

Application Methods Affect Phosphorus-Induced Lead Immobilization from a Contaminated Soil

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ABSTRACT

Phosphate rock (PR) and phosphoric acid (PA) are an effective combination of P sources for immobilizing Pb in contaminated soils. This column experiment examined the effectiveness of different application methods on Pb immobilization in a contaminated soil. Phosphate was applied at a P/Pb molar ratio of 4 with half as PR and half PA. While PR was mixed with the soil or placed as a layer, aqueous PA was applied from the top of the column as one or two applications. After 4 wk of incubation, total and soluble Pb and P, TCLP-Pb (toxicity characteristic leaching procedure) and PBET-Pb (physiologically-based extraction test) in the P-treated soil were determined. Phosphate addition effectively reduced leachable Pb to below the EPA drinking water standard of $15 \mu\text{g L}^{-1}$ in all treatments. Mixing both PA and PR with the soil was the most effective method in Pb immobilization, reducing TCLP-Pb by up to 95% and PBET-Pb by 25 to 42%. Application of PR as a layer in the soil column was the most effective in reducing Pb migration (by 73–79%) and minimizing soil acidification and P entrophication, potential drawbacks of PA. Applying PA in two applications was less effective than one application. Mixing PR and PA with the soil plus placing PR as a layer can be employed for effective remediation of Pb-contaminated soils, reducing Pb leachability, bioavailability, and mobility while minimizing soil acidification and P entrophication.

LEAD contamination in soils is of major concern due to not only its toxicity to humans and animals, but also to its ease of exposure through ingestion or inhalation. Activities such as mining and manufacturing, and the use of synthetic products (e.g., pesticides, paints, batteries, and industrial waste) have resulted in many Pb-contaminated sites. Over time, the Pb loading rate in soil exceeds its natural removal rate by more than 20-fold (Nriagu, 1978). A soil is generally considered contaminated with Pb when its total Pb concentration exceeds 400 mg kg^{-1} (USEPA, 1996), and remediation is required at this level (OSWER, 1994).

Various remediation technologies have been developed to clean up Pb-contaminated soils. Among those, in situ Pb stabilization using binding agents is a promising approach due to its sustainability and cost-effectiveness. Other remediation technologies, including excavation, solidification, and chelation/extraction, are either very costly or only partially effective. The estimated cost of solidification is about $\$750 \text{ m}^{-3}$ and that of stabilization $\$250 \text{ m}^{-3}$. Stabilization seems to be a more feasible option due to its ease of operation and relatively low cost (Wang et al., 2001).

In situ Pb immobilization in soil using phosphate has been considered a cost-effective and environmentally-benign remediation technology. When P reacts with Pb in a soil, it transforms reactive and bioavailable Pb species into more stable forms. Pyromorphite is one of the least soluble forms of Pb found in soils under a wide range of environmental conditions. The bioavailability and mobility of soil Pb can be drastically reduced when unstable Pb forms, such as cerussite (PbCO_3), are converted into pyromorphite (Zhang and Ryan, 1999). During the last decade, many researchers have successfully demonstrated the effectiveness of phosphate-induced Pb immobilization by mixing phosphate minerals with Pb-contaminated soils (Ma et al., 1993, 1994; Cotter-Howells, 1996). Dissolution of Pb compounds followed by precipitation of Pb-phosphate has been considered as a primary mechanism for Pb immobilization in soils (Ma et al., 1993). Thus, successful immobilization of Pb in soil requires enhanced solubility of soil Pb and P by decreasing soil pH and/or applying sufficient amount of soluble P.

Among various P sources, phosphate rock (PR) has been proved to be feasible to immobilize Pb in soils. Phosphate rock, a complex assemblage of phosphate minerals, is mainly composed of microcrystalline carbonate fluor-apatite (Ma et al., 1995). Its effectiveness in immobilizing Pb primarily depends on its ability to provide soluble P (Ma et al., 1993, 1995). To compensate for its low solubility in a soil, soluble phosphoric acid (PA) has been used in combination with PR. This approach has been used to effectively immobilize Pb from a Pb-contaminated soil (Cao et al., 2001). The role of PA in the mixture was to solubilize Pb minerals in soils and PR, thereby increasing the available Pb and P in the soil. This, in turn, facilitates more precipitation of Pb-phosphate compounds. Application of PA promoted the greatest soil pH reduction while a mixture of PA and PR yields the best overall results for in situ Pb immobilization with less soil pH change and less P leaching (Cao et al., 2001).

