EPA Public Access

Author manuscript

Environ Pollut. Author manuscript; available in PMC 2020 May 15.

About author manuscripts

Submit a manuscript

Published in final edited form as:

Environ Pollut. 2017 January ; 220(Pt A): 549–556. doi:10.1016/j.envpol.2016.10.002.

Soil solution interactions may limit Pb remediation using P amendments in an urban soil

John F. Obrycki, Kirk G. Scheckel, Nicholas T. Basta

School of Environment and Natural Resources, 210 Kottman Hall, 2021 Coffey Road, The Ohio State University, Columbus, OH 43210, United States, U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Land Remediation and Pollution Control Division, Cincinnati, OH 45224-1701, United States

Abstract

Lead (Pb) contaminated soils are a potential exposure hazard to the public. Amending soils with phosphorus (P) may reduce Pb soil hazards. Soil from Cleveland, OH containing 726 ± 14 mg Pb kg^{-1} was amended in a laboratory study with bone meal and triple super phosphate (TSP) at 5:1 P:Pb molar ratios. Soil was acidified, neutralized and re-acidified to encourage Pb phosphate formation. PRSTM-probes were used to evaluate changes in soil solution chemistry. Soil acidification did not decrease in vitro bioaccessible (IVBA) Pb using either a pH 1.5, 0.4 M glycine solution or a pH 2.5 solution with organic acids. PRSTM-probe data found soluble Pb increased 10-fold in acidic conditions compared to circumneutral pH conditions. In acidic conditions ($p = 3-4$), TSP treated soils increased detected P 10-fold over untreated soils. Bone meal application did not increase PRSTM-probe detected P, indicating there may have been insufficient P to react with Pb. X-ray absorption spectroscopy suggested a 10% increase in pyromorphite formation for the TSP treated soil only. Treatments increased soil electrical conductivity above 16 mS cm^{-1} , potentially causing a new salinity hazard. This study used a novel approach by combining the human ingestion endpoint, PRSTM-probes, and X-ray absorption spectroscopy to evaluate treatment efficacy. PRSTM-probe data indicated potentially excess Ca relative to P across incubation steps that could have competed with Pb for soluble P. More research is needed to characterize soil solutions in Pb contaminated urban soils to identify where P treatments might be effective and when competing cations, such as Ca, Fe, and Zn may limit low rate P applications for treating Pb soils.

Keywords

Lead (Pb); Phosphorus (P); Bioaccessibility; In vitro; Remediation

Publisher's Disclaimer: Disclaimer

Publisher's Disclaimer: Although EPA contributed to this article, the research presented was not performed by or funded by EPA and was not subject to EPA's quality system requirements. Consequently, the views, interpretations, and conclusions expressed in this article are solely those of the authors and do not necessarily reflect or represent EPA's views or policies. MRCAT operations are supported by the Department of Energy and the MRCAT member institutions. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

1. Introduction

Lead (Pb) contaminated soils are a public health concern because they can act as one of several potential exposure sources to elevate blood lead levels in children (Mielke et al., 2011, Binns et al., 2007). One potential management strategy is treating soils with phosphorus (P), specifically phosphates (PO_4^{3-}), to encourage formation of several types of Pb phosphates, including chloropyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$). These Pb phosphates are less soluble than other Pb mineral forms and could pose less of a Pb soil ingestion hazard when compared to other more soluble Pb minerals (Scheckel et al., 2013).

The reduced Pb ingestion hazard for human intake can be evaluated using in vitro bioaccessible (IVBA) extractions. Two extractions used are US EPA Method 1340 (US EPA, 2013), a pH 1.5 0.4 M glycine solution, and a physiologically based extraction test (PBET) pH 2.5 solution with organic acids as buffering agents (Attanayake et al., 2014). Within the range of pH 1.5–2.5, IVBA Pb treatment effects tend to be more pronounced at pH 2.5 because Pb solubility decreases as pH increases. For example, a P treated soil containing approximately 45% pyromorphite had 50% IVBA Pb when evaluated using US EPA 1340 (US EPA, 2013). A soil with 0% pyromorphite had 65% IVBA Pb in this same extraction solution (Scheckel et al., 2005). The difference in Pb solubility between these two samples doubled when evaluated using pH 2.5 solutions with 0.4 M glycine. The same 45% pyromorphite sample had 20% IVBA Pb in this pH 2.5 solution, and the 0% pyromorphite sample had approximately 50% IVBA Pb (Scheckel et al., 2005).

Determining how much P to add to Pb contaminated soils to reduce IVBA Pb hazards remains an open question. Higher P application rates, such as above 4:1 P:Pb molar ratios, may increase P runoff and have negative effects on water quality (Basta and McGowen, 2004, Osborne et al., 2015, Weber et al., 2015, Yang et al., 2001). Amendment rates of 4:1 P:Pb may not be effective in reducing IVBA Pb for the human ingestion exposure pathway (Obrycki et al., 2016, Yang et al., 2001). Higher application rates, such as 15.4:1 P:Pb molar ratio, reduced IVBA Pb on a smelter Pb contaminated soil containing $4361 \pm 24 \text{ mg Pb kg}^{-1}$ (Ryan et al., 2004, Yang et al., 2001). This 15.4:1 P:Pb molar ratio treatment caused approximately 45% of Pb to be converted to pyromorphite as discussed above (Ryan et al., 2004).

One explanation for why these higher P:Pb molar ratios are necessary to reduce IVBA Pb is interactions between soluble P and soil solution constituents reduce Pb phosphate formation (Hettiarachchi and Pierzynski, 2004, Porter et al., 2004). For example, this means P must be added in excess of the P:Pb 0.6 M ratio that occurs in chloropyromorphite. In situ decreases in soil pH are needed as Pb solubility is the rate-limiting step in mineral formation (Ryan et al., 2001). Increasing P application rates, in excess of the rates used by Ryan et al. (2004), but without soil acidification, did not consistently reduce IVBA Pb or increase Pb-phosphate formation (Obrycki et al., 2016).

Reducing soil pH may be a key component of remediating Pb contaminated soils to ensure sufficient Pb and P within the soil solution. However, decreases in soil solution pH increase the solubility of other metals that can interact with P and subsequently limit Pb phosphate

formation. When soil pH is reduced below point of zero charge for Fe and Al oxide surfaces (i.e. below pH ~7–9), P can also be adsorbed onto these now positively charged surfaces (Essington, 2004). However, reductions in soil pH coupled with increases in P content may also lead to increased dissolved organic matter in soil solutions that could chelate Pb and prevent Pb phosphate formation (Lang and Kaupenjohann, 2003). Concentrations of 72 mg C l⁻¹ were found to contain nearly 10,000 fold higher Pb concentrations compared to pure solutions without soluble C added. Additionally, soluble carbon extracted using a 5:1 water:soil extract kept more Pb in solution, particularly in pH 4 solutions (Lang and Kaupenjohann, 2003).

