Phosphate Based Pb Immobilization in a Contaminated Soil

Frantisek Majs, John C. Seaman*, and A. Kelsey-Wall

AACES; Savannah River Ecology Laboratory; The University of Georgia; Drawer E; Aiken; SC 29802. * Corresponding author: seaman@srel.edu

Abstract

A batch equilibration study was conducted to compare the effectiveness of different forms of P on immobilizing heavy metals in polluted soil. Hydroxyapatite (HA), trisodium trimetaphosphate (TP3) and dodecasodium (Na-IP6) phytate and calcium (Ca-IP6) phytate were added to a coarse-textured, Pb-contaminated, highly weathered soil. Equilibrium in 0.01 *M* $CaCl_2$ was established and dissolved organic carbon (DOC) and pH of the supernatant were measured. Solubility differences for Pb in the residual soils of the three P amendments were determined with the USEPA Toxicity Characteristic Leaching Procedure (TCLP). Bioavailability of heavy metals from treated soils was evaluated using MetPLATE. The Na-IP6 amendment increased soil pH from 5.5 to nearly 10; no pH increase was observed for HA or Ca-IP6 or TP3. The DOC for Na-IP6 increased tremendously in contrast with HA or Ca-IP6 or TP3 (from 5 to 2000 mg L-1). The increase beyond phytate solubility was caused by the dispersion of the soil organic matter. Initial decreases in Pb TCLP solubility was measured for all four treatments. However, further additions of Na-IP6 led to a large increase in Pb solubility; increased TP3 addition led to a steady increase in Pb solubility; and solubility of Pb decreased with increasing amounts of P added for HA and Ca-IP6 treatments. This study illustrates the importance of the initial P speciation in controlling heavy metal immobilization.

Objectives

- Evaluate alternative sources of phosphorus for *in-situ* remediation of lead contamination compared to hydroxyapatite
- Compare commercially available dodecasodium phytate with precipitated calcium phytate

Materials and Methods:

I. Batch Equilibration:
- 3 g of lead (Pb) contaminated soil equilibrated in 15 mL 0.01 *M* $CaCl_2$ for seven days on a reciprocal shaker in 50 mL centrifuge tubes
- Centrifuged and 0.22-µm filtered
- Supernatant analyzed for dissolved organic carbon (DOC; Shimadzu)
- Supernatant aliquot acidified with 5µL mL^{-1}ultra pure HNO_3 and analyzed for dissolved phosphorus (P) and Pb on ICP-MS (Elan 6000; Perkin Elmer)

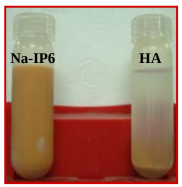

Figure 1. Dispersing effect of dodeca-sodium phytate (Na-IP6) compared to hydroxyapatite (HA).

	Mean	SD
Sand, %	97.12	1.25
Clay, %	2.27	1.15
Organic Matter, %	3.91	0.90
Lead, g kg^{-1}	7.47	0.83

Table 1. Basic characteristic of the coarse-textured, lead (Pb) contaminated, highly weathered soil from a shooting range used in Pb immobilization study.

II. Toxicity Characteristic Leaching Procedure (TCLP):
- 0.5 g of air-dried residue from phase I extracted with 10 mL of TCLP reagent (0.1 *M* glacial CH_3COOH / 0.0643 *M* NaOH with final pH 4.93)
- Centrifuged, 0.22-µm filtered, and analyzed for dissolved P and Pb on ICP-MS
- Values corrected for metal removed during the initial equilibration

III. Sequential Extraction Steps:

A.	Water soluble	DI water
B.	Exchangeable	0.5 *M* $CaNO_3$
C.	Acid soluble	0.44 *M* CH_3COOH + 0.1 *M* $CaNO_3$
D.	MnO_2 occluded	0.01 *M* NH_2OH-HCl + 0.1 *M* HNO_3
E.	Organically bound	0.1 *M* $Na_4P_2O_7$
F.	Amorphous Fe oxides	0.175 *M* $(NH_4)_2C_2O_4$ + 0.1 *M* $H_2C_2O_4$
G.	Crystalline Fe oxides	0.15 *M* $Na_3C_6H_5O_7$ + 0.05 *M* $C_6H_8O_7$ with 0.5 g $Na_2S_2O_4$ / 10 mL of reagent
H.	Total digestion	HF/HNO_3 microwave assisted digestion

IV. Heavy Metal Toxicity:
- MetPLATE™ used to test the toxicity of supernatants based on enzyme inhibition in non-viable *E. coli* strain by bioavailable heavy metals from phase I
- Assay measured at 575 nm using a spectrophotometric microplate reader (Molecular Devices)