The objective of this study was to evaluate the effectiveness of different application methods on Pb immobilization in a soil using a mixture of PR and PA as P source. This was accomplished by (i) determining Pb leaching characteristics and bioavailability; and (ii) to evaluate Pb distribution in a soil after P application.

MATERIALS AND METHODS

Site Characterization

The soil used for this study was collected from a Pb-contaminated site in an urban area of northwest Jacksonville,

Abbreviations: XRD, X-ray diffraction; TCLP, toxicity characteristic leaching procedure; PBET, physiologically-based extraction test; PR, phosphate rock; PA, phosphoric acid.

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Florida. The site is located in a vacant, fenced rectangular area (4100 m²), and covered by vegetation (mainly grasses). Past industrial activities, which included a gasoline station, salvage yard, auto body shop, and recycling operation for lead batteries, have all contributed to the contamination of this site. The total Pb concentrations in the soil ranged from 36 to 21 074 mg kg⁻¹. Lead concentration decreased with soil depth, with the majority of the Pb present near the soil surface (0–20 cm). Mineralogical characterization of the site by X-ray diffraction (XRD) reveals that PbCO₃ (cerussite) is the predominant Pb mineral in the sand fraction and PbO in the silt and clay fraction (Cao et al., 2001).

Soil Characterization

Soil samples were collected from the top 20 cm at the Jacksonville site. They were collected from a location where high concentrations of Pb are present (Cao et al., 2001). They were air-dried, sieved through a 2-mm stainless steel screen and stored at room temperature. The soil sample was thoroughly mixed to ensure uniformity. They were then digested using the hot-block digestion procedure (USEPA Method 3050A) for total Pb concentration. The clean soil sample was collected from outside the fence directly adjacent to the site. The Pb contents and pH in the clean and contaminated soils were 77 and 5017 mg kg⁻¹, and 6.7 and 6.2, respectively.

Column Preparation

The column test was used to simulate field conditions. A total 400 g of soil was packed into a PVC column (40 cm height by 3.5 cm diameter), with the top half (0–20 cm) being filled with the contaminated soil and the lower half (20–40 cm) the clean soil to approximate the Pb distribution at the site. The bulk density of packed soil was 1.2 g cm⁻³.

A total of 18 columns were mounted with each treatment replicated three times. The phosphate application rate was based on a P/Pb molar ratio = 4, which was the optimum rate for Pb-immobilization in a contaminated soil (Cao et al., 2001). A fixed amount of P was applied to all columns except for the control, with half as PR (R) and half as PA (A). Both PR and PA were applied only to the first 20 cm of the soil column, i.e., the contaminated soil. Phosphate rock was added in two ways: either mixed (M) with the contaminated soil or added as a layer (L) placed between the contaminated and clean soil. Phosphoric acid was added in three ways, added simultaneously with the PR (S1), one application a week later (W1), or two applications with a week apart (W2). While PR was added as powder without grinding, PA was added from the top as a solution to 75% field capacity of the soil.

A total of five different P application methods were used in this experiment and they were as follows:

- R_{MA}S₁: PR was mixed with the contaminated soil and PA was added at the same time;
- R_{MA}W₁: PR was mixed with the contaminated soil (Day 1) and PA was added 1 wk later (Day 8);
- R_{LA}S₁: PR was added as a layer and PA was added at the same time;
- R_{MA}W₂: PR was mixed with the contaminated soil (Day 1) and PA was added two times (Day 1 and Day 8) with 1 wk apart;
- R_{LA}W₂: PR was added as a layer (Day 1) and PA was added two times (Day 1 and Day 8) with 1 wk apart.

A fine textured glass wool was placed at the bottom of all columns, acting as a filter for the leachate. The soil columns were leached with deionized distilled water twice up to 2 pore volumes 1 and 4 wk after the last application of PA. After

incubation at 75% field capacity of the soil, the PA in the treatments R_{MA}S₁, R_{LA}S₁, and R_{MA}W₁ was in the soil for 5 and 4 wk, whereas half of the PA in the treatment R_{MA}W₂ was in the soil for 5 wk and the other half 4 wk. By comparing these treatments, the effects of incubation time and application methods on phosphate-induced Pb immobilization can be obtained.