Potentially up to 80% of soil P amendments are unavailable for plant uptake, and by extension Pb phosphate formation, due to soil chemical reactions with Al, Fe, and Ca (Withers and Sharpley, 1995). Detailed thermodynamic modeling conducted by Porter et al. (2004) indicated phosphate treatments could have limited interactions with soil Pb due to competition for soil solution P from aluminum (Al), iron (Fe), calcium (Ca), magnesium (Mg), and manganese (Mn). When remediating Pb contaminated soils with an end goal of forming Pb phosphates, such as chloropyromorphite, all Ca must be converted to hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) and all Mn must be converted to manganese hydrogen phosphate (MnHPO₄) (Porter et al., 2004). Of these two elements, Ca is more likely to limit Pb phosphate formation in most soils due to its higher relative abundance in soils compared to Mn (Porter et al., 2004).

Thermodynamic modeling is useful for theoretically defining possible long-term endpoints for soil solution equilibria conditions. However, as noted previously with the kinetics of Pb solubility being the rate-limiting step for Pb-phosphate mineral formation (Ryan et al., 2004), many reactions in soils are kinetically controlled and not thermodynamically controlled. Therefore, the ability of thermodynamic equilibrium models to predict Pb in the soil solution and its availability to potentially form Pb phosphates must be evaluated as a potential predictor.

If the Ca:P soil solution molar ratio in the soil is 1.67, then chloropyromorphite formation is promoted (Porter et al., 2004). Using data from Lindsay, 1979, Porter et al., 2004 estimated an average soil contains a Ca:P ratio of 20, or 12-fold higher than the thermodynamically favorable ratio. These conclusions were made using a detailed modeling experiment with an assumed average soil concentration and assumed P and Ca solubility. Data from a recent nationwide survey of United States soils from the top 5 cm of the soil profile indicated the average total Ca:P mol ratio was 21.9 (Smith et al., 2013). These data were calculated using total Ca and total P concentrations rather than soil solution values. However, given these total molar ratios, excess soluble Ca relative to soluble P may be encountered in surface soils within the United States at potential soil Pb remediation locations. This excess Ca could potentially limit Pb phosphate formation.

Adding dilute phosphoric acid (H₃PO₄) is a treatment which provides the additional soluble P to change all Ca to apatite, adds sufficient P to react with Pb, and reduces soil pH (Porter et al., 2004, Ryan et al., 2004, Scheckel et al., 2013, Yang et al., 2001). A treatment such as 10 g P kg⁻¹ as H₃PO₄ lowered surface soil pH from 7.1 to approximately 4, increased Pb

phosphate formation 45% in the previously discussed smelter waste soil, and reduced IVBA Pb from approximately 60%–20% when evaluated at pH 2.5 with 0.4 M glycine (Ryan et al., 2004, Scheckel et al., 2005, Yang et al., 2002). This treatment applied P at a 15.4 P:Pb molar ratio and added 1000 mg P kg⁻¹ beyond the soil P sorption capacity (Yang et al., 2001). The amendment caused surface soils (0–2.5 cm) to have 10,500 mg P kg⁻¹ (Yang et al., 2002). This surface soil P concentration is higher than the greatest total soil P value found by Smith et al. (2013) of 9120 ppm P. A surface soil with this elevated concentration could be a future P runoff source if not managed properly.

Modeled data using assumed soil solution concentrations are useful to generate theoretical guidelines for P amendment potential and limit excessive P additions (Porter et al., 2004). Several techniques exist for quantifying soil solution components to provide site-specific empirical data which can be compared to theoretical calculations. Soil solutions can be evaluated by extracting pore water using several methods, including centrifugation and in situ soil water samplers (Fisher and Reddy, 2013, Thibault and Sheppard, 1992, Wolt, 1994). Other methods include placing ion-exchange resins into the soil to measure soil solution chemistry over time (Qian and Schoenau, 2002). Ion-exchange resins offer a potential for widespread measurement of soil pore water to evaluate P treatments in situ.

Using soil solution measurements with IVBA Pb combines techniques not commonly used in Pb contaminated soil literature (Yang et al., 2001). Instead, studies focus upon evaluating IVBA Pb (Attanayake et al., 2014, Obrycki et al., 2016, Scheckel et al., 2013). For water soluble and plant uptake Pb studies, collected soil solution data was modeled to estimate the types of minerals controlling Pb solubility (Cao et al., 2002, Strawn et al., 2007). Soil solution data in combination with IVBA Pb results may help explain why treatments are effective on certain soils but not others.

Based on previous findings, in vitro pH conditions influence Pb solubility with lower pH conditions showing P treatments to be less effective. Additionally, in situ soil P treatments might not be effective due to soil solution chemistry interactions. These in vitro and in situ questions remain at the forefront of soil Pb research. This study used a novel approach combining PRS^{TM}-probes (Western Ag Innovations Inc., Saskatoon, Canada), two IVBA Pb tests conducted at pH 1.5 and pH 2.5, and X-ray absorption spectroscopy to quantify changes in the soil solution and soil Pb during the remediation process. The objective was to determine the effect of varying soil pH on in vitro extractable Pb and evaluate the suitability of PRS^{TM}-probes as indicators of how well treatments promoted increased Pb and P solubility.

2. Materials and methods

This study used a residential soil from Cleveland, OH which had been air dried, sieved to <2 mm, and homogenized through repeated mixing. Three subsamples were collected from the bulk soil and analyzed for soil texture following Kettler et al. (2001). Six bulk soil subsamples were analyzed for organic carbon following Heanes (1984) using a CEM-MARS 5 (CEM Corporation, Matthews, North Carolina) and a Genesys 10 spectrophotometer

(Thermo Electron Corporation, Waltham, Massachusetts). The bulk soil texture was loamy sand ($n = 3$), and the bulk soil organic carbon was $29.7 \pm 1.1 \text{ g C kg}^{-1}$ ($n = 6$).

