992). Therefore, effective Pb-immobilization using phosphate amendments requires enhanced solubility of Pb minerals by inducing acidic conditions that will promote their solubility as well as pyromorphite formation. The Pb in the pyromorphite is much less bioavailable than Pb associated with cerrucite. However, resulting acidic conditions will also enhance the mobility of other heavy metals, increasing the risk of their leaching into groundwater. In order to enhance the solubility of solid Pb-mineral phases in the existing soil environment, phosphoric acid has been selected as a source of both soluble phosphorus and acidity required to increase the Pb mineral solubility in the contaminated soils.

The reactive sinks that compete for soil amendments such as phosphate, however, can significantly reduce the effectiveness of metal-phosphate precipitation. Therefore, phosphate amendments must be site specifically characterized under a range of field conditions (e.g., metal concentrations, organic carbon content, pH, and soil mineralogy). For example, mineralogical characterization of soil from the Jacksonville site indicated that cerussite ($PbCO_3$) was the major Pb-mineral. It was mainly concentrated in the sand and silt fractions, and was not detected in the clay fraction. Additionally, few studies have characterized the long-term mobility and bioavailability of the amended soils and sediments, a critical factor in determining the effectiveness of any stabilization method.

The objective of this study was to evaluate the efficiency and capability of various phosphate amendments including soluble P to immobilize metals in contaminated soils via evaluating their leaching characteristics. Our efforts focused on screening suitable soluble phosphorus sources by 1) minimizing their application rates for optimum immobilization with minimum resulting adverse impact on soil physico-chemical characteristics, 2) evaluating vertical effectiveness, and 3) testing various design parameters for the field scale applications. However, prior to gaining regulatory approval for the pilot-scale field demonstration, phosphate amendments must demonstrate effective immobilization capacity with minimum leaching of other metals and applied phosphorus to ground water.

MATERIALS AND METHODS

Effectiveness of $Ca(H_2PO_4)_2$ H_2O in Immobilizing Pb

Batch Test

Four grams of air-dry soil were placed into 40mL polycarbonate centrifuge tubes. Phosphate amendment solution was prepared by dissolving $Ca(H_2PO_4)_2$ H_2O into 0.05 M H_3PO_4 and 0.002 M $CaCl_2$ solution so that 20 mL solution may be equivalent to 22.5 tons of phosphate per acre. Phosphate amendment solution was added to a centrifuge tube. In addition to soluble phosphate sources, we also used 5% phosphatic rock and phosphatic clay. Samples were equilibrated on a reciprocating shaker for 24 h at 25°C. Supernatants pH reading was taken after suspensions were allowed to settle. Samples were centrifuged at 10,000 rpm for 20 minutes using a Beckman model J2-21 and filtered through 0.45 μm membrane filters. A fraction of the filtered supernatant was analyzed for dissolved organic carbon (DOC) using a Shimadzu TOC 5050 analyzer and soluble orthophosphate using the molybdate ascorbic acid method (Olsen and Sommers 1982). The remaining supernatant was acidified and analyzed for metals by using either flame atomic absorption spectrometer (Perkin Elmer 3030) or atomic absorption spectrophotometers equipped with graphite furnace (Perkin Elmer SAMMA 6000). After batch equilibration, the residue was evaluated by using a toxicity characteristic leaching procedure (TCLP) as described below.

Column Test

In this investigation, column tests were used to evaluate the effectiveness of selected treatments for further detailed evaluation. A total of 25 g air-dry soil was mixed with $Ca(H_2PO_4)_2$ H_2O salt at an application rate equivalent to 22.5 ton per acre for the

Jacksonville contaminated soil. After uniform mixing, mixture was placed in 60-mL syringes containing 0.5 g coarse washed-sand to prevent soil loss during leaching. Mixed solution of 0.005 M H_3PO_4 and 0.001 M $CaCl_2$ was added to bring soil to near field capacity. Each column was covered with polyurethane film to avoid moisture loss but allow adequate air exchange. It was incubated at room temperature. After one week of incubation, 25 mL of deionized water was leached through columns under gravity and samples were returned for continued incubation and were extracted after 4 week. Leachate was filtered through 0.45 μm membrane filters. The supernatant was analyzed for dissolved organic carbon (DOC), phosphate, and metals as described above. The TCLP test was used to evaluate the effectiveness of applied treatment by taking soil sample from one of the column replicates.

Sequential Extraction

Sequential extractions were performed in duplicate for the selected column test after 2 week of incubation to evaluate the effectiveness of applied treatments on solid phase distribution of target metals. The procedure of Tessier and others (1979) was adopted for this investigation. Each extraction step and the target phase is listed in the order of least to most chemically aggressive:

- **Exchangeable**: Soil samples are extracted with 8 ml of 1M $MgCl_2$ (pH 7) for 1h
- **Carbonate bound**: The residue from exchangeable fraction is extracted with 8 mL of 1 M NaOAc (adjusted to a pH 5 with HOAc)
- **Fe-Mn Oxide**: The residue from carbonate fraction is extracted with 0.04 M NH_2OH-HCl in 25 % v/v HOAc at 96 °C with occasional agitation for 6h
- **Organic bound fraction**: The residue from Fe-Mn oxide fraction is extracted with 3 mL of 0.02 M HNO_3 and 5 mL 30 % H_2O_2 (adjusted to pH 2 with HNO_3). The mixture is heated to 85°C for 2 hours with occasional agitation. A second 3 mL aliquot of 30 % H_2O_2 is added again and mixture is heated again. After cooling 5 mL of 3.2 m NH_4OAc in 20 % nitric acid and sample diluted to 20 mL. and agitated for 30 minutes continuously.
- **Residual fraction**: The residue from organic matter fraction was digested using a microwave-based EPA Method 3051a (HNO_3/HCl).

After each successive extraction, separation was done by centrifugation (Beckman Model J-2-21) at 10,000 rpm for 30 minutes. The supernatants were removed with pipette and filtered through 0.45 μm polycarbonate membrane filters. The residue was washed with 8 mL water followed by vigorous hand shaking, then followed by 30 minutes of centrifugation before the next extraction.

Effectiveness of H_3PO_4 in Immobilizing Pb

Initially 200 g air-dried contaminated soil sample (0-10 cm), collected from the Jacksonville field demonstration site, was taken in plastic containers. Phosphoric acid

(1M) was chosen as a source of soluble phosphorus in this experiment. Lead solubility in the contaminated soil will be enhanced because it was dominated mainly by the cerussite ($PbCO_3$) solid phase. Three levels of soluble P were applied at 2, 4, and 8 molar ratios of P/Pb. By mixing appropriate amounts of 1M phosphoric acid with deionized water, individual samples were brought to approximately 70 % of their field capacity. After equilibrium of 24 hours, these samples were air dried at room temperature. These phosphate-treated soil samples were used in both batch and column tests.

Batch Test

For the batch extractions, 5 g of control and P treated air-dried soil samples were placed in polycarbonate 40 mL centrifuged tubes. In addition to phosphoric acid, phosphatic clay and phosphatic rock at 5 % level were also evaluated for their effectiveness. These were equilibrated with 25 mL of deionized water on a reciprocating shaker for 24 hours at 25 °C. Supernatant pH reading was taken after suspensions were allowed to settle. Samples were centrifuged at 10,000 rpm for 15 minutes using Beckman model (J2-21) and filtered through 0.45 μm membrane filters. A fraction of dissolved supernatants was analyzed for DOC using a Shimadzu TOC 5050 analyzer, and soluble orthophosphate using the molybdate ascorbic acid method (Olsen and Sommers 1982). The remaining supernatant was acidified and analyzed for metals by using either flame atomic absorption spectrometer (Perkin Elmer 3030) or atomic absorption spectrophotometers equipped with graphite furnace (Perkin Elmer SAMMA 6000). After batch equilibration, the remaining solid residue was evaluated for their Pb-mobility by using TCLP.

Column Test

Column tests were also used to evaluate the effectiveness of selected treatments at low liquid:solid (LS) ratio. A total of 25 g of air-dry contaminated soil, previously treated with phosphoric acid, was placed in a 60-mL plastic syringe containing 0.5 g coarse washed-sand in the bottom to prevent the soil losses during leaching. Deionized water was added to bring the soil to approximately 70 % of its field capacity. Each column was covered with polyurethane film to avoid moisture loss but allowing adequate air exchange during the incubation period at room temperature. After one week of incubation, 25 mL of deionized water was leached through columns under gravity and samples were returned for continued incubation and to be extracted again after 4 weeks. Leachate was filtered through 0.45 μm membrane filters. The supernatant was analyzed for DOC, phosphate, and metals as described above. The TCLP test was used to evaluate the effectiveness of applied treatment by taking soil from one of the column replicates.

Effectiveness of $Ca(H_2PO_4)_2/H_3PO_4$ Combination in Immobilizing Pb

The main objective of this column experiment was to test the hypothesis that metals mobilized from surface soils due to increasing phosphate applications are re-adsorbed back onto subsurface soils. In addition to the phosphoric acid treatments, other soluble phosphorus sources such as $Ca(H_2PO_4)_2$ were also evaluated for their effectiveness in immobilizing heavy metals in contaminated soils using a column experiment under existing field conditions.

The Pb-contaminated soil used in this study were the same as in the previous batch and column tests. An acrylic column measuring 25 cm in length and 2 cm diameter was used. The column was sealed from the bottom using a rubber stopper with small holes for glass outlet tube to collect leachate. A thin film of glass wool was placed in the column bottom to prevent soil flow into the leachate. First 100 g non-contaminated air-dried soil was placed in the column, which made ~20 cm column length. On top of this, 50 g of contaminated soil (air-dried) was filled, which took approximately 10 cm of soil column length. The following treatments were selected for this experiment:

- Control: no soluble phosphorus;
- P-2: H_3PO_4 (P/Pb=2)
- PC-4: $H_3PO_4 + Ca(H_2PO_4)_2$ (P/Pb=4, 50% each)
- P-4: H_3PO_4 (P/Pb=4)
- PC-8: $H_3PO_4 + Ca(H_2PO_4)_2$ (P/Pb=8, 50% each)
- P-8: H_3PO_4 (P/Pb=8)

The above amounts of soluble phosphorus from selected sources and deionized water were mixed together to provide desired phosphorus application rate, and were added together to bring soil column moisture ~75 % of field capacity. Each column was covered with polyurethane film to avoid moisture loss while allowing adequate air exchange during incubation period at room temperature. After one week of equilibrium, columns were leached twice with 65 mL deionized water (~2 pore volume each time) at one week intervals. Leachate was filtered through 0.45 μm membrane filters. The supernatant was analyzed for DOC, phosphate, and metals as described above. The TCLP test was also used to evaluate the effectiveness of applied treatment by taking soil sample from both surface and bottom layers of contaminated soil from each column after leaching.

Effectiveness of Selected Treatment in Immobilizing Pb Using an Intact Core

Batch Test

For the batch extractions, 5 g of air-dried soil samples were placed in a 40-mL polycarbonate tubes. Potential P-amendments screened in the batch test include H_3PO_4, $Ca(H_2PO_4)_2$, KH_2PO_4 and mixture of H_3PO_4 and $Ca(H_2PO_4)_2$ with equal quantity of phosphorus. Phosphorus application rate was based on the stoichiometric molar ratio of P to total Pb content in soil. Six different molar ratio of P were used in these batch tests. Mixtures were equilibrated with 25-mL of deionized water on a reciprocating shaker for 24 hours at 25 °C. Supernatant pH reading was taken after suspensions were allowed to settle. Samples were centrifuged at 10,000 rpm for 15 minutes using Beckman model (J2-21) and filtered through 0.45-μm membrane filters. A fraction of dissolved supernatants was analyzed for DOC and soluble orthophosphate as previously described. The remaining supernatant was acidified and analyzed for metals as previously described. After batch equilibration, the remaining solid residues were evaluated for their metal mobility using TCLP.

Undisturbed Soil Columns

Undisturbed soil columns were used to simulate the field scenario after application of phosphate amendments and to evaluate the effectiveness of applied treatments at relatively low liquid to solid (LS) ratio. Undisturbed soil columns of 4-cm internal diameter and 106 cm length were collected from the highly contaminated zone of the demonstration site using a mechanical Geoprobe. For the intact soil columns, we used three combinations of P amendments. For calculating P application rate, we took top 30-cm soil into account and P-treatments were applied in two steps. In the first step, 50 % of P-dose equivalent to 4P/Pb SMR was applied to all three treatments using H_3PO_4 mixed with 75-mL $CaCl_2$ solution. After one week of incubation, second half of P dose was applied by mixing appropriate amount of H_3PO_4 or $Ca(H_2PO_4)_2$ H_2O in 75-mL 0.05 M $CaCl_2$ solution for the first and second treatments. For the third treatment, 5% phosphate rock was mixed thoroughly in first 10-cm. After two weeks of incubation, soil columns were leached with deionized water. Leachates were collected in the increments of ~100 mL per day initially and 300 mL at the end of the experiments. A total of ~3-L of water was leached through each column. The volume of effluent and time of collection was recorded. The pH, EC, and total soluble carbon were measured immediately after each collection. Leachate was filtered through 0.45-µm membrane filters. The heavy metal concentrations in each extract were also measured by atomic absorption spectrometry as described previously.

After leaching, each soil column was sliced into 6 sections of 0-10, 10-20, 20-30, 30-40, 40-60 and 60-80 cm in length. Collected soil was dried at room temperature. The final soil pH was measured in water at solid:liquid ratio of 1:2 after 24 h of equilibrium. The TCLP test was used to evaluate the vertical effectiveness of applied phosphate amendments.

RESULTS AND DISCUSSION

Effectiveness of $Ca(H_2PO_4)_2$ H_2O in Immobilizing Pb

The results from the batch and column test were summarized in Table 2. We observed that application of P amendments (combined mixture of $Ca(H_2PO_4)_2$ +H_3PO_4 + $CaCl_2$) at an application rate equivalent to 22.5 ton P per acre effectively immobilized target metal (Pb) to below its regulatory level (TCLP test).

Table 2. Lead Concentrations (μ g L^{-1}) in Batch and Column Leachates and in the TCLP Solution.

Treatments	Batch Test		Column Test	
	Leachate Pb	TCLP-Pb	Leachate Pb	TCLP-Pb
Control	422	194	12	154
Soluble P¶	150	5.5	40	4.7
Soluble P+ 5 % PR§	73	5.1	47	4.2
Soluble P+ 5 % PC§	75	4.4	69	4.1

¶ Soluble P stands for $Ca(H_2PO_4)_2 + CaCl_2 + H_3PO_4$
§ PR and PC stand for phosphatic rock and phosphatic clay, respectively

Application rate of P amendments will depend on the contamination levels as well as soil physicochemical properties and soil mineralogy. It also depends on the percentage of metals present in their labile forms because proposed *in situ* remediation technology minimizes the mobility of target contaminants by transferring them to non-labile phases via chemically induced transformations. Reactive sinks that compete for soil additives such as P amendments, however, can reduce the effectiveness of metal precipitation. In this experiment, we optimized P amendments rates according to the site specific field conditions (e.g., metals concentrations, organic carbon levels, and soil mineralogy). Based on our batch and column experimental data, combined application of $Ca(H_2PO_4)_2$ H_2O, $CaCl_2$ and H_3PO_4 at a rate of P/Pb 8 was sufficient to immobilize target contaminant (Pb) to below its regulatory level. Applied treatment is not only effective for Pb, but it also immobilized other metals such as cadmium, copper and zinc to a significant extent (data not shown).

In addition, the addition of PR and PC further reduced both soluble and TCLP Pb. Although, it is not feasible to use phosphatic clay at present due to high transportation costs, but it could be important alternative in near future. We replaced phosphatic clay with phosphate rock due to its long-term capability to immobilize metals via low solubility. In case of coarse textured soils, it will be very important to use either phosphate rock or phosphatic clay for the effective long term metal immobilization due to their capability to supply and retain applied phosphorus.

Subsequent chemical fractionation results showed that most of the lead in these soils was concentrated in the potentially bioavailable fraction (Figure 6). Application of P amendment significantly reduced extractable Pb in the non-residual fractions and increased Pb concentration in the residual fraction. Lead reduction from the non-residual fractions was mainly from the exchangeable, carbonate bound fraction, Fe-Mn oxide fraction. These fractions represent approximately 60-80% of the total lead. Exceptionally, lead associated organic fraction was reduced significantly from 23% to less than 4%. This demonstrated the effectiveness of applied P amendments to transform Pb associated with the water soluble, exchangeable, carbonate, Fe-Mn oxide and organic bound fractions to more stable residual fraction. Applied P amendment treatment remained more effective when it was combined with 5% phosphatic clay.

Applied P amendments are not only effective for Pb, it also reduced labile fraction of heavy metals such as Cd, Cu and Zn. Figure 7 demonstrated the effect of applied P amendments on copper immobilization. Cd and Zn showed the same trends as Cu (data not shown)

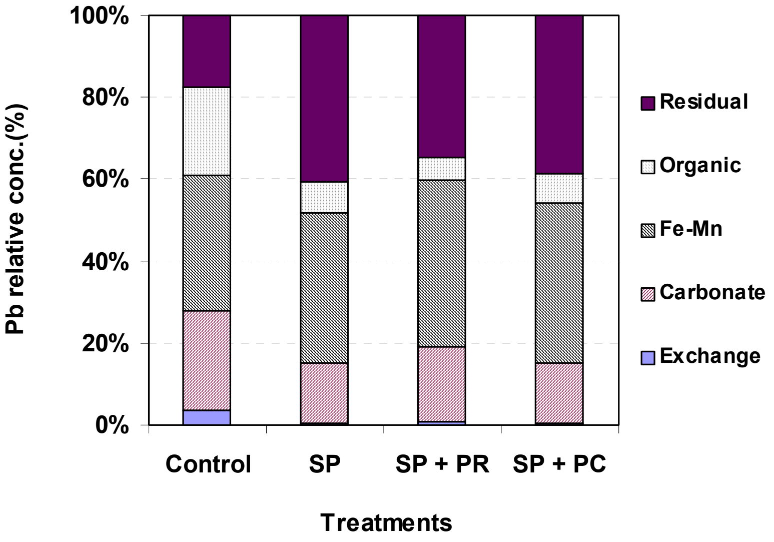


Figure 6. Lead Distribution in Different Fractions of the Contaminated Soils After Application of P Amendment (2 Weeks After Incubation at Field Capacity in Columns).

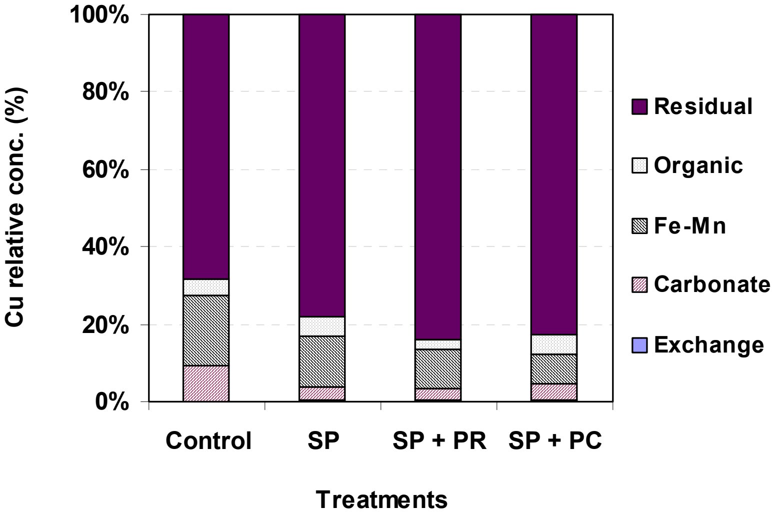


Figure 7. Copper Distribution in Different Fractions of Contaminated Soils After Application of P Amendments (2 Weeks After Incubation at Field Capacity in Columns).

The results from the batch and column experiments indicated that a combined application of soluble phosphorus (a mixture of $Ca(H_2PO_4)_2\ H_2O$, $CaCl_2$ and H_3PO_4) at a rate of 25 tons P per acre and 50 tons phosphate rock (dry weight) per acre immobilized Pb to below its regulatory level. The effective transformation of Pb from the non-residual fractions to the residual fraction demonstrated the effectiveness of applied P-amendments. However, further investigation is needed to reduce the metal concentration in leachates to below the drinking water standard. More laboratory experiments should be conducted to study the vertical effectiveness of these applied treatments.

Effectiveness of H_3PO_4 in Immobilizing Pb

The results of both batch and column tests were summarized in Table 3. They demonstrated that applications of phosphate rock and phosphatic clay remained slightly effective for reducing the Pb-concentrations in TCLP extractions due to limited phosphorus availability caused by low phosphate mineral solubility. For effective immobilization in highly contaminated soils, supplementary doses of soluble phosphorus became necessary to economically reduce Pb concentration to below the regulatory level.

In both column and batch experiments, TCLP-Pb was reduced to below its regulatory limit of 5 mg L^{-1} at the soluble phosphorus application rate of P/Pb=4 obtained from the H_3PO_4 without much decrease in treated soil pH (~5.2). Although with increasing application rate from 4 to 8, the TCLP-Pb decreased less than 2.5 mg Pb, the high phosphorus dose reduced treated soil pH to below 4. Also with increasing application rate, risk of surface and ground water contamination with soluble phosphorus increased significantly. Overall, observed leachates concentrations for the selected trace metals increased with increasing phosphate application rate, particularly for Cd, Cu and Zn due to the enhanced solubility of soil organic matter and activity of soil legends.

Both DOC and trace metal concentrations remained high in the column leachate compared to batch test leachate. This may be caused by much longer equilibrium time of column tests and relatively low liquid solid ratio. The dilution due to high L/S ratio reduced leachate trace metal concentrations in the batch test.

Table 3. Lead Concentrations in Batch and Column Leachates and in TCLP Solution.

