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SOIL LEAD REMEDIATION: IS REMOVAL THE ONLY OPTION?

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INTRODUCTION

Lead, a naturally occurring metal, has always been present in soils, surface waters and ground waters. Lead content of agricultural soils ranges from > 1 mg/kg to 135 mg/kg with a median value of 11 mg/kg (1). Inner-city neighborhoods in most of our major cities have mean or median soil Pb concentrations in excess of 1000 mg/kg (2-6) with values as high as 50,000 mg/kg being reported (7). Most of these elevated lead concentrations observed in the urban soils are assumed to come from various anthropogenic sources: industrial emissions, vehicular emissions and exterior lead paint (8). Additionally, lead has been added to soil as the insecticide lead arsenate, impurity in fertilizers as well as from mining and smelting activities (9). Further, lead is a contaminant of concern in about one third of the National Priority List (NPL) sites and over 400 Superfund sites have excessive soil Pb concentrations (10). Thus, its use by society; paints, chemical additives, tools and weapons, as well as other consumer and industrial products, coupled with inadequate disposal or recycling by society have caused environmental systems (soils) to become repositories for the metal. It is also apparent that not only are soils the repository for environmentally released Pb, but it is retained in the zone of addition (9).

According to the Center for Disease Control (CDC) lead poisoning is the most common and most devastating environmental disease affecting young children. Over the past decade the blood Pb level associated with impairment has decreased from 25 µg/dL to 10 µg/dL, as we have learned that levels above 10-15 µg/dL can significantly reduce IQ and learning ability in children (11). Because of the reduction of Pb in automotive emissions, and reduction of Pb in food due to changes in canning technology, both food and automotive emission Pb levels have decreased nearly 10 fold in the past 15 years (12). During the same time frame median blood Pb levels in suburban children have fallen from about 20-25 µg/dL in 1970 to 3-4 µg/dL in 1990. With the normal variance (and varied amounts from Pb in plumbing systems) some suburban children exceed 15 µg/dL. But over 50% of children in the center city exceed 15 µg/dL limit (13). Thus, lead risk to young children is now recognized as the most sensitive limit for Pb in the environment (11). CDC estimates that Pb poisoning in children costs billions of dollars in medical and special education expenses and decreased future earnings. Lead paint, Pb in drinking water and Pb in soil are the major sources of exposure. Children exposed to high levels of soil and dust Pb have been found to have high blood Pb in numerous cases (7). Lead in soils contaminated by smelter emissions, automotive emissions, or paint residue have been found to cause increased blood Pb in children when soil Pb exceeds 500-1000 mg/kg (14-17). In other cases, social factors and/or soil chemical factors alter exposure and/or bioavailability of the soil Pb and little or no increases in blood Pb are observed even with soils containing 5000 mg Pb/kg (18). Further, Pb in mining soils appears to have lower bioavailability than Pb in urban dusts (19-21). Cotter-Howells and Thornton (18) reported low blood Pb levels in children living in an area with soils (about 5000 mg/kg) derived from PbS mining wastes. Studies have found the relationship (slope of blood Pb/soil Pb) for children in smelter and urban areas to range from 1.1 to 7.6 µg/dL/1000 mg/kg, while for children in mining areas the relationship ranges from 0 to 4.8 µg/dL/1000 mg/kg (22). Suggesting that Pb in soils contaminated from mining activities is less bioavailable than Pb in soil derived from urban and smelting sources. Three possible explanations have been offered for the observations: the size of the Pb containing particle, the species of Pb in soil, and the geochemical matrix incorporating the Pb species. These results are interpreted as indicating that because of specific adsorption, soil Pb bioavailability increases with increasing soil Pb concentration and that the form of soil Pb alters its bioavailability.

Programs to reduce exposure from Pb paint and Pb in drinking water are moving forward. No program exists on contaminated soil Pb because, according to CDC and EPA, there is insufficient

information available on which to base such a program. They state that far less is known about the hazards of soil Pb-- and how to address those hazards-- than about paint or water. Thus, information is needed to better characterize the problem, determine pathways of exposure, and determine effective remediation methods.

