Use of Phosphates to Immobilize Lead in Community Garden Soils

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INTRODUCTION

The effectiveness of using phosphate-based compounds to immobilize lead (Pb) in soils is well established (Hettiarachchi and Pierzynski 2004). This technique is based on the observation that insoluble Pb compounds are produced after adding phosphates. For example, adding phosphate to lead-contaminated soils reduced water soluble Pb by 40-95% (Ma et al. 1995), gastro-intestinal available Pb in humans by 23-92% (Ruby et al. 1996; Ruby et al. 1999; Basta et al. 2001), and in feeding experiments, phosphate-amended soil significantly lowered Pb in rat tissue (Hettiarachchi et al. 2003).

Most of this work, however, was focused on lead immobilization using soils from mining and industrial sites and not garden soils (McGowen et al. 2001). In garden soils, the soil is typically rich in phosphorus and there is a continual phosphorus flux due to additions by fertilization and removal by plant uptake. Hettiarachchi and Pierzynski (2002) studied the influence of plant growth in lead-contaminated soils stabilized using phosphorus and manganese. They concluded that it was important to monitor the amount of phosphorus in the soil, since its removal by plants negated its capacity to reduce lead bioavailability. Conversely, excess levels of phosphorus added to the soil can: 1) damage plants by causing iron chlorosis (Smith 1988); 2) release arsenic (As) from the soil (Peryea and Kammereck 1997); and 3) be a major pollutant in watersheds (McDowell and Sharpley, 2001; Torrent and Delgado, 2001; Young and Ross, 2001; Maguire and Sims 2002).

In this study, we used EPA method 1312, the Synthetic Precipitation Leaching Procedure (SPLP), to predict the relative effectiveness of three types of phosphate, ranging from soluble to highly insoluble (Sodium Dihydrogen Phosphate (NaP), Triple Super Phosphate (TSP) and Rock Phosphate (RP)) to bind lead in garden soils.

PROCEDURE

Eight soil sets were used in this study, 5 from Connecticut community gardens (CG1-CG5), one from soil contaminated with lead arsenate, one from a soil contaminated with CCA leachate (a wood preservative containing copper, chromium and arsenic) (Stilwell and Gorny, 1997), and one uncontaminated farm soil from Lockwood Farm in Hamden, CT. The soils were dried and passed through a 2 mm sieve prior to use. For each sample, 40 g of dry soil was weighed into a 120 ml plastic container, the P amendments were then added at 0, 0.1, 0.5 percent by weight total P and mixed in the container, prior to adding 10-15 ml of distilled water (to approximate 90% water holding capacity). The soil/water mixture was stirred using a glass rod to keep the soil from compacting and then the moist soil was placed into uncovered 50ml polypropylene tubes. In two cases (CG2 and CG5), insufficient sample dictated use of 30 g (CG2), and 20 g (CG5) of soil, and all subsequent water and phosphorus additions were adjusted accordingly. The soils were kept in the open air and water was added weekly to account for evaporation, as monitored by total weight. After 60 days of aging the soils were dried at 60 ºC. Each trial was run in duplicate.

The phosphorus compounds were Sodium Dihydrogen Phosphate, ($NaH_2PO_4H_2O$, Analytical Grade, Fisher Scientific), Triple Super Phosphate, TSP, ($Ca(H_2PO_4)_2H_2O$, Kirby Agriculture, Lancaster PA), and Rock Phosphate, RP, ($Ca_3(PO_4)_2$, Espoma Co., Millville, NJ). Rock phosphate (RP) is a naturally occurring mineral containing calcium phosphate ($Ca_3(PO_4)_2$), which is highly insoluble in water and, therefore, the phosphorus is not readily available to plants (Merck 1983). Consequently, fertilizer manufacture's add phosphoric acid to the RP, forming TSP (Merck 1983). In this form, the phosphorus is more soluble and plant available (40-50% available as P_2O_5). The phosphate in the NAP is freely soluble in water (Merck 1983). The amount of each amendment to equal 0.1%, and 0.5% P was based on a calculated %P of 22.4% in the $NaH_2PO_4H_2O$ (NAP), and on triplicate analysis (see below) of the P content in the RP (7.7 ± 1.5% P), and in the TSP (21.1 ± 0.5 % P). For example, in 40g of soil 0.53g of RP, or 0.19g TSP, or 0.18g of NAP was used to equal 0.1% added P.

