



Reducing Children's Risk from

LEAD in SOIL

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Lead poisoning is the most common and serious environmental disease affecting young children, according to the U.S. Centers for Disease Control and Prevention (CDC). During the past 25 years, researchers have gathered extensive information that verifies the adverse effects of elevated levels of lead in the blood on cognitive development. CDC recognized this research and lowered the definition of elevated blood lead level for children under age 6 from 25 to 10 micrograms lead per deciliter ($\mu\text{g Pb/dL}$) (1). Evidence for potential effects at even lower levels continues to accumulate (2). The median levels in children under age 6 fell from about 15–18 $\mu\text{g Pb/dL}$ blood in 1970 to 2–3 $\mu\text{g Pb/dL}$ in 1994 as a result of the concurrent reduction of lead in automotive emissions, paint, drinking water, and soldered food cans (3). Yet, more than 2.2% of children ages 1–5 still have blood lead concentrations higher than 10 $\mu\text{g Pb/dL}$ (3). Children living in central cities exhibit a higher prevalence of elevated blood lead levels (4).

**A field experiment in
Joplin, Mo., demonstrates
alternatives to traditional
cleanups.**

CDC estimates that lead poisoning in children costs billions of dollars for medical treatment and special education as well as losses in the children's future earnings. Paint, drinking water, soil, and dust that contain lead are the major remaining sources of exposure. Although programs to reduce children's exposure to lead from paint and drinking water have been implemented in the United States, no program exists for lead-contaminated soil beyond Superfund sites. According to CDC and the U.S. EPA, insufficient information is available on which to base such a program. Far less is known about the hazards of lead in soil—and how to address them—than about lead in paint or water. Thus, information is needed to better characterize the effects of soil properties on the levels of lead associated with risk from soil, to determine the effects of lead speciation on risk from soil, and to identify successful remediation methods.

Traditional methods for reducing the risk of elevated levels of soil lead include removal, covering, or dilution by mixing with uncontaminated soil. EPA's National Risk Management Research Laboratory (NRMRL) and DuPont Co. collaborated to evaluate in situ remediation technologies. This article describes the resulting field experiment at a lead-contaminated urban site in Joplin, Mo., which demonstrated that reducing risk from lead does not require removing soil.

The gravity of lead

Lead, a naturally occurring metal, has always been present in soils, surface waters, and groundwaters. Flaking paint, decades of leaded gasoline use, mining operations, smelter and industrial emissions, waste incineration, and application of pesticides all contributed to elevating lead to harmful levels in soils. Agricultural soils have a median content of 11 milligrams of lead per kilogram (mg Pb/kg) and range from less than 1 to 135 mg Pb/kg (5). Because of their high concentration of industries, aging buildings, and vehicular traffic, urban environments have a median lead level in soil of more than 1000 mg Pb/kg (6, 7) and reported values as high as 50,000 mg Pb/kg (8). According to the EPA CERCLIS database, lead is also a contaminant of concern in about half of the National Priority List sites for which soil is the contaminated media (9). To complicate matters, lead usually remains near the surface of soil, which increases the chance of exposure.

Children who reside in areas where soils contaminated by smelter emissions, automotive emissions, or paint residue have exceeded 500–1000 mg Pb/kg often have increased blood lead levels (10). In other cases, social reasons or chemical factors in the soil altered exposure or bioavailability of lead in the soil; little or no increase in blood lead was observed, even with soils containing 5000 mg Pb/kg (11).

Soils contaminated by mining activities appear to have less bioavailable lead than urban soils (12–15). Studies show the relationship of blood lead to soil lead for children in smelter and urban areas range from 1.1 to 7.6 ($\mu\text{g Pb/dL blood}/(1000 \text{ mg Pb/kg soil})$), whereas for children in mining areas the relationship ranged from 0 to 4.8 ($\mu\text{g Pb/dL blood}/(1000 \text{ mg Pb/kg}$

soil) (15). Three explanations have been offered for this observation: the size of the lead-containing particle, the solid-state species of lead in soil, and the geochemical matrix incorporating the lead species. These characteristics affect dissolution and solubility of the soil lead. In addition, the complex soil matrix may alter the exposed receptor's ability to absorb lead.

The effects of both lead compounds and particle size were reported in soil-dosing studies with cattle (16) and rats (17, 18). Chaney et al. found the bioavailability of lead from lead acetate in a purified rat diet was significantly reduced when amended with a soil containing a low concentration of the metal (8). When the rats were fed urban garden soils with about 1000 mg Pb/kg, bone lead was only about 20% as high as when equivalent lead acetate was added to the control diet. Another soil with 10,200 mg Pb/kg caused bone lead to be 70% as high as with an equivalent lead acetate dosing, suggesting that the levels of both soil lead contamination and lead species are important in determining lead bioavailability.