The bulk soil was separated into 9 containers (2.4 l capacity). Subsamples were taken from each container ($n = 9$) for pre-incubation analysis prior to any P addition. Container soil masses were each adjusted to 2.365 kg. The experimental design included three replicates of a control, bone meal (BM) amendment, and triple super phosphate (TSP) amendment. BM (4-12-0) and TSP (0-46-0) (The Espoma Co., Millville, New Jersey) were added at a 5:1 P:Pb molar ratio. Both amendments contain Ca and P. The BM contains $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and TSP is $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. The amendment ratio was calculated assuming initial soil Pb concentration of $800 \text{ mg Pb kg}^{-1}$ and did not account for existing P in the soil. To their respective containers, 27.01 g BM and 7.07 g TSP were added. Additionally, 1.1825 g KCl were added to BM and TSP containers. This KCl addition followed the $500 \text{ mg of Cl kg}^{-1}$ rate used by Yang et al. (2001) to increase chloropyromorphite formation.

After the amendments were added and mixed, containers were subjected to three conditions. First, containers were watered with deionized water to allow the native soil pH to control soil solution chemistry. Second, containers were watered with 0.36 M HCl (3% v:v) (Fisher Scientific, CAS 7647-01-0) to reduce soil pH and increase Pb solubility. Third, soils were returned to a circumneutral pH using liming material and watered with deionized water. The process of acidifying and returning soils to circumneutral pH followed Ryan et al. (2004) and Yang et al. (2002). Soils were maintained at 25–30% gravimetric moisture content to ensure saturated soil and provide sufficient soil solution to react with PRS^{TM}-probes (Western Ag Innovations Inc., Saskatoon, Canada). After each treatment step, containers were air-dried, mixed, and approximately 100 g of soil was subsampled from each container for analysis.

Soil pH was allowed to stabilize prior to using the PRS^{TM}-probes in each of the described treatment steps. For example, containers were watered with 0.36 M HCl for 7 days prior to inserting the PRS^{TM}-probes for the second, acidic treatment step to allow soil pH to decrease. To raise the soil pH following the acidic condition, hydrated horticultural lime (7.5 g) (A.H. Hoffman Inc., Landisville, PA) was added to containers. Amendment rate was calculated by the amount of lime needed to neutralize the volume of 0.36 M HCl added to the containers. pH paper (pHydrion Vivid 1–11, Micro Essential Laboratory, Brooklyn, NY, US) verified soil water pH within the containers. The pH paper was placed directly into free water on the soil surface in the containers. At the conclusion of the 3% HCl acidic condition, pH paper indicated soil solution pH was 3–4. Following liming, pH paper indicated soil pH was pH 6–7.

During each of these treatment steps, 8 PRS^{TM}-probes were placed within each container, 4 anion probes and 4 cation probes. Containers were watered to maintain 25–30% gravimetric moisture content but not mixed while PRS^{TM}-probes were in place. Probes were kept in place for 5 days, after which probes were removed from each container, washed with deionized water, sealed in plastic bags, and stored in a refrigerator. PRS^{TM}-probes analytical blanks were prepared by following the same washing procedure. PRS^{TM}-probes were shipped to Western Ag Innovations (Saskatoon, SK, Canada) for analysis. The 2015 Western

Ag Innovations Student Research Award provided PRS™-probes for 30 samples, and these three treatment steps described above used all available PRS™-probes.

Two additional treatments were conducted as additional proof-of-concept steps to evaluate IVBA Pb changes by adding extra acid and extra P to containers. Soil pH was lowered further by watering containers with 25 ml of 12.1 M HCl, and 0.36 M HCl was used to maintain the 25–30% gravimetric moisture content. Following this application, soils were placed in a fume hood and allowed to react and dry for 2 weeks. Next, extra P was added to the containers at the same 5:1 P:Pb molar ratio used previously. This application took into consideration the mass of soil removed during subsampling, resulting in 22.95 g of Bone Meal and 5.98 g TSP being added. Soils were watered with 0.36 M HCl and allowed to react and dry for 9 days. Subsamples were collected in the same manner described above after each of these additional treatment steps. The total experiment, including days to transition containers between conditions, lasted 75 days.

Soil samples of the <2 mm fraction were analyzed for soil pH and electrical conductivity (EC) using a 1:2 soil:solution ratio. Soil pH was measured using an accumet pH probe (Fisher Scientific, Pittsburgh, PA) calibrated in pH 2.0, 4.0, 7.0, and 10.0 buffers. Soil electrical conductivity (EC) was measured using an ECTest® (Oakton Instruments, Vernon Hills, IL) calibrated with an 1414 $\mu\text{S cm}^{-1}$ Traceable® Conductivity Standard (Fisher Scientific). Soil solution EC in the 1:2 soil to solution ratio was converted to a soil paste EC by multiplying by 6. This multiplication factor was selected to avoid underestimating changes in EC due to treatments (Sonmez et al., 2008).

The <2 mm fraction samples were sieved to <250 μm and analyzed for total metal content using acid digestion following US EPA Method 3051a (US EPA, 2007) and a CEM-MARS 5 (CEM Corporation, Matthews, North Carolina). Bioaccessible Pb was evaluated using US EPA Method 1340 (US EPA, 2013) and a physiologically based extraction test (PBET) using pH 2.5 extracting solution (Attanayake et al., 2014). NIST 2711a (Montana II Soil) was used as a quality control soil. IVBA Pb was calculated by taking the in vitro method extractable Pb divided by the US EPA Method 3051a Pb. All soil solutions were analyzed with ICP-OES (Varian 720, Varian, Inc., Australia).

Samples of the <250 μm fraction were pelletized and Pb L-edge XAS spectra were recorded at the Materials Research Collaborative Access Team's (MRCAT) beamline 10-ID at the Advanced Photon Source (APS), Argonne National Laboratory (ANL), Argonne, IL (Segre et al., 2000). The electron storage ring operated at 7 GeV in top-up mode. A liquid nitrogen-cooled double-crystal Si(111) monochromator was used to select incident photon energies, and a platinum coated mirror was used for harmonic rejection. The reference signal from a lead metal foil was collected congruently with each sample scan to correct for energy drifts. Five XAS scans were collected for each sample in transmission mode and fluorescence mode using a four-element silicon drift detector.

A total of 25 Pb standards were analyzed to facilitate linear combination fitting (LCF) of the sample spectra to investigate the likely Pb mineral forms in the samples. Principal

component analysis and target transformation were conducted using Athena (Ravel and Newville, 2005) as described by Gräfe et al. (2014).

To check for potential dissolved carbon interference with Pb phosphate formation, samples of the <250 μm fraction were analyzed from the following three treatment steps: watering with deionized water, watering with 0.36 M HCl, and following the final extra P + 0.36 M HCl. Samples were extracted following the 5:1 water:soil extraction solution ratio and 1 h shaking recommended by Jones and Willett (2006). Five g of soil and 25 g of deionized water were shaken on a reciprocating shaker for 1 h, centrifuged, and filtered through 0.45 μm nylon filters. Five ml of each solution was analyzed using the extraction solution of Heanes (1984) and the associated microwave and spectrophotometer instrumentation mentioned previously. Dissolved organic carbon values were reported on a mg l^{-1} basis to allow comparison with data from Lang and Kaupenjohann (2003).