The amounts of As, P and Pb in soil extracts were obtained using EPA method 1312, the Synthetic Precipitation

Leaching Procedure (Townsend et al. 2002). This method is used to predict the potential for pollutants, including phosphates and heavy metals such as Pb, to leach into surface and ground waters after rain events. To account for the difference in rainwater pH, the SPLP solution pH is 5.00 for tests conducted west of the Mississippi River, and 4.20 east of the river. The pH is adjusted using a mixture of 60/40 % by weight sulfuric and nitric acid and a 20:1 liquid/solid mixture is shaken for 18 hours. Thus, following this procedure, 1.5±0.02 g dry soil were weighed, in duplicate, into 50 ml polypropylene centrifuge tubes, 30 ml of extraction fluid was added to each sample, the mixture was shaken for 18 hours using a Wrist Action Shaker (Burrell 75, Pittsburgh, PA), and centrifuged at 3000 rpm for 10 minutes. The supernatant was filtered through a 1 micron syringe filter (Puradisc, Whatman), 25 ml portions were transferred to polypropylene containers and 2.5 ml of concentrated nitric acid was added to each sample. Thus, for each of the 8 soil sets, 28 extracts were obtained for analysis: two from each duplicate soil sample with no added P (total of 4), 2 from each duplicate of the 3 amendments at 0.1% added P (2x2x3=12) and 2 from each duplicate at 0.5% added P (2x2x3=12).

The As, P and Pb in the acidified extracts were determined by atomic spectroscopy using a TJA Atom Scan 16 (Thermo Fisher Scientific) inductively coupled plasma atomic emission spectrometer (ICP-AES). To adjust for the acid addition, a dilution factor of 1.1 was entered into the raw data. To calculate the fraction extracted, the SPLP solution concentration/soil concentration was multiplied by 20 to account for the solution to soil ratio (30 ml solution, 1.5 g soil). The total amount of inorganic analytes in the soil was determined in triplicate by ICP-AES after digestion of 0.5g samples in 50 ml tubes using concentrated nitric acid and a hot block digester (Stilwell et al. 2008). The procedure is summarized in the flowchart below (Figure 1).

Figure 1. Outline of Experimental Conditions.

(I) Soil set (n-8) sieved 2mm or less

(II) for each soil set, weigh 20-40g of soil into 14 containers, keep 2 as is, add amendments at the 0.1% and 0.5% levels, in duplicate to the remaining 12 containers, mix, add water, mix, transfer into 50ml tubes (14 per soil set, times 8 soil sets =112 test soils)

(III) Age 60 days in open air. Add water weekly to maintain 90% water holding capacity

(IV) Dry, weigh 1.5 g (in duplicate), extract SPLP solution, filter, acidify (n=28 per soil set, times 8 soil sets 224= extracts).

(V) Analyze for As, P, and Pb by IC-OES

RESULTS AND DISCUSSION

Soil Analysis

Shown in Table 1 is the soil pH and the average amounts of Pb, As and P in the soils, prior to amendments. The community garden soils were selected for their high Pb content with a wide range in P content.

TABLE 1. Average and Standard Deviation of As, P, and Pb (mg/kg) in the soil samples.

	pH	Pb			As			P		
CG1	6.4	480	±	49	2.9	±	0.6	586	±	16
CG2	5.2	879	±	8	11	±	2	1558	±	74
CG3	6.8	1060	±	45	4.5	±	0.04	546	±	9
CG4	6.5	1273	±	279	5.2	±	0.4	1009	±	83
CG5	5.8	6474	±	368	10.4	±	0.3	956	±	27
FS	5.4	32	±	2	4	±	2	945	±	5
PBAS	4.9	255	±	26	30	±	1.4	1096	±	72
CCA	4.3	198	±	2	168	±	20	572	±	6

CG- Community Garden Soils
FS- Farm Soil
PBAS- Lead Arsenate Contaminated Soil
CCA- Soil Composite Under CCA Pressure Treated Decks

Lead and Phosphorus in SPLP Extracts of Unamended Soils.

