In-Place Inactivation of Pb in Pb-Contaminated Soils

WILLIAM R. BERTI* AND SCOTT D. CUNNINGHAM

Environmental Biotechnology Program, DuPont Central Research & Development, Glasgow Business Community 301, P.O. Box 6101, Newark, Delaware 19714-6101

There has been increasing attention to the use of soil amendments and green plants to remediate surface soils contaminated with Pb. We call one form of this technique in-place inactivation. In-place inactivation reduces the hazards associated with contaminated soils through the use of chemicals that change the molecule species of the Pb to stabilize the soil Pb chemically and physically in situ. We have seen significant changes in soil Pb chemistry, Pb leached from soil, and Pb measured by a physiologically based extraction test (PBET) after incorporating inexpensive and readily available materials to three soils. The soils have total Pb concentrations that range from 1200 to 3500 mg kg⁻¹. The leachable soil Pb was significantly reduced in all cases from as high as 30 mg Pb L⁻¹ to below the regulatory limit of 5 mg Pb L⁻¹ after soil treatment. The PBET mimics the mammalian gastric—intestinal tract solutions. In the simulated intestinal phase of the PBET, Pb in solution was reduced by 72% in one of the soils treated with a high Fe-containing industrial byproduct. These results help to illustrate the utility of incorporating soil amendments to reduce hazards associated with Pb-contaminated soils.

Introduction

Current soil remediation often relies either on a “capping strategy” or an excavation of the contaminated soil and burial in a landfill. Some highly contaminated soils are solidified and stabilized with portland cement prior to disposal. Cost of these types of site remediation typically ranges from about USD15 m⁻² for a 60-cm-thick soil cap to USD730 m⁻² for excavating to 60 cm, stabilizing, and off-site disposal. An agricultural-based alternative to current remediation methods may be appropriate at many contaminated sites. Cost for this remediation strategy has been estimated at USD6 m⁻² for incorporation of materials 60 cm deep (USD is U.S. dollars, 1996 estimates; Quinton, G., DuPont Corporate Remediation Group, personal communication, 1996)

This alternative uses green plants and soil amendments to remediate contaminated soils through the biological, chemical, and physical “in-place inactivation” of heavy metals, including Pb. This stabilization technique depends on changing the contaminant chemistry by adding and incorporating soil amendments. The soil amendments must be able to effectively change trace elemental chemistry while having a neutral to positive effect on plant growth. Measuring these changes in soil chemistry can be somewhat problematic. Our current ability to speculate trace elements in complex matrices such as soil is limited because they are found in relatively low concentrations and in a variety of physicochemical forms (1, 2).

One speciation technique, sequential chemical extractions, separates forms of trace elements into operationally distinct fractions, such as water-soluble, exchangeable, carbonate, oxhydroxide, organic, and precipitated. This is accomplished by using progressively harsher solutions to dissolve trace elements from the soil matrix. We have developed and are using a sequential chemical extraction technique for our Pb-contaminated soils based on our own work (3) and that of others (4, 5). Our method differs from that of others by using AgNO₃ in the first solution. Silver nitrate was chosen because Ag⁺ has an ionic potential and Misono softness similar to that of Pb (6). Silver ions should therefore be effective for exchanging with Pb⁺ that occurs on surfaces as inner-sphere complexes. Additionally, because Ag⁺ is highly reactive with anions, the formation of Ag precipitates should reduce the redistribution of Pb to solid forms in this fraction.

Sequential chemical extractions should help provide an indication of the hazard the contaminated soil poses to the environment due to similarities between extraction solutions and environmental conditions. The inherent hazard posed by Pb contained in a soil matrix is a function of its relative mobility and bioavailability. Not all soil Pb is equally bioavailable or mobile. It forms associations with numerous organic and inorganic phases in soils. The nature of its chemical distribution within the soil, and thus the inherent hazard posed by the matrix, is often a function of soil pH, mineralogy, texture, organic matter content, source and quantity of Pb in the soil, and time. Several of these factors can be modified by soil amendments. Sequential chemical extraction techniques can be used to measure these modifications. They fill a need for other techniques currently offered when applied to the examination of soil—chemical changes that occur on the same or similar soils to which different treatments have been imposed (7).