Data were analyzed using Minitab (v. 16, State College, PA), Microsoft Excel (v. 2010, Redmond, WA) and SigmaPlot (v. 12.5, San Jose, CA). ANOVAs were conducted using Minitab to evaluate PRS^{TM}-probe data results regarding Pb solubility and the in vitro results. In vitro results were analyzed using a general linear model with IVBA Pb as the response variable, fixed factors of experimental condition (i.e. neutralized soil pH, extra acid, extra P), in vitro test (US EPA 1340 or PBET for a specific soil treatment), and the interaction condition*in vitro test. Pairwise comparisons were analyzed by condition*in vitro test. For these ANOVAs, posthoc Tukey Honest Significant Difference was computed using a confidence level of 0.95. Dissolved organic carbon data were analyzed using experimental condition, type of amendment added, and the interaction between experimental condition*amendment type.

3. Results and discussion

3.1. In vitro methods QA/QC

NIST 2711a IVBA Pb in the pH 1.5 solution (US EPA, 2013) was $88.4\% \pm 0.02$ and in the pH 2.5 PBET solution (Attanayake et al., 2014) was $50.2\% \pm 0.01$. Both calculations used $1300 \text{ mg Pb kg}^{-1}$ for NIST 2711a total soil Pb (US EPA, 2013). IVBA Pb from 2711a in pH 1.5 with 0.4 M extracting solution was within acceptable limits (US EPA, 2013). Final solution pH for in vitro extractions remained within 0.5 pH units of pH 1.5 or 2.5. This 0.5 pH range is the currently acceptable range for the pH 1.5 extraction (US EPA, 2013). Variability in final extracting solution pH is an important consideration when evaluating IVBA Pb (Obrycki et al., 2016).

3.2. Treatment results

The pre-incubation subsamples had an IVBA Pb of $77\% \pm 2\%$ ($n = 9$) in the pH 1.5, 0.4 M glycine solution and $38\% \pm 1\%$ in the pH 2.5 PBET solution. No decrease for IVBA Pb was observed in either the BM or TSP treated soils for either in vitro extraction (Fig. 1). Treatments did not reduce soil Pb ingestion hazard as indicated by the general linear model results for interaction terms (condition*in vitro test) for US EPA 1340 ($p = 0.342$) or PBET

($p = 0.073$). As shown in Fig. 1, IVBA Pb had a slight, but not statistically significant, increase across the three conditions.

The initial soil total metal concentrations in the containers ($n = 9$) for the $<250 \mu\text{m}$ fraction was Pb $726 \pm 14 \text{ mg kg}^{-1}$, P $1315 \pm 10 \text{ mg kg}^{-1}$, and Ca $7525 \pm 55 \text{ mg kg}^{-1}$. Prior to adding any P amendments, all containers had similar total P:Pb molar ratios (Table 1). Amendments were effective in increasing total soil P:Pb molar ratios relative to the control soil (Table 1), as seen in samples analyzed following the neutralization, extra acid, and extra P treatment conditions. The increase in soil P:Pb molar ratios in the BM treated soils following adding 12.1 M HCl could be indicative of increased dissolution under the more concentrated HCl treatment, allowing the amendment to become more distributed in the soil. The Ca:P molar ratio for the BM soil following the 12.1 M HCl treatment step also increased, which supports this finding because bone meal contains Ca.

Soil pH measurements on the air dried samples indicated treatments reduced soil pH, raised it back to circumneutral, and acidified the soils again (Table 2). Soil water pH was between 3 and 4 during the 0.36 M HCl acidification condition when checked with pH paper. The pH increased to pH 6.5–6.7 upon air drying post-incubation, indicating the soil was able to buffer these pH changes. As the experiment progressed, the soils would be classified as strongly saline ($>16 \text{ mS cm}^{-1}$) by the US National Soil Survey Handbook (USDA NRCS, no date). This finding raises questions regarding the effectiveness of acidifying soils using this study's methods when the resulting soils may be too saline to support general plant growth. The incubation containers were not able to drain which could have led to a buildup of salts.

PRST^{TM}-probe data indicated the P amendments and varied pH conditions were effective in changing soil solution chemistry. Under 0.36 M HCl acidic conditions, the PRST^{TM}-probe data detected soluble Pb increased by at least a factor of 10 for control and treated soils compared to the other circumneutral conditions (Table 3) ($p < 0.001$). Within the 0.36 M HCl acidic conditions, the PRST^{TM}-probe data indicated the control soil had 2-fold more soluble Pb compared to amended soils (Table 3) ($p < 0.001$). There were no differences in soluble Pb between soils at initial soil pH and soils neutralized with lime following acidification. The difference in soluble Pb during the 0.36 M HCl acidic condition between treated and untreated soils (Table 3) is similar to the results from Strawn et al. (2007), in which P treatments reduced Pb solubility relative to untreated control soils. This could potentially be due to increased Pb sorption with the P amendments (Basta et al., 2005).

The amended soils had more total P than the control soils (Table 1) and should have more P available to react with the increased soluble Pb during the acidification process. PRST^{TM}-probe measured P in the TSP treated soils increased 10-fold compared to the control and bone meal treated soils during 0.36 M HCl conditions (Table 3) ($p < 0.001$). The PRST^{TM}-probes did not detect an increase in soluble P for the BM treated soils under acidic conditions. PRST^{TM}-probe detected Ca was not as affected by the pH changes as P and Pb as seen by the coefficients of variation across all PRST^{TM}-probe data. The coefficient of variation across all Ca samples and conditions was 13%, compared to 191% for all P data, and 147% for all Pb data. Detected Ca tended to be higher in the control soils compared to the treated soils, which could potentially be due to PRST^{TM}-probe ion exchange resin competition

amongst the increased soil solution cations in the treated soils. Geochemical modeling using Visual Minteq showed saturation and potential formation of several Ca, Mn, and Pb phosphate minerals.