Shown in Figure 2 is the SPLP Pb versus the soil Pb in unamended soils. From the data in Figure 2 the best fit line (fixing the origin equal to zero) is: $[Pb]_{in\ solution} = 0.0003*[Pb]_{in\ soil}$ ($R^2=0.944$). Using this equation we calculate a threshold soil Pb content of 50 ppm based on the suggested limit of 0.015 ppm Pb (0.015/0.0003=50) in the SPLP solution (Hardison Jr. et al. 2004). This threshold concentration should be compared with the background level of 10-20 ppm Pb in uncontaminated US soils (Holmgrem et al. 1993, Frink 1996). It is also much lower than the 400 ppm Connecticut limit for Pb in residential soils (State of CT. 1996).
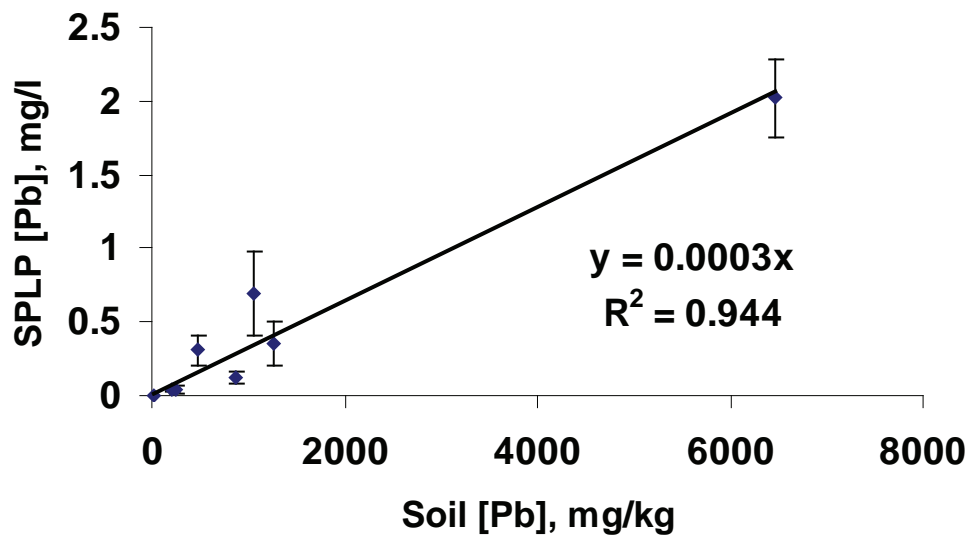

$$y = 0.0003x$$
$$R^2 = 0.944$$

Figure 2. SPLP Pb in solution (mg/l) versus Pb in soil (mg/kg).

Shown in Figure 3 is the SPLP P concentration in solution versus the unspiked amount of total P in the soils. No drinking water limit exists for P, so the SPLP test is not directly applicable as it was for Pb. However, the USEPA has established a 0.1 mg/l water quality criterion for total P in agricultural runoff discharging into streams (Zvomuya et al. 2006). Based on this criterion all of the P in the extracts exceeds these levels (0.1 mg/l) prior to the addition of any P containing amendments. Clearly, phosphorus as well as lead levels need to be considered when developing a remediation strategy. Phosphorus in solution could be reduced by adding alum and iron (Zvomura et al. 2006), as well by choice of amendment (shown below), but its concurrent effects on Pb have not been investigated. Note that associated correlation ($R^2=0.368$) is less than that with Pb ($R^2=0.944$, Figure 2), but as the amount of P in the soil increases, there is a noticeable trend for P to increase in solution as well.
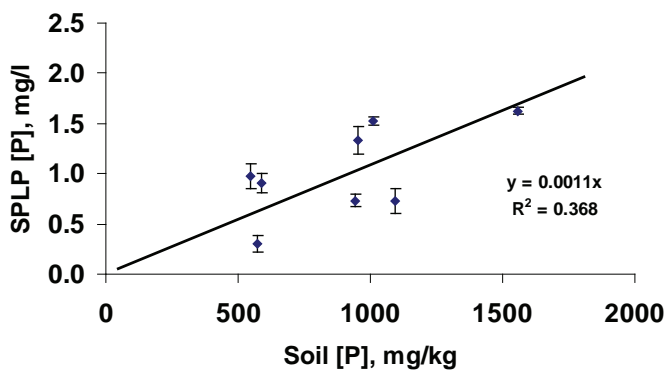