Analytical Procedure

Soil pH was measured with deionized water at a 1:1 soil/solution ratio after 24 h of equilibrium. Total P was measured colorimetrically with a Shimadzu 160U spectrometer using the molybdate ascorbic acid method (Page et al., 1982).

At the end of the experiment, the soil columns were divided into four sections (0–10, 10–20, 20–30, and 30–40 cm). The modified physiologically-based extraction test (PBET) (the soils were mixed with 0.011 M HCl solutions at a 1:100 soil/solution ratio at pH of 1.95) and toxicity characteristic leaching procedure (TCLP) were conducted in each section to determine the effectiveness of P-induced Pb immobilization in the soil. Total Pb in each soil layer was also determined to compare the downward movement of Pb among different treatments. After leaching columns with up to 2 pore volumes of distilled deionized water (DDW) twice, column leachates were analyzed for Pb and P concentrations.

Lead analysis was performed using a flame atomic absorption spectrophotometer (AAS, 220 FS with SIPS, Varian, Walnut Creek, CA) or a graphite furnace atomic absorption spectrophotometer (SIMMA 6000, PerkinElmer Corp., Norwalk, CT). Standard soil reference materials (2709 San Joaquin soil and 2710 Montana soil) from the National Institute of Science and Technology (NIST, Gaithersburg, MD) were carried through the digestion and analyzed as a part of quality control (within 100 ± 20%). Reagent blanks and internal standards were used where appropriate to ensure accuracy and precision. Differences among different means were determined by analysis of variance.

Soil clay fractions were separated by centrifugation and analyzed using XRD to detect the formation of pyromorphite in the soil.

All results are expressed as an average of triplicates ± standard deviation. The effect of treatment was determined by analysis of variance using the Statistical Analysis System (SAS Institute Inc., 1987).

RESULTS

Soil Characterization

The soil is sandy with a pH of 6.2 to 6.7 (data not shown), which is greater than typical Florida soils (Chen et al., 1999). Lead was the main contaminant with a concentration of 5017 mg kg⁻¹, exceeding the critical level of cleanup for industrial soils (1400 mg kg⁻¹). More detailed description of the site can be found in Cao et al. (2001). Generally, Pb was concentrated at the surface soil (0–20 cm) and its concentrations decreased with soil depth.

Effects of Phosphorus Application on Soil pH

The pHs of the P-treated soils were measured to evaluate the degree of soil acidification. As seen from Table 1, reduced soil pH in the surface soil (0–20 cm) was observed in all P-treated soils due primarily to the addition of PA. Significant reduction in pH, approxi-

Table 1. Effects of P treatments on soil pH.

Soil layer	Control	R _M AS ₁ †	R _M AW ₁	R _L AS ₁	R _M AW ₂	R _L AW ₂
cm						
0–10	6.21 ± 0.12	5.2 ± 0.16	5.25 ± 0.07	5.12 ± 0.17	5.21 ± 0.08	5.26 ± 0.06
10–20	6.16 ± 0.08	5.75 ± 0.12	5.99 ± 0.07	5.89 ± 0.05	5.87 ± 0.02	5.89 ± 0.04
20–30	6.78 ± 0.02	5.93 ± 0.02	6.08 ± 0.04	6.12 ± 0.06	6.35 ± 0.01	6.46 ± 0.02
30–40	6.74 ± 0.16	6.07 ± 0.06	6.11 ± 0.01	6.18 ± 0.05	6.41 ± 0.04	6.46 ± 0.06

† R_MAS₁: Phosphate rock (PR) was mixed with the soil and phosphoric acid (PA) was added simultaneously; R_MAW₁: PR was mixed and PA was added 1 wk later; R_LAS₁: PR was added as a layer and PA was added simultaneously; R_MAW₂: PR was mixed and PA was added two times with 1 wk apart; R_LAW₂: PR was added as a layer and PA was added two times with 1 wk apart.

mately 1 pH unit, was limited to only the top 10 cm. Yang et al. (2001) added 5000 mg kg⁻¹ of P as PA to immobilize Pb and reported a reduction of soil pH by three units from 7.22 to 4.34. The presence of PR in the soil has buffered soil pH in our experiment. The fact that reduction in soil pH was mostly limited to the top 20 cm of the soil column (Table 1) indicates limited movement of P in the soil profile.