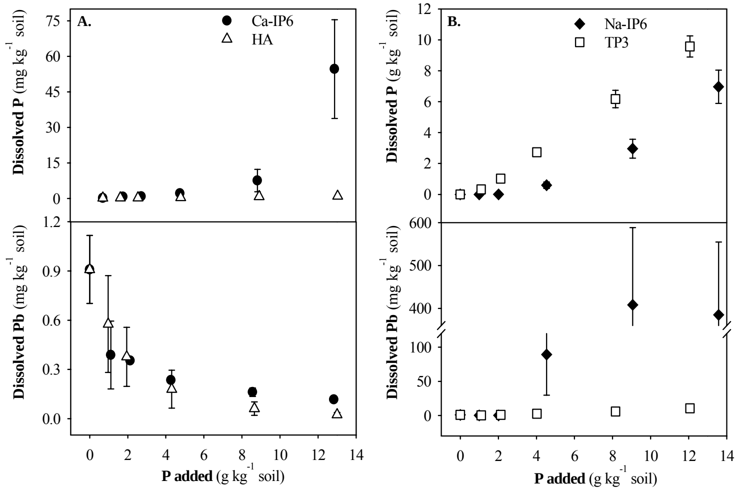

Figure 2. Changes in dissolved phosphorus (P) and lead (Pb) concentrations with increasing P addition during a seven day batch equilibration study (0.01 *M* $CaCl_2$) comparing the effectiveness of various forms of P on decreasing Pb solubility in highly contaminated soil, including **A.)** hydroxyapatite (HA) and calcium phytate (Ca-IP6) and **B.)** dodecasodium phytate (Na-IP6) and trisodium trimetaphosphate (TP3).

Results

- Dissolved P increases significantly as a function of P addition in form of Na-IP6 and TP3, increase for Ca-IP6 is two orders of magnitude smaller, and slight for HA (Figure 2.)
- Application of Na-IP6 above 6 mg kg^{-1} soil cause dispersion of mineral particles and organic matter (Fig. 1 and Tab. 2), which causes large increase in Pb solubility (Fig. 2)
- TP3 application caused soluble Pb to increase from 1 to 10 mg kg^{-1} soil
- HA and Ca-IP6 application led to decrease in TCLP leachability of Pb (Fig. 3)
- Lower rates decreased Pb TCLP leachability with TP3 application; however, leachability increased at larger P levels (Fig. 3)
- Na-IP6 and application to a large increase in Pb solubility mainly due to the dispersion of the mineral particles and organic matter (Fig. 3)
- Decrease in acid soluble and increase in MnO_2 occluded fraction with increasing P level is clear for Ca-IP6 (Fig. 4)
- Opposite is true for HA, no clear trend was observed for Na-IP6 (Fig. 4)
- MetPLATE supernatant toxicity decreased in order Na-IP6 > Ca-IP6 ≈ HA; toxicity was not determined for TP3 soil extract

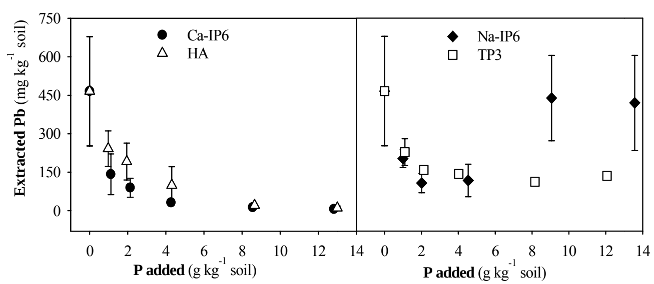

Figure 3. Corrected TCLP extractability of lead (Pb) from residual soil treated with HA, Ca-IP6, Na-IP6 and TP3.

	Pb Soil		HA		Ca_n-IP6		Na_{12}-IP6		TP3	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
DOC, mg L^{-1}	2.9	0.3	6.7	0.8	10.5	0.3	2222.8	151.5	52.1	14.0
pH	6.4	0.1	6.7	0.1	5.6	0.1	9.9	0.1	5.7	0.1

Table 2. Maximum changes of DOC concentration and pH after seven day equilibration study in highly contaminated soil. Soil (Pb soil) was treated with the four sources of phosphorus

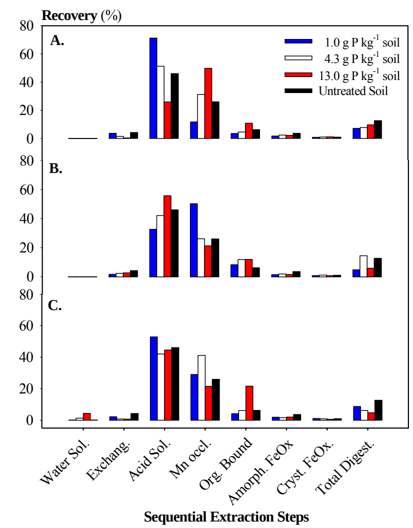

Figure 4. Sequential extraction of residual lead (Pb) contaminated soil treated with A.) Ca-IP6, B.) HA, and C.) Na-IP6 compared to Pb extractability in untreated soil. Stepwise changes of Pb extractability with increasing P level correspond to total Pb concentration.

Conclusions

- Ca-IP6 application does not cause increase in lead (Pb) solubility nor TCLP leachability and is fully comparable with traditional HA treatment in lowering Pb solubility
- Mechanisms of lowering Pb solubility for Ca-IP6 and HA are different. Major difference is found in acid soluble and manganese oxide occluded fractions of the extractable Pb.
- Sodium phytate causes overall increase in Pb solubility due to the dispersion of mineral particles and organic matter
- TP3 increases immediate Pb solubility upon application and increases Pb TCLP leachability at amendment levels above 8 g P kg^{-1} soil

Acknowledgments

The authors would like to thank Jane Logan and Jennifer McIntosh for their assistance. This research was funded by Financial Assistance Award Number DE-FC09-96SR18546 from the Department of Energy to the University of Georgia Research Foundation.