Remediation treatments for soils attempt to capitalize on the differences in physical and chemical properties between a contaminant and soil constituents. For example, remediation efforts for metal contaminated sites use properties such as solubility, density, particle size distribution, surface chemistry, boiling point or magnetic susceptibility to allow separation and recovery. Metals found as relatively soluble species or weakly sorbed to soil clays might be solubilized by the application of mild organic acids. If the metals are present as separate mineral particulates, then their typically higher density might permit the physical separation of these species from the less dense aluminosilicate and organic constituents of soils. Otherwise, these forms could be bound in a solid cement or vitreous glass matrix. If the metal species are volatile, then a soil heating method might allow recovery. Separation methods relying on the magnetic susceptibility of ferromagnetic or strongly paramagnetic metal species have also been attempted. More detailed discussions of remediation technologies can be found in the literature (23-28).

Many biological, chemical and physical process have been proposed for soil remediation. Some of the processes can be either applied to excavated soil or used in situ. However, reduction in exposure to soil Pb has typically been accomplished by soil removal for off site disposal, covering, or diluting by mixing with uncontaminated soil. Cost, logistical concerns, and regulatory requirements associated with excavation, ex situ treatment and disposal can make in situ treatment an attractive option. Our current understanding of Pb exposure and factors which effect its bioavailability as well as its environmental chemistry may allow development of less costly and environmentally less disruptive methods of remediation.

METHODOLOGY

In response to the need for cost effective technology to immobilize Pb, we have collaborated with Ohio State University to examine the feasibility of Pb immobilization by phosphate rocks. This approach is based on the hypothesis that Pb phosphates are the most insoluble Pb minerals, these materials are resistant to acid weathering, and these materials are less bioavailable than other Pb forms. The experimental approaches utilized in this research have been laboratory scale solution studies, resin studies, dialysis studies, soil studies, and feeding studies.

RESULTS

We have shown that Pb is rapidly and effectively precipitated from solution by orthophosphate (aqueous P, hydroxyapatite, or phosphate rock) to form a series of Pb phosphates (29-31). We have used hydroxyapatite and phosphate rock as the primary P source and have shown that they are effective in attenuating Pb in aqueous solution, exchangeable form and contaminated soil material, to below the U.S. EPA action level of 15 μg/L dissolved Pb. Phosphate rocks from Florida, North Carolina and Idaho are also shown to be effective in removing Pb from aqueous solution (29). The final product of Pb immobilization is primarily hydroxypyromorphite ($Pb_{10}(PO_4)_6(OH)_2$), which is stable even at pH as low as 3. Results of chemical and x-ray diffraction (XRD) analysis, scanning electronic microscopy (SEM), and scanning transmission electronic microscopy (STEM) strongly support the mechanism of dissolution of hydroxyapatite and precipitation of hydroxypyromorphite. Aqueous P concentration is a key factor in determining the effectiveness of Pb immobilization and the formation of hydroxypyromorphite. Thus pH is important since it determines solubility of hydroxyapatite or phosphate rock. Hydroxyapatite or phosphate rock not only supplies P to immobilize Pb, but also provides Ca to replace Pb from exchange sites. This is especially important in contaminated soils and solid wastes where the bulk of the Pb is in labile rather than soluble form.

We have also shown that hydroxyapatite can effectively immobilize aqueous Pb in the presence of common soil solution anions: NO_3^-, Cl^-, F^-, SO_4^{2-}, and CO_3^{2-} (30). Lead concentrations were reduced from initial levels of 5 - 100 mg/L to below the EPA dissolved Pb action level of 15 μg/L except at very high CO_3^{2-} concentrations, whose levels are unlikely to be found in contaminated soils and wastes. Hydroxyapatite was transformed to hydroxypyromorphite after reaction with $Pb(NO_3)_2$ in the presence of NO_3^-, SO_4^{2-}, and CO_3^{2-}; to chloropyromorphite ($Pb_{10}(PO_4)_6Cl_2$) after reaction with $PbCl_2$; and to fluoropyromorphite ($Pb_{10}(PO_4)_6F_2$) after reaction with PbF_2, respectively. Hydroxyapatite dissolution followed by precipitation of hydroxypyromorphite, chloropyromorphite, or fluoropyromorphite was the main process during the reaction, but Pb adsorption by hydroxyapatite and cation substitution of Pb for Ca on hydroxyapatite may also have occurred.