The human health and environmental hazard posed by Pb-contaminated soils is primarily through direct ingestion of the contaminated soil. The hazard to children by direct soil ingestion is generally acknowledged as the hazard of greatest concern. Ruby et al. (8, 9) have developed a physiologically based extraction test (PBET) that determines soil Pb bioaccessibility, a chemically surrogate measurement for soil Pb bioavailability in animals as a result of soil ingestion. This surrogate measurement for soil Pb bioavailability fills a need in research and development of remediation technologies for a test that is an appropriate measure of the soil Pb hazard and that is quick and inexpensive as compared to the animal models that are normally used to assess bioavailability. Bioaccessibility is defined as the solubility of soil Pb in simulated stomach and intestinal solutions of the PBET relative to the total Pb in the soil. Soil Pb bioaccessibility determined in both the simulated stomach and intestinal phases of the PBET was shown to be well correlated with soil Pb bioavailability using a Sprague-Dawley rat model (9). The simulated stomach phase of the PBET, however, was more highly correlated to the rat model than the intestinal phase of the PBET. Our own research and that conducted at DuPont’s Haskell Laboratory indicated that soil Pb bioaccessibility determined in the simulated stomach phase of the PBET correlated well with the results of absolute soil Pb bioavailability using microswine as the animal model (unpublished results).

This paper builds on our earlier work that grew out of phytoremediation of Pb-contaminated soils (3), further examining the effects of materials such as phosphate fertilizer and iron oxhydroxides to change soil Pb chemistry and...
reduce the hazard of soil Pb, as measured by sequential chemical extractions, the toxicity characteristic leaching procedure, and a physiologically based extraction test.

**Experimental Section**

Soils were collected from the surface to 60 cm of three former industrial areas, screened through a 9.5-mm sieve, and homogenized. Total soil Pb (using a nitric acid/perchloric acid open vessel microwave digestion technique), Pb leachability (modified from the toxicity characteristic leaching procedure, TCLP (10)), and percent gravel (particles > 2 mm) by sieving were performed on air-dry samples. Soil tests (e.g., soil pH, extractable P, Ca, Mg, K; organic matter; and texture (11)) and sequential chemical extractions were performed on air-dry material passing a 2-mm sieve. The PBET [modified from Ruby et al. (9)] was performed on air-dried soil material smaller than 250 µm.

We tested a wide range of soil amendments including KH₂PO₄, agricultural limestone, gypsum, sulfur, iron oxyhydroxides (e.g., humate from TiO₂ mining, which has also been tested as a soil amendment in plant nutrition and growth (Mollerup, D. A., DuPont White Pigments and Mineral Products, personal communications, 1994)), and composted leaves (i.e., natural humus from Twin Oaks Mulch, Quarryville, PA). Of all amendments tested, only amendments whose addition resulted in significantly reduced leachable Pb (as measured by the TCLP) at rates that are compatible with plant growth are included in this report. A standard engineering stabilization method (portland cement) was also used at rates high enough to reduce the TCLP Pb values of the resulting soil materials to below the regulatory limit of 5 mg Pb L⁻¹.

Applications were on a dry-weight basis. Soil amendments were mixed by hand into 100 g of soil, the mixture was placed into 500-mL glass jars, and water was added to attain a moisture content of about 30%, which is in a range considered optimum for microbial activity (13). The jars with soil were covered with laboratory film (i.e., Parafilm “M”) to allow gas exchange and to minimize moisture loss. The samples were placed in a dark incubation chamber at about 30°C. Two-milliliter samples were taken at 30 and 60 min of the simulated stomach phase of the test controlled at a pH of 2.5 ± 0.1. The simulated intestinal phase of the test, controlled at pH 7.0 ± 0.1, was sampled at 60 and 120 min. Sampling was done without replacing the sample solution with an equal-size aliquot. The final volume in the flask was determined at the end of the test. Pb bioaccessibility was determined by dividing the Pb concentration measured in the supernatant by the total Pb concentration in the supernatant at the end of the test determined separately for each sample.