Treatment	Batch Test				Column Test			
	pH	Water-Soluble		TCLP	pH	Water-Soluble		TCLP
		OC	Pb	Pb		OC	Pb	Pb
		mgL^{-1}	μg L^{-1}	mg L^{-1}		mg L^{-1}	μg L^{-1}	mg L^{-1}
C[#]	7.36	14.9	21.0	126	7.45	35.3	52.5	146
C +5% PC	7.31	16.9	19.0	109	7.69	39.9	42.5	125
C +5% PR	7.49	16.0	5.5	104	7.73	37.7	37.0	118
P/Pb=2	5.84	17.7	40.0	8.63	5.84	42.5	10.5	8.2
P/Pb=2 +5% PC*	5.60	18.9	57.5	6.28	5.88	58.6	8.5	7.9
P/Pb=2 +5% PR*	5.87	16.1	39.5	5.32	5.90	31.6	8.0	6.3
P/Pb=4	5.29	16.9	60.5	3.42	5.14	54.2	6.0	3.2
P/Pb=4 +5% PC	5.16	18.9	50.0	2.42	5.14	72.8	4.4	2.7
P/Pb=4 +5% PR	5.18	16.6	54.0	2.37	5.05	68.7	6.0	2.5
P/Pb=8	4.39	21.2	106	0.78	3.98	101	35.0	1.8
P/Pb=8 +5% PC	4.46	27.9	72.0	0.97	3.95	150	22.0	0.6
P/Pb=8 +5% PR	4.47	26.0	72.5	0.80	4.00	104	26.5	1.0

C stands for control;
* PR and PC stand for phosphate rock and phosphatic clay, respectively.

The results from both the batch and column experiments demonstrated that application of soluble phosphorus equivalent to 2775 kg P per acre obtained from H_3PO_4 immobilized soil Pb concentration to below its regulatory levels. Additional column experiments will be required to test the hypothesis that metals mobilized from surface soil under resulting acidic conditions are sorbed back onto subsurface soils. Re-adsorption should reduce metal concentration in leachates to below drinking water regulatory levels. Column experiments will be conducted to evaluate the vertical effectiveness of these applied treatments.

Effectiveness of $Ca(H_2PO_4)_2/H_3PO_4$ Combination in Immobilizing Pb

The present column experiment was designed to obtain detailed leaching data on the capacity and efficiency of Pb-immobilization in contaminated soils treated with phosphorus obtained from the phosphoric acid and other soluble phosphorus sources. Our results suggested that a 4 molar ratio of P/Pb using H_3PO_4+$CaCl_2$ or H_3PO_4 +$CaCl_2$ + $Ca(H_2PO_4)_2$ proved to be optimum for Pb-immobilization in contaminated soils (Tables 4 and 5). The concentration of most leachable trace metals from phosphorus amended soils decreased sharply and remained below their regulatory levels in drinking water particularly for the Cd and Pb. Applied P amendments were effective not only to limited surface layer, but remained effective > 10 cm depth from surface.

Table 4. Chemical Characteristics and Trace Metal Concentrations in the Column Leachates.

Treatments	First Leaching ~2 Pore Volume						
	pH	TOC (mg/l)	Pb (µg/l)	Cd (µg/l)	P (mg/l)	Cu (mg/l)	Zn (mg/l)
Control	8.26	96.2	8.5	0.2	0.68	0.15	0.04
P-2	8.14	113.2	3.3	0.3	1.14	0.19	0.02
PC-4	6.72	105.0	0.8	1.2	46.9	0.17	0.01
P-4	7.43	94.2	5.1	0.2	42.0	0.41	0.17
PC-8	5.52	108.3	3.2	2.6	214.4	0.37	0.11
P-8	5.43	103.5	4.6	2.4	257.5	0.39	0.08
	Second Leaching ~4 Pore Volume						
Control	7.54	59.2	5.0	1.2	0.64	0.18	0.02
P-2	7.65	64.2	6.0	1.0	1.64	0.18	0.04
PC-4	7.30	90.6	5.5	2.2	35.5	0.37	0.01
P-4	6.93	51.1	2.0	1.3	69.5	0.57	0.13
PC-8	6.64	63.3	5.1	1.9	112.5	0.39	0.10
P-8	6.64	49.1	4.1	2.6	160.6	0.35	0.07

Table 5. TCLP-Pb in Contaminated Soils After Treating with Phosphorus Using Phosphoric Acid and Calcium Monophosphate.

Treatment	TCLP Pb (mg L^{-1})	
	Surface	Below 10 cm Depth
Control	143.4	122.8
P-2	60.6	18.6
PC-4	4.4	4.6
P-4	3.6	4.4
PC-8	2.3	4.2
P-8	1.9	1.2

Effectiveness of Selected Treatment in Immobilizing Pb Using an Intact Core

The effects of applied phosphate amendments on selected leachate characteristics and their resulting effects on metal leachability are shown in Figures 8 and 9, respectively. Generally for all phosphate amendments, increasing application rate caused a decrease in leachates pH in the following order: H_3PO_4 > Mixture of $Ca(H_2PO_4)_2$ H_2O and H_3PO_4 >$Ca(H_2PO_4)_2$ H_2O> KH_2PO_4. The amount of unused soluble phosphorus in leachates varied among various P-amendments. For example, up to 1 of P/Pb application rate, soluble P in leachate remained relatively low in the case of H_3PO_4 and mixture amendments compared to other amendments, which indicates efficient utilization of applied phosphorus. In the case of $Ca(H_2PO_4)_2$ H_2O and KH_2PO_4 amendments, higher soluble P concentration in the leachate enhanced the risk of P migration to the surface and groundwater.

The amount of DOC in leachates increased more significantly with increasing application rate of KH_2PO_4 as compared to other P-amendments at the same application rate (Figure 8).

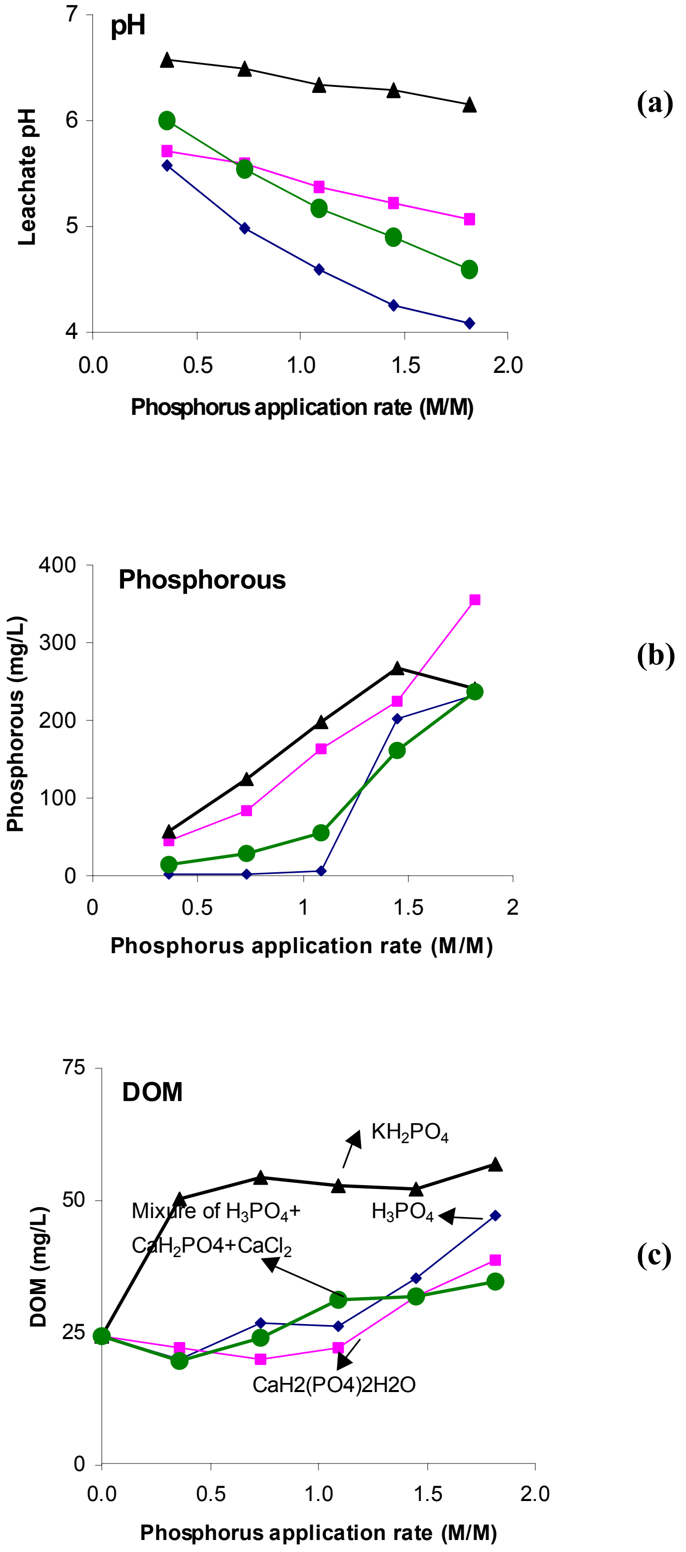


Figure 8. Chemical Characteristics of Batch Leachates: (a) pH, (b) Soluble Phosphorus Concentration (mg L^{-1}), and (c) Dissolved Organic Matter (mg L^{-1}).

The increase in metal leachability of phosphate-amended soil at a relatively high application rate (Figure 9) may be attributed to a decrease in pH and enhanced solubility of soil organic carbon resulting in the formation of stable organo-metallic complexes. These organo-metallic complexes are unable to form metal phosphate although a sufficient amount of soluble P was present in these leachate solutions. Our data showed a positive correlation between the leachability of Pb and Cu, and DOC concentration in the leachate solution. This is why $CaCl_2$ was added as an amendment to reduce DOM concentration.

In the second step of the batch test, the effectiveness of applied P-amendments was measured by using a standard TCLP test. Generally, with increasing phosphate application rate, a decrease in TCLP extractable metal concentrations was observed for most applied amendments (Figure 10). However, the observed reduction remained more pronounced, particularly for Pb. Among screened P-amendments, H_3PO_4 and a mixture of H_3PO_4, $Ca(H_2PO_4)_2\ H_2O$, and $CaCl_2$ at the SMR of 1was sufficient to immobilize target contaminant Pb to below its regulatory level in highly contaminated soil from the demonstration site, which represents one of the worst case scenarios. Their application rate remained relatively low compared to other amendments. Based on these batch test results, a mixture of H_3PO_4 $Ca(H_2PO_4)_2\ H_2O$, and $CaCl_2$ outranked P-amendments for the effective immobilization of metal in highly contaminated soil from the Jacksonville demonstration site.

The effects of applied P-amendments on leachate pH and dissolved organic matter in the cumulative leachates of intact soils columns are shown in Figure 11. Initially, leachate pH decreased significantly for Treatments 1 and 2, respectively, compared to Treatment 3. However, an application of 5% phosphate rock in Treatment 3 was able to maintain leachate pH near neutral. With increasing leachate volume, leachate pH tends to be stable after two weeks of leaching. However, unexpected behavior of dissolved organic matter was observed (Figure 11), which may be attributed to the decrease in leachate pH and the development of reducing conditions in the soil columns.

The amounts of metals leached as a function of cumulative leaching volume are shown in Figure 12. Among the investigated metals, leachability patterns varied widely.

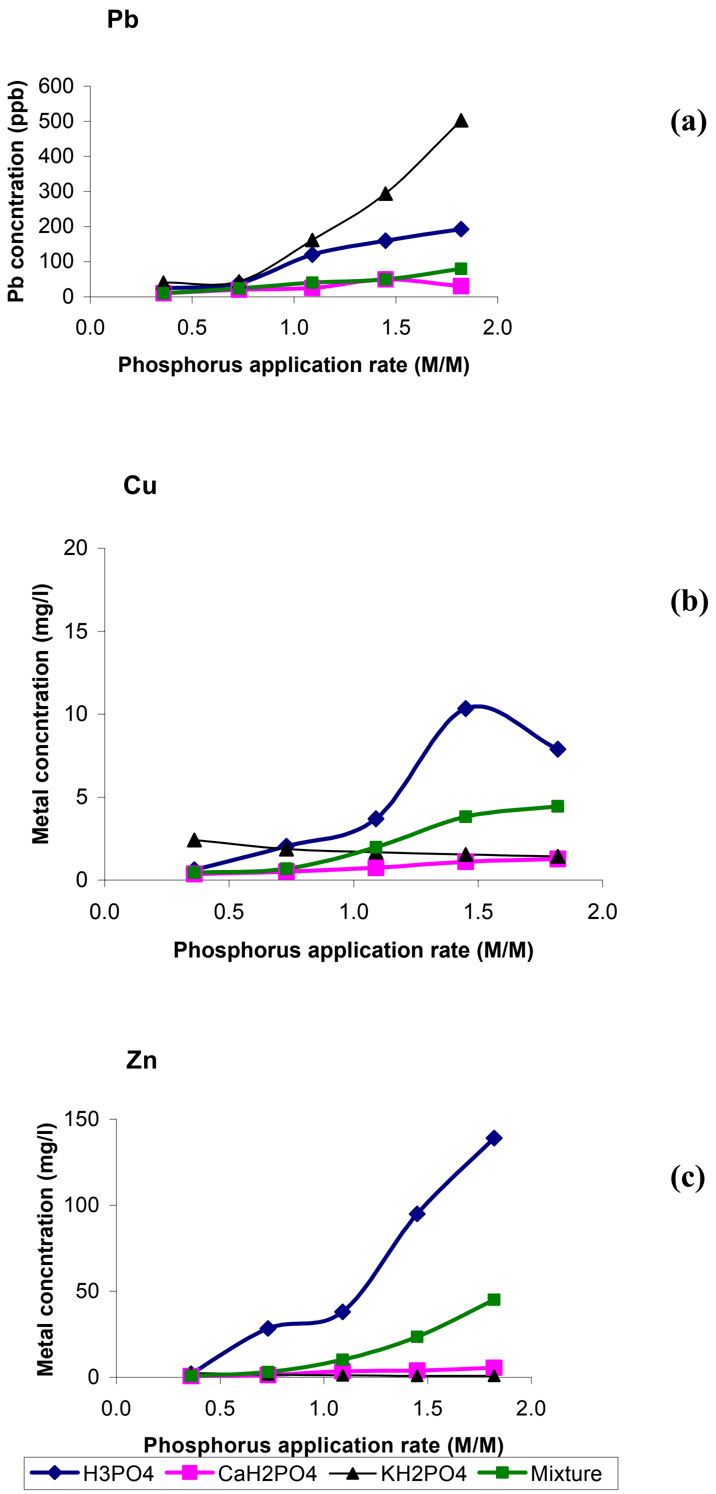


Figure 9. Heavy Metal Concentrations in Batch Test Leachates: (a) Pb Concentration (μg L^{-1}), (b) Cu Concentration (mg L^{-1}), and (c) Zinc Concentration (mg L^{-1}).

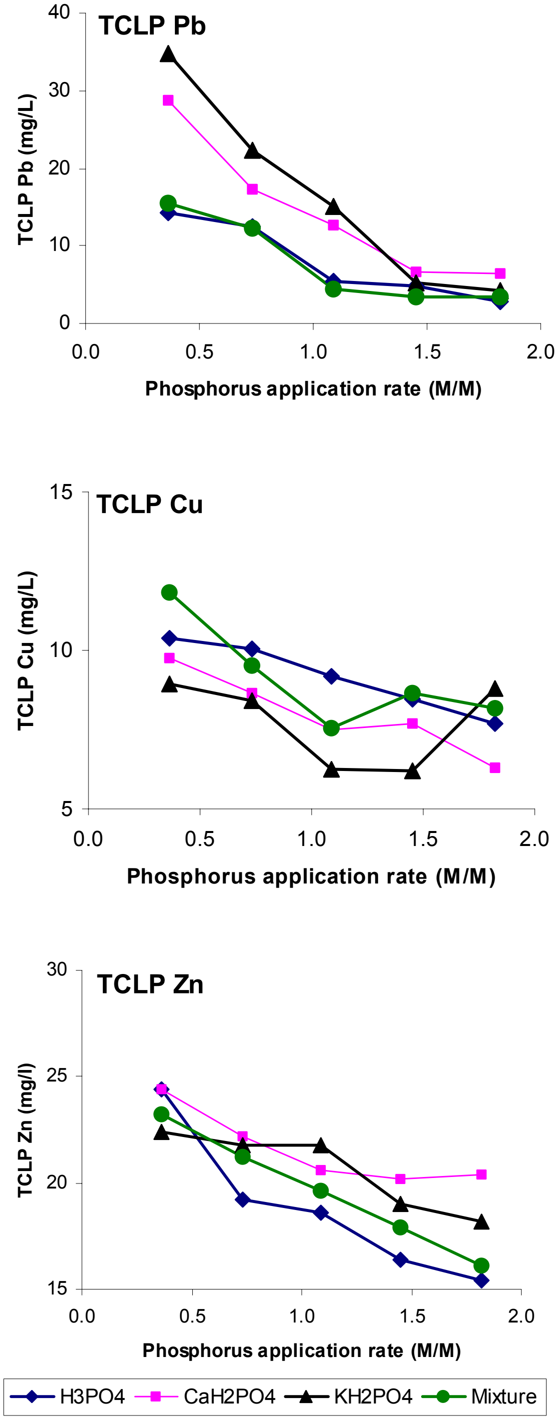


Figure 10. TCLP- Extractable Metals (mg L^{-1}) in Phosphate-Amended Soil.

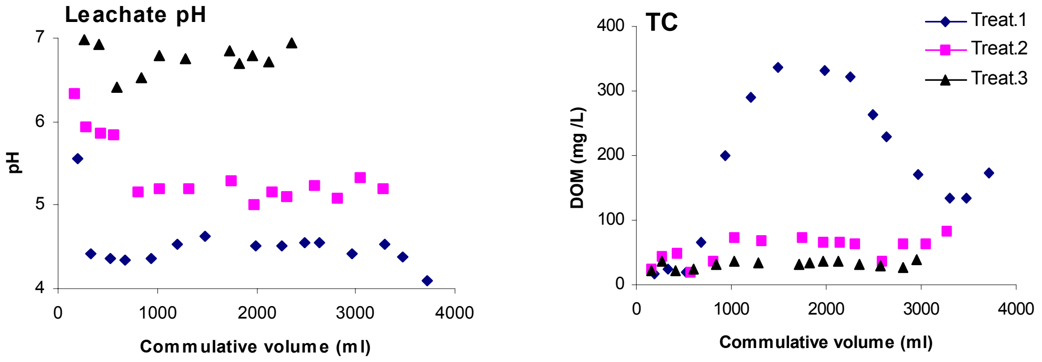


Figure 11. Effects of Applied P-Amendments on Leachate Characteristics of Intact Soil Columns.

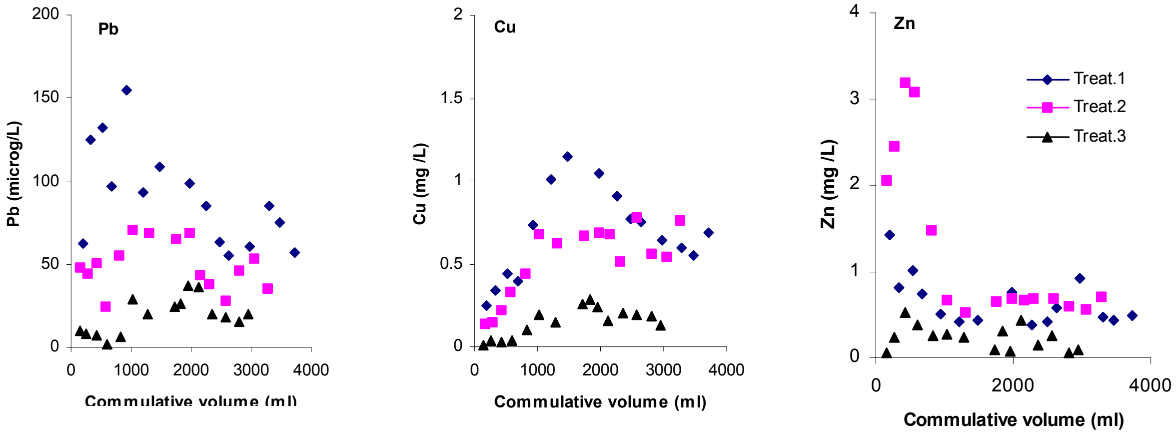


Figure 12. Effects of Applied P-Amendments on Leachability of Heavy Metals in Intact Soil Columns as a Function of Increasing Leachate Volume.

For Pb and Cu leachability patterns remained consistent with the increasing solubility of DOC in the leachates. Dissolved organic carbon may increase metal solubility by formation of stable aqueous metal complexes (Zhu and others 1999). Therefore, successful immobilization treatment for Pb is expected to depend on pH and similar behavior is expected for other metals. Oxidation-reduction potential (Eh) is another property affecting metal solubility in columns that was not monitored in this experiment.

TCLP Leachability

The vertical effectiveness of applied P-amendments for metal immobilization was measured by USEPA TCLP and these results are shown in Figure 13. TCLP-Pb leachability in surface soil (0-10 cm) was reduced to below its regulatory limit of 5 mg L^{-1} for all three treatments. The vertical effectiveness of these treatments depends largely on the variability of soil characteristics and the nature of filled material in the selected demonstration site. A variable depth of sand layer was observed in the contaminant section of the site and the observed depth varied between 25 to 50 cm from the surface. Although TCLP leachability of metals decreased significantly for most investigated metals (Figure 13), the observed effects remained more pronounced for Pb. All three treatments reduced the leachability of heavy metals; overall, the highest reduction was observed for Treatment 1 followed by Treatments 2 and 3.

The decrease in pH of the sectioned soil columns after their leaching remained lowest for Treatment 1 followed by Treatments 2 and 3 (Table 6). The highest reduction in soil pH remained limited to surface layers. The vertical effects of applied phosphate amendments depend mainly on soil physical variability within the contaminated section of the demonstration site. We can conclude that reduction in soil pH to ~5-5.50 may provide optimum metal immobilization because several solid phase fractionation studies reported complete solubilization of carbonate-bound metals in soils and sediments (Tack and Verloo 1997). Soluble metals in soil solution may easily form stable metal phosphate in the presence of soluble phosphorus, which needs further investigation.

