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Modifying Soil Lead Bioavailability by Phosphate Addition

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Lead contamination of soil has become recognized as a public health hazard. Young children ingest daily, unintentional and otherwise, milligram quantities of soil and dust derived from soil. When the soil is contaminated with lead, the children's blood lead levels rise (Beck, 1992). Although behavioral factors may modify a child's uptake of soil, the link between soil and blood lead levels is distinct, even among children who mouth less than others (Rabinowitz and Bellinger, 1988). Currently several Superfund abatement projects are underway in urban settings and near smelters to rectify specific sites.

The typical remedies include soil removal for off site disposal, fencing to limit access, covering, or dilution by roto-tilling with uncontaminated soil (Elias, 1989). Some have attempted to chemically leach the lead from the soil for removal (Brown and Elliot, 1992). These methods are often effective, but their costs and disruptive nature often prevent them from being employed in situations where they might be useful. We have sought methods to reduce the toxic potential of lead in place without the expenses associated with cartage.

Lead in soil is mostly present as ionic lead absorbed onto clays, hydroxides or organic matter or as lead oxide, sulfide, or other ionic salt, rather than as lead metal. Soil treatments with lime, peat or chelators may modify plant uptake of metals (Abesel and Cottenie, 1985), but under gastric conditions these modifications do not influence uptake (Ruby et al, 1992). Even lead sulfide, normally insoluble, is absorbed as readily as lead nitrate by fasting humans, because of the acidity in the digestive tract(Rabinowitz et al, 1980). However, the geochemical behavior of lead, indicates that phosphate, when present in sufficient amounts,

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immobilizes lead, even at low pH (Nriagu, 1974). Since solubility, bio-availability and toxicity are all closely linked (Channey et al, 1989), we sought to immobilize lead in soil by phosphate addition.

A recent report illustrates indirectly how added phosphate binds soil lead (Davenport and Peryea, 1991). After phosphate fertilizer application, arsenic was more rapidly removed by water from an old orchard that had been sprayed with lead arsenate. This mobilization of arsenate was presumably due to double displacement, phosphate displacing the arsenic from the lead. We therefore attempted to make lead from contaminated soil less soluble, even under gastric conditions, by the addition of phosphate.

MATERIALS AND METHODS

The amount of leachable lead in soil was measured with and without any soil phosphate pretreatment. Three different leachates were used: 10% nitric, 0.3% hydrochloric or 10% citric acid.

Two different sources of lead contaminated soils were investigated, both kindly provided by regional US EPA offices. One from Boston is a composite from residential yards of lead painted homes, and it had originally been prepared as an internal standard for x-ray florescence studies (xrf). Thus, it was expected to be representative and very homogeneous. Its lead is mostly in the form of carbonate or oxide, although some could also be as the sulfate or bound to the humic soil components. The second sample from Helena, Montana was from near a smelter and contains lead minerals, slag, and smelter fall-out in unknown proportions amounting to 1233 ppm lead, 34 ppm arsenic and 21 cadmium by xrf.

Soil samples were dried at 65 C and sieved (1.5 mm), rejecting the coarse fraction without grinding. One gram portions were weighed into a 15 ml conical polystyrene centrifuge tube. Any pre-treatment would then be done. That consisted of mixing the soil with 10 ml of 0.03 M di-sodium hydrogen phosphate and 0.015 M sodium chloride. The mixture was agitated for 1, 3, or 7 days, and then centrifuged, discarding the supernate. The lead content of this discard was found to be negligible, less than 1.5 percent of the lead in the sample. The residual soil was then treated with one of the extractants.

Ten ml of either a) 10 percent nitric acid, b) 0.1N HCl, or c) 10 % citric acid was added and the mixture

Table 1. Extractable lead in replicates of two soil samples with and without phosphate treatment using three different solvents. Mean ± SD

Boston	Soil Lead (ug/g)				
	Treatment				
Solvent	No	N	Yes	N	Decline
10 % Nitric	1644 ± 24	3	1556 ±171	4	5 %
0.1 N HCl	1424 ±233	3	953 ±118	9	33
10 % Citric	1337 ±156	3	764 ±171	3	43
Montana	Soil Lead (ug/g)				
	Treatment				
Solvent	No	N	Yes	N	Decline
10 % Nitric	1182 ±45	3	1159 ±222	2	2 %
0.1 N HCl	667 ± 25	3	161 ± 36	2	76
10 % Citric	605 ±102	3	342 ± 38	3	43

shaken on its side for 24 hours at room temperature. Then after centrifugation a portion of the supernate was removed for lead determination using a flame atomic absorption spectrophotometer (Perkin Elmer model 2380) with a background corrector. An air-acetylene flame (18 fuel, 36 air flow rates) from a single slot burner and a continuous 10 mA lamp current were used with the 217 lead line. Standards and samples were both prepared in 3 percent solutions of tetra-sodium EDTA, electrophoresis grade, to reduce any potential chemical interferences. Results were then expressed as micrograms of extractable lead per gram of dry soil.