Lead was determined in all solutions using inductively coupled plasma—atomic emission spectrometry (ICP—AES). Standard soil reference materials from the U.S. Department of Commerce National Institute of Science and Technology were used to assess accuracy and precision of methods.

**Results and Discussion**

Characterization data of the three Pb-contaminated soils that were used for laboratory experiments are presented in Table 1. These soils represent a range of total Pb contamination that is higher than the current limit for residential land use in the United States [about 400 mg of Pb (kg⁻¹ of soil)⁻¹]. The Pb in soil 1 resulted from manufacturing the anti-knock gasoline additives tetraethyl lead and tetramethyl lead (i.e., TEL and TML) from about 1920 to 1989. Analytical testing, however, indicated that the sample did not contain TEL, TML, or their known intermediate breakdown products (data not presented). Soil 2 was a blasting cap destruction area. The source of Pb in soil 1 is most likely from lead azide (Pb(N₃)₂) used in the blasting caps. The Pb in soil 3 came from the manufacturing of explosives. Lead azide was probably the main source of Pb in this sample also.

The soils in this study represent not only a range of Pb concentrations but also a range of chemical and physical characteristics (Table 1). The soils vary in pH, texture, and plant macronutrients. They also have low to moderately high organic matter content. Soils 1 and 2 are poor plant growth media. Soil 1 is a poor material for plant growth because of its alkaline pH, high gravel, low organic matter content, low plant-available P, and excessive levels of plant-available Mg and Ca. Soil 2 is poor because of its acid pH and low levels of plant-available nutrients. Both of these soils require plant fertilizers and other soil amendments to quickly establish a robust plant cover. Soil 3 is more easily amended for plant growth. It has a near-neutral pH and moderate concentrations of most plant nutrients. Of the three soils in this study,
only this one had abundant plant growth in its native state. It also contained the highest concentration of total Pb (Table 1).

The sequential chemical extractions (Figures 1 and 2) resulted in a “fingerprint” of the soil Pb, which we believe gives information on its potential for leaching, plant uptake, and mammalian bioavailability through soil ingestion. Soils in which the Pb resides mostly in the first fractions are potentially of greatest hazard when compared to soils in which the Pb resides primarily in later fractions, especially the last. Lead in the first two fractions is extractable by relatively mild solutions and would be most available to the effects of water leaching through the soil, plant uptake into roots, and bioavailability through soil ingestion. Lead resistant to extraction until the last two fractions, which include boiling nitric–perchloric acids, would be available only under the harshest chemical conditions rarely found in the environment or only over geological time–frames.

The sequential chemical extractions of the three soils suggests that Pb resides in different chemical forms (Figure 1). In all three untreated soils, the majority of the Pb was extracted in the first two fractions. In soil 1, more than 50% of the Pb, however, resided in the second fraction alone. Three-quarters of the Pb in soil 2 was extracted from the first two fractions. In soil 3, almost 70% of the total Pb resided in fractions 1 and 2. The relative availability of the Pb in these samples, as determined by the sequential chemical extractions, would suggest that these soils present a potential hazard to human health and the environment through direct soil ingestion and leaching to groundwater.

Lead in soil 1, with a total concentration of 1200 mg of Pb kg\(^{-1}\), was primarily in fractions 2, 5, and 6. We would not expect the Pb in this soil to be readily available for plant uptake. Lead forms in this soil as well as in the other two, however, will be easily extractable in an acid solution, such as that used in the TCLP. Also, the sequential chemical extraction results suggest that forms of Pb in all three soils are available for dissolution in the acid portions of the GI tract of mammals, which may result in Pb poisoning.