Table 6. Final pH of Phosphate-Amended Soil Columns After Their Leaching.

Depth (cm)	Control	Treatment 1	Treatment 2	Treatment 3
0 -10	6.41	3.81	5.18	5.85
10-20	6.54	3.72	5.10	6.04
20-30	6.88	3.74	5.52	6.12
30-40	7.04	3.52	5.45	6.03
40-60	7.02	4.61	5.16	6.11
60-80	6.66	4.55	5.41	6.22

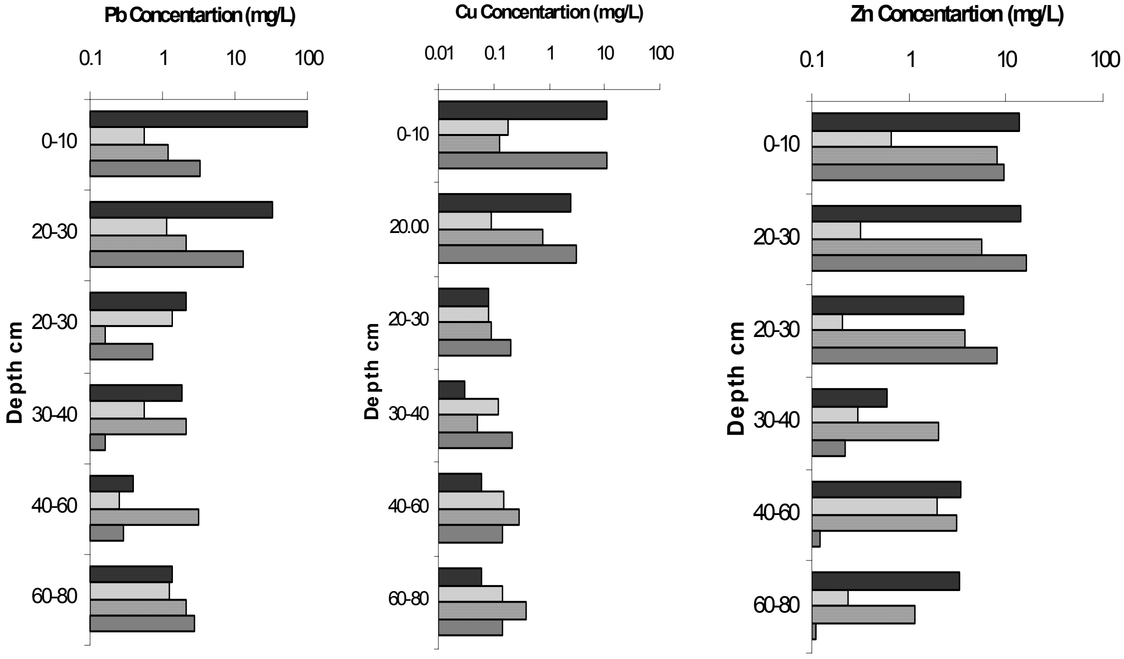


Figure 13. TCLP-Metal Contents in Sectioned Intact Soil Columns After Their Leaching.

CONCLUSIONS

Based on the results of the column and batch experiments, several conclusions can be drawn:

- Among various phosphate amendments, mixtures of H_3PO_4+$Ca(H_2PO_4)_2$ H_2O+$CaCl_2$ or H_3PO_4+phoshphate rok+$CaCl_2$ at application rate of 4 P/Pb was the most effective in achieving a low leachability of regulated metals with minimum adverse effects on soil physicochemical characteristics and leachability of P and DOC.

- For efficient immobilization, pH reduction with H_3PO_4 became necessary to dissolve carbonate-bound metals and make them readily available for the geochemically stable metal phosphate formation.

- Intact soil column results remained consistent with batch test results. Using batch experiment is easy and fast for optimizing phosphate application rate and evaluating metal immobilization in contaminated soils

INTERACTIONS OF HEAVY METAL WITH PHOSPHATIC CLAY: SORPTION AND DESORPTION BEHAVIOR

BACKGROUND

Phosphate mining in Florida produces large quantities of phosphatic clay as by-products. At current mining rates nearly 100,000-ton day^{-1} of phosphatic clay is produced, creating a major disposal problem for the phosphate mining industry. Phosphatic clay characteristically has a high content of apatite (up to 24-32 % of total dry weight), which is too fine to recover during processing. In addition to apatite, phyllosilicate minerals (mainly smectite, palygorskite, and kaolinite) constitute a major fraction of phosphatic clay (Hawkins 1973; Blue and Mislevy 1980). This clay has high CEC and neutral to slightly acidic pH. These properties suggest that addition of phosphatic clay as a binding agent to immobilize heavy metals would be an innovative approach for the remediation of soils and sediments polluted with heavy metals.

Land disposal of municipal and industrial wastes and applications of fertilizers and pesticides in agriculture have contributed to a continuous rise of toxic metals in the soil environment. The bioavailability and fate of these heavy metals in soil strongly depend on the extent of their sorption onto solid phases. Partitioning of trace metals between solid and aqueous phases is controlled by properties such as surface area, surface charge induced by the formation of organic coatings on the surface, and variables such as pH, ionic strength and concentration of complexing ligands (Petrovic and others 1999). Metal immobilization through precipitation and adsorption is also considered a common mechanism to reduce metal toxicity in contaminated soil environment (Malakul and others 1998).

In situ immobilization and geochemically reactive barriers are two promising approaches that have the potential to remove metals from solutions and/or stabilize metals in soils, sediments, water and wastes. In the development of in situ immobilization technology and reaction barrier remedial systems, two important factors need to be considered: (i) the system must be effective under a variety of existing geochemical conditions and (ii) immobilized metals should be stable and remain non-leachable under variable environmental conditions. Generally, in situ immobilization of metals involves minimization of contaminant mobility by transferring them from labile to non-labile phases via physically, chemically or biologically induced transformations. Behaviors of heavy metals in the soil environment are governed to a large extent by their sorption and desorption reactions with different soil constituents. Although desorption is a key factor controlling the availability and mobility of metal ions in contaminated soils and sediments, it has received much less attention than to the sorption process. It is therefore important to understand various processes and factors controlling the desorption behavior of sorbed metals.

Metal bioavailability is tied to solubility rather than total concentration, and must be considered in developing remediation strategies (Traina and Laperche 1999). For example, a major limitation for in situ immobilization of Pb in contaminated soils is the limited solubility of lead minerals, present in the existing soil environment. Lead carbonate (cerussite) has been identified as a major Pb mineral in many soils from contaminated sites, particularly from battery recycling sites (Nedwed and Clifford 1997; Royer and others 1992). Effective Pb-immobilization using phosphorus amendments requires enhanced solubility of existing Pb minerals by inducing acid conditions that promote pyromorphite formation. The Pb in the pyromorphite is much less bioavailable than Pb associated with cerrucite. The resulting acidity will also enhance the mobility of other metals, causing risk of their leaching to ground water. Phosphatic clay possesses high potential to adsorb these mobilized metals in the resulting soil environment and provide an additional phosphate source for pyromorphite formation. Phosphatic clay could also have the secondary benefits of improving fertility, structure, and soil moisture-holding capacity when added to sandy soils (Gonzalez and others 1992).

Most studies on heavy metal sorption and related mechanisms have been focussed on individual synthetic mineral sorbents. For example, hydroxyapatite has been investigated as a potential agent to treat heavy metal-contaminated soils, sediments, wastes, and wastewater, especially in the cases of Pb, Cd, Zn and U (Arey and others 1999; Chen and others 1997; Ma and others 1993; Xu and Schwartz 1994; Suzuki and others 1988). However, minerals such as smectite, illite, kaolinite and Fe-Mn oxides are also considered potential binding agents for heavy metals. Adsorption behaviors of these individual minerals have been studied by several workers (Griffin and Au 1977; Kraepiel and others 1999; Lothenbach and others 1998; Siantar and Fripiat 1995; Spark and others 1995; Yong and others 1990). To our knowledge, no efforts have been made to evaluate the sorption and desorption behavior of phosphatic clay with respect to heavy metals. Phosphatic clay is a heterogeneous mixture of several minerals, which interact with heavy metals in a variety of ways. Reaction kinetics and mechanisms of heavy metal sorption onto phosphatic clay are still not well understood. Identifying the sorption mechanisms of heavy metals on phosphatic clay is important to predict the efficiency of phosphatic clay for heavy metals immobilization in variable soil environments.

The main objective of this study was to evaluate the heavy metal immobilization potential of phosphatic clay. The specific goals were to: (i) examine the sorption of heavy metals onto phosphatic clay, (ii) estimate leachabilities of the reaction products using both acidic and basic extracting solutions, (iii) characterize the reaction products of phosphatic clay after interaction with aqueous Cd, Pb, and Zn solutions, and (iv) elucidate the mechanisms of heavy metal sorption and desorption in the presence of phosphatic clay. The results of this study indicate phosphatic clay has a potential to immobilize heavy metals in contaminated soils, sediments, wastes and wastewater due to a high capacity to adsorb and retain metals.

MATERIALS AND METHODS

Characterization of Phosphatic Clay

Phosphatic clay used in this study was obtained from the PCS Phosphate Mining Company, White Springs, Florida. Clay sample preparation included air drying, crushing by mortar and pestle, passing through a 60-mesh sieve, and pre-rinsing with deionized water.

Characterization of the clay included surface area measurement, mineralogical analysis, particle morphology assessment, and elemental analysis. Surface area was determined by the BET-N_2 adsorption procedure. Mineralogy was determined prior to and following various treatments using x-ray diffraction and standard cation-saturation procedures for identification of expansible phyllosilicates (Whittig and Allardice 1986). X-ray diffraction analyses were conducted on a computer-controlled x-ray diffractometer equipped with stepping motor and graphite crystal monochromatore. Scans were conducted from 2 to 60° at a rate of 2° per min. Particle morphology was assessed by scanning electron microscopy (SEM), and elemental spectra for individual particles were obtained using energy-dispersive x-ray elemental spectroscopy during SEM observations.

Table 7. Selected Properties of Phosphate Rock.

Formula	Surface Area	pH	P	Si	Ca	Al	Fe	Mg	Pb	Cu	Zn	Mn	Cd
	m^2/g		..……………..%…………….						……….mg/kg……….				
$Ca_{10}(F_2)(PO_4)_6(CaCO_3)_x$	33.6	7.10	14.3	17.5	34.3	0.66	0.63	0.22	<1	7.02	110	650	20.2

Sorption Experiment

Deionized water from a Barnstad Nano-Pure system was used in rinsing and preparation of samples. Labware used for each experiment was cleaned in detergent first, then acid-washed, and finally rinsed with deionized water. Metal concentrations of Cd, Pb, and Zn stock solutions were 2.50×10^{-2} mol L^{-1}, 4.50×10^{-2} mol L^{-1}, and 7.50×10^{-2} mol L^{-1} prepared from their nitrate salts. All chemicals used in these experiments were analytical reagent grade.

All metal sorption experiments were performed in batch mode. A 30 ml aliquot of 0.05 mol L^{-1} KNO_3 background electrolyte solution containing a known amount of metal ions was equilibrated with 0.1 g phosphatic clay powder in 40 ml polycarbonate centrifuge tubes. The slurries were shaken on a reciprocating shaker operated at 30 ±1 rpm at room temperature of 25 ± 3 °C for 24-hours, which has proven to be sufficient for the reaction to reach equilibrium (Ma and others 1993; Xu and others 1994). The supernatant was separated by centrifugation (Beckman G-2-21) at 10,000 rpm for 20-minutes. Metal concentrations in the filtrate were analyzed as previously described. Multi-level standards (Fisher Scientific) were prepared in 2 % of nitric acid. Total phosphate (PO_4) concentrations were determined by spectrophotometer using the ascorbic acid method (Olsen and Sommers 1982). Solution pH was determined using a Fisher Scientific Accumet model 20 pH/conductivity meter. The amount of adsorbed metal was taken as the difference between the amount added initially and that remaining in solution after equilibration. All measurements were in duplicate. After sorption experiments, the remaining solid residue in the centrifuge tubes were thoroughly washed three times with deionized water and supernatants were discarded immediately after 15-minutes of centrifugation. The washed residue was stored for the following desorption experiments.

Desorption Experiment

To determine the stability of heavy metal ions adsorbed to phosphatic clay, desorption characteristics were also determined. Four extracting solutions of varying pH were prepared to evaluate the leachability of phosphatic clay after interaction with aqueous solutions. Two acidic solutions were prepared from acetic acid at pH 2.93 and 4.93 following the preparation of the extraction fluids used in the EPA Toxicity Characteristic Leaching Procedure (EPA 1990). The other two extracting solutions used in this study were 0.1mol L^{-1} ammonium acetate at pH 7 and basic solution of pH 10 prepared by diluting concentrated NaOH solution and deionized water.

The washed residues from sorption experiments were treated with 30-ml of each leaching solution and slurries were shaken on a reciprocating shaker for 24-hours. Slurries were centrifuged and their supernatants were filtered and analyzed for the metals of concern as described above in the sorption section.

Sorption Kinetics Experiments

A total of 0.5-g phosphatic clay powder, previously passed through a 60-mesh sieve, was weighed into 250-mL polycarbonate bottles. A 150 ml aliquot of 0.1 mol L^{-1} KNO_3 electrolyte solution was added to each bottle. In this experiment, the liquid to solid ratio (L/S) was the same as for the sorption and desorption experiments (L/S = 300). Concentrated metal solutions were added to each bottle to provide an initial metal concentration of ~ 50 mg L^{-1}. Bottles containing these slurries were shaken on a reciprocating shaker for 120 hours at room temperature (25 ±3 ^{0}C). Periodically, 10-ml slurry samples were taken from each bottle using plastic syringes and filtered immediately through 0. 45-µm syringe filters. Filtrates were analyzed for pH, Ca, P, Cd, Pb, and Zn as described in the previous section.

RESULTS AND DISCUSSION

Sorption Isotherms

Phosphatic clay was effective in sorbing all three metals, with the amount of metals sorbed ranging Pb > Zn > Cd (Figure 14a). Though the sorption isotherms of Pb, Cd and Zn by phosphatic clay differed, each followed type-L shape based on the classification of Giles and others (1960). The Pb sorption isotherm remained nearly a vertical line for initial concentrations from 0 to 50 mg, because equilibrium concentrations were near the detection limit of the employed analytical method. According to Brümmer and others (1983), isotherms with similar equilibrium concentrations for different amounts of added metal suggest a precipitation mechanism. Our sorption data show that precipitation and coprecipitation mechanisms played a more significant role for removal of Pb and Cd as compared to Zn (Figure 14a). Precipitation is often associated with neutral to alkaline conditions, relatively high metal concentrations, low solubility of metal compounds and low amounts of specific sorption sites (Brümmer 1986). Most sorption isotherms were characterized by their decreasing slopes as equilibrium metal concentration increased indicating high affinity of the adsorbent for low concentrations of adsorbate (Wu and others 1999). Metal sorption by phosphatic clay showed Langmuir-type isotherms, which can be described by the equation:

$$q = \frac{Q_{\max} C_e}{K + C_e} \qquad (1)$$

where q is the amount of heavy metals sorbed on phosphatic clay (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}), Q_{max} is the maximum sorption capacity (mg g^{-1}) and K is the affinity constant (mg L^{-1}).

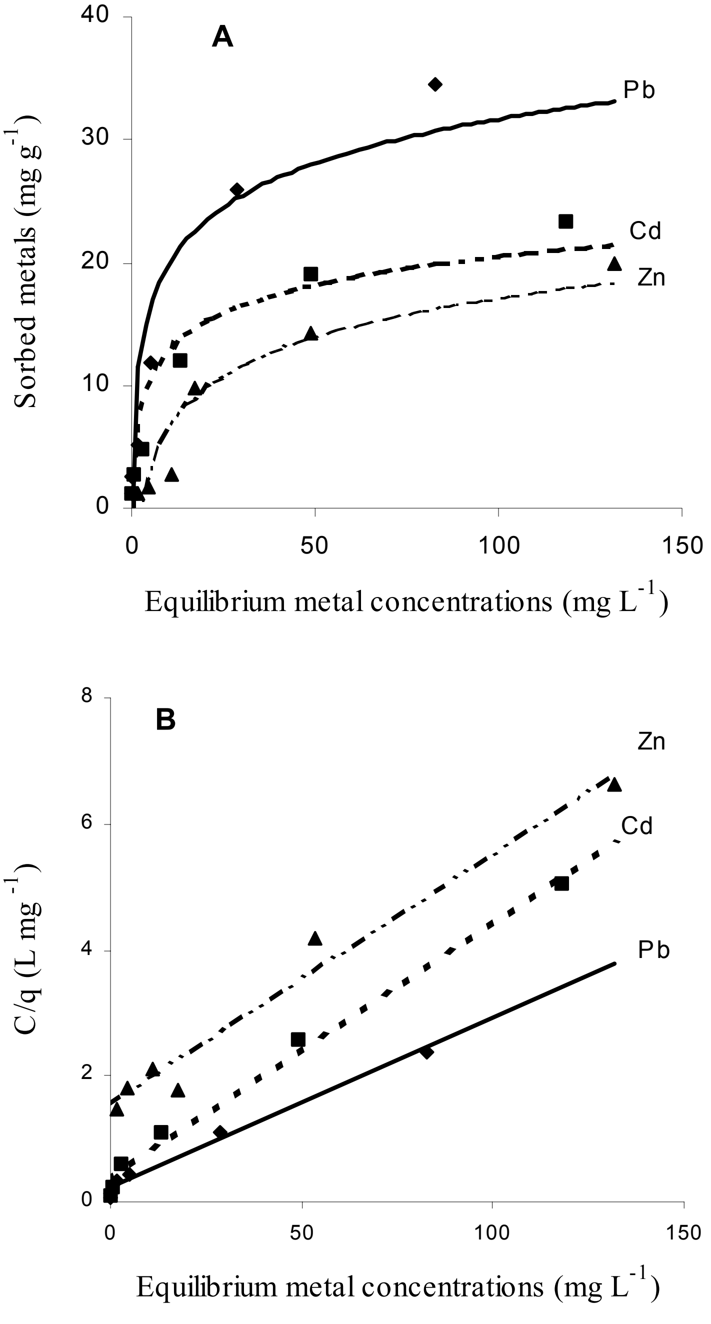


Figure 14. Sorption Isotherm Curves of Heavy Metals onto Phosphatic Clay Before (a) and After (b) Linear Langmuir Transformation. The Data Are from 24-Hour Sorption Experiments.

The equilibrium sorption data were fitted to the linear form of the Langmuir equation and are plotted in Figure 14b. Langmuir sorption parameters of phosphatic clay for each of the three metals were calculated by using the least square fitting, and are shown in Table 7. In most cases, correlation coefficients (R^2) for the linear regression fit were > 0.97. Sorption parameters of phosphatic clay showed variability among the three metals, as reflected by their sorption maxima and affinity constants (Table 8).

Results showed that Q_{max} of phosphatic clay remained highest for Pb, followed by Zn and Cd respectively. This suggests that the presence of fluoroapatite and other minerals in phosphatic clay significantly increased sorption capacity through a precipitation mechanism. Small K values for phosphatic clays suggested higher affinity for Pb and Cd than for Zn. Phosphatic clay possesses high CEC (~26.9 cmole kg^{-1}). In a high ionic strength background electrolyte system (0.05 KNO_3), metals competed with other ions for sorption sites on the phosphatic clay, resulting in reduced uptake of Pb, Cd and Zn (Hirsch and others 1989; Holm and Zhu 1994). Because no additional complexing ligands were added during the experiment, phosphate ions originating from fluoroapatite were the major ligands that could form complexes with metals. The fit of our sorption data to a linear form of Langmuir equation is generally good for the investigated metals, though with slight deviations at higher concentrations. These deviations suggest that other possible mechanisms in addition to precipitation and coprecipitation may be taking place simultaneously (Sparks 1995).

During sorption experiments, pH and concentrations of Ca and PO_4 in the equilibrium solutions were also measured. After interaction of heavy metals with phosphatic clay, phosphorus concentrations in the equilibrium solutions were reduced to below the detection limit (approximately equivalent to the P concentration in the reagents blank) due to P's rapid consumption and limited availability from phosphatic clay. Reactions of metal solution with phosphatic clay can decrease solution pH and equilibrium pH decreased by ~2 units as the amount of sorbed metals increased. The magnitudes of pH change were in proportion to the amounts of individual amount of metals sorbed (Figure 15), which were in the order Pb >> Cd > Zn.

Table 8. Langmuir Parameters for Heavy Metal Adsorption onto Phosphatic Clay.

Metals	Q_{max} (mg g^{-1})	K mM	R^2
Cd	24.5	0.3653	0.98
Pb	37.2	0.2156	0.99
Zn	25.1	1.5338	0.97

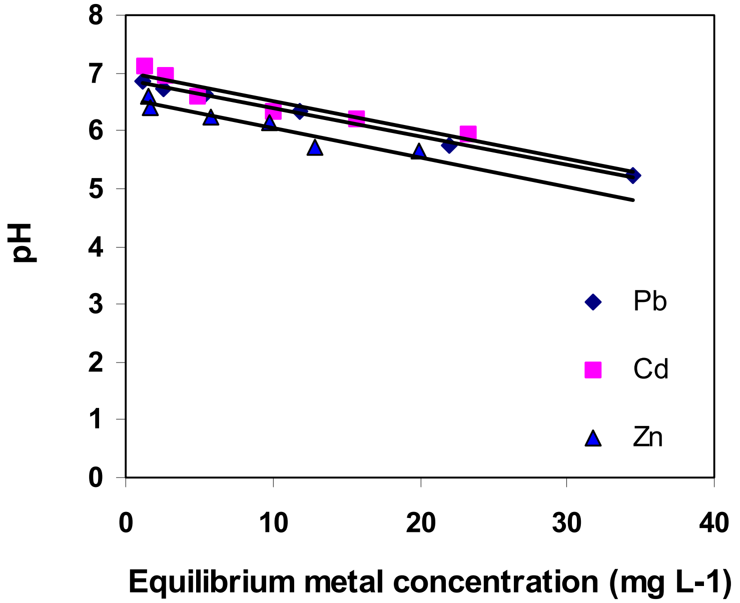


Figure 15. Relationship Between Sorbed Metals and pH After 24 Hours of Interaction Between Metal and Phosphatic Clay.

