OKLAHOMA

Remediation of Heavy Metal-Contaminated Soil Using Rock Phosphate

By N.T. Basta and R. Gradwohl

Research over the past few decades has focused on the use of "chemical immobilization" products to chemically alter soil heavy metals to less soluble and less bioavailable forms. Organic amendments (municipal biosolids, composts, manures), alkaline materials (limestone, cement kiln dust, fly ash), and phosphate amendments [rock phosphate (RP), commercial fertilizers, phosphoric acid] have been studied for remediation of heavy metal-contaminated soil.

Objectives of this work were to evaluate (1) the ability of RP treatment to reduce plant and oral bioavailability of cadmium (Cd), Pb and Zn, and (2) the long-term stability of phosphate-treated soil.

Extensive lead (Pb) and zinc (Zn) ore mining and smelting have resulted in contamination of soil that poses risk to human and ecological health. Many reclamation methods used for these sites are lengthy and expensive and may not restore soil productivity. Soil heavy-metal environmental risk to humans is related to bioavailability. Assimilation pathways include the ingestion of plant material grown in (food chain), or the direct ingestion (oral bioavailability) of, contaminated soil.

Plant and Oral Bioavailability

Soil (loam, pH 6.4) contaminated by Zn and Pb milling and smelting was mixed with North Carolina RP at 1 lb RP per 10 lb soil. Triplicate treated soils and an unamended control were wet to 25 percent moisture and incubated at 80ºF for 90 days. During the incubation, water was added to maintain moisture, and the soils were mixed weekly. After incubation, lettuce was grown under controlled conditions until maturity in 6-inch pots containing soil. Lettuce was harvested and analyzed for Cd, Pb and Zn. Oral bioavailability of heavy metals was estimated by the Physiologically Based Extraction Test (PBET). This test simulates human gastrointestinal chemistry. The PBET procedure has two extraction phases: gastric and intestinal. Heavy metal dissolved by the PBET method was used to estimate oral bioavailability.

Lettuce did not grow on the control soil because the soil had greater than 0.01 lb plant available Zn/10 lb of soil...extracted with 0.01 M calcium nitrate [$Ca(NO_3)_2$] ...resulting in Zn phytotoxicity. Therefore, it is not possible to determine reductions in heavy metal content of lettuce due to RP. Treatment of contaminated soil with RP reduced plant available Pb, Cd and Zn

Lettuce grown in control and treated contaminated soil. Photo taken at time of harvest. Treatments are lime-stabilized municipal biosolid (LS), a blend of municipal biosolids and alkaline admixtures (NV), rock phosphate (PO_4), and an anaerobically digested municipal biosolid (SS).

TABLE 1. Plant and oral bioavailability of heavy metals in RP-treated contaminated soil.

Heavy metal	Plant available, ppm[1] soil		Oral bioavailability: Gastric phase, ppm soil		Oral bioavailability: Intestinal phase, ppm soil	
	Control	RP	Control	RP	Control	RP
Pb	0.54	0.37	7.1	5.5	1.8	0.2
Cd	186	98	6.4	5.3	4.0	1.0
Zn	1,090	740	266	250	163	38.1

[1]ppm = parts per million

(**Table 1**). Reduction of plant available Zn by RP and several other treatments allowed growth of lettuce on treated soil (see photo on previous page). The RP treatment resulted in small, but not significant ($P<0.05$), reductions in heavy metal oral bioavailability measured by the PBET gastric phase (**Table 1**). The intestinal-phase concentrations of Cd, Pb and Zn were lower than their respective gastric-phase concentrations. Rock phosphate treatment reduced intestinal-phase Pb by 90 percent, Cd by 75 percent, and Zn by 77 percent (**Table 1**).

The PBET results do not represent actual amounts of bioavailable metal absorbed into the body. However, they may represent metal fractions potentially bioavailable for absorption. Our results show RP amendments are more efficient in reducing soluble metals in the intestinal phase. However, the PBET method has never been evaluated for treated contaminated media. Therefore, we do not know if the gastric or intestinal phase is the best predictor of bioavailability. Although metal absorption occurs in the intestine, the higher gastric phase metal concentrations may be used as a conservative worse-case scenario. The actual oral bioavailability of these metals may occur at values between those predicted by the gastric and intestinal phases.