It may be possible to significantly reduce the hazard presented by the soils by in-place inactivation. In-place inactivation builds on the excellent work of many previous research groups, who have demonstrated that soil amendments can change soil Pb chemistry, reducing the soil Pb hazard (14–18). Application of these amendments should cause the Pb to shift from forms with high relative availability (fractions 1 and 2) to those with low or no relative availability (fractions 3–6). Amendments are chosen to be compatible with plant growth and microbial activity so that soil productivity is maintained or increased. Also, amendments should be locally available, relatively low in cost, easy to apply and incorporate, benign to the people using them, and not cause further environmental degradation (e.g., nitrates in biosolids at rates excessive for plant N requirements). To this end, we selected eight materials and incorporated them at varying rates in the three soils. These materials were chosen because of their known positive effects on plant growth at certain application rates. They were also chosen for their potential abilities to inactivate soil Pb in forms not available to plant growth, soil ingestion, and leaching and to reduce the characteristic hazard of a material to acceptable levels.

The sequential chemical extraction was significantly altered as a result of adding materials, especially IRM and P (Figure 2). Lead extracted in the first fraction was reduced, and a greater percentage was extracted in subsequent fractions. Others (14, 18) have shown that the addition of P to soil containing Pb results in the formation of lead phosphate with low water solubility. The iron oxides in the IRM probably affect soil Pb chemistry through surface adsorption (19) and solubility mechanisms. Humate and natural humus applications seemed to have less overall effect on changing the results of the sequential chemical extraction when compared with IRM and P. Sequential chemical extractions of samples amended with humate and natural humus showed reduced Pb extracted in the first fraction and increased Pb in subsequent fractions. Organic materials, such as humate and natural humus, most likely worked in ways similar to that of IRM through surface adsorption (19) and solubility mechanisms.

Certain soil amendments at relatively low rates, such as KH\(_2\)PO\(_4\), dramatically reduced the leachable Pb (Figure 3A). Phosphate added as low as 0.1% P was able to reduce leachable Pb to below 5 mg of Pb L\(^{-1}\) (which is the regulatory limit of the TCLP) in soils 1 and 3. Potassium phosphate added at 0.5% P reduced leachable Pb in all three soils to less than 5.0 mg of Pb L\(^{-1}\). IRM applications of at least 6% were needed to reduce the leachable Pb to below 5 mg of Pb L\(^{-1}\) in any of the soils (Figure 3B). In two soils, IRM alone at rates up to 10% (the highest level in the study) significantly reduced leachable Pb as compared to the untreated soils. IRM at 10% was not sufficient, however, to reduce the leachable Pb below 5 mg of Pb L\(^{-1}\) for soils 2 and 3. Other materials, such as CaSO\(_4\), CaCO\(_3\), and biosolids, when applied at rates as high as 10% also were not as effective as P for reducing leachable Pb (see Figure 3C for natural humus; other data not presented). Furthermore, some of these materials at high levels are probably incompatible with optimal plant growth.

Portland cement is often used to immobilize metals in a solid matrix, such as soils, prior to landfilling. For the three soils, empirically derived additions of 11.6%, 11.6%, and 12.2% portland cement resulted in leachable Pb concentrations of 0.6, 1.6, and 1.0 mg of Pb L\(^{-1}\), respectively. Portland cement, however, significantly increased the pH of the leachate solution from 4.9 to 6.9 or higher. The other amendments shown (i.e., IRM, KH\(_2\)PO\(_4\), and natural humus) had little effect on the pH of the leaching solution (data not shown). Portland cement probably resulted in the production of lead carbonates (Figure 2A–C), which are not highly soluble in a leachate with a pH of 6.9 or higher.