The correlation between the amount of Ca remobilized into the equilibrium solution and total amounts of metals sorbed onto phosphatic clay was approximately linear (Figure 16). Slope for the Pb sorption isotherm vs. Ca concentration was 0.97 with ($R^2 = 0.97$). The nearly 1:1 ratio indicated displacement of Ca by Pb, to form $PbCO_3$, $Pb_3(OH)_2CO_3)_2$ and $Pb_5(PO_4)_3(F,OH)$ (Santillan-Medrano and Jurinak 1975; Ma and others 1993). On the other hand, slopes for Cd and Zn were 0.77 ($R^2 = 0.97$) and 0.67 ($R^2 = 0.92$), suggested additional retention mechanisms without cationic exchange, such as surface complexation (Echeverria and others 1998). We assumed that most Ca in the equilibrium solution was obtained from dissolution of phosphatic clay components (e.g. fluoroapatite and carbonate minerals) after interactions with aqueous metal solutions.

Simultaneous changes of equilibrium solution pH and Ca concentration make it difficult to determine whether the increase in Ca concentration was the consequence of ion exchange with heavy metals, further phosphatic clay-component dissolution due to the decrease in pH or other mechanisms. According to LeGeros and LeGeros (1984), cations with ionic radii smaller than Ca^{+2} (0.99 °A) have less chance to be incorporated into an apatite structure compared to cations with larger ionic radii. Therefore, precipitation of Zn^{2+} (0.69°A) with Ca^{+2} would be less likely compared to the larger cations Pb^{+2} (1.18 °A) and Cd^{+2} (0.97 °A). This explanation is consistent with our data. In the case of phosphatic clay, it appears that several mechanisms are involved in removal of metals from aqueous solution. It would be difficult to determine the proportions of metals removal due to any specific mechanism.

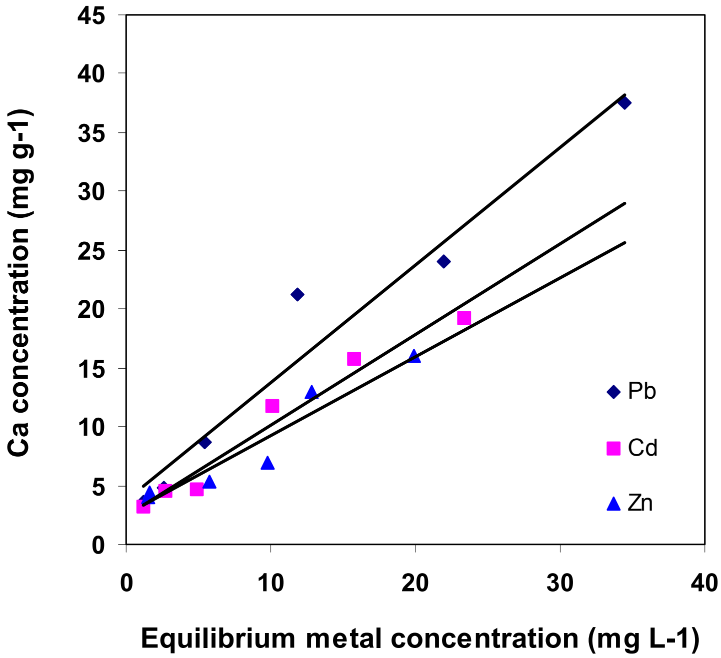


Figure 16. Relationship Between Amounts of Metals Sorbed onto Phosphatic Clay and Resulting Ca Concentrations in the Equilibrium Solution After 24 Hours of Interaction.

Table 9. Desorption Percentage of Heavy Metals from Phosphatic Clay.

Metals sorbed		Desorption %			
Metals	mg g-1	TCLP pH 3	TCLP pH 4.9	H_2O pH 7	H_2O pH 10
Pb	11.7	23.1	17.9	0.8	1.5
Pb	21.0	20.0	13.8	0.4	0.5
Pb	93.0	9.8	8.1	nd*	2.4
Cd	10.1	23.2	17.4	0.6	1.2
Cd	19.9	45.0	33.0	0.8	0.3
Cd	35.9	8.4	14.5	nd	2.4
Zn	7.3	73.9	28.7	0.4	0.4
Zn	22.5	46.6	33.3	0.4	1.7
Zn	40.8	29.8	21.9	nd	6.0

* nd: Not determined

Desorption Experiment

Desorption percentage of heavy metals sorbed onto phosphatic clay was based on concentrations in the extracting solutions used for desorption. The amounts of Cd and Zn desorbed by acidic extracting solutions remained high compared to Pb. Depending upon sorbed amount of metals, their percentage of desorption into the TCLP extracting solution at pH 2.93 varied from 9.8 to 23.1 for Pb, 8.4 to 45.0 for Cd and 29.8 to 73.9 for Zn (Table 9). Also the amount of metals desorbed into extracting solutions decreased with their increasing sorption onto phosphatic clay. Low metal leachability with increasing sorption can be explained by blockage of exchange sites with metal ions and competitive sorption because of increased metal ions in the extracting solutions (Tyler 1978). For investigated metals, the desorbed amount decreased continuously with increasing pH of the extracting solution and it became only trace amounts above pH 7. Therefore, sorption-desorption of heavy metals on phosphatic clay exhibits a hysteresis with respect to pH.

Desorption of sorbed metals from phosphatic clay revealed clear differences in surface affinity. Among the studied metals, Pb showed the greatest resistance to desorption followed by Cd and Zn, respectively (Table 9). Xu and others (1994) and Chen and others (1997) observed similar desorption behavior for metals sorbed onto hydroxyapatite. Exceptionally low desorption of Pb from phosphatic clay confirmed the importance of apatite in retaining Pb, since only a small percentage of sorbed Pb was released even by TCLP extracting solution at pH 2.93. Lead was tenaciously held to phosphatic clay dominated by substantial amounts of fluoroapatite, only small percentages of which could be removed because the TCLP extracting solution was not able to destroy the newly formed pyromorphite compound during reaction. This suggests that phosphatic clay could be used effectively to remediate Pb-polluted soils and sediments.

From comparison of sorption and desorption data, it is apparent that, in addition to metal phosphate formation, several other mechanisms including surface complexation, ion exchange, diffusion and precipitation of metal carbonates may have contributed simultaneously to heavy metals removal by phosphatic clay. The significant differences between percentage of sorbed metals desorbed into extracting solutions during the desorption experiments suggest differences in their sorption mechanisms. In contrast to Pb and Cd, substantial amounts of sorbed Zn were released into the TCLP extracting solutions. This preferential release suggests that Zn was sorbed to surface sites of phosphatic clay with no or very small incorporation. Lothenbach and others (1998) also observed similar behavior for desorption of sorbed Cd and Zn from montmorillonite. Such results clearly demonstrate that waste phosphatic clay could potentially be a cost-effective stabilization agent for treating contaminated soils, thereby meeting essential requirements of environmentally sustainable technology.

Solid Phase Examination

X-ray diffraction analysis of phosphatic clay after its interaction with aqueous Pb solutions at the highest concentration (~5000 mg L^{-1}) confirmed the formation of fluoropyromorphite (Figure 17). In the case of Cd and Zn sorption onto phosphatic clay, XRD patterns were identical with the original phosphatic clay, with no significant morphological differences (data not shown) even at the highest concentrations. This suggests that new crystalline solid phases were not formed or at least could not be detected due to the detection limit of XRD.

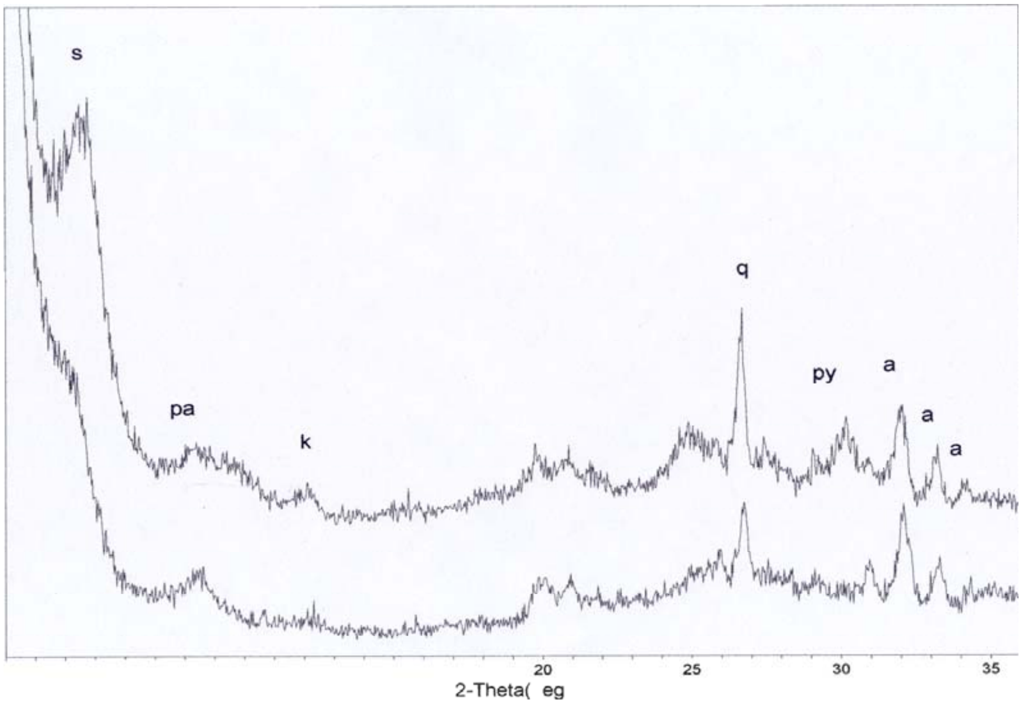


Figure 17. X-Ray Diffraction Patterns of Phosphatic Clay with the Following Treatments: (a) Untreated and (b) Lead-Treated Phosphatic Clay.

Scanning electron microscopy and energy-dispersive elemental X-ray analysis corroborated the presence of fluoropyromorphite (Figures 18 and 19). Backscatter imaging, which is sensitive to atomic number, was useful in locating the crystals of Pb-bearing fluoropyromorphite. Xu and others (1994) suggested possible coprecipitation of Cd and Zn with Ca to form a solid solution residue when aqueous metal solutions interacted with apatite. However, we were unable to confirm a clustering of these metals with Ca or in any other form using SEM and energy-dispersive techniques.

Coprecipitation of Cd and Zn into phosphatic clay components (apatite) can not be excluded on the basis of our measurements, because the analytical methods used failed to detect minor substitutions. Co-precipitation has been advanced as the explanation for the slow uptake often observed in metal sorption experiments (McBride 1980).

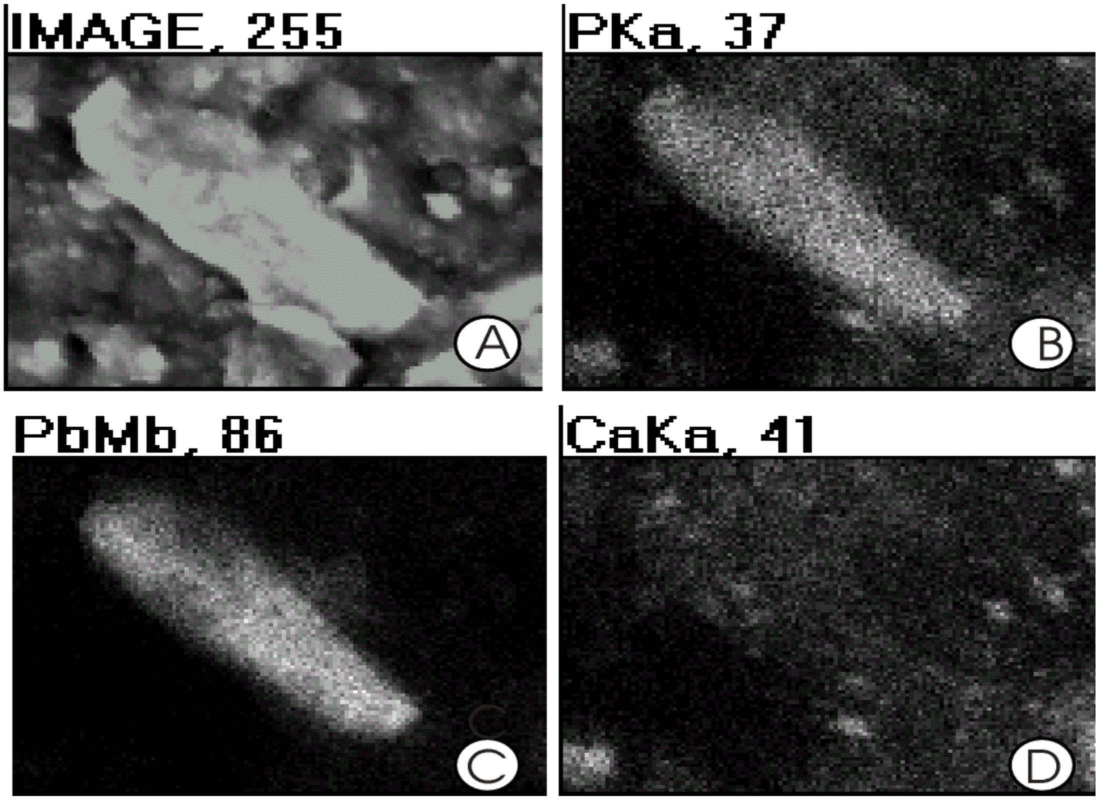


Figure 18. SEM Element Map of Pb-Rich Pyromorphite Particle in Lead-Treated Phosphatic Clay.

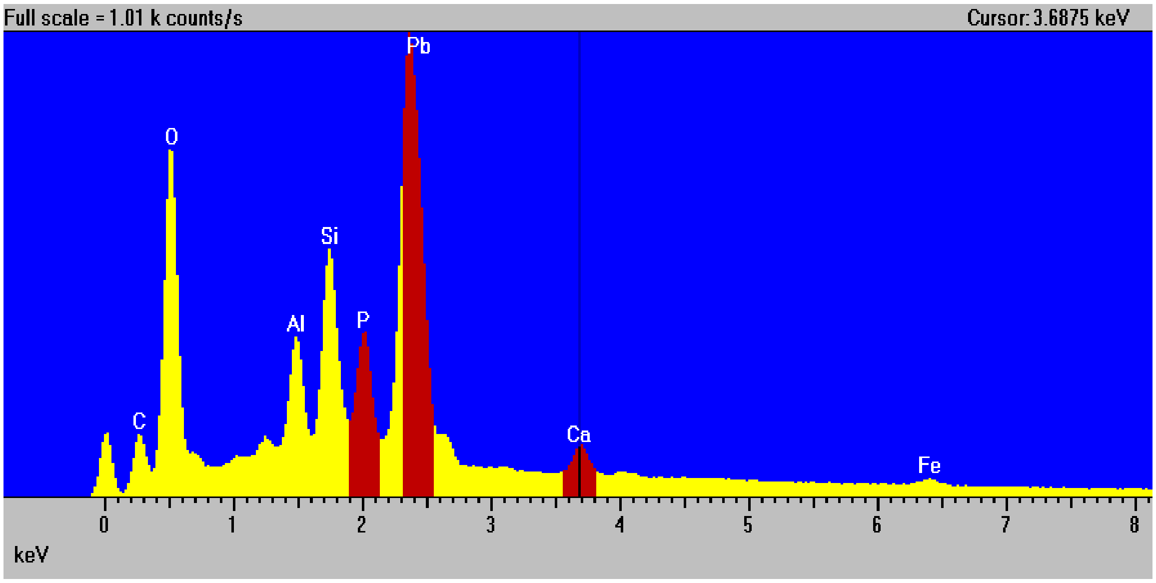


Figure 19. Elemental Spectrum of Pyromorphite Particle Obtained by Energy-Dispersive X-Ray Analysis.

Sorption Kinetics

Heavy metal sorption kinetics for phosphatic clay could be influenced by the dissolution of phosphatic clay components, because metals may interact with dissolution products during sorption. Initially, we evaluated phosphatic clay dissolution in 0.05 mol L^{-1} KNO_3 background electrolyte without adding metals ion at the same liquid: solid ratio (L/S) of 300 as a function of increasing reaction time. After 45-hours of dissolution, Ca concentration (15 ± 0.2 mg L^{-1}) leveled off, but PO_4 concentration and pH still increased continuously at slow rate (Figure 20).

Changes occurring in solution chemistry during heavy metal interactions with phosphatic clay were monitored for an initial concentration of 50 mg L^{-1} for each individual metal as a function of increasing reaction time (Figure 21). First, equilibrium pH decreased sharply and then it increased slowly with increasing reaction time as the metal solutions interacted with phosphatic clay. However, with ~50 mg L^{-1} metal in the initial solution, pH dipped more than one unit in the first 5-min, so reaction with the phosphatic clay may neutralize solution pH. The magnitude of pH change was proportional to the amount of metals sorbed on phosphatic clay, in the order Pb >> Cd >Zn.

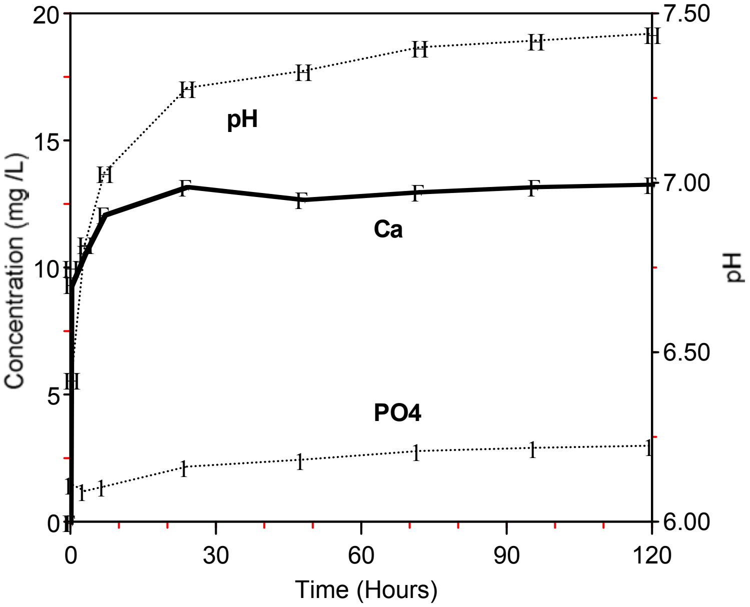


Figure 20. Changes in Leachate Chemistry During Interaction Between Phosphatic Clay and 0.05 Mole L^{-1} KNO_3 Background Electrolyte Without Any Metal Ions.

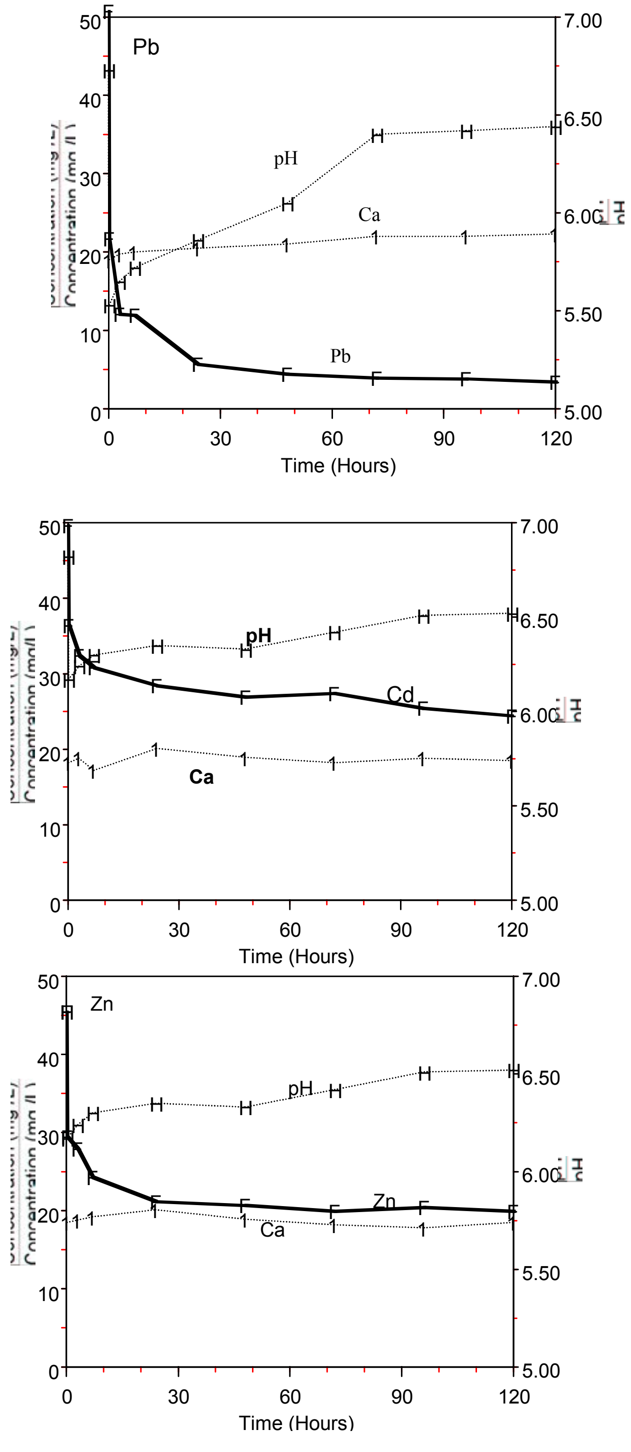


Figure 21. Changes in Leachate Chemistry During Interaction Between Phosphatic Clay and Metal Ions (50 mg L^{-1}) in the Presence of 0.05 Mole KNO_3 Background Electrolyte Solution.