The XAS results (Fig. 2) did not indicate an increase in Pb phosphate formation comparable to other studies when 15.4 P:Pb mol ratios caused 45% pyromorphite formation above untreated controls (Ryan et al., 2004). Pb carbonate, Pb sorbed hydroxyapatite (HAP), and $\text{Pb}_3(\text{PO}_4)_2$ (data not shown) were unchanged across all incubation conditions. Pb carbonate varied between 10 and 20%, Pb sorbed hydroxyapatite (HAP) varied between 0 and 12%, and $\text{Pb}_3(\text{PO}_4)_2$ varied between 0 and 7%. These three Pb mineral forms did not demonstrate increasing or decreasing trends across the experimental conditions. Presented results are single replicates collected from a control, BM, or TSP container following each of the incubation conditions for pyromorphite, mineral sorbed Pb, and organic bound Pb. Three replicates of subsamples collected prior to adding any P amendments were also analyzed to evaluate pre-incubation Pb mineral forms. Fig. 2 suggests the TSP treated soil had pyromorphite formation increase 10% over initial soil samples. Additionally, Fig. 2 suggests the mineral sorbed Pb in the TSP treated soil decreased 19% compared to initial TSP samples. These data suggest some mineral sorbed Pb transitioned to pyromorphite. Bone meal treated soils and the control soil did not demonstrate this same treatment effect. As the mineral sorbed Pb remained constant throughout the treatment conditions, this may indicate Pb solubility remained limiting, even as soil pH decreased. Obrycki et al. (2016) reported TSP was more effective than BM in reducing IVBA Pb and pyromorphite formation for the non-acidified soil in this study. Mineral sorbed Pb remained the dominant XAS identified Pb form throughout the experiment. XAS results suggest organic bound Pb decreased in control and BM treated soils by 5–10%, and increased 8% in TSP treated soils. However, as shown in Fig. 2, the absolute difference in the three preincubation replicates was approximately 15%. Given this normal variation seen in XAFS fitting using LCF, the above note percentages are suggested only. The speciation data suggest a potential trend may have occurred with regard to the TSP treated soils.

If Pb phosphates were forming at the 45% rate seen by Scheckel et al. (2005), including pyromorphite, the soils analyzed using PBET pH 2.5 (Attanayake et al., 2014) (Fig. 1) would be more likely to demonstrate a treatment effect. As discussed above, this pH level has more pronounced IVBA Pb effects when compared to pH 1.5 extractions (Scheckel et al., 2005). Comparisons between Figs. 1 and 2 demonstrate though the XAS data suggest some alterations in Pb mineral forms, these differences were not substantial enough to cause detectable changes in Pb solubility using in vitro extractions. These results suggest the soils may have been P limited, as the final extra P treatment added to the TSP container led to a potential increase in pyromorphite formation.

Dissolved organic carbon increased across the three tested treatment steps (Table 4), but remained similar across containers (control, BM, TSP) within each treatment step. Two-way ANOVA indicated dissolved organic carbon differed only by treatment step ($p < 0.0001$) and not by treatment ($p = 0.51$) or sample*treatment step ($p = 0.56$). Values remained below the 72 mg C l^{-1} value from Lang and Kaupenjohann (2003) that demonstrated approximately 10,000 fold higher soluble Pb compared to pure solutions without dissolved C. Given the

similarities in dissolved organic carbon within each treatment step, dissolved organic carbon was not differentially affecting the containers in potential for Pb chelation.

4. Implications

When the results from Ryan et al., 2004, Yang et al., 2001, Yang et al., 2002 using a smelter waste soil are compared to the results in this current study, a similar P:Pb ratio was unable to lead to a similar decrease in IVBA Pb. However, the previous studies added soluble P to the soil system and this current study utilized solid P amendments. In both this study's soil and the smelter waste soil, excessive Ca relative to P may have been reducing Pb phosphate formation. Prior to P amendments, the smelter waste contained 4361 ± 24 mg Pb kg⁻¹, P:Pb molar ratio of 0.9, and a Ca:P molar ratio of 15.8 (Yang et al., 2001). Reductions in IVBA Pb following P treatments started to occur at a Ca:P molar ratio of 2.07 (5000 mg P kg⁻¹), but it was the 15.4 P:Pb mol ratio (10,000 mg P kg⁻¹, 1.03 Ca:P) that caused the reported reductions in IVBA Pb (Ryan et al., 2004, Yang et al., 2001). Treatment effects were found once the Ca:P molar ratio was 1.67, the modeled threshold value from Porter et al. (2004).

The soil used in this current study had a higher P:Pb molar ratio (12.2 in untreated control) and a lower Ca:P molar ratio (4.4 in untreated control) compared to the smelter waste (Table 1), indicating the soil may be a more suitable candidate for lower P application rates. Soil amendments increased the P:Pb mol ratio above 15.4:1. Increased total P did not always lead to increased soluble P (Table 3). Under acidic conditions, only TSP treated soils had an increase in P to react with Pb and theoretically form chloropyromorphite. These results indicate the soil pH in this study may not have been low enough to dissolve sufficient P to react with Pb. However, the smelter waste soil had 6-fold higher Pb content compared to this study's soils (4361 ± 24 mg Pb kg⁻¹ vs. 726 ± 14 mg kg⁻¹). When soils were acidified, the smelter waste soil likely had higher soluble Pb concentrations available to react with P. As discussed in the introduction, Ryan et al. (2001) noted soluble Pb is the rate limiting step for Pb phosphate formation. Depending upon the Pb minerals present in the soil that are required to dissolve prior to this formation, Pb mineral solubility increases approximately 1000 fold between pH 6 and pH 4, demonstrating the importance of reducing soil pH for Pb solubility (Hettiarachchi and Pierzynski, 2004).

Other urban soils could have similar Pb, Ca, and P concentrations compared to this study's soil from Cleveland, OH. Potential Pb remediation treatments could use non-Ca containing P amendments (ammonium and potassium phosphates) at rates which could reduce Ca and P competition and ensure sufficient P is available to react with Pb. These amendments would need to be readily soluble, and even under acidic conditions the bone meal did not increase the PRS^{TM}-probe measured P. Most commonly available liming materials contain Ca, which could serve as an additional sink for P.

Liming materials may contain CaO (quick lime), the addition of could interfere with pyromorphite formation (Porter et al., 2004). However, Chappell and Scheckel (2007) found in a pure system, CaO may have enhanced pyromorphite formation. These results highlight the importance of addressing x-ray methodological issues associated with identifying Pb minerals and the challenges from applying theoretical modeled data to empirical situations

(Chappell and Scheckel, 2007). Calcareous, Pb contaminated urban soils could be difficult to treat with low P amendment rates due to the excess Ca. P treatment options for urban soils deserves future study.