There was concern for any possible chemical interference during the spectrometry from residual phosphate in the EDTA solution from incomplete decanting after centrifugation. A series of standards with constant lead amounts but varying phosphate contents was prepared, up to 1.6 M. It was found that the lead signal varied in strength by less than 2 percent over this wide range in phosphate levels. Thus any decrease in the lead signal is not an analytical artifact of any phosphate residue.

As a further test of the overall analytical system, known amounts of lead were added to soil extracts. This was done over a range of lead concentrations from 150 to 1740 ug/g. For seven trials, recoveries averaged 100.7 percent (std err 2.0).

The amounts of lead extracted by each solvent is shown in Table 1. The strong nitric acid is assumed to represent essentially the total lead in the sample (Tessler et al, 1979). Although silicate minerals

Table 2. pH of some leaching fluids.

Leachate	pH
EP Toxicity Test 1986, Acetic acid	5.0
TCLP Extraction, US EPA, 1990	4.9 and 2.9
This Study	
10 % 2.2 N Nitric Acid	< 0.1
0.5 % .1 N Hydrochloric Acid	1.1
10 % .5 N Citric Acid	1.5
Soil samples with water 1:1	near 5
Human gastric contents	1 to 3

resist this acid treatment, nearly all of the lead contamination dissolved, whether the lead was a sulfide, sulfate, phosphate, carbonate or adsorbed on oxides or organic matter. From the Montana soil, 96% of the lead detected by xrf was mobilized by 10% nitric acid (1182 vs 1233 ug/g). The two milder acids dissolved only 50 to 80 % the total lead in this soil before treatment.

The phosphate treatment has no apparent effect on the nitric acid soluble fraction. This strong acid could dissolve any lead phosphate formed. However, using the two milder acids, the phosphate treatment markedly reduced the amounts of soluble lead. The size of this decline averaged 49 percent and ranged from 33 to 76 percent.

All of the lead in soil is not in one chemical or physical form and thus may not be uniformly bioavailable (Freeman et al, 1991). The rationale for our approach is that the bioavailable portion of soil lead can be approximated by the soluble fraction, because lead must first be dissolved to be absorbed. Since we do not have a reliable in vitro model of gut absorption with simulated digestive enzymes and transport mechanisms, we rely on selective leaching to characterize the lead and infer its bioavailability (Davis et al 1992). Selective leaching has long been used to study the speciation of nutrient elements. Also, the bioavailabilities of minerals in soil are measured to determine micronutrient requirements of crops (Harter, 1983; Shuman, 1985).

The use of various leachates to estimate the hazardous nature of wastes has also found legal application (United States Federal Register, 1990). Table 2 shows the pH of various proposed leaching agents, those used in this study, and human gastric contents. The milder acids used here approximate physiological pH. The time course of the phosphate reaction has been crudely examined by subjecting samples to 1, 3, and 7 days'

Table 3. Predicted distributions of blood lead in two hypothetical groups of children, with and without phosphate treatment of soil. This example uses the values from the Boston soil in Table 1.

Phosphate	Available	Blood Lead Distribution		
Treatment	Soil Lead	Median	≥ 10	≥ 15 ug/dL
No	1337 ug/g	8.5 ug/dL	32 %	5.2 %
Yes	764	5.4	4	0.2

exposures to phosphate prior to acid extractions. Using the 0.1N HCl extractable lead as a guide, there appears to be no difference among these times: 884, 1083, and 989 respectively. The reaction is essentially complete within a day under these conditions. For that reason, the values for the different times were pooled for this presentation.

The longer term stability of products of this phosphate treatment has not been examined. The phosphate reaction produces only a lead phosphate corrosion rim of unknown thickness, which may be physically abraded and worn down as soil particles push against each other. With time, fresh lead surfaces would again become available from the cores of these particles. The permanence of the modification may depend on the physical properties and depth of this rim of reaction product. Similarly, thermal or moisture cycling of the soil may effect the permanence of the phosphate-induced modifications.

The consequences of reducing the soil lead on a population's blood lead distribution are shown in Table 3. The Lead5 biokinetic uptake model was used with standard default parameters: 100 mg/day of soil and dust ingestion, outdoor air lead 0.2 ug/cu M, tap water 4 ug/L, maternal blood lead 7.5 ug/dL, no lead paint, and a population geometric standard deviation of 1.42 (US EPA, 1991). Two values of soil lead were chosen based on our pilot study, 1337 and 764 ppm. This 43 % difference in soil lead yielded median blood lead levels of 8.5 and 5.4, a 36 % reduction. However, if considered as the difference in the numbers of children with blood leads over 15 ug/dl, the effect is more pronounced, a 25 fold reduction. Only 0.2 % rather than 5 % would be expected to be over 15 ug/dl. Using 10 ug/dl as a level of concern, there would be an 8 fold decline in the number of children affected. If similar reductions could be accomplished in the real world using a familiar chemical of small cost, then significant improvements would follow.

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