Major changes in the metal concentrations occurred in two distinct stages: a rapid decrease in metal concentration, which occurred during first 10-20 minutes followed by a slow decrease as a function of increasing reaction time. Fast reactions are most likely the result of chemical reaction with surface sites on phosphatic clay that are readily accessible by metal ions (Strawn and others 1998). In all cases, total P concentration decreased to below its detection limit (approximately equivalent to concentration in blank) due to geochemically stable metal phosphate formation and its limited availability from phosphatic clay. Among the studied metals, decreases in Pb initial concentration remained highest for the kinetic sorption experiments, followed by decrease in Cd and Zn concentrations.

CONCLUSIONS

The results of this study clearly demonstrate that phosphatic clay is a very effective adsorbent for heavy metals removal from aqueous solutions. The amounts of metals sorbed onto phosphatic clay decreased in the order Pb > Cd > Zn. Although metal sorption onto phosphatic clay followed the Langmuir isotherm, apparent sorption mechanisms remained variable among investigated metals as evidenced by differences in their sorption and desorption behavior. Formation of fluoropyromorphite after reaction of aqueous Pb with phosphatic clay confirmed that precipitation is the dominant mechanism for Pb removal from aqueous solution. In addition to precipitation mechanisms, there exists the possibility of other sorption mechanisms such as surface complexation, co-precipitation and diffusion (particularly for Cd and Zn). These results imply that phosphatic clay could be a cost-effective option in the remediation of metals contaminated soils and sediments.

LEAD IMMOBILIZATION IN CONTAMINATED SOILS USING SOLUBLE PHOSPHATE AS AFFECTED BY THE PRESENCE OF VARIOUS LEAD SOLID PHASES

BACKGROUND

The primary mechanism of pyromorphite formation in the Pb-P-H_2O system has been reported as precipitation of soluble lead and phosphate and it has been considered a rapid process. Soluble Pb can be depleted rapidly if a stoichiometric amount of phosphorus is provided and well mixed. A potential limitation of in situ Pb immobilization in contaminated soils is the limited solubility of lead minerals in the existing contaminated soil environment. The solubility of Pb-bearing solids will be determined by the Pb release rate (desorption, dissociation and dissolution).

Because of high metal concentrations, different sources of metal input to the soil, and weathering, contaminated soils contain not only sorbed metals, but also various mineral forms of metal. In soils from contaminated soils, lead and lead compounds appear in a variety of physical (dust, chips, and chunks) and chemical (oxides, carbonates, hydroxides, and sulfates) forms (Royer and others 1992). The major lead species found in contaminated soils include lead carbonate, lead oxides, basic lead carbonate, and lead sulfate (Nedwed and Clifford 1997). Lead contaminated sites containing carbonate usually contain lead carbonate, basic lead carbonate or basic lead carbonate sulfate ($Pb_4(SO_4)(CO_3)_2(OH)_2$) (Royer 1992). These minerals were identified with SEM as major lead phases in contaminated soils from several US industrial sites (Van Benschoten 1997). Hessling and others (1990) also found lead carbonate, basic lead carbonate, lead sulfate and lead oxides as major lead compounds in contaminated soils from several US battery recycling sites.

Because forms of soil Pb vary widely and depend upon the sources of Pb contamination and environmental conditions, knowledge of the reaction behavior of primary Pb solid phases with phosphate becomes important in assessing the efficiency of Pb immobilization by addition of phosphate. The knowledge of reaction kinetics in the Pb- contaminated soils dominated with different Pb-minerals will provide additional information essential in the evaluation of the in situ remediation technology for different soils. It will be useful to optimize treatment application rate as well as design parameters for the in-situ remediation technology.

Because of the complexity, experimental and theoretical studies that probe the nature of these processes at a fundamental level are difficult to perform on natural samples and results are difficult to interpret because of the large number of interacting abiotic and biotic process. It is also essential to carry out parallel studies of the natural system to place constraints on the variable and types of process that control contaminant speciation and distribution and to develop testable hypothesis that can be chosen by appropriate model systems. Zhang and Ryan (1999 a,b) used different lead minerals individually to study the formation of chloro-pyromorphite in the presence of synthetic apatite under varying pH conditions in pure systems. To date, the role of Pb-mineral dissolution in contaminated soil and its effects on the pyromorphite formation at different pH has not been investigated using soluble phosphorus. We adopted this combined approach to interpret analytical results on natural soil material containing different Pb compounds.

The main objective of this study was to evaluate the potential role of various lead minerals present in the contaminated soils on the formation of pyromorphite in the presence of soluble orthophosphate at controlled pH varying from 7 to 3. The mineralogy of the treated soil residue has been assessed by using X-ray diffraction.

MATERIALS AND METHODS

Deionized water from a Nano-Pure Barnstad reverse osmosis ion exchange was used in rinsing and preparation of samples. Lab-ware used for each experiment were previously rinsed in soap water, acid washed, and finally rinsed with deionized water.

Two soil samples collected from the selected field demonstration site in Jacksonville, Florida were used in this experiment. Soil samples were collected 0-20 cm below surface. These were air dried at room temperature and sieved to pass through a 2 mm sieve. Soil 1 was not contaminated and spiked with different lead minerals, while Soil 2 was contaminated. Properties of these two soils are presented in Table 10.

Table 10. Selected Physicochemical Characteristics of Soils Used in Experiment.

Characteristics	Soil 1	Soil 2
pH	7.58	7.21
Sand	89.2	85.9
Silt	8.1	6.7
Clay	2.8	3.7
Organic matter (%)	2.96	5.09
CEC cmoles kg^{-1}	4.7	6.7
Texture classification	Sandy Loam	Sandy Loam

Soil-1: Uncontaminated; Soil-2: Contaminated soil (Total 5,550 mg Pb kg^{-1})

Lead minerals used in this investigation were either specimen grade or reagent grade obtained from various sources. These were initially analyzed to confirm their Pb-mineral forms by using X-ray diffraction analysis. The X-ray diffraction patterns confirmed that selected Pb-solids were pure cerussite, anglesite and litharge. 20 g of the uncontaminated soil was spiked with different lead minerals to provide approximately 10,000 mg kg^{-1} of total Pb. For comparison purpose Pb-contaminated soil (total Pb ~ 5,550 mg kg^{-1}) from the same site was also used in this investigation.

Dissolution of Pb from Pb Contaminated Soils

Dissolution of lead minerals in contaminated soils was conducted in a 500 mL glass beaker, containing 200 mL solution of 0.005 M KCl and 0.1 M KNO_3 as background electrolytes and adjusted to designated pH with 0.1 M HNO_3 or NaOH. Spiked soil with lead mineral was then added to the solution. Static pH control was achieved by acid and base titration using a Metrochem Auto titro-processor 686. The suspension was continuously stirred with a Teflon magnetic stirrer and sampled after 5, 10, 15, 30, 60, 90,120, 150, 180 minutes using a plastic syringe. Samples were filtered immediately through 0.20 μm filters and the filtrate was acidified and refrigerated until analyzed. Soluble lead concentrations were measured as a function of time to determine the dissolution kinetics of Pb minerals in the contaminated soils.

Reaction Between Soluble Phosphate and Pb-Contaminated Soils

Determination of the kinetics of pyromorphite formation in lead contaminated soil dominated by various Pb-solid phase minerals in the presence of soluble phosphorus was conducted in the same glass beaker containing background solutions used previously in the dissolution study. In the pH constant study, the pH was adjusted to 3, 5, 7 and held constant for 180 minutes during reaction period. The amount of added soluble phosphorus from CaH_2PO4 was based on the stoichiometric molar ratio of phosphorus to lead (P/Pb) and ratio remained equal to the amount needed to transform the total added Pb from lead minerals into pyromorphite based on 3/5 (P/Pb) ratio of chloro-pyromorphite $Pb_5(PO_4)_3Cl$. The soluble phosphorus and contaminated soil spiked with Pb-mineral solid phases was added to the 200 mL of 0.005 KCl and 0.1 M KNO_3 solution previously adjusted pH. The pH of the suspension was maintained by the auto titro-processor and the suspension was sampled periodically after 5, 10, 15, 30, 60, 90,120, 150, 180 minutes by using a plastic syringe while the system was continuously stirred with a Teflon magnetic stirrer. Samples were filtered immediately through 0.20 μm syringe filters. The filtrate was acidified and refrigerated until analyzed for Pb and P concentrations.

In addition to the analysis of solution constituents, the solid residue in the reactor was collected at the end of reaction and dried at 35 °C. Solid residue was separated into sand and silt+clay fractions by using a wet sieving technique. For X-ray diffraction analysis, tiles were prepared using the concentrated silt+clay slurry

Analytical Procedure

The acidified filtrate was analyzed for the total Pb as described previously. Multilevel standards (Fisher Scientific) were prepared in 2 % nitric acid. The total phosphate concentrations $(PO_4)_T$ was determined by using a spectrophotometer (Beckman DU-6) using the ascorbic acid method (Olsen and Sommers 1982). Solution pH was measured with by a glass electrode, which was connected, to 686 Titroproccesor (Metrohem).

RESULTS AND DISCUSSION

Lead Solubility in Contaminated Soils

The dissolution of different lead minerals in soil expressed as a function of soluble Pb concentration vs. reaction time at pH varying from 7 to 3 are shown in Figure 22. Overall, Pb dissolution in the litharge and cerussite-spiked soils significantly increased with decrease in soil suspension pH, especially at pH=3. However, there was low solubility and no significant effect of pH on the cumulative Pb concentrations in soil suspensions spiked with anglesite. These cases were reflected by dissolution reactions of the three compounds are (Lindsay 1979):

$$PbO+2H^{+} \Leftrightarrow Pb^{2+}+H_2O \qquad \log K^0=12.7 \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$PbCO_3+2H^{+} \Leftrightarrow Pb^{2+}+CO_2+H_2O \qquad \log K^0=4.65 \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$PbSO_4 \Leftrightarrow Pb^{2+}+SO_4^{2-} \qquad \log K^0=-7.79 \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

From Equations (1) and (2), PbO and $PbCO_3$ dissolution strongly depended on the pH, increasing with pH reduction. $PbSO_4$ dissolved respective of pH (Equation 3), even at a high acidity of pH=3. When pH<5.0, observed lead minerals dissolution in soil was similar to their respective predicted solubility in pure system: PbO > $PbCO_3$ > $PbSO_4$. The Pb was retained in the soil matrix via adsorption and possibly a fraction of Pb was precipitated as lead hydroxide. At neutral pH, lead was adsorbed through surface complex formation with soil minerals and /or to the organic fraction of soil (Yong and others 1990).

Observed dissolution patterns in the contaminated soil remained similar to the cerussite- and litharge-spiked soils at all studied pH values. Mineralogical characterization of the contaminated soil identified cerussite as one of the dominant lead minerals. Observed Pb- concentrations were not constant within the 3 hours of reaction time.

Lead Dissolution in the Presence of Soluble Phosphate

It has been demonstrated that the dominant reaction in an aqueous system containing Pb and soluble P is the formation of pyromorphite (Ma and others 1993; Zhang and Ryan 1999). Soluble phosphorus mixed with Pb-mineral spiked soil material was tested for its feasibility to reduce aqueous lead from suspension and to transformation Pb in spiked solid phases to pyromorphite. Soluble lead concentration showed highest reduction in cerussite-spiked soil followed by litharge- and anglesite-spiked soils (Figure 23). In addition, results clearly demonstrated the similar behavior between cerussite-amended soil and contaminated soils, particularly at pH 3. Normally, soluble Pb can be depleted rapidly in a pure system, if a stoichiometric amount of phosphorus is provided and well mixed. In case of soil suspensions, Pb concentrations remained significantly high at pH 3, even when excess of soluble phosphorus was present in the soil suspensions. This contradictory behavior may be attributed to Pb association with other ligands, causing interference for pyromorphite formation. These observed effects remained more pronounced in the case of cerussite-spiked and contaminated soils compared to other studied Pb-solid phases.

Table 11. Solubility (mg) of Pb in the Contaminated Soils After 3 Hr Test With or Without the Presence of P.

	With P			Without P		
	pH=7	pH=5	pH=3	pH=7	pH=5	pH=3
$PbCO_3$	0.004	1.97	109	0.001	0.029	0.80
$PbSO_4$	0.023	0.24	4.14	0.019	0.006	0.019
PbO	0.16	4.48	110	0.002	0.051	1.81
NCS	0.03	0.89	42.6	0.002	0.042	0.98

Reaction Product Characterization

The X-ray diffraction patterns of the reaction products of lead contaminated soils and soluble phosphorus showed evidence of transformations of Pb-minerals into geochemically stable chloro-pyromorphite (Figures 24 to 27). The intensity and magnitude of pyromorphite showed its highest rate at low pH 3 due to enhanced dissolution of Pb minerals. However in case of contaminated soils, no obvious changes in magnitude of newly formed minerals was observed because its concentration remained below the detection limit of XRD, which is approximately ~1% Pb.

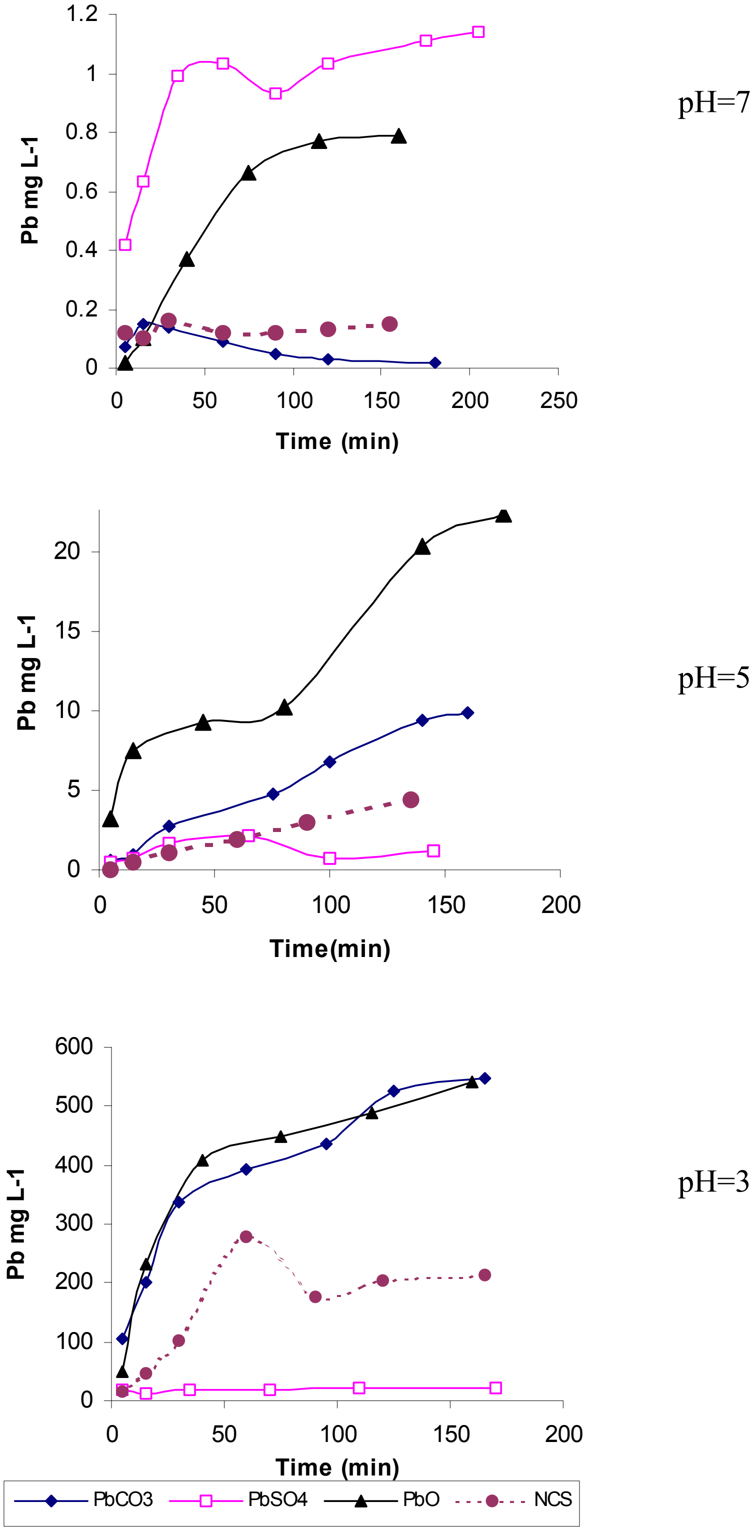


Figure 22. Effect of pH on the Dissolution of Various Lead Minerals in the Soil as a Function of Time. Loading ~10,000 mg Pb Kg^{-1}, L/S = 10, KNO_3 = 0.1 Mole and KCl = 0.005 Mole; NCS, Naturally Contaminated Soil.

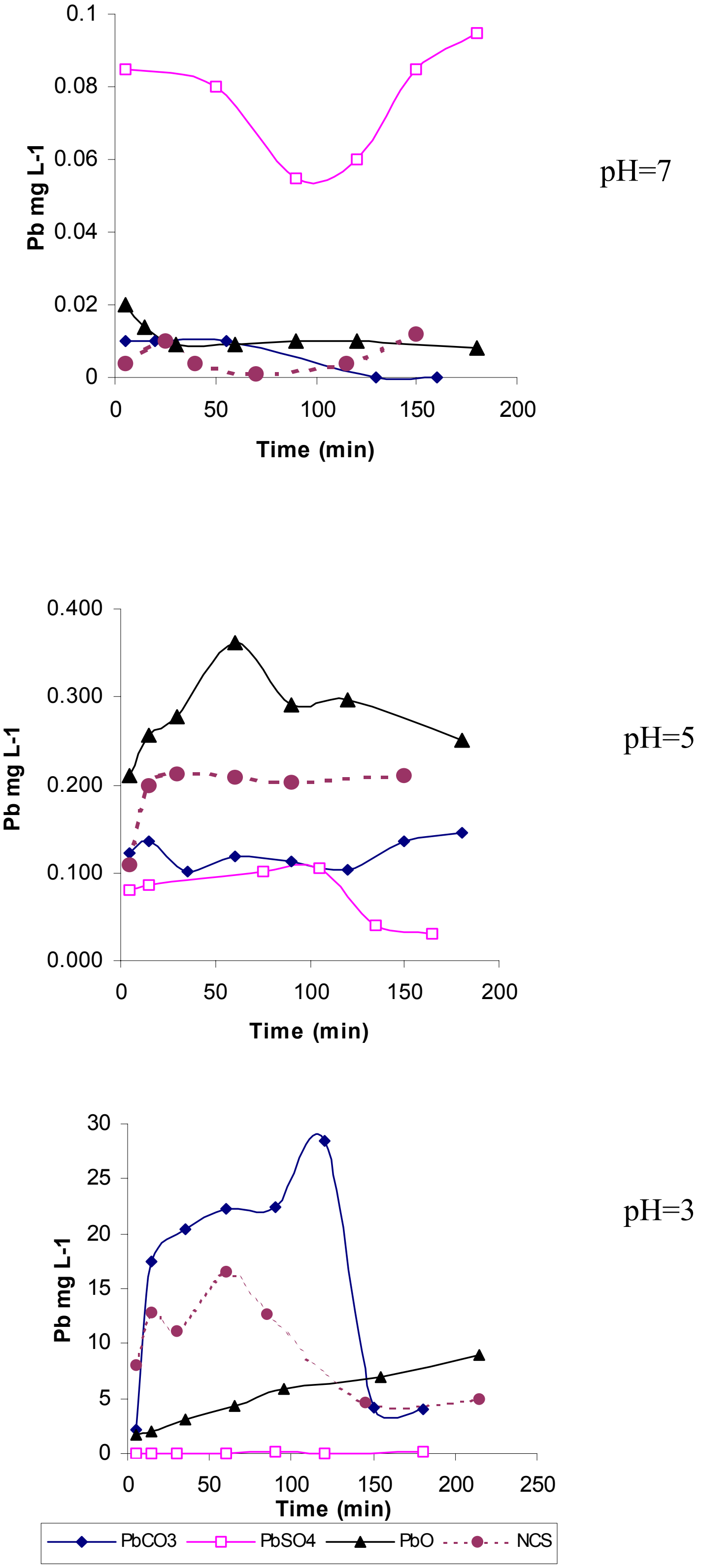


Figure 23. Effect of pH on the Dissolution of Various Lead Minerals in the Soil with the Presence of Phosphorus as a Function of Time. Loading ~10,000 mg Pb Kg^{-1} L/S=10, KNO_3 = 0.1 Mole and KCl =0.005 Mole.

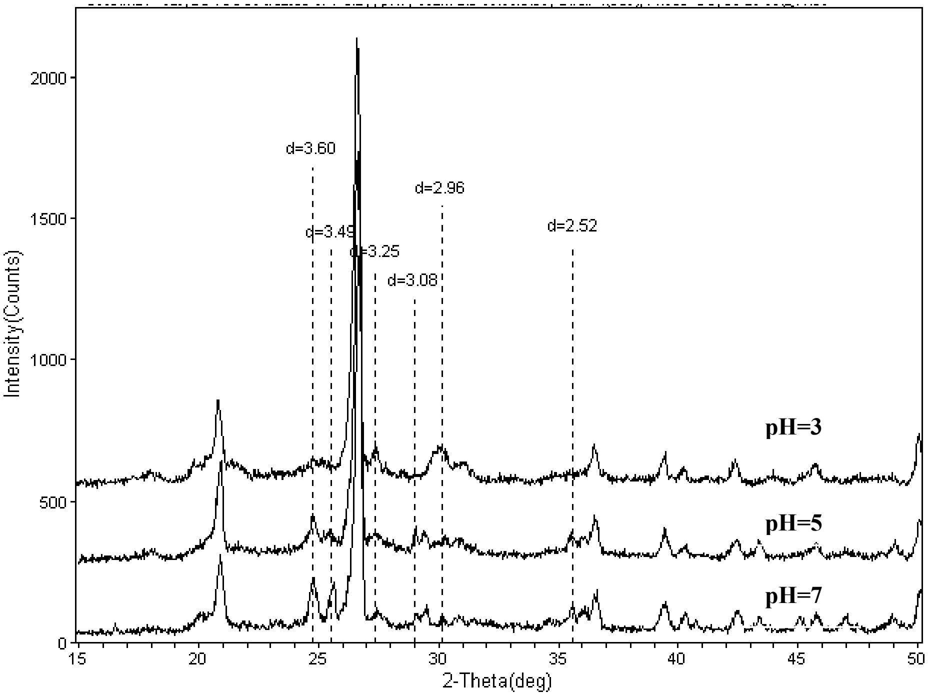


Figure 24. X-Ray Diffraction Patterns of the Reaction Products of Cerussite-Contaminated Soil with Soluble P Application at Constant pH Varying from 3 to 7.