Figure 3. SPLP P in solution (mg/l) versus P in soil (mg/kg).

Lead in SPLP Extracts of Soils Amended with Phosphates.

In Figures 4 and 5, the average percent change in SPLP Pb in solution and the average percent Pb leached from the soil with 0.1% and 0.5% P treatments is given. The most noticeable decrease was at the 0.5% P level for both TSP and RP. At the 0.1% added P level only a small decrease in SPLP Pb was observed using the RP amendment (17% reduction). At the 0.5% added P level the SPLP Pb was reduced to 39 ± 20 % (RP) and 58±27% (TSP) of the levels in unamended soils. Using NAP, the SPLP Pb increased by 32±21 and 90±67%. The percentage of lead leached from soil followed the same trend as the SPLP Pb in solution (Figure 4). The average percent

lead extracted from unamended soils was 0.7±0.4, while they were 0.3±0.1 in the RP amended soils and 0.4±0.2 in the TSP amended soils at the 0.5% level. Thus, at the 0.5% amendment level for RP or TSP the lead extracted is reduced by roughly 50% compared to the unamended soils, which in turn, increases the threshold limit for Pb in soil from 50 to roughly 100 mg/kg..
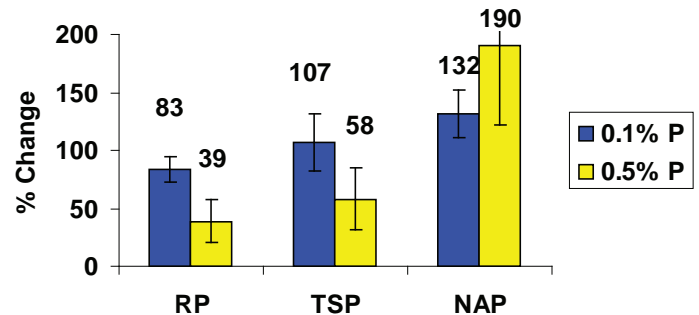

Figure 4. Percentage (%) change in SPLP Pb with P amendments. Numbers within graph are the percent increase or decrease compared to no amendment (100%).
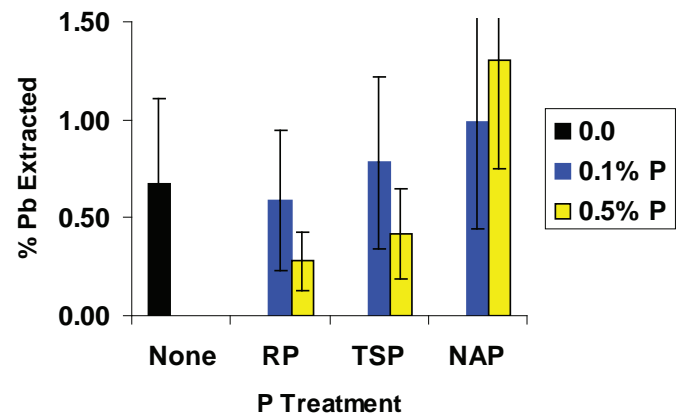

Figure 5. Percentage (%) of Soil Pb Extracted into SPLP solution with treatment

The pH of the extracts from unamended soils linearly correlated with the pH of the soils (Table 1), with the Extract pH = 0.7x Soil pH + 2.5 ($R^2= 0.90$). We could, however, find no correlation between the fraction of Pb extracted and the final pH of the extraction fluid ($R^2=0.33$-0.42). The effects on pH in the extracts of the amended soils were all minimal and averaged less than ± 0.25 pH unit change compared to the unamended soil, except for the 0.5% TSP amendment extracts where the average pH was lowered by 0.6±0.4. The lowering of the pH by this amount may have increased the fraction leached in the 0.5% TSP to some extent, since a lower pH will

increase the solubility of lead in solution (Pendias and Pendias 1992). The significant increase in the Pb content in SPLP extractions from the NAP amended soils was not due to pH, since the average pH increased from 0.1±0.3 in 0.1% NAP amended extracts to 0.2±0.6 in the 0.5% NAP amended extracts, which would tend to decrease the Pb solution concentration (Pendias and Pendias 1992).