As discussed previously, many other soil constituents other than Ca could interact with P amendments. In mining waste soils, Fe rather than Ca was more likely a competitive sorption site for P (Strawn et al., 2007). These mining wastes contained 3560–5180 mg Pb kg⁻¹ and 40,200–84,800 mg Fe kg⁻¹. Soils were amended with 1% (10,000 mg P kg⁻¹) P which achieved an approximate 13–18.8 P:Pb mol ratio and a 2.2–4.7 Fe:P mol ratio (Strawn et al., 2007). These treatments did not lead to increased Pb phosphate formation, and instead the added P formed associations with Fe (Strawn et al., 2007). At a different mining waste site, elevated Zn could have interacted with added P and reduced Pb phosphate formation (Brown et al., 2007). Amendment rates of 10,000 mg P kg⁻¹ and 30,000 mg P kg⁻¹ were added to the mining waste tailings (Brown et al., 2007).

The addition of both Ca and P as a treatment for Pb contaminated soils has been suggested as a treatment to reduce soluble Pb and plant uptake Pb (Li et al., 2014). Li et al. (2014) used a spiked 500 mg Pb kg⁻¹ soil and applied P and Ca to encourage Pb phosphate formation. The proportions of Pb mineral forms in the soils changed less than 15% relative to the control soil (Li et al., 2014). The findings from Li et al. (2014) highlight potential difficulties in using Ca and P as co-amendments to modify Pb mineral forms. Additionally, the use of spiking solutions may affect the Pb minerals forms when compared to non-spiked Pb contaminated soils studies.

Soil solution chemistry must be evaluated prior to widespread recommendations for P amendments in urban areas to reduce Pb bioaccessibility. Multiple soil constituents should be considered beyond solely considering the soil P:Pb ratio. Future studies should evaluate soil solution components, particularly Ca and P, in other Pb contaminated urban soils as the Ca:P mol ratio may be a limiting factor for Pb phosphate formation. These urban soils may have Pb contaminant levels below the several thousand mg Pb kg⁻¹ encountered in industrial wastes. If acidification is used as a treatment step to increase Pb solubility, amendments must supply sufficient P to react with the Pb. These evaluations will be useful to identify soils which may be potential successful remediation candidates and which soils may require other treatment options, such as capping or removal.

5. Conclusion

The in vitro results indicated no reduction in IVBA Pb during the experiment. The XAS results indicated limited increase in pyromorphite for TSP treated soils only. Experimental conditions did change soil solution chemistry as indicated by PRS^{TM}-probe data. Acidic conditions increased soluble Pb 10-fold over circumneutral pH conditions. Bone meal amendment did not increase soluble P under acidic conditions. Triple super phosphate amendment increased PRS^{TM}-probe detected P 10-fold over untreated soils. Total elemental soil analysis indicated P:Pb molar ratios of over 30:1, in excess of previously effective molar ratios for reducing IVBA Pb. These multiple lines of evidence, in the context of previously published literature, suggest soil solution chemistry could be interfering with pyromorphite

formation. PRS^{TM}-probes indicated soil solution Ca was a potential interfering cation. This study demonstrated PRS^{TM}-probes could be used for in situ monitoring of the soil solution to identify if P amendments are increasing soluble P as they are intended. Applying sufficient P for favorable Pb reactions to occur, while reducing water runoff problems, is a challenge for remediating Pb contaminated soils. Competing soil solution constituents may limit widespread use of P treatments on soils with similar characteristics to reduce in vitro Pb hazard. This study identified this potential issue in one urban soil, and future research across many soil types is necessary to document the extent of this potential issue.

Funding

PRSTM-probe analysis supported by a 2015 Western Ag Innovations Student Research Award. Other support included partial salary for N.T. Basta by state and federal funds appropriated to the Ohio Agricultural Research and Development Center (USDA NIFA OHO01336), The Ohio State University, Columbus, OH, 43210. Other support included graduate student support for J.F. Obrycki from The Ohio State University, Columbus, OH, 43210 through a Distinguished University Fellowship, Ohio Agricultural Research and Development Center College of Food, Agricultural, and Environmental Sciences Graduate Research Fellowship, and School of Environment and Natural Resources funding.

Abbreviations

ANOVA	Analysis of Variance
IVBA	in vitro bioaccessible
PRS^{TM}	plant root simulator
US EPA	United States Environmental Protection Agency
USDA NRCS	United States Department of Agriculture Natural Resources Conservation Service
XAS	X-ray absorption spectroscopy

References

- Attanayake CP, Hettiarachchi GM, Harms A, Presley D, Martin S, Pierzynski GM. Field evaluations on soil plant transfer of lead from an urban garden soil. *J. Environ. Qual*, 43 (2) (2014), pp. 475–487. [PubMed: 25602649]
- Basta NT, McGowen SL. Evaluation of chemical immobilization treatments for reducing heavy metal transport in a smelter-contaminated soil. *Environ. Pollut*, 127 (2004), pp. 73–82. [PubMed: 14553997]
- Basta NT, Ryan JA, Chaney RL. Trace element chemistry in residual-treated soil: key concepts and metal bioavailability. *J. Environ. Qual*, 34 (2005), pp. 49–63. [PubMed: 15647534]
- Binns HJ, Campbell C, Brown MJ. Interpreting and managing blood lead levels of less than 10 µg/dL in children and reducing childhood exposure to lead: recommendations of the Centers for Disease Control and Prevention advisory committee on childhood lead poisoning prevention. *Pediatrics*, 120 (5) (2007), pp. e1285–e1298. [PubMed: 17974722]
- Brown SL, Compton H, Basta NT. Field Test of *In Situ* Soil Amendments at the Tar Creek National Priorities List Superfund Site. *J. Environ. Qual*, 36 (2007), pp. 1627–1634. [PubMed: 17940262]
- Cao X, Ma LQ, Chen M, Singh SP, Harris WG. Impacts of phosphate amendments on lead biogeochemistry at a contaminated site. *Environ. Sci. Technol*, 36 (24) (2002), pp. 5296–5304. [PubMed: 12521153]