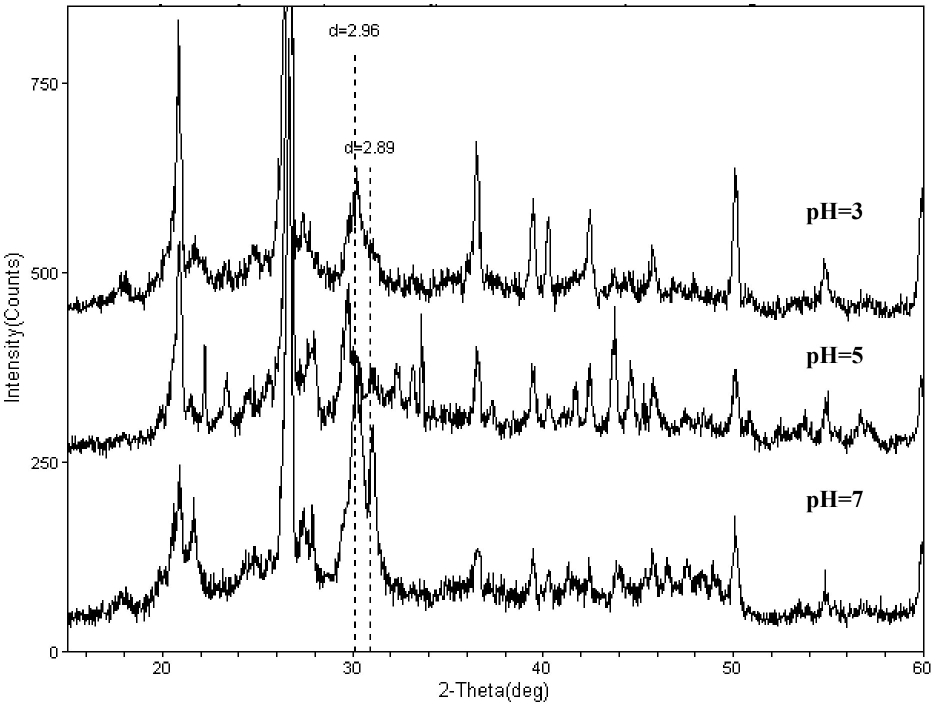


Figure 25. X-Ray Diffraction Patterns of the Reaction Products of Anglesite-Contaminated Soil Reaction with Soluble P at Constant pH Varying from 3 to 7.

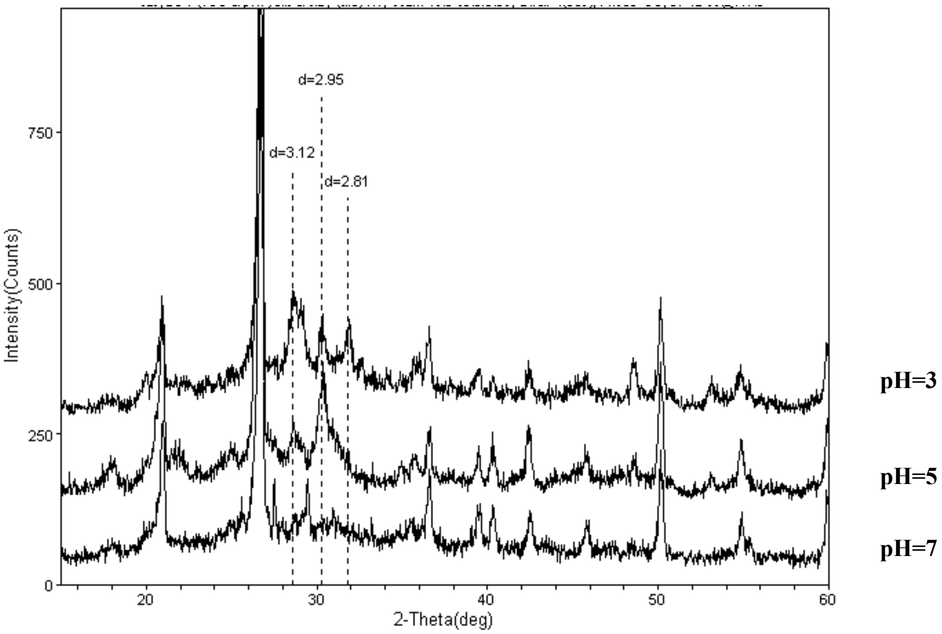


Figure 26. X-Ray Diffraction Patterns of the Reaction Products of Litharge-Contaminated Soil with Soluble P Application at Constant pH Varying from 3 to 7.

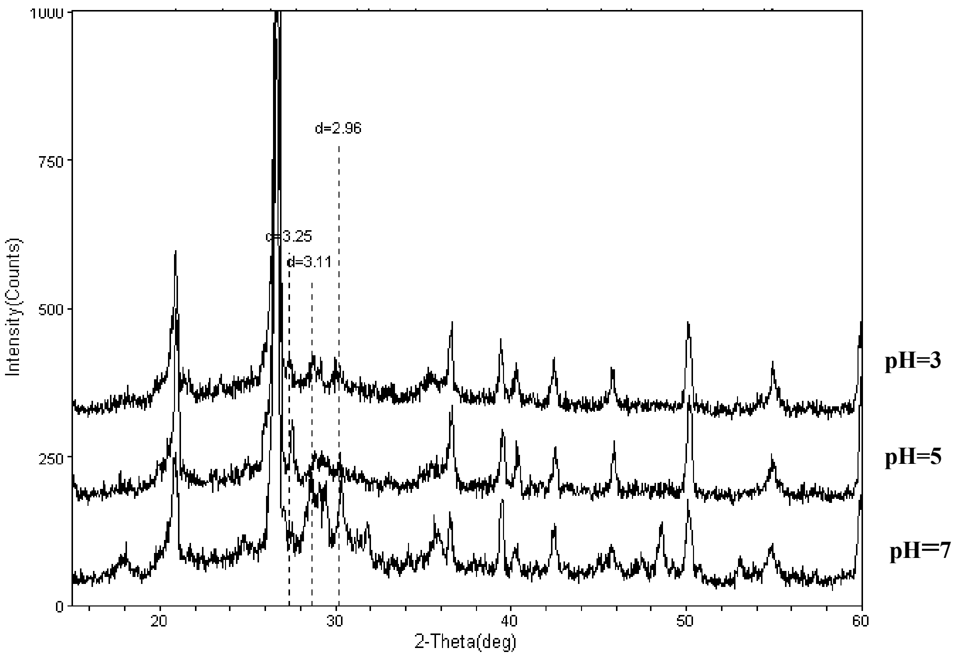


Figure 27. X-Ray Diffraction Patterns of the Reaction Products of Naturally Pb Contaminated Soil with Soluble P Application at Constant pH Varying from 3 to 7.

CONCLUSIONS

Soil samples artificially contaminated with solid phase lead minerals to produce 10, 000 mg Pb/kg and contaminated soil were evaluated for their dissolution and immobilization efficiency in the presence of soluble phosphorus at pH varying from 3 to 7. Results demonstrated that dissolution and transformation of Pb-solid phases into geochemically stable chloro-pyromorphite was dependent on pH and nature of different lead minerals. Higher acid ($pH<5$) was favorable for the lead phosphate formation from $PbCO_3$ and PbO minerals, while the formation of lead phosphate from $PbSO_4$ occurred at all tested pH range (3-7). Lead dissolution behavior in contaminated soils was similar to cerussite-spiked soil.

FIELD DEMONSTRATION OF LEAD IMMOBILIZATION IN CONTAMINATED SOIL AFTER APPLICATION OF PHOSPHORUS AMENDMENTS

INTRODUCTION

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, 1997). Conversion of soil Pb to lead phosphate could immobilize soil Pb and reduce its bioavailability. Among all the lead phosphate minerals, chloropyromorphite has the lowest solubility, thus, it is most stable under favorable environmental conditions. Ma and others (1993) showed that hydroxyapatite ($Ca_5(PO_4)_3OH$) has the potential to immobilize Pb in solution by formation of hydroxypyromorphite. Phosphate rock (primarily $Ca_{10}(PO_4)_5F_2$) is also shown to effectively immobilize Pb from aqueous solution 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 immobilized 22% to 100% aqueous Pb from 13 Pb contaminated soils. In these studies, the effectiveness of phosphate rock to immobilize Pb was based on formation of insoluble lead phosphate. In addition, formation of pyromorphite upon addition of apatite or soluble inorganic P amendments has been observed in Pb-contaminate soils (Cotter-Howells 1996; Laperche and others 1997). The formation of Pb 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 isolated Pb-enriched fractions from contaminated soil at pH values between 5 and 8. Dissolution of the initial Pb phase appeared to limit the formation rate of hydroxypyromorphite ($Pb_5(PO_4)_3OH$). Conversion to $Pb_5(PO_4)_3OH$ was fastest at pH=5. Zhang and others (1997) performed similar experiments and found that dissolution of anglesite ($PbSO_4$) and cerussite ($PbCO_3$) limited their rate of conversion to $Pb_5(PO_4)_3OH$. Thus, acidity of soil takes an important role in the immobilization of metal using phosphate amendment. The mechanism of phosphate amendment could be considered as the dissolution of metal compounds in soils and followed by the precipitation of insoluble metal phosphates. Under existing soil environments, observed solubility of Pb compounds and phosphate minerals remained limited, a major limitation for their effective and efficient immobilization. For example, lead carbonate (cerussite) 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 enhanced solubility of Pb minerals by inducing acidic conditions that will promote their solubility as well as lead phosphate formation.

In addition, because this in situ technique doesn't change the total Pb concentration in soil, information on the amount of time required for reducing soil Pb bioavailability after P application as well as the long-term stability of Pb immobilization is very important.

Although much knowledge about the mechanisms and requirements involved in the immobilization of heavy metals using phosphate amendments has been acquired and laboratory experiments using phosphate treatment has been successful, to our knowledge, the implementation of this technology has not been yet tested *in situ* in the field. Thus, a field demonstration of this technology, at a site heavily contaminated with Pb and other heavy metals, was conducted in the present study. The main objectives are (1) to demonstrate the effectiveness of pre-acidified phosphate amendments on the in *situ* immobilization of lead in a contaminated field; (2) to measure the mobility and phytoavailability of Pb in the contaminated soil after application of phosphate treatments; and (3) to assess long-term stability for the in situ immobilization of lead in a contaminated field.

MATERIALS AND METHODS

Experimental Plot Establishment

The P-treated plots were established on the hotspot zone with the Pb concentration of >2,000 mg Pb kg^{-1} in the selected Jacksonville site. We prepared circular P-treated plots of ~4 m^2 using plastic lawn-edger by inserting them half into the soil and half above surface which would be useful to prevent free flow of surface water into plot or versa. P amendments were applied to each plot, at a 4 molar ratio of P to Pb based on our lab test results. On 02/17/2000, half of the amount of P was applied as H_3PO_4 to all plots, by mixing it into 25 L of water and spraying it uniformly in each area and covering with a plastic sheet to maintain moisture contents in the surface layers (Figure 28). On 03/27/2000, 40 days after the first application, the second half of the P amendments was applied as H_3PO_4 in T1, $Ca(H_2PO_4)_2$ in T2 and 5% phosphate rock in T3 by mixing them to a depth of 20cm. Phosphate rock consists mainly of $Ca_5(PO_4)_3F_2$ with substantial CO_3^{2-} substitution in the structure (Ma and others 1995). Monitoring wells (MW1, MW2, and MW3) were installed in the centers of T1, T2, and T3 plots, respectively. The wells consisted of PVC with 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 (Figure 29).

Figure 28. Application of P in the Jacksonville Demonstration Site.

Figure 29. Geoprobe Used for Well Installation in the Jacksonville Demonstration Site.

Soil, Vegetation and Groundwater Sampling

Composite soil samples were collected at 6 depth intervals of 0-10, 10-20, 20-30, 30-40, 40-60, and 60-80cm, respectively, from the 3 treated plots and the control site (T0) at 7, 50, 130, 220, 330, and 480 days after the application of P-treatments. Immediately after returning to the laboratory, all soil samples were air-dried and passed through 2-mm stainless steel sieve. St. Augustine grass (*Stenotaphrum secundatum*) that predominantly grew in the tested plots were harvested. After rinsed with deionized water, the shoots were oven-dried and digested with USEPA 3050 procedure. Some of roots were rinsed with deionized water and vacuum dried for microscopic analysis. Groundwater samples were collected with a suction lift pump from each of three monitoring wells. Samples were filtered through Whatman 42 filter paper and acidified to below pH 2 for analysis.

X-ray Diffraction (XRD) Analysis

The crystalline components in soils from the control and P-treated plots were characterized by X-ray diffractometer (Philips Electronic Instruments, Inc., Mahwah, NJ) using Cu Kα radiation at 35 kV and 20 mA. Measurements were made using continuous scanning techniques, and XRD patterns were obtained from 2 to 60^0 2θ.

Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis

Selected samples analyzed by XRD were further examined by using scanning electron microscope (SEM, JSM-6400/TN500, JEOL, USA), equipped with a energy dispersive x-ray elemental spectrometry (EDX). Vacuum-dried root samples were mounted on carbon tubes using double stick tape and then carbon coated. The analysis of roots necessitated a longer vacuumation time to obtain a sufficient vacuum than was required for the soil particles.

Chemical Analysis

Soil organic matter was determined using the Walkley-Black procedure (Nelson and Sommers 1982); CEC was examined using the method of Rhoades (1982). Total phosphorus was measured colorimetrically with a Shimadzu 160U spectrometer using the molybdate ascorbic acid method (Olsen and Sommers 1982). All metal elements of concern were determined as previously described. Quality control samples included Standard Reference Materials of soil (2709 San Joaquin Soil, 2710 Montana Soil) and plant (1547 Peach Leaves) (U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899).

RESULTS AND DISCUSSION

Effects on Soil pH from Phosphate Treatment

As expected, application of P amendments impacted the pH of this sandy soil with relatively low buffer capacity. Soil pH was reduced in all P-treated plots due to the addition of H_3PO_4. Figure 30 shows pH values of surface soil from the control and P-treated plots. Among all treatments, H_3PO_4 (T1) promoted the highest decrease in soil pH, while T3 promoted the least decrease. Soil pH changes showed the same trends for all treatments, i.e., initial reduction followed by a gradual increase with time. Soil pH in the T3 plot decreased to the lowest (pH=5.2) on day 7 after the treatment, and then gradually recovered, and finally reached equilibrium on day 130. For the T1 and T2 treatments, soil pH reached at the lowest on day 50, and reached equilibrium on days 220 and 330, respectively. Only H_3PO_4 was added in the T1 treatment, which caused a great decrease of soil pH. It was not until 330 days later that the soil pH could be recovered and reached equilibrium. Obviously, application of calcium phosphate (T2) and phosphate rock (T3) increased soil pH back near to the control. The least decrease and earliest recovery of pH value in the soil of the T3 plot may be interpreted by neutralization of phosphate rock dissolution.

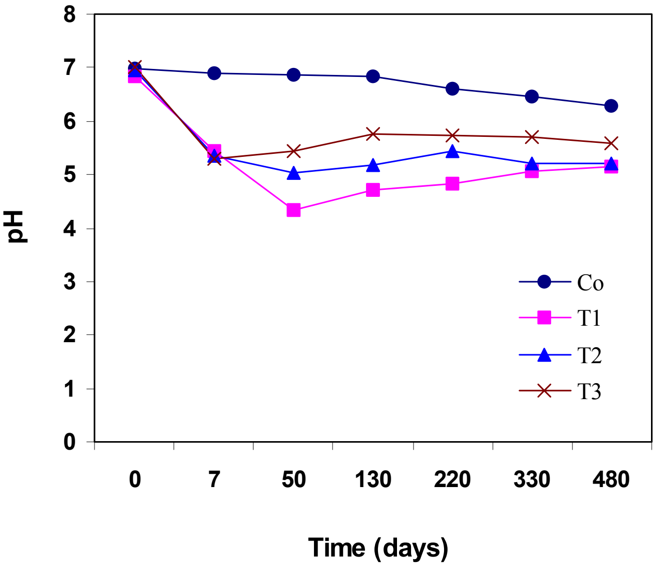
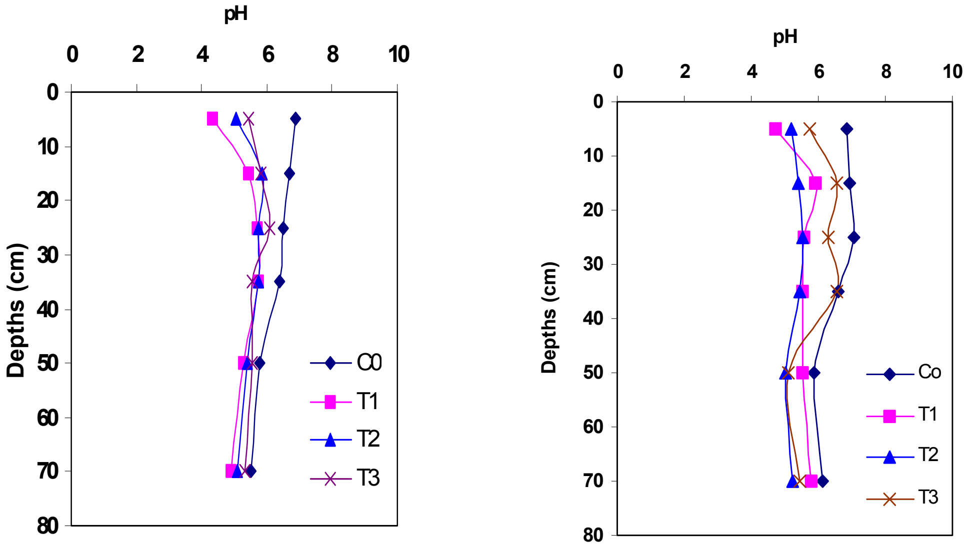


Figure 30. pH Changes in the Surface Soil as a Function of Time.



Day 50 Day 130

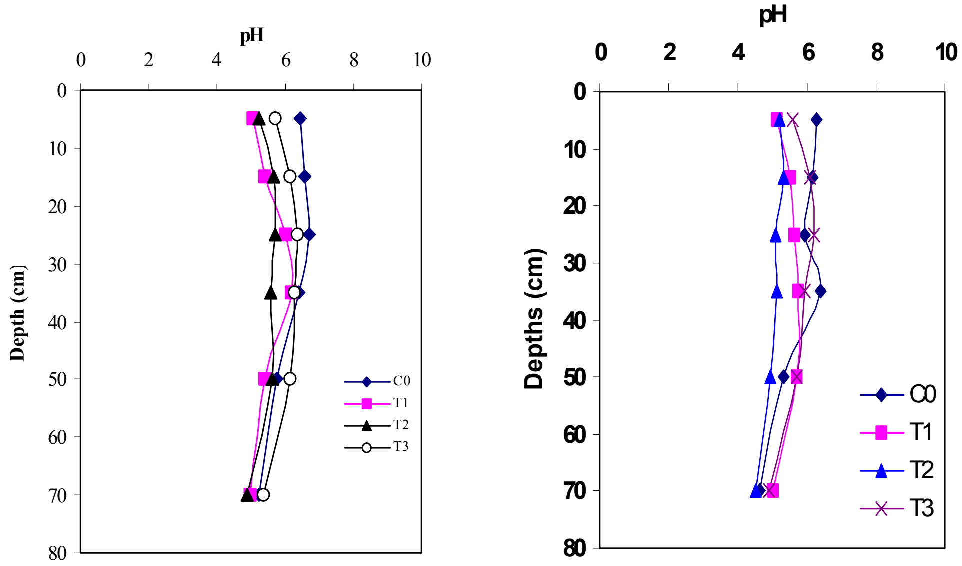


Figure 31. pH Changes in the Soil Profile as a Function of Time After P Treatments.

Also, downward movement of H_3PO_4 occurred in the soil profile, resulting in pH decrease (Figure 31). Before 130 days, all treatments resulted in much decrease of soil pH at each depth, which was not unexpected. At 330 days, the soil profile pH values in the P-treated sample recovered and were close to those in the control. The variations in pH, at lower depths, may be attributed to various factors in addition to the associations with P treatment sources at the top, such as, redox conditions associated to fluctuations in water table, lower levels of CO_3^2 as compared to the surface, and possibly the effects of sorption-desorption of metals during leaching.

Although application of H_3PO_4 caused a decrease in soil pH, it was necessary to reduce soil pH to near 5~6 in the first phase of the treatment for efficient metal immobilization in this demonstrate site. As discussed in the section "Selection and Characterization of Heavy Metal Contaminated Site," lead in this site was mainly associated with carbonate. Therefore, it was essential to add H_3PO_4 into the soil to dissolve carbonated associated Pb for the subsequent precipitation of insoluble pyromorphite-like mineral.