Long-Term Chemical Stability of Treated Soils

Long-term stability of chemical immobilization of heavy metals using RP methods was examined by acidifying soils with nitric acid to target pH levels of 6, 5.5 and 4 to mimic natural soil acidification. Changes in readily available Cd, Pb and Zn were determined by extraction with 0.01 M $Ca(NO_3)_2$. Acidification resulted in an increase of available Cd, Pb, and Zn in the control soil (**Table 2**).

In general, soil treatment with RP reduced available heavy metal. Soil acidification of RP-treated soil decreased Pb availability, unlike the control. Apparently soil acidification dissolved the carbonated apatite RP which resulted in formation of insoluble Pb phosphate minerals. Results from other studies suggest the formation of extremely stable pyromorphites is responsible for Pb immobilization in soil systems as well as apatite ion exchange, adsorption, and coprecipitation. Unlike Pb, Cd and Zn availability increased with soil acidification. However, increases of heavy metal availability in RP-treated soil was smaller than in control soils.

Summary

Treatment of smelter-contaminated soil with RP reduced Zn phytotoxicity and

TABLE 2. Changes in heavy metal availability due to soil acidification.

Heavy metal	Soil pH	Available metal, ppm soil: Control	Available metal, ppm soil: RP
Pb	6.5 (initial)	6.2	6.9
	6.0	17	2.4
	5.5	32	4.0
	4.0	55	1.5
Cd	6.5 (initial)	194	96
	6.0	256	129
	5.5	263	150
	4.0	287	254
Zn	6.5 (initial)	1,300	784
	6.0	3,130	3,530
	5.5	9,630	5,990
	4.0	12,040	7,760

In Memory of Santford W. Martin, 1922-1998

Santford W. Martin

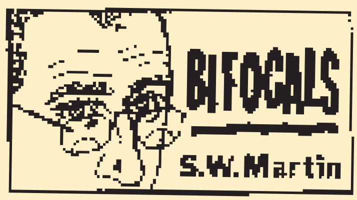
Mr. Santford W. Martin, who served as Editor for PPI and its forerunner organizations for more than 30 years, passed away September 18, 1998. Mr. Martin, who was age 76 at the time of his death, began his career with the Institute in 1957.

A native of Winston-Salem, North Carolina, he served 3 years in the military during 1943 to 1946. Mr. Martin was a graduate of Wake Forest University with B.A. (1947) and M.A. (1948) degrees, majoring in English-Journalism.

With a widely recognized talent for improving the readability of agronomic information, Mr. Martin edited *Better Crops with Plant Food* magazine and other Institute publications. He also wrote a popular column called “Bifocals,” which appeared in the magazine until 1980.

Before joining the Institute staff, Mr. Martin was Publications Editor for the Development Program of North Carolina State College. Earlier, he was Director of Publicity and Department Head at Gardner-Webb College, and also served as Director of Information for the North Carolina Alcoholic Rehabilitation Program.

“Santford Martin was a talented and respected man of highest integrity. He will be dearly missed by his family and all who knew him. There are many people who never met Santford, but yet thought of him as a friend because of his writing. He was a creative and productive individual and inspired many others to higher standards through his dedication and example,” said Dr. David W. Dibb, PPI President.



reduced plant available Cd, Zn and Pb. Oral bioavailability of Pb, Cd and Zn was also reduced by RP treatment, but the extent of reduction is uncertain. Small reductions in oral bioavailability were measured by the PBET gastric phase, but large reductions were obtained by the PBET intestinal phase. Lead immobilized by RP is very stable to soil acidification. In fact, acidification increases the amount of Pb immobilized. Increased available Cd and Zn suggests some of the fraction immobilized by RP may not be stable to soil acidification. However, available Cd and Zn in acidified RP-treated soil was less than that in the acidified control soil. Rock phosphate may serve as an inexpensive alternative method for remediation of smelter contaminated soil.

Research investigating use of RP and other phosphate sources (commercial fertilizer, phosphoric acid) is in progress at several universities (Florida, Kansas State, University of Missouri, Ohio State, Oklahoma State), the U.S. Environmental Protection Agency, and private industry.

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