Reduction of soil pH to near 5.5 is necessary for efficient Pb immobilization in soils. Since a large fraction of the Pb in the soil is associated with carbonate (Cao et al., 2001), addition of PA to the soil is essential for the dissolution of PR and Pb carbonate. Soluble P and Pb may enhance precipitation of insoluble pyromorphite-like minerals in a soil, which at given Pb and phosphate concentrations are formed at a greater rate at pH 5 than at pH 6 or 7 (Laperche et al., 1996). Other researchers have used liming materials along with phosphate treatments to buffer against a decrease in pH (Basta and McGowen, 2004; Brown and Elliott, 1992). Also the application of PA to acidify soil may increase the risk of ground water contamination with P and other heavy metals, so care should be exercised

Toxicity Characteristic Leaching Procedure Lead

The toxicity characteristic leaching procedure is designed to evaluate the potential for migration of hazardous constituents through the vadose zone soils to water table under landfill conditions. Higher Pb concentration in TCLP extracts is indicative of higher potential for Pb mobility in soil. Toxicity characteristic leaching procedure-Pb in the contaminated soil, i.e., top 20 cm of the column, was determined. The TCLP-Pb concentrations in the control soil without P treatment were as high as 127 mg L⁻¹, significantly greater than the regulatory level of 5 mg L⁻¹ (Fig. 1). This is because most of the Pb in this soil is in the carbonate fraction, which would readily dissolve in an acidic TCLP solution (Melamed et al., 2003). Phosphate addition, on the other hand, greatly reduced TCLP-Pb, i.e., by >95% (Fig. 1). As a result of P application, TCLP-Pb in the contaminated soil (0–20 cm) was reduced to below 5 mg L⁻¹ (the EPA criteria for TCLP-Pb) in all five treatments (Fig. 1). This is consistent with the results by Hettiarachchi et al. (2000) and Chen et al. (2003) who reported the addition of P significantly reduced TCLP-Pb in contaminated soils to below the critical level of 5 mg L⁻¹.

Among the five P treatments, the highest reduction in TCLP-Pb was observed for treatment R_MAS₁ (PR was mixed and PA was added simultaneously), which had

less than 3 mg L⁻¹ in the contaminated soil (Fig. 1). On the other hand, treatment R_MAW₂ (PR was mixed with and PA was added two times with 1 wk apart) was the least effective in reducing TCLP-Pb in the soil. This makes sense since the PA in the treatment R_MAS₁ was in the soil more than a week longer than that in R_MAW₂. This indicates that not only the method of P application is important, but the reaction time of P with Pb is also critical. Phosphate-induced Pb immobilization occurred during the 4 wk of incubation in addition to during the TCLP extraction.

Lead Bioavailability

Incidental ingestion of Pb-contaminated soil has been reported as a primary exposure pathway to humans for elevated blood Pb levels (Chen et al., 2003). A physiologically-based extraction test has been used to estimate Pb bioavailability (in vivo), which simulates Pb dissolution under gastrointestinal conditions using a chemical extraction (Yang et al., 2001). Lead bioavailability in contaminated soils has been shown to vary with its mineralogical forms (Davis et al., 1993). In vivo and in vitro assays have indicated that the mammalian gastrointestinal availability of Pb is controlled by the form and relative solubility of Pb solids (Ruby et al., 1996). The PBET has been used to assess the Pb bioavailability

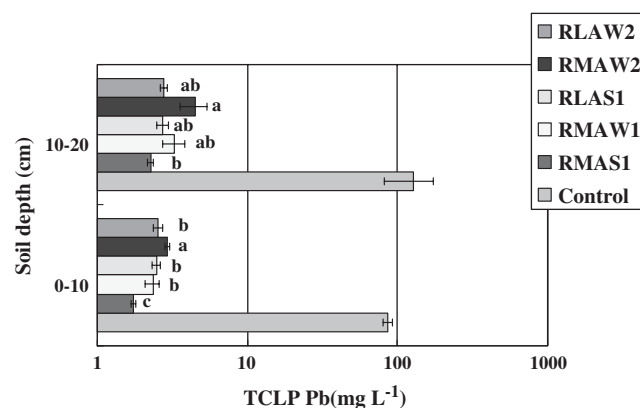


Fig. 1. Toxicity characteristic leaching procedure (TCLP) metal contents in sectioned soil columns (0–20 cm) after leaching. Detection limit = 0.2 mg L⁻¹. R_MAS₁: Phosphate rock (PR) was mixed with the soil and phosphoric acid (PA) was added simultaneously; R_MAW₁: PR was mixed and PA was added 1 wk later; R_LAS₁: PR was added as a layer and PA was added simultaneously; R_MAW₂: PR was mixed and PA was added two times with 1 wk apart; R_LAW₂: PR was added as a layer and PA was added two times with 1 wk apart. Columns with the same letter are not significantly different at $p < 0.05$.

in a contaminated soil after receiving various amounts and sources of P (Hettiarachchi et al., 2000).