Concerning the precipitation of pyromorphite-like mineral, it was shown that at a given lead and phosphate concentration, more pyromorphite-like mineral was formed at pH 5 than at pH 6 or 7 (Laperche and others 1996). Zhang and others (1999) studied the formation of pyromorphite from combinations of different Pb solids and apatite suspensions under varying pH conditions. They found that the dissolution of apatite or dissolution of both apatite and Pb bearing solids was the rate-limiting step of the reaction involving formation of pyromorphites. This suggests that acidification prior to P addition might enhance the formation of pyromorphite in soils.

Leaching Characteristics of Lead After P Application

The toxicity characteristic leaching procedures (TCLP) test is designed to evaluate whether hazardous constituents may migrate through the vadose zone soils to the water table by simulating landfill conditions. TCLP level reflects the mobility of hazardous. Higher Pb concentration in TCLP extracts means higher mobility of Pb in the soil. Figure 32 shows the TCLP-Pb levels in the control and P-treated soils. TCLP-Pb concentrations in the control were more than 100mg/l, significantly exceeding the regulatory level of 5mg/l. The site would be characterized as hazardous waste by the TCLP-Pb. As a result of P application, TCLP extractable Pb was significantly reduced for all P amended plots (Figure 32). After 130 days, all P treatments reduced TCLP to below regulatory level with reduction of TCLP-Pb by over 95% relative to the control. TCLP-Pb did not change with time, showing a long-term immobilization. In addition, TCLP-Pb decrease was also observed in the deep soils in all P-treated plots (Figure 33). TCLP-Pb decreased in the profile, especially in the upper depth of 0-30cm. This phenomenon may due to the downward movement of H_3PO_4, resulting in the formation of insoluble pyromorphite.

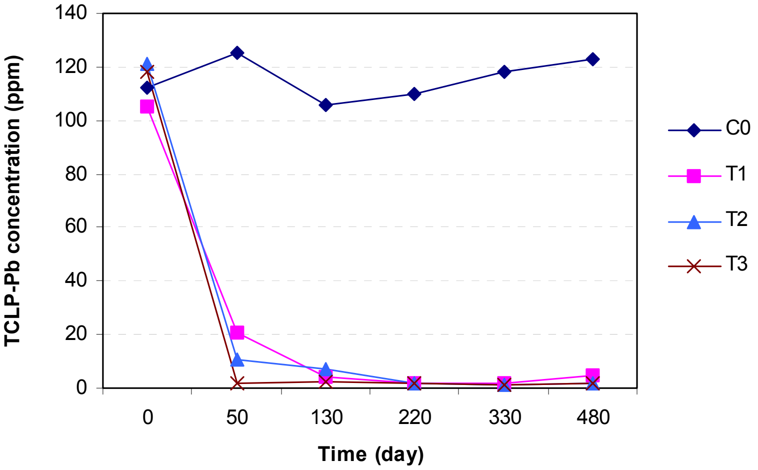


Figure 32. TCLP-Pb Concentration in the Surface Soil of the Control and All P-Treated Plots as a Function of Time.

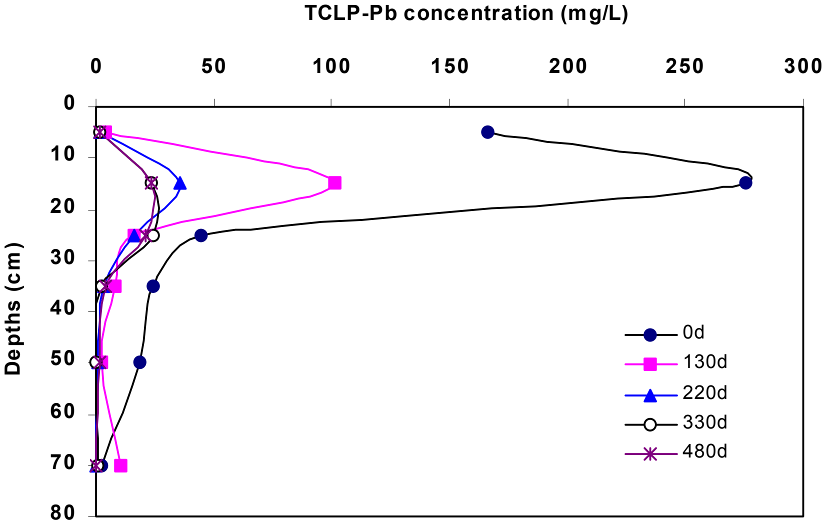


Figure 33. TCLP-Pb Concentration in the Soil Profile of T1 Treated Plot as a Function of Time.

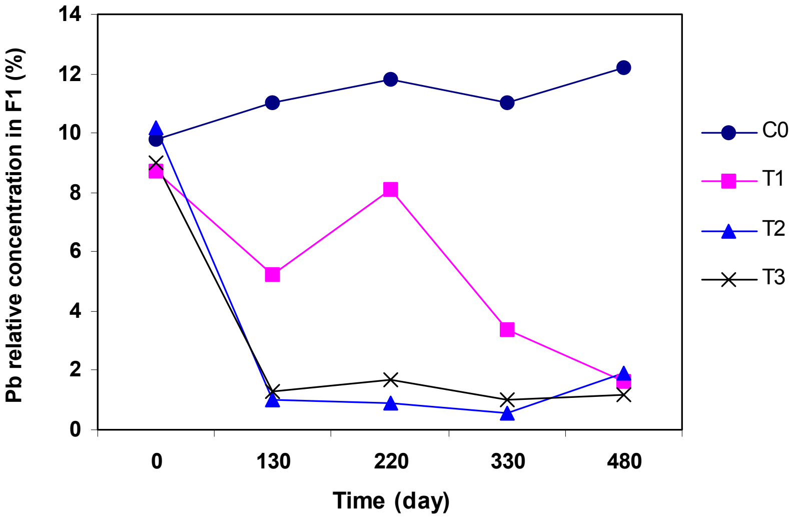
Pb Distribution in the Control and P-Treated Soils

Chemical fractionation has been extensively used to assess diagenetic processes, especially mobility and bioavailability of heavy metals. Assuming the non residual metal (sum of the 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, with more effective treatments converting greater amounts of metal from the non residual to the residual fraction or from more or less bioavailable forms, i.e., from the exchangeable to carbonate, Fe-Mn oxide, or organic fraction.

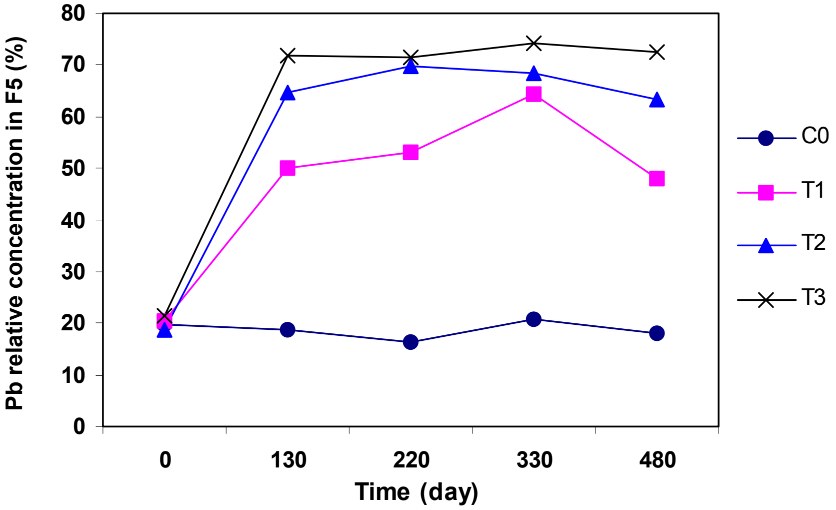
The sequent extraction scheme of Tessier (1988), one of the most widely used, has been selected to evaluate the efficacy of decontamination treatments (Ma and Rao 1997; Pardo and others 1990; Rauret and others 1988). The scheme is based on operationally defined fractionation procedures: water soluble and exchangeable, carbonate, Fe-Mn oxides, organic, and residual fractions. However, the scheme is occasionally limited by redistribution of metals during extraction. Thus, a comparison of summed fractions for SRM2710 was made with total content data via single concentrated HNO_3 digestion. The summed fractions averaged 103±10% of the total Pb, indicating good recovery using the fractionation scheme.

Figure 34 shows the Pb concentration changes in the water soluble and exchangeable as well as residue fractions from the control (T0) and in the P-treated surface soils (T1, T2 and T3). The data indicated that P treatments reduced the lead concentrations in the water and exchangeable fraction, while residue Pb was significantly elevated. The T1, T2, and T3 treatments increased residue Pb by 30-40%, 42-50%, and 50-55%, respectively in the test period, it implied that all P treatments were able to modify the partitioning of Pb from the non-residual/potentially available phase to the residual/unavailable phase. It was consistent with our hypothesis of dissolving cerussite with phosphoric acid, followed by the precipitation of geochemical stable pyromorphite (Ma and others 1995).

Among three P treatments, phosphate rock (T3) showed the most conversion of Pb from the non-residual to residual fraction, while the H_3PO_4 treatment (T1) showed the least (Figure 34). It may be attributed to more P available for the Pb phosphate formation from the long-term release of phosphate rock at the surface soil. Less P available at the surface due to H_3PO_4 leaching may interpret the least transformation of lead in the H_3PO_4 treatment. Similarly, Hettiarachchi and others (2000) also reported that phosphate rock was more effective than triple superphosphate or phosphoric acid in reducing Pb bioavailability for the Zn-Pb contaminated soils in their experiment.



(a)



(b)

Figure 34. Pb Distribution in the Water and (a) Exchangeable Fraction and Residue; (b) Fractions as a Function of Time.

Mineralogical Analysis for the Control and P-Treated Soils

Direct identification of mineralogical changes resulting from P addition is possible with physical methods. Figure 35 shows XRD patterns for the soil of P-treated plot T1 as a function of time. Compared to the control soil, $PbCO_3$ peak (3.51Å) disappeared in the H_3PO_4 treated soil, while some new peaks were observed at sampling time. Of the three most prominent peaks of pyromorphite-like mineral ($Pb_5(PO_4)_3X$, X=OH, Cl), two can be seen at 2.98 Å and 2.87 Å, and their intensities did not change with time. These suggested that pyromorphite-like mineral was formed *in situ* in H_3PO_4 treated soils and the formation of pyromorphite-like mineral showed a long-term stability. X-ray diffraction patterns for P-treated soil T2 are shown in Figure 36. Two peaks at 2.98Å and 2.87Å, attributed to pyromorphite-like mineral, were also present in the H_3PO_4+$Ca(H_2PO_4)_2$ treated soils after day 220. However, they were not observed at day 50, indicating that the formation of pyromorphite-like mineral takes time in the H_3PO_4+$Ca(H_2PO_4)_2$ treated soils. Similarly, no pyromorphite-like minerals were initially formed in phosphate rock treated soil T3 at day 50 (Figure 37). After 220 days, phosphate rock gradually dissolved and produced enough soluble P to form a pyromorphite-like mineral. At days220, 330 and 480, two peaks (2.98Å and 2.87Å) showing the presence of a pyromorphite-like mineral were clearly visible, indicating that the formation of the pyromorphite-like mineral in the presence of phosphate rock is a slow process.

Cotter-Howells and others (1991) and Laperche and others (1996) observed a new peak at 2.87Å upon phosphate addition to a Pb-contaminated soil. *In situ* formation of lead phosphate has been reported in some contaminated soils. Ruby and others (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 and others (1996) reported the presence of a substantial amount of pyromorphite in contaminated gardens, urban and motorway roadsides.

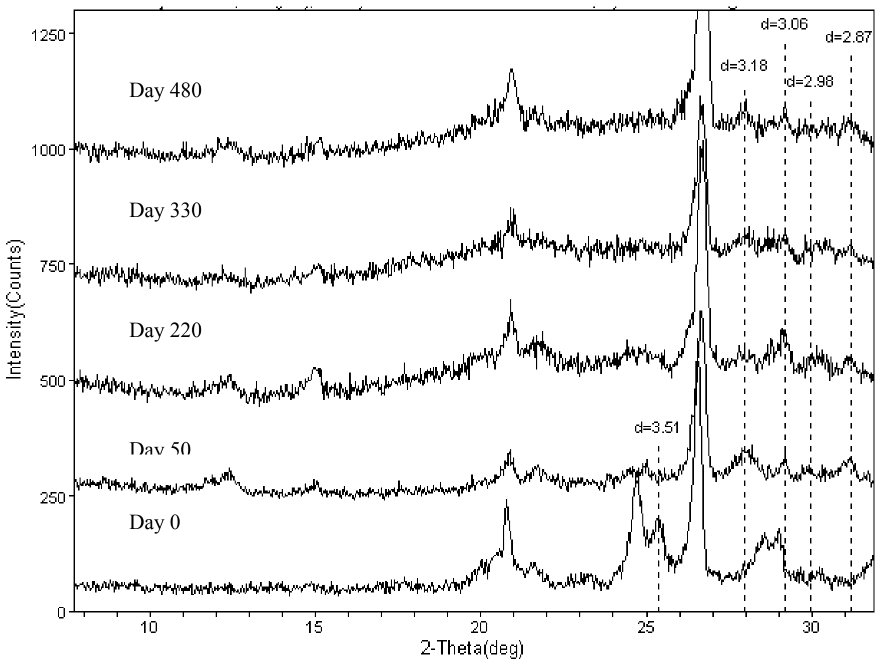


Figure 35. X-Ray Diffraction Patterns of Soil in P-Treated Plot T1 as a Function of Time.

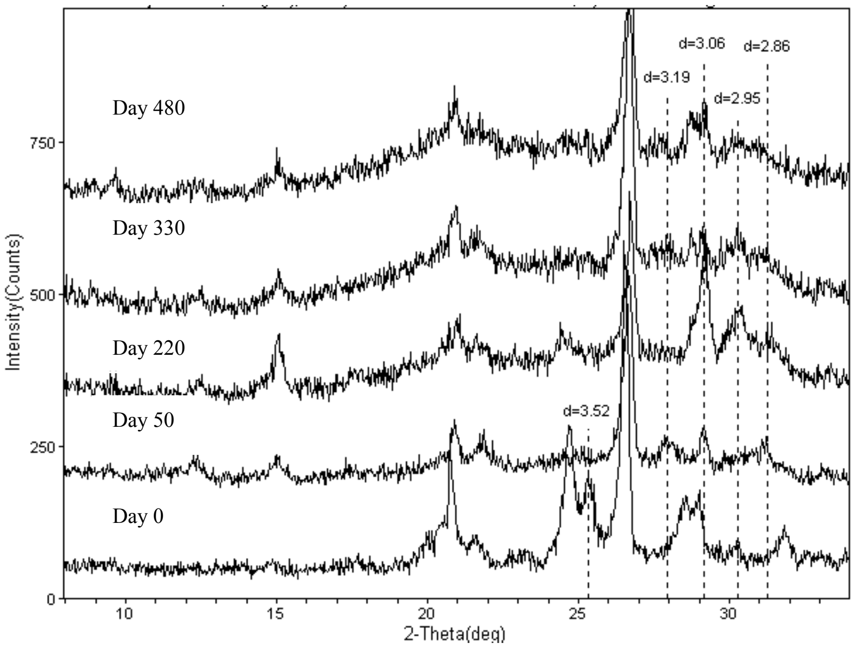


Figure 36. X-Ray Diffraction Patterns of Soil in P-Treated Plot T2 as a Function of Time.

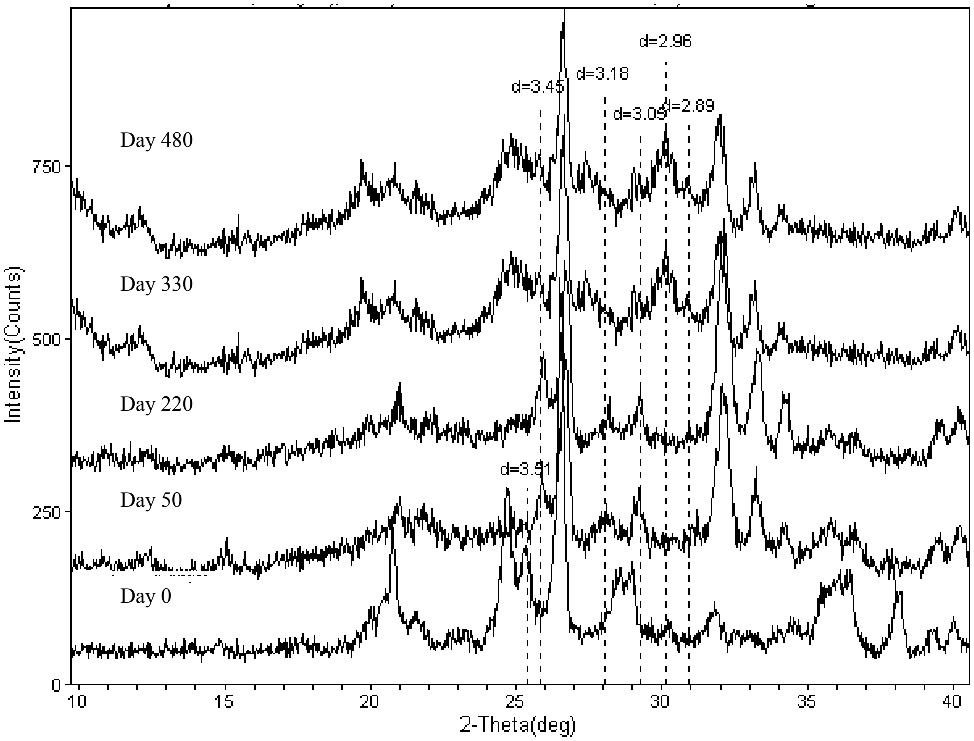
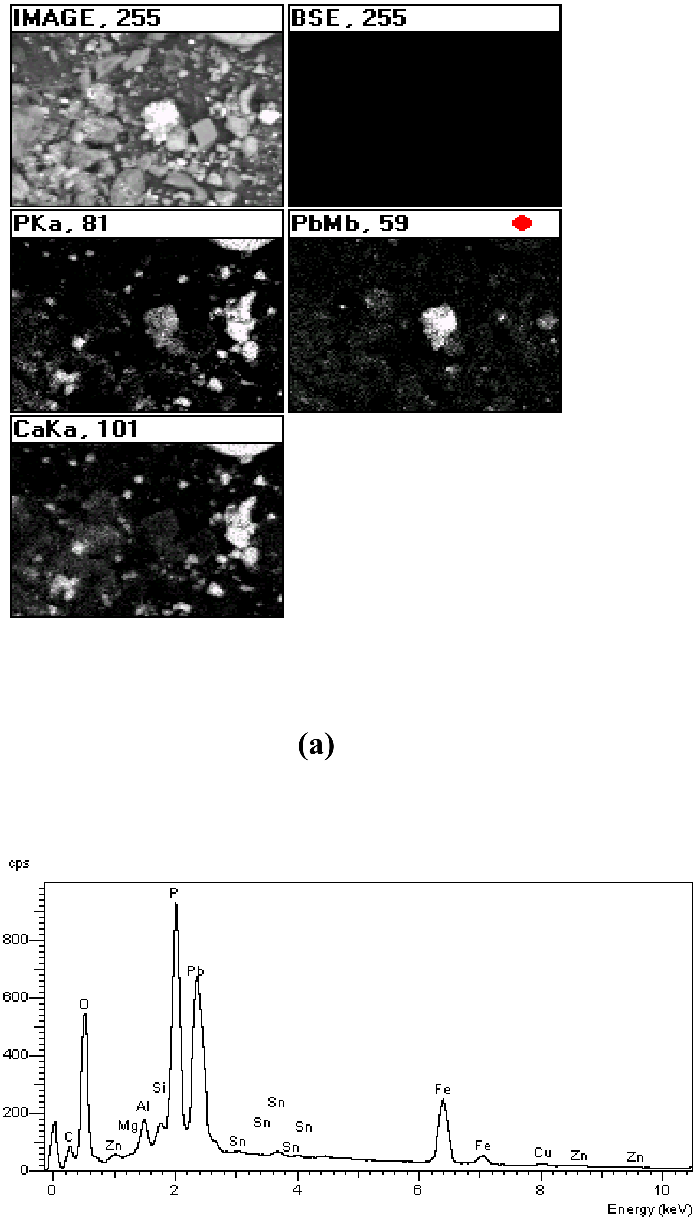


Figure 37. X-Ray Diffraction Patterns of Soil in P-Treated Plot T3 as a Function of Time.

In Figure 35 to Figure 37, we observe two other distinctive peaks (3.19Å and 3.05Å) in addition to 2.98Å and 2.87Å. The occurrence of 3.19Å and 3.05Å may be attributed to coprecipitation or adsorption of other metals (Cu, Zn, and Ca) onto lead phosphate. Figure 38a shows SEM image and elemental dot maps of a soil samples taken from P-treated plot T3, further confirming the presence of pyromorphite at the surface soil in T3 and the association of Pb with P. The elemental dot map also shows the presence of Ca with P, coherent with addition of phosphate rock. EDX of Figure 38b suggests that association of Zn and Cu with Pb-P. The similar cases were observed in P-treated soil T1 and T2 (data not shown). 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. The main mechanism of Pb immobilization is via dissolution of phosphate source or meta-stable Pb and subsequent precipitation of a pyromorphite-like mineral.

Although phosphate rock is less soluble, it could provide a long-term source of phosphorus. It was worthwhile to note that in T3 treatment, the intensities of phosphate rock peaks (2.80Å, 2.77Å, 2.70Å) on days 330 and 480 were lower compared to those on days 50 and 130. The reduced intensity of the phosphate rock with time might be an indication of further dissolution of PR. The presence of metals can induce further dissolution of PR by removal of soluble phosphates from soil solution through precipitation reactions. Moreover, reduced phosphate rock also could indicate increased sorption of metals onto PR. Increased sorption of metals onto phosphate rock surfaces can be responsible for reduced intensity of XRD peaks because of the increased mass absorption coefficient of X-rays upon adsorption of metals (McKenzie and others 1980). Strong adsorption of Pb onto apatite surfaces or simultaneous adsorption of Pb and surface precipitation of Pb phosphate on the apatite surfaces also might be possible in PR-treated soils (Ma and others 1994).