Arsenic in SPLP Extracts of Soils Amended with Phosphates

Some garden soils can be contaminated with both Pb and As. For example, soils for housing built on old orchard sites or other agricultural land where lead arsenate was used as a fungicide/herbicide (Peryea and Kammereck 1997), or Pb contaminated soils near CCA pressure treated decks (Stilwell and Gorny 1997, Peryea 1999). Soils contaminated with both Pb and As as a result of these conditions are the PBAS and CCA soils (Table 1). Addition of P to As contaminated soils can have the undesired side effect of releasing As into the soil solution, thus increasing its potential to contaminate runoff water. This increase in solution phase As occurs because added phosphate (PO_4^-3) can replace arsenate AsO_4^{-3} in the soil particle (Peryea and Kammereck 1997, Peryea 1999). An example of this releasing effect on As is shown in Figure 6 for CCA soil. Using TSP or NAP amendments the SPLP As (mg/l) increased from 0.15±0.02 in the unamended soil, to 0.9±0.1 and 1.6±0.3 in 0.5% amended TSP and NAP, respectively. In the RP SPLP extracts the As did not increase. Similar trends were observed in the PBAS soil extracts. In all of the other soils, the As levels in the extracts were below the detection limit. Based on these data, if significant As contamination is known, or suspected, then additional phosphate additions to the soil, other than that required for growing crops, is not warranted. More specific guidelines are available for gardening in Pb and As contaminated soils (Peryea 1999).

Phosphorus in SPLP Extracts of Soils Amended with Phosphate.

Shown in Figure 7 is the SPLP P concentration in solution (mg/l) versus the total P (mg/kg) in the soils. The SPLP P in TSP and NAP extracts tended to increase with soil P following a second power relationship (SPLP P = Constant x Soil P ^1.9-2.3, R^2 >0.9). The average SPLP P (mg/l) in the 0.1% and 0.5% TSP amended soils were 7±3 and 47±13, respectively, while the average P in SPLP extracts from NAP soils were much higher 13±5 (0.1% NAP) and 101±20 (0.5% NAP). In soils amended with RP, the

SPLP P remained flat over the entire concentration range. The average SPLP P (mg/l) in the RP amended soils were 1.1±0.5 and 1.0±0.5 in the 0.1% and 0.5% amended soils, compared to 0.9±0.4 in the unamended soils. Clearly, using RP as an amendment was vastly superior to TSP and NAP in minimizing soluble P. However, as was the case in unamended soil the P levels in the RP, TSP and NAP extracts exceed the USEPA 0.1 mg/l water quality criterion for total P in agricultural runoff discharging into streams (Zvomuya et al. 2006).

The percent of P extracted from the soil with P treatment is given in Figure 8. Using no amendments or using RP as an amendment the %P extracted is around 1% or less, while in 0.1% TSP or NAP amended soils the % P extracted averaged between 8% (TSP) and 16% (NAP), and in the 0.5% amended soils the % P extracted averaged between 15-35%.
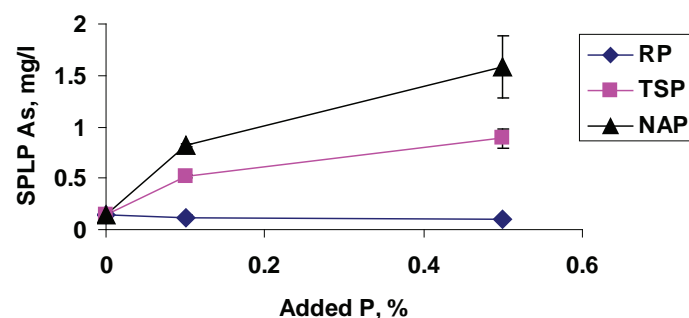