- Chappell MA, Scheckel KG. Pyromorphite formation and stability after quick lime neutralization in the presence of soil and clay sorbents. *Environ. Chem*, 4 (2007), pp. 109–113.
- Essington ME. *Soil and Water Chemistry: An Integrative Approach*. CRC Press, Boca Raton (2004).
- Fisher MM, Reddy KR. Soil pore water sampling methods DeLaune RD, Reddy KR, Richardson CJ, Megonigal JP (Eds.), *Methods in Biogeochemistry of Wetlands*. SSSA Book Series 10, SSSA, Madison, WI (2013), pp. 55–70.
- Gräfe M, Donner E, Collins RN, Lombi E. Speciation of metal(loid)s in environmental samples by X-ray absorption spectroscopy: a critical review. *Anal. Chim. Acta*, 822 (2014), pp. 1–22. [PubMed: 24725743]
- Heanes DL. Determination of total organic- C in soils by an improved chromic acid digestion and spectrophotometric procedure. *Commun. Soil Sci. Plan*, 15 (10) (1984), pp. 1191–1213.
- Hettiarachchi GM, Pierzynski GM. Soil lead bioavailability and in situ remediation of lead-contaminated soils: a review. *Environ. Prog*, 23 (1) (2004), pp. 78–93.
- Jones DL, Willett VB. Experimental evaluation of methods to quantify dissolved organic nitrogen (DON) and dissolved organic carbon (DOC) in soil. *Soil Biol. Biochem*, 38 (2006), pp. 991–999.
- Kettler TA, Doran JW, Gilbert TL. Simplified method for soil particle-size determination to accompany soil-quality analyses. *Soil Sci. Soc. Am. J*, 65 (2001), pp. 849–852.
- Lang F, Kaupenjohann M. Effect of dissolved organic matter on the precipitation and mobility of the lead compound chloropyromorphite in solution. *Eur. J. Soil Sci*, 54 (2003), pp. 139–147.
- Li L, Scheckel KG, Zheng L, Liu G, Zing W, Xiang G. Immobilization of lead in soil influenced by soluble phosphate and calcium: lead speciation evidence. *J. Environ. Qual*, 43 (2014), pp. 468–474. [PubMed: 25602648]
- Lindsay WA. *Chemical Equilibria in Soils*. John Wiley & Sons, New York (1979).
- Mielke HW, Covington TP, Mielke PW, Wolman FJ, Powell ET, Gonzales CR. The New Orleans lead-safe childcare playground project. *Environ. Pollut*, 159 (2011), pp. 2071–2077. [PubMed: 21131114]
- Obrycki JF, Basta NT, Scheckel KG, Stevens BN, Minca KK. Phosphorus amendment efficacy for in situ remediation of soil lead depends on the bioaccessible method. *J. Environ. Qual*, 45 (1) (2016), pp. 37–44. [PubMed: 26828158]
- Osborne LR, Baker LL, Strawn DG. Lead immobilization and phosphorus availability in phosphate-amended, mine-contaminated soils. *J. Environ. Qual*, 44 (1) (2015), pp. 183–190. [PubMed: 25602333]
- Porter SK, Scheckel KG, Impellitteri CA, Ryan JA. Toxic metals in the environment: thermodynamic considerations for possible immobilization strategies for Pb, Cd, As, and Hg. *Crit. Rev. Environ. Sci. Technol*, 34 (2004), pp. 495–604.
- Qian P, Schoenau JJ. Practical applications of ion exchange resins in agricultural and environmental soil research. *Can. J. Soil Sci*, 82 (2002), pp. 9–21.
- Ravel B, Newville M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat*, 12 (4) (2005), pp. 537–541. [PubMed: 15968136]
- Ryan JA, Zhang P, Hesterberg D, Chou J, Sayers DE. Formation of chloropyromorphite in a lead-contaminated soil amended with hydroxyapatite. *Environ. Sci. Technol*, 35 (2001), pp. 3798–3803. [PubMed: 11783662]
- Ryan JA, Scheckel KG, Berti WR, Brown SL, Casteel SW, Chaney RL, Hallfrisch J, Doolan M, Grevatt P, Maddaloni M, Mosby D. Reducing children's risk from lead in soil. *Environ. Sci. Technol*, 38 (1) (2004), pp. 18A–24A.
- Scheckel KG, Ryan JA, Allen D, Lescano NV. Determining speciation of Pb in phosphate-amended soils: method limitations. *Sci. Total Environ*, 350 (2005), pp. 261–272. [PubMed: 16227085]
- Scheckel KG, Diamond GL, Burgess MF, Klotzbach JM, Maddaloni M, Miller BW, Partridge CR, Serda SM. Amending soils with phosphate as means to mitigate soil lead hazard: a critical review of the state of the science. *J. Toxicol. Env. Heal. B*, 16 (6) (2013), pp. 337–380.
- Segre CU, Leyarovska NE, Chapman LD, Lavender WM, Plag PW, King AS, Kropf AJ, Bunker BA, Kemner KM, Dutta P, Duran RS, Kaduk J. The MRCAT insertion device beamline at the advanced

- photon source Pianetta P, et al. (Eds.), CP521 Synchrotron Radiation Instrumentation: Eleventh U.S. National Conference, American Institute of Physics, New York (2000), pp. 419–422.
- Smith DB, Cannon WF, Woodruff LG, Solano F, Kilburn JE, Fey DL. Geochemical and mineralogical data for soils of the conterminous United States: U.S. Geological Survey Data Series (2013). 801, 19 pp. <http://pubs.usgs.gov/ds/801/> accessed 14.04.16.
- Sonmez S, Buyuktas D, Okturen F, Citak S. Assessment of different soil to water ratios (1:1, 1:2.5, 1:5) in soil salinity studies. *Geoderma*, 144 (2008), pp. 361–369.
- Strawn DG, Hickey P, Knudsen A, Baker L. Geochemistry of lead contaminated wetland soils amended with phosphorus. *Environ. Geol*, 52 (2007), pp. 109–122.
- Thibault DH, Sheppard MI. A disposable system for soil pore-water extraction by centrifugation. *Commun. Soil. Sci. Plant Anal*, 23 (13&14) (1992), pp. 1629–1641.
- US EPA. Method 3051A Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils SW-846 Hazardous Waste Test Methods. US EPA (2007). <https://www.epa.gov/sites/production/files/2015-12/documents/3051a.pdf> accessed 30.06.16.
- US EPA. Method 1340 In Vitro Bioaccessibility Assay for Lead in Soil SW-846 Hazardous Waste Test Methods. US EPA (2013). <https://www.epa.gov/sites/production/files/2015-12/documents/1340.pdf> accessed 30.06.16.
- USDA NRCS. No date. National soil survey handbook, title 430-VI. Available online. http://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/ref/?cid=nrcs142p2_054242 (accessed 2 December 2015).
- Weber JS, Goynes KW, Luxton TP, Thompson AL. Phosphate treatment of lead- contaminated soil: effects on water quality, plant uptake, and lead speciation. *J. Environ. Qual*, 44 (2015), pp. 1127–1136. [PubMed: 26437094]
- Withers PJ, Sharpley AN. Phosphorus fertilizers Reheigl JE (Ed.), *Soil Amendments and Environmental Quality*, CRC press, Boca Raton, FL (1995), pp. 65–107.
- Wolt JD. *Soil Solution Chemistry: Applications to Environmental Science and Agriculture*. John Wiley & Sons, New York (1994).
- Yang J, Mosby DE, Casteel SW, Blanchar RW. Lead immobilization using phosphoric acid in a smelter-contaminated urban soil. *Environ. Sci. Technol*, 35 (2001), pp. 3553–3559. [PubMed: 11563662]
- Yang J, Mosby DE, Casteel SW, Blanchar RW. In vitro lead bioaccessibility and phosphate leaching as affected by surface application of phosphoric acid in lead- contaminated soil. *Arch. Environ. Contam. Toxicol*, 43 (2002), pp. 399–405. [PubMed: 12399910]

Fig. 1.
In vitro bioaccessible pb using US EPA Method 1340 and PBET pH 2.5 solution
(Attanayake et al., 2014).