We have also investigated the effects of metals such as Zn, Cd, Ni, Cu, Fe^{2+}, and Al on Pb immobilization by hydroxyapatite as well as the effectiveness of hydroxyapatite in attenuating these metals (31). We have shown that not only do these metals have no significant effect on Pb immobilization by hydroxyapatite at low concentrations (<20 mg/L), but also these metals themselves are removed by hydroxyapatite. The amount of metals removed depends on the concentrations of Pb and metals, as well as the types of metals. At higher concentrations (>20 mg/L), Cu is most effective in inhibiting Pb immobilization by hydroxyapatite, followed by Fe^{2+}, Cd, Zn, Al, and Ni. Hydroxypyromorphite was the only mineral detected by XRD besides hydroxyapatite after Pb reaction with hydroxyapatite in the presence of these metals. The amounts of hydroxypyromorphite formed decreased with an increase in metal concentrations, according to XRD. The order of inhibition of hydroxypyromorphite formation is positively correlated with the solubility of the other metal phosphates and supports a mechanism of competitive precipitation.

Hydroxyapatite also removed Pb^{2+} from Pb-EDTA solution in the presence of excess EDTA. Indicating that basic Ca-phosphates can sequester Pb even in the presence of strongly complexing organic ligands. In longer term experiment, hydroxyapatite was effective in immobilizing Pb^{2+} for up to 16 weeks, confirming the stability of the reaction product. In another experiment, a mixture of hydroxyapatite and hydroxypyromorphite were reacted with anion exchange resin. Lead concentrations in the suspension of hydroxyapatite and hydroxypyromorphite were low (< 168 nmol/L) in spite of the fact that the anion exchange resin extracted PO_4^{3-} from solution, which again demonstrated the stability of hydroxypyromorphite over hydroxyapatite. Additionally, the mixture of hydroxyapatite and hydroxypyromorphite was also reacted with aqueous Ca^{2+} to study the possibility of Ca^{2+} substitution for Pb^{2+} on hydroxypyromorphite. Higher Ca^{2+} concentrations resulted in slightly higher Pb^{2+} concentrations (< 158 nmol/L), possibly as a result of hydroxyapatite precipitation and hydroxypyromorphite dissolution. We have illustrated that exchangeable Pb can be precipitated by reacting hydroxyapatite with a cation exchange resin saturated with Pb. No hydroxypyromorphite was detected in the hydroxyapatite residue, indicating the reaction did not occur in bulk solution. The resin was coated with hydroxypyromorphite indicating that hydroxyapatite not only immobilized Pb, but supplied cations (Ca) to displace Pb from the resin which, was immediately precipitated as hydroxypyromorphite. In further evaluations of the reaction we mixed hydroxyapatite with several Pb contaminated soils and allowed them to react for several days. Sequential extraction of the samples illustrated that the hydroxyapatite addition reduced the labile fractions of soil Pb (soluble and exchangeable) and increased the residual fraction of soil Pb.

In animal feeding experiments we have illustrated that Pb bioavailability followed the order: Pb-acetate >> contaminated soil> pyromorphite = control and that the addition of apatite or rock phosphate to the contaminated soil reduced the bioavailability of the contaminated soil Pb. Thus, illustrating that the formation of phyromorphite in soils not only reduce the solubility of the soil Pb, but reduce its bioavailability. In fact even without allowing time for reaction, the addition of the phosphate (apatite or rock) to the contaminated soil was effective at reducing soil Pb bioavailability.

CONCLUSIONS

Our results strongly demonstrate that both hydroxyapatite and phosphate rocks were effective in reducing Pb solubility and bioavailability through dissolution of hydroxyapatite or phosphate rocks and precipitation of pyromorphite. The effective and rapid Pb^{2+} immobilization from solution and contaminated soils by hydroxyapatite or phosphate rock, the limited effects from other minerals, anions, and cations, the apparent environmental stability of the reaction products, along with the ready availability and low-cost of hydroxyapatite or phosphate rock suggest that this approach might have great merit for cost-effective in situ immobilization of Pb contaminated water, soils, and wastes.

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