Figure 39 illustrates the SEM elemental dot maps and EDS of a soil sample taken at the depth of the 30~40cm layer of T2, revealing the presence of pyromorphite after P application. *In situ* formation of pyromorphite in a deep soil profile should be favorable for the vertical immobilization of lead.



(a)

(b)

Figure 38. Element Distribution (a) and Relative Elemental Concentrations (b) of a Surface Soil Sample Taken from Plot T3 at Day 330.

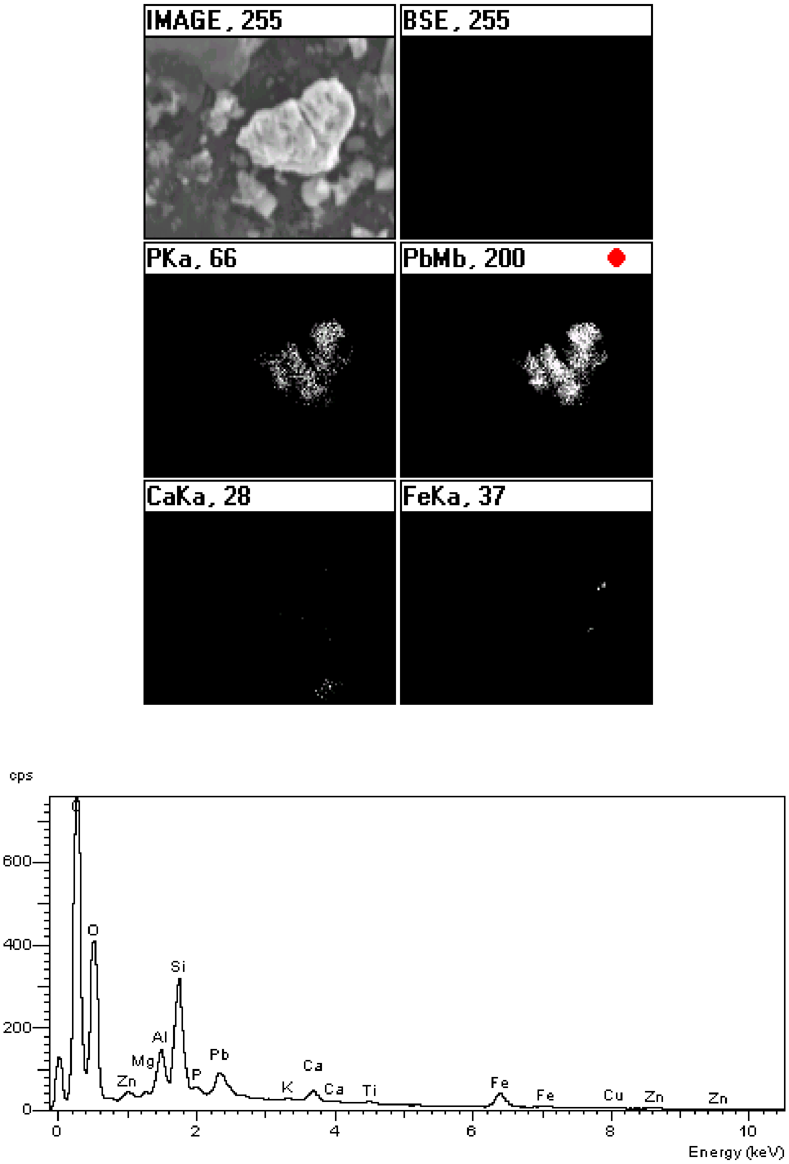


Figure 39. Element Distribution (a) and Relative Concentrations (b) of a Soil Sample Taken from Treatment Plot T2 at a Depth of 30-40 cm at Day 330.

Phosphorus Movement and Mass Balance in the Soil Profile

Special attempts were made in this study to determine the mass balance for phosphorus, taking into account P leaching and mass balance in the soil after P application. This was an important task for the field test from the viewpoint of the secondary contamination. Although it is well recognized that phosphate amendment is an effective method to immobilize metals in contaminated soil, some elevated soluble phosphorus may enhance eutrophication risk.

Generally, vast majority of added phosphorus was retained in the soil, leading to the formation of pyromorphite-like minerals, but there is still limited amount of P which may be taken up by vegetation, migrate down to the groundwater or even move into surface water as runoff. In most soils, the amount of phosphorus available to plants from soil is very low, seldom exceeding about 0.01% of the total phosphorus in the soil (Brady and Weil 1999). The principal pathway by which P is lost from the soil system may be phosphorus dissolved in surface runoff water, which would cause an eutrophication risk. Therefore, it is of significance to assess the P movement within P-treated fields from both P utility and P eutrophication risk.

Figure 40 illustrates the P retardation in the surface soil of three P-treated plots as a function of time. Phosphorus in all treatments existed mainly on the surface. Approximately 45-48% of the P added as H_3PO_4 (T1) remained on the surface , 52-58% as H_3PO_4+$Ca(H_2PO_4)_2$ (T2) , and 72-73% as H_3PO_4+ phosphate rock (T3). Little changes occurred over time for all P treatments, especially for phosphate rock application.

As expected, limited downward migration of P was observed in this soil with low buffering capacity (data not shown), which should enhance the vertical immobilization of Pb, Zn and Cu. Concentrations of P declined as the depth increased. Phosphorus loss in Treatment T1 was slightly more than that of treatment T3 (data not shown). Figure 6-14 shows that 94-96% of the added P remained in the soil in treatments T3 at sampling time, while treatments T1 and T2 kept 80-92% and 83-93%, respectively. Little changes of phosphorus occurred over time for phosphate rock application. It indicated that, in term of eutrophication risk, phosphate rock treatment (T3) has the lowest.

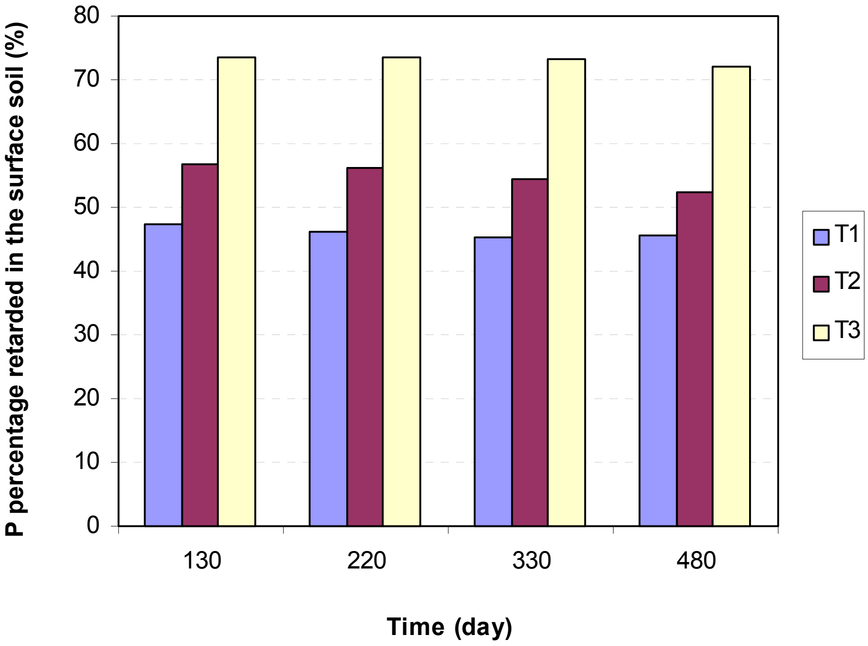


Figure 40. P Retained in the Surface Soil from P-Treated Plots H_3PO_4 (T1), H_3PO_4+$Ca(H_2PO_4)_2$ (T2), and H_3PO_4+ Phosphate Rock (T3).

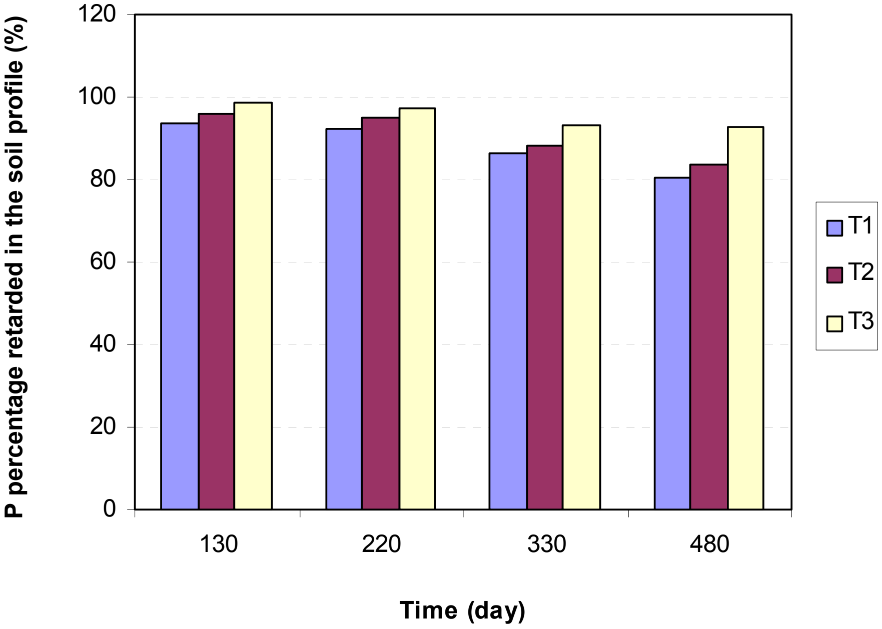


Figure 41. P Retained in the Soil Profile from P-Treated Plots H_3PO_4 (T1), H_3PO_4+$Ca(H_2PO_4)_2$ (T2), and H_3PO_4+ Phosphate Rock (T3).

P and Pb Phytoavailability in P-Treated Plots

In this study, P amendment was applied at a 4 molar ratio of P to Pb. A considerable amount of phosphate was added to the soil, resulting in more phosphorus taken up by St. Augustine grass (*Stenotaphrum secundatum*). Three cuttings of grass were collected at 220, 330, and 480 days, respectively. Shoot P concentrations were elevated in treatments T1, T2, and T3 after application of phosphate amendment compared to the control (Figure 42). P concentration increased with time in both the control and treatments. In contrast, shoot tissue Pb contents decreased significantly after P amendment (Figure 43).

Laperche and others (1997) reported that the addition of HA (0.6%, 1.16%, 1.74%, and 2.32% by weight) to Pb polluted soils led to a strong decrease of the Pb concentrations in shoots of sudax (*Sorghum bicolor L. Moench*). It is generally agreed that phosphorus is an essential element for plants and is one of the most limiting factors for plant growth in soil. Phosphate that is available to plant roots would also be available to heavy metal compounds to form metal phosphates (Cotter-Howells and Caporn 1996). Thus, it is reasonable to expect that the more plant takes up phosphorus, the more Pb accumulated in the roots. Consequently, we hypothesized that Pb accumulate inside the root or on the root surface as lead phosphate. Figure 44 shows an SEM element map and EDX of root rhizosphere grown in P-treated soil T2 at day 330. Obviously, Pb was associated with P and accumulated on the surface of root hair.

Earlier studies have been conducted on the location and chemical state of Pb in plant tissues, using solvent extraction or light and electron microscopy. These studies reported that Pb was bound to cell walls (Koeppe 1977; Samardakiewicz and Wozny 2000). Koeppe (1977) concluded that Pb translocation is highly dependent on physiological status and, under conditions of optimal growth, that Pb precipitates on root cell walls in an insoluble, amorphous form which, in maize, has been identified as a lead phosphate. Similarly, analysis of root section by TEM showed Pb deposited next to cell walls of root grown in hydroxyapatite or phosphate rock treated soils (Laperche and others 1997). The effect of apatite amendments on Pb concentration in roots was studied by Traina and others (1999). These authors showed that the presence of rhizosphere created local acidity which may have enhanced the local dissolution of apatite grains and precipitation of pyromorphite on the root surface. The association of pyromorphite with roots and the contribution of root exudates in pyromorphite formation were found by Cotter-Howells (1999). In addition, Cotter-Howells (1996) demonstrated that it was possible to induce the formation of lead phosphate by growing *Agrostis capillaris* on contaminated soils and amending it with organic matter (horticultural peat). Grains of lead phosphates were detected by SEM in the rhizosphere of *Agrostis capillaris.*

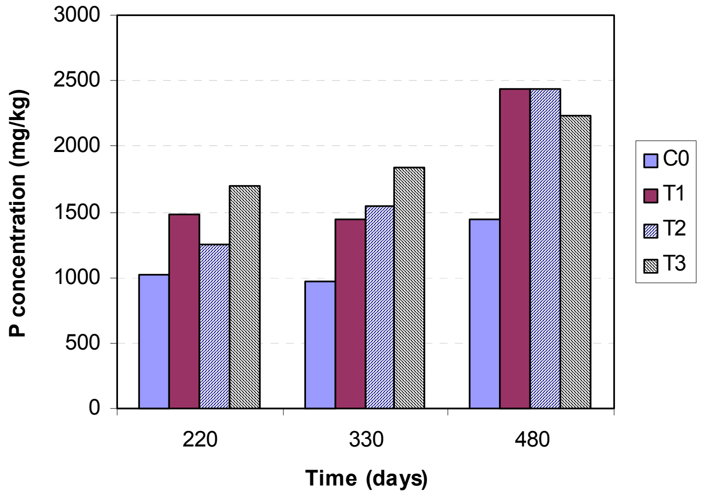


Figure 42. P Concentration in the Grass (*Stenotaphrum secundatum*) Shoots Grown in the Control and P-Treated Plots.

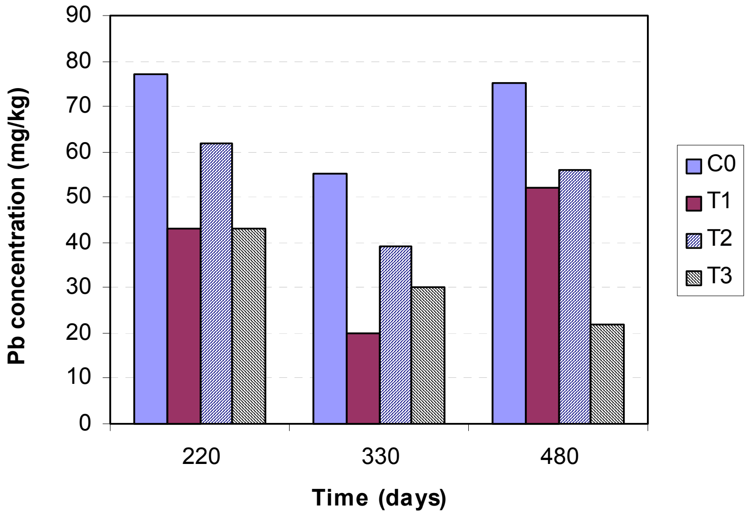
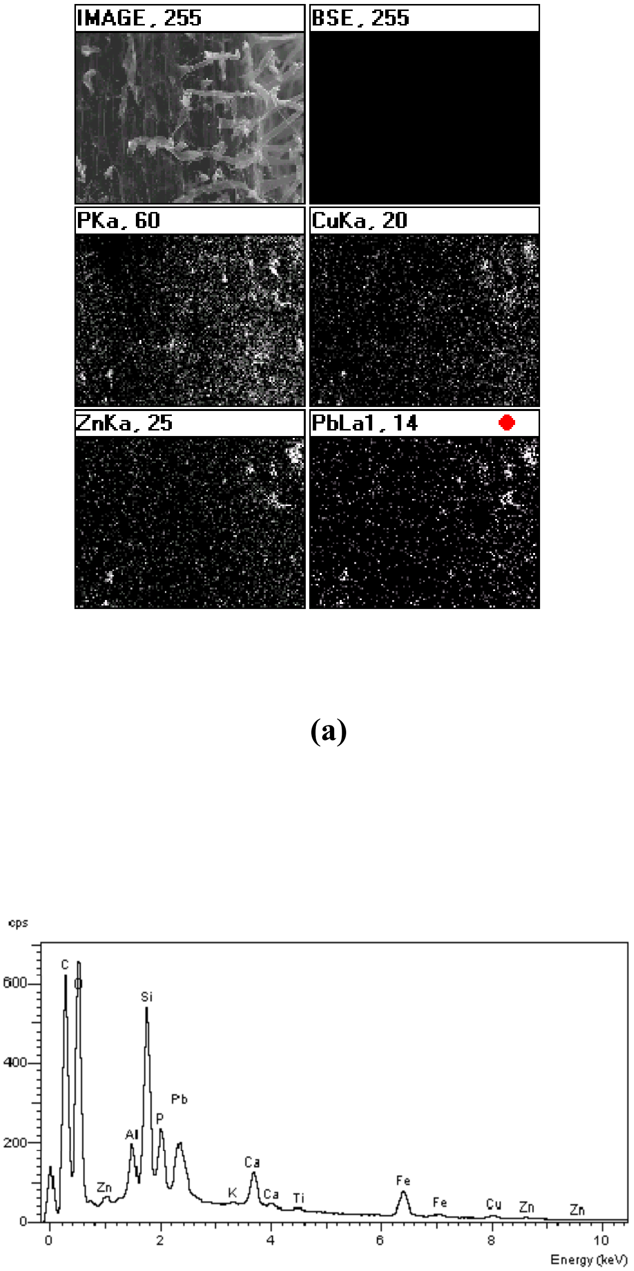


Figure 43. Pb Concentration in the Grass (*Stenotaphrum secundatum*) Shoots Grown in the Control and P-Treated Plots.



(a)

(b)

Figure 44. Element Distribution (a) and Relative Concentration (b) of the Grass Root Grown in T2 Treatment Soil at Day 330.

Groundwater Analysis

Figure 45 illustrates the groundwater pH changes with time. Generally, groundwater pH after P treatment was close to that before P application in the test period except on day 7 and day 330. On these two days, pH was slightly reduced. The reduction of groundwater pH on day 7 may be due to the leaching of H_3PO_4 resulted from pre-acidification.

P treatment resulted in a Pb decrease in groundwater taken from the three monitoring wells installed in the plots (MW1, MW2, and MW3) compared to samples taken before P application (Figure 46). However, elevation of Pb concentrations were observed on day 7 and day 330; this may be attributable to lead leaching from the soil due to low soil pH value. Fluctuations in Pb concentrations have paralleled, in general, fluctuations in groundwater pH. In addition, special attention should be given to the effect of the rainfall event.

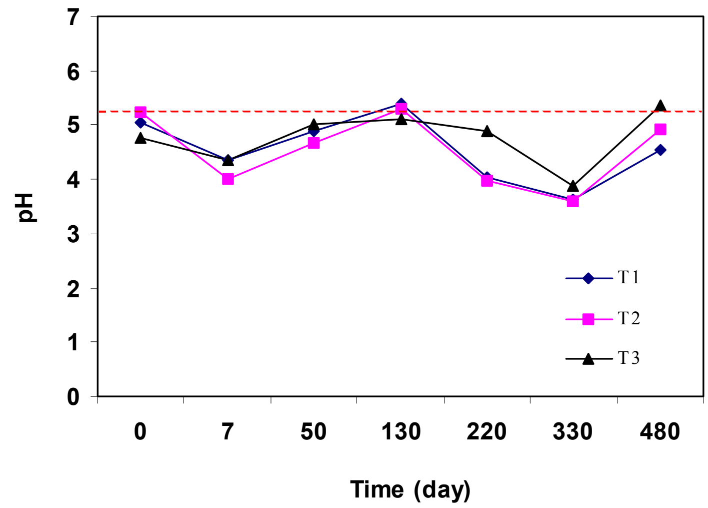


Figure 45. pH Changes in the Groundwater as a Function of Time.

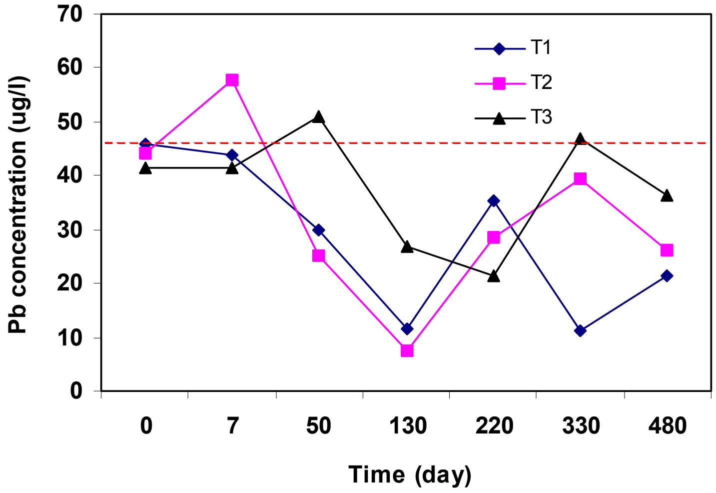


Figure 46. Pb Concentration Changes in the Groundwater as a Function of Time.

CONCLUSIONS

We have reported the results of a pilot-scale field experiment on the efficiency of P amendments to immobilize Pb at an extremely contaminated site. To our knowledge, it is one of the first field experiments to assess a broad *in situ* implementation of this technology.

The results of the pilot-scale field study at this particular site indicate that P amendments are efficient in transforming lead from non-residual into residual form. The effective immobilization of lead is attributed to the *in situ* formation of insoluble pyromorphite-like minerals after P application. Phosphate amendment is more effective for Pb immobilization than Cu, Zn or Cd. Phosphate amendment resulted in decrease of Pb phytoavailabilities. Pb concentration in groundwater was reduced after P application although there is a high variation of Pb concentration. A mixture of H_3PO_4 and rock phosphate yielded the best results in Pb immobilization, with least impact on soil pH, and least risk of potential eutrophication. In addition, the results of this field test were consistent with those of lab experiments.

Based on our laboratory experiment and 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 excised to maximize lead immobilization and minimize potential adverse impacts caused by application of phosphate amendments to soils. Although H_3PO_4 is needed to catalyze the dissolution of 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 invert the phases 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 formation of pyromorphite-like minerals and minimizing potential P and Pb leaching.

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