Fig. 2.
X-ray absorption spectroscopy identified Pb forms in soils.

Table 1 Mol ratios for <250 μm samples based on total element concentrations.

	Treatment	n	Condition ^a			
			Initial	Lime + DI water	Extra acid	Extra P + 0.36 M HCl
P:Pb	Control	3	12.2 $\pm$ 0.2	12.3 $\pm$ 0.3	12.5 $\pm$ 0.3	12.5 $\pm$ 0.2
	TSP	3	11.9 $\pm$ 0.7	21.3 $\pm$ 0.2	21.2 $\pm$ 0.5	33.6 $\pm$ 3.1
	Bone meal	3	12.3 $\pm$ 0.2	16.7 $\pm$ 0.5	20.6 $\pm$ 0.1	31.1 $\pm$ 1.1
Ga:P	Control	3	4.4 $\pm$ 0.0	5.1 $\pm$ 0.1	7.1 $\pm$ 0.1	7.0 $\pm$ 0.3
	TSP	3	4.4 $\pm$ 0.0	3.3 $\pm$ 0.1	4.4 $\pm$ 0.1	2.8 $\pm$ 0.2
	Bone Meal	3	4.4 $\pm$ 0.0	4.1 $\pm$ 0.1	5.0 $\pm$ 0.1	3.9 $\pm$ 0.1

^aCondition: Initial-Subsample prior to incubation or adding any P; Lime + DI Water-Neutralized with horticultural lime and watered with deionized (DI) water; Extra acid-Watered with 0.36 M HCl + 12.1 M HCl; Extra P+0.36 M HCl-Extra 5:1 P:pb amendments added and watered with 0.36 M HCl.

Table 2

Soil pH and electrical conductivity (EC) across treatments and conditions.

	Treatment	n	Condition ^a					
			Initial	DI water	0.36 M HCl	Lime + DI water	Extra acid	Extra P + 0.36 M HCl
pH	Control	3	7.3 ± 0.0	7.8 ± 0.0	6.6 ± 0.1	7.6 ± 0.1	5.9 ± 0.3	5.6 ± 0.1
S.U.	TSP	3	7.3 ± 0.0	7.2 ± 0.0	6.5 ± 0.0	7.6 ± 0.0	5.9 ± 0.1	5.1 ± 0.2
	Bone Meal	3	7.3 ± 0.0	7.6 ± 0.0	6.7 ± 0.0	7.7 ± 0.1	6.3 ± 0.2	6.1 ± 0.1
EC	Control	3	1.2 ± 0.0	0.6 ± 0.0	17.6 ± 1.1	17.8 ± 3.3	59.2 ± 8.2	81.2 ± 6.0
mS cm ⁻¹	TSP	3	1.2 ± 0.0	3.0 ± 0.0	15.0 ± 1.0	13.4 ± 1.6	58.6 ± 5.4	74.8 ± 1.7
	Bone Meal	3	1.2 ± 0.0	2.6 ± 0.2	19.8 ± 4.3	18.0 ± 4.6	49.4 ± 7.1	83.4 ± 8.9

^aCondition: Initial-Subsample prior to incubation or adding any P; DI Water-Watered with deionized (DI) water; 0.36 M HCl-Watered with 0.36 M HCl; Lime + DI Water-Neutralized with horticultural lime and watered with DI; Extra Acid-Watered with 0.36 M HCl + 12.1 M HCl; Extra P + 0.36 M HCl Extra 5:1 P:Pb amendments added and watered with 0.36 M HCl.

Table 3

PRSTM-probe supply rates ($\mu\text{g}/10\text{cm}^2/5$ days] for Pb, P, and Ca across treatments and conditions.

	Treatment:	n	Condition ^b		
			DI water	0.36 M HCl	Lime + DI water
Pb ^a	Control	3	11.1 $\pm$ 0.9c	216.3 $\pm$ 10.9a	3.3 $\pm$ 0.2c
	TSP	3	8.6 $\pm$ 0.5c	106.8 $\pm$ 5.2b	1.9 $\pm$ 0.1c
	Bone Meal	3	4.1 $\pm$ 0.4c	90.7 $\pm$ 11.0b	1.0 $\pm$ 0.1c
P	Control	3	6.5 $\pm$ 0.6a	11.3 $\pm$ 0.5a	2.2 $\pm$ 0.2a
	TSP	3	19.7 $\pm$ 0.9a	134.7 $\pm$ 20.7b	6.3 $\pm$ 0.2a
	Bane Meal	3	10.8 $\pm$ 0.4a	3.6 $\pm$ 0.3a	3.3 $\pm$ 0.1a
Ca	Control	3	2194.2 $\pm$ 37.1a	1979.6 $\pm$ 43.2ab	1809.4 $\pm$ 7.9bc
	TSP	3	1997.2 $\pm$ 36.6ab	1599.0 $\pm$ 123.0cd	1674.7 $\pm$ 42.2cd
	Bone Meal	3	2015.4 $\pm$ 33.6ab	1506.5 $\pm$ 51.8d	1628.2 $\pm$ 7.3cd

^aLetters indicate statistically significant differences across treatments and conditions for each element at $P < 0.001$ using separate ANOVA with Tukey HSD using a 95% confidence interval for each individual element.

^bCondition: DI Water-Watered with deionized (DI) water; 0.36 M HCl,-Watered with 0.36 M HCl; Lime + DI Water-Neutralized with horticultural lime and watered with DI.

Table 4

Dissolved organic carbon extracted from <250 µm soil samples using 5:1 water:soil extraction.

	Treatment	n	Condition		
			DI water	0.36 M HCl	Extra P + 0.36 M HCl
Dissolved organic carbon (mg C l ⁻¹) ^a	Control	3	4.5 ± 0.4c	12.5 ± 1.7b	35.3 ± 7.4a
	TSP	3	4.8 ± 0.3c	11.4 ± 1.6b	36.6 ± 2.7a
	Bone Meal	3	5.9 ± 0.4c	12.0 ± 0.7b	44.4 ± 9.5a

^a Letters indicate statistically significant differences across treatments and conditions for each element at P < 0.001.