The bioavailability of soil Pb is associated with its solubility and dissolution rate in the gastrointestinal tract. Bioavailable Pb in the contaminated soil based on PBET was reduced after P application in all five treatments (Fig. 2). The control soil showed 50 to 51% of bioavailable fraction Pb while P-treated soils showed of 30 to 45% bioavailable fraction Pb. Reduction of bioavailable Pb was similar to the 25 to 35% reduction reported by Hettiarachchi et al. (2000) and 39% by Yang et al. (2001). The greatest reduction in PBET-Pb was obtained again from the treatment R_{MAS1} , similar to the TCLP results (Fig. 1), but no significant differences were found between treatments.

Lead Migration in Soil

In most contaminated soils, metals do not appear to leach downward in significant quantities in the short term primarily due to their strong interactions with the soils. However, in the long run, metals can leach downward in a soil due to their complexation with solubilized organic matter, especially in an alkaline environment where organic matter is more soluble (Marschner and Wilczynski, 1991). This may be true at this site where soil organic matter (3.91%) and pH (6.95) are much higher than those of typical Florida soils (Chen et al., 1999).

To determine the effectiveness of P treatment to prevent Pb downward migration, total Pb concentrations in bottom half of the column (20–40 cm) were determined (Fig. 3). As expected, significant downward movement of Pb was observed in the control soil, especially in the 20- to 30-cm fraction, which was located directly under the contaminated soil (0–20 cm). The initial Pb concentration in the lower half of the column (20–40 cm) in the control soil was 77 mg kg^{-1} (data not shown). After being in contact with the Pb-contaminated soil for 5 wk under 75% field capacity, the Pb concentration in the 20- to 30-cm soil column fraction increased to 365 mg kg^{-1} . However, Pb migration was mostly limited to that sec-

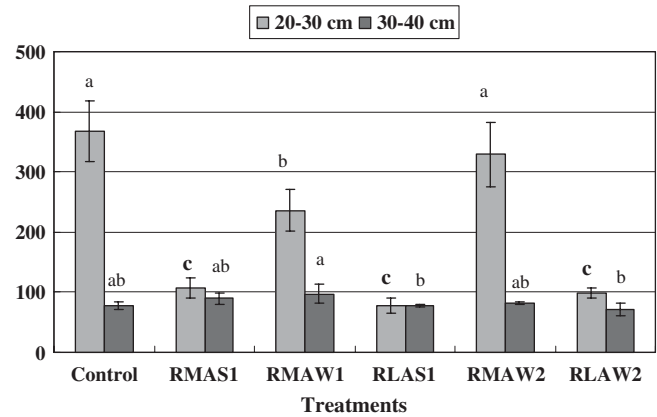


Fig. 3. Total Pb concentration in sectioned soil columns (20–40 cm). Detection limit = 0.2 mg L^{-1} . R_{MAS1} : Phosphate rock (PR) was mixed with the soil and phosphoric acid (PA) was added simultaneously; R_{MAW1} : PR was mixed and PA was added 1 wk later; R_{LAS1} : PR was added as a layer and PA was added simultaneously; R_{MAW2} : PR was mixed and PA was added two times with 1 wk apart; R_{LAW2} : PR was added as a layer and PA was added two times with 1 wk apart. Columns with the same letter are not significantly different at $p < 0.05$ for the same depth.

tion of the column as Pb concentration in the 30- to 40-cm fraction remained at 77 mg kg^{-1} and little difference was observed among the five treatments in 30- to 40-cm fractions (Fig. 3).

All treatments were effective in reducing Pb migration except R_{MAW2} where PR was mixed with the contaminated soil in the top 20 cm, and PA was applied two times with 1 wk between applications. Since PA was added in two aliquots, the amount of acidity was probably insufficient to dissolve enough Pb from the soil to induce the precipitation of Pb-phosphate minerals. This was confirmed by the P data where P concentration in the leachate of R_{MAW2} was the lowest (Fig. 4). This was also consistent with the highest TCLP-Pb (Fig. 1) and PBET-Pb (Fig. 2) observed in the treatment R_{MAW2} .