The results of the PBET showed that treating the soil with IRM, P, and portland cement may be effective in reducing Pb bioaccessibility in these soils when compared to the untreated soils (Figure 4). This can be seen for soil 1 in which Pb bioaccessibility was reduced in the stomach phase (pH 2.5) from about 40% (standard error of the mean (SE) = 3%, n = 6) of the total for the untreated soil when averaged over both time points to about 11% (SE = 1%, n = 6) of total after treatment with 10% IRM. Phosphorus (added at the rate of 0.5% P as KH\(_2\)PO\(_4\)) was also highly effective in reducing Pb bioaccessibility in the stomach phase of this soil to about 20% (SE = 2%, n = 6).

The IRM and portland cement soil treatments were also effective in reducing Pb bioaccessibility in the simulated intestinal phase of soil 1 (Figure 4A). Lead absorption into the blood of animals occurs primarily in the small intestines (20), the chemistry of which we attempted to simulate in the intestinal phase of the PBET. As shown by Ruby et al. (9), the
bioaccessibility of Pb in the simulated stomach phase, however, correlated better than Pb bioaccessibility in the simulated intestinal phase with a Sprague–Dawley rat model. Also, because Pb bioaccessibility is usually higher in the acid
solution of the simulated stomach phase, it is a more conservative estimate of the Pb bioavailability potential than the simulated intestinal phase.

The P and IRM treatments were also effective for reducing Pb bioaccessibility in soil 2 (Figure 4B). The IRM and P treatments had the lowest overall Pb bioaccessibility in the simulated stomach solution, although the IRM treatment was initially the highest. Furthermore, Pb bioaccessibility in the soil treated with IRM or P was significantly lower than untreated or portland cement-treated soil in the simulated intestinal phase.

The effect of soil amendments on Pb bioaccessibility was highly variable in soil 3, which had the highest total Pb concentration of the three soils (Figure 4C). Pb bioaccessibility in the simulated stomach phase of soil 3 was highest in the 10% IRM treatment and lowest in 0.5% phosphorus treatment. The P treatment was significantly lower ($p < 0.05$) as compared to untreated soil and the other two treatments. For the simulated intestinal phase of this soil, the Pb bioaccessibility of the portland cement treatment was significantly greater than the other treatments shown. This result suggests that, in the short term, these stabilization techniques will most likely be empirically derived. Additional work, however, is necessary to help predict a mix of amendments that are needed to reach an acceptable Pb bioavailable or bioaccessible end point for all soils.

Remediation criteria for Pb in soils are set primarily to protect children, who may incidentally ingest small quantities of soil. It is thought that exposure to Pb can increase the risk of irreversible neurobehavioral damage at concentrations as
low as 10 µg of Pb dl⁻¹ of blood (21). The integrated exposure uptake biokinetic model for lead in children (IUBK) was designed to estimate Pb uptake from Pb in soil and dust that is ingested or inhaled (22). The default value for the bioavailability of Pb in soil that is ingested is 30% of the total Pb, meaning that 30% of the total Pb in the ingested soil enters the blood. In this study, lead bioaccessibility varied from 6 to 42% of the total in the three untreated soils used. This variability in bioaccessibility indicates the variability of soil Pb bioavailability in animal models (8) and that Pb bioavailability may differ significantly from 30%. The default value of 30% may underestimate or overestimate the risk posed by a Pb contaminated soil. More importantly, the data indicate that if the PBET can be used to help generate site-specific data on Pb bioavailability, it may also be useful in helping to determine site-specific soil treatment strategies that reduce the risk of Pb poisoning due to soil ingestion. These strategies may include cost-effective soil treatments that can help lower the bioavailability of Pb in soil by changing the solubility of Pb in the GI tract.

Reducing metal availability and maximizing plant growth through in-place inactivation may prove to be an effective method of in situ soil Pb remediation on industrial, urban, and mining sites. In addition, these stabilization techniques can occur as part of a treatment train with other phytoremediation methods now under development, the most intriguing of which may be “biomining” the available fraction of metal pollutants with plants.

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