Figure 6. SPLP As versus added P (%) in CCA soil. As content in soil was 198±2 mg/kg (Table 1).
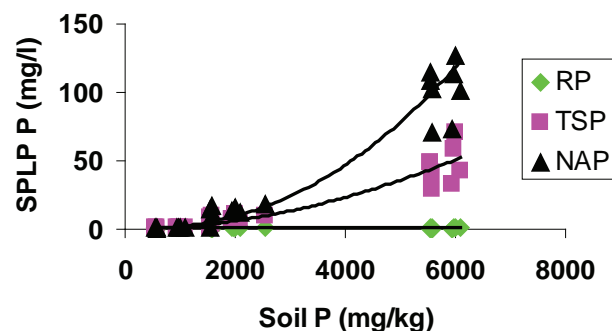

Figure 7. SPLP P in solution extracts (mg/l) versus total soil P (mg/kg).
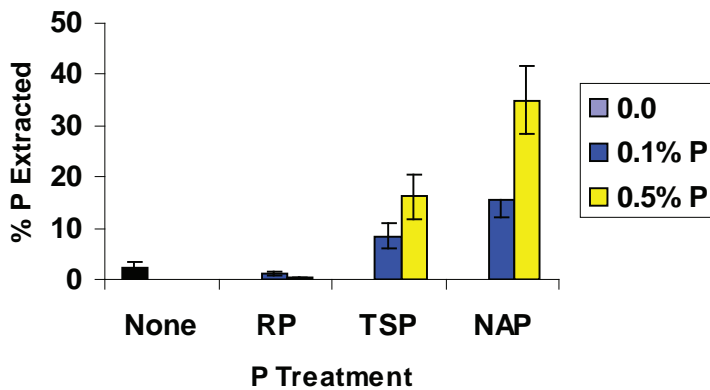
Figure 8. Percent (%) P extracted from soil by treatment.

CONCLUSIONS

Clearly, even modestly contaminated garden soils (between 100-300 ppm Pb) can exceed the suggested SPLP limit for Pb (0.015 ppm). The threshold value calculated from a best fit linear relationship was 50 ppm.

The average percent lead extracted was 0.7±0.4 in unamended, 0.3±0.1 in the RP amended soils at the 0.5% P level and 0.4±0.2 in the TSP amended soils at the 0.5% level. Thus, at the 0.5% amendment level for RP or TSP the lead extracted is reduced by roughly 50%. However, no benefit was found in reducing extractable Pb when using soluble phosphate in the form of NAP.

The percent of P extracted from the soil with P treatment was quite significant in the TSP and NAP amended soils, ranging between 8% in 0.1% TSP to 16% in 0.1% NAP amended soils, and increasing to 15-35% in the 0.5% amended soils. Using no amendments or using RP as an amendment the %P extracted was around 1% or less. Clearly, using RP as an amendment is vastly superior to TSP and NAP in minimizing soluble P. However, the P levels in all of the SPLP extracts (unamended, RP, TSP and NAP) exceeded the USEPA 0.1 mg/l water quality criterion for total P in agricultural runoff discharging into streams (Zvomuya et al. 2006).

Use of RP as the P amendment was also superior to TSP and NAP in minimizing As extraction in As and Pb co-contaminated soils.

In the context of potential runoff, RP performed best and

should be the amendment of choice when developing remediation strategies to minimize both P and Pb in solution. However, the results presented here reflect laboratory conditions carried out in a relatively short duration (2 months aging). A field study undertaken over multiple seasons would be needed to confirm these results since natural, climatic, and biological conditions can influence soil chemistry. Nonetheless, it is also clear that any action, which reduces both the inflow of water into the soil and the direct runoff of water off the soil, would reduce the amount of P and Pb in runoff feeding streams and lakes. An example of such action would be to cover the soil with a geo-textile, followed by with 15-20 cm of mulch, which could be readily replenished as needed.

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