Treatments with PR placed as a layer (e.g., R_{LAS1} and R_{LAW2}) were more effective in reducing Pb migration

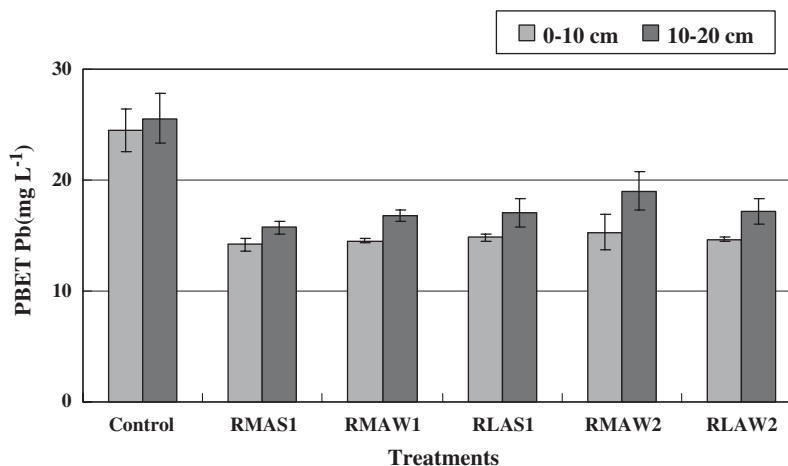


Fig. 2. Physiologically based extraction test (PBET)-extractable Pb contents in sectioned soil columns (0–20 cm) after leaching. Detection limit = 0.2 mg L^{-1} . R_{MAS1} : Phosphate rock (PR) was mixed with the soil and phosphoric acid (PA) was added simultaneously; R_{MAW1} : PR was mixed and PA was added 1 wk later; R_{LAS1} : PR was added as a layer and PA was added simultaneously; R_{MAW2} : PR was mixed and PA was added two times with 1 wk apart; R_{LAW2} : PR was added as a layer and PA was added two times with 1 wk apart.

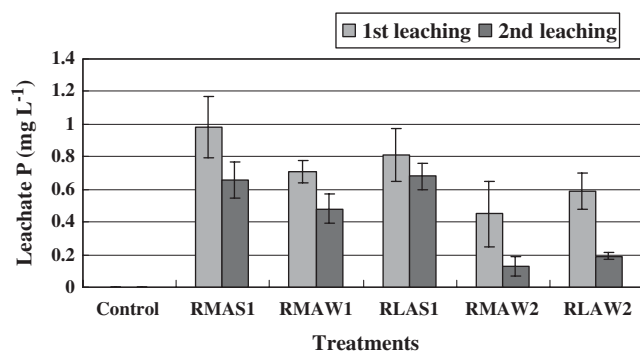


Fig. 4. Phosphorus concentrations (mg L^{-1}) in column leachate (0–20 cm). R_{MAS1}: Phosphate rock (PR) was mixed with the soil and phosphoric acid (PA) was added simultaneously; R_{MAW1}: PR was mixed and PA was added 1 wk later; R_{LAS1}: PR was added as a layer and PA was added simultaneously; R_{MAW2}: PR was mixed and PA was added two times with 1 wk apart; R_{LAW2}: PR was added as a layer and PA was added two times with 1 wk apart.

than those where PR was mixed with the soil (R_{MAS1}, R_{MAW1}, and R_{MAW2}; Fig. 3). This may be due to the formation and/or containment of stable Pb minerals within the PR layer. Among the treatments where PR was mixed with the soil, treatment R_{MAS1}, where PA was applied at the same time with PR, was the most effective.

To determine the mechanism of reduction in Pb downward movement, the soil around the PR layer was separated and analyzed with XRD. Previous analysis of mineralogical changes over time resulting from P addition using XRD showed formation of stable pyromorphite-like minerals in P-treated soil (Cao et al., 2002). However, no Pb-phosphate was identified in the clay fractions in this research (data not shown). With the Pb concentration in the soil being lower than the detection limit for XRD (~1%), formation of Pb-phosphate in the soil cannot be ruled out.

Leachable Lead and Phosphorus

Column studies more closely simulate field conditions than TCLP extraction does. To simulate field conditions, soil columns were leached twice with DDW and the leachate was collected. The leachate was analyzed for total Pb and P concentrations. All P-treated soils showed that leachable Pb had been reduced to below the EPA drinking water regulatory level of $15 \mu\text{g L}^{-1}$ or nondetectable (Table 2). The highest Pb concentration was again observed in the treatment R_{MAW2}, comparable to the control soil. Lead concentrations in the second leachate were lower than those in the first leachate. Significant differences were seen in the release of Pb between treatments with different application methods of PA, where the treatment R_{MAW2} was observed to be the

least effective yet still below the EPA regulatory level ($15 \mu\text{g L}^{-1}$). All five treatments proved to be effective in reducing Pb solubility in the soil.

The addition of large amounts of P to a contaminated soil may increase the risk of eutrophication in water bodies (Basta and McGowen, 2004). Taking P leaching in the soil into account is important with respect to secondary contamination. Although it is well recognized that phosphate amendment is an effective method for immobilizing metals in contaminated soils, it is unavoidable that some elevated soluble P may enhance eutrophication risk (Cao et al., 2001). This was not the case in this study as P leached from the P-treated soil columns was less than 1 mg L^{-1} for all treatments (Fig. 4). Treatments where PA was applied in two aliquots (R_{MAW2} and R_{LAW2}) had lower P concentrations in the leachate than in the other treatments. This may indicate that the application of P in small quantities can limit the downward movement of PA, however, with correspondingly lower efficiency in immobilizing Pb in the soil (Fig. 1 and 2).

Though P release from P-treated soil was limited, some of the P, which was not converted to Pb-phosphate or sorbed by the soil, was released from the soil. Therefore, caution is needed to assess the P movement within P-treated fields to minimize eutrophication risk, and consideration should be given to soil type and the amount of P added.

CONCLUSIONS

The efficiency of in situ P-induced Pb immobilization depends on the type and rate of P amendment, along with appropriate application methods. This study has shown that applying a mixture of PA and PR effectively reduced TCLP-extractable Pb, bioavailable Pb (PBET), and vertical Pb migration in a Pb-contaminated soil. All P-treated soil resulted in significant reductions in bioavailable and leachable Pb as compared with the control soil. Of all the treatments, mixing of PR with the soil coupled with simultaneous application of PA (R_{MAS1}) was the most effective in decreasing leachable and bioavailable Pb with the least impact on soil pH and lowest eutrophication risk. The treatment that included PA being applied in two aliquots and PR being applied as a layer was the least effective overall. These results also indicate that simultaneously applied PA with the PR is necessary for effective immobilization of Pb in soils. The fact that layered PR showed lower efficiency in Pb immobilization as compared with the other treatments may be due to an insufficient amount of P supplied to the soil. However, the PR layer showed improved re-

Table 2. Effects of P treatments on Pb concentrations ($\mu\text{g L}^{-1}$) in soil leachate.

Leaching	Control	R _{MAS1} †	R _{MAW1}	R _{LAS1}	R _{MAW2}	R _{LAW2}
First leaching	33.6 ± 1.5	ND‡	ND	ND	11 ± 1.9	2.3 ± 0.45
Second leaching	14.5 ± 1.74	ND	ND	ND	5.7 ± 0.91	ND

† R_{MAS1}: Phosphate rock (PR) was mixed with the soil and phosphoric acid (PA) was added simultaneously; R_{MAW1}: PR was mixed and PA was added 1 wk later; R_{LAS1}: PR was added as a layer and PA was added simultaneously; R_{MAW2}: PR was mixed and PA was added two times with 1 wk apart; R_{LAW2}: PR was added as a layer and PA was added two times with 1 wk apart.

‡ ND, not detected; Detection limit = $1 \mu\text{g L}^{-1}$.

duction of Pb migration over the mixing treatments. Furthermore, these results suggest layered PR below contaminated soil may serve as a reactive barrier to prevent Pb from migrating into the ground water. Although the effects of PA on pH and leachable P were acceptable in this experiment, Pb leaching and eutrophication may be potential drawbacks of its indiscriminate utilization. The combination of the soil-PR mixture and PR layer can be considered as well for remediation of Pb-contaminated soils, and with reduced leaching, bioavailability and mobility of Pb.

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