Nutritional studies, mostly with rats, have shown that when dietary calcium or iron was deficient, the circulatory system absorbed more lead (19, 20). In human studies, dietary components, calcium, phosphorus, phytate (inositol hexaphosphate), and fiber reduced lead absorption (21–23). Combinations of calcium and phosphorus reduced lead absorption more than the presence of increased levels of calcium or phosphorus alone (22, 24). Results from the U.S. National Health and Nutrition Examination Survey, conducted by CDC's National Center for Health Statistics, support this finding, which showed that children with lower intakes of dietary calcium had increased levels of lead in their blood (25).

Collectively, these results indicate nutritional status alters lead absorption into the body, the form of lead affects its bioavailability in soil, and bioavailability from soil increases with increasing soil lead concentrations. However, we will only be able to quantify and predict these observed changes in lead bioavailability when the mechanisms that affect lead solubility and absorption by the receptors are understood. Additionally, we need to develop standardized procedures to account for and quantify the environmental availability of lead in soil and the amount delivered to the site of toxic action. Most importantly, as we understand the mechanisms for sequestering lead in environmentally stable forms, our ability to develop appropriate risk standards and remediation treatments for soils will improve.

Reducing exposure

Techniques to reduce exposure traditionally focus on blocking the pathway to the human receptors, such as soil removal and offsite disposal. Cost, logistical concerns, and regulatory requirements associated with excavation, ex situ treatment, and disposal, however, can make in situ treatment an attractive option.

Soil bioavailability strongly depends on the metal's mineral form, particle size, and soil chemistry; this relationship is illustrated in the development and calibration of an in vitro bioaccessibility technique in which various primary lead minerals and soil forms

ranged from 0 to 100%, depending on the form of the lead (26). The *in vitro* bioaccessibility measurement was related to *in vivo* swine bioavailability (26). Thus, it should be possible to relate soil lead bioavailability to a quantitative description of the mineral and/or adsorbed form of soil lead. Further, if the soil forms are converted to lead forms that have reduced bioavailability, the overall bioavailability of lead in the soil should be reduced. Therefore, NRMRL started a research program to demonstrate the connection between the mineralogy of lead in soil, the soil chemistry, and the lead bioavailability (27). The program is complicated by the requirement that changes in the chemical form of the lead in soil be evaluated in relation to changes in the bioavailability of the lead.

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Children face the greatest risk from soil lead exposure. In a review of drug absorption, Kararli (28) concluded that no single animal can mimic the gastrointestinal tract characteristics of humans, although it is possible to select the right animal model for a specific purpose. Thus, the debate about which animal model (e.g., weanling pigs or weanling rats) is most appropriate as a surrogate for children has become a subset of issues that need to be addressed (14, 29–32). Animal-dosing studies are complex, expensive, and time-consuming; it is preferable therefore to ultimately identify a battery of chemical or physical tests that will dependably mimic and predict the bioavailability of soil lead to humans (see Supporting Information).

Understanding lead exposure; the chemical, biochemical, and physical factors that affect lead bioavailability; and how environmental chemistry influences bioavailability may allow development of less costly and environmentally disruptive methods of soil lead remediation. At this time, there is insufficient evidence of the relationship between these surrogate measures and bioavailability of soil lead to animals to conclude from any one measurement that bioavailability has changed. Rather, a change in these surrogate mea-

asures must be related to a change in an appropriate measure of lead bioavailability. Moreover, without an understanding of the reasons for the variations, a change in measured lead bioavailability is of limited value. Chemical and physical surrogates are therefore required to understand the reason for the change in lead bioavailability as measured by an animal model.

Laboratory studies. The NRMRL research program's initial goal was to demonstrate the feasibility of altering the mineralogy of lead in soil in a laboratory setting by using thermodynamic and kinetic studies. Orthophosphate (aqueous phosphorus, hydroxyapatite, or phosphate rock) rapidly and effectively precipitates lead from solution to form a series of lead phosphates of low aqueous solubilities (27, 33–43). The final product of lead immobilization is primarily pyromorphite [$\text{Pb}_5(\text{PO}_4)_3\text{X}$, where X is OH, Cl, or F], which is stable under normal soil environmental conditions.

Children with lower intakes of dietary calcium had increased levels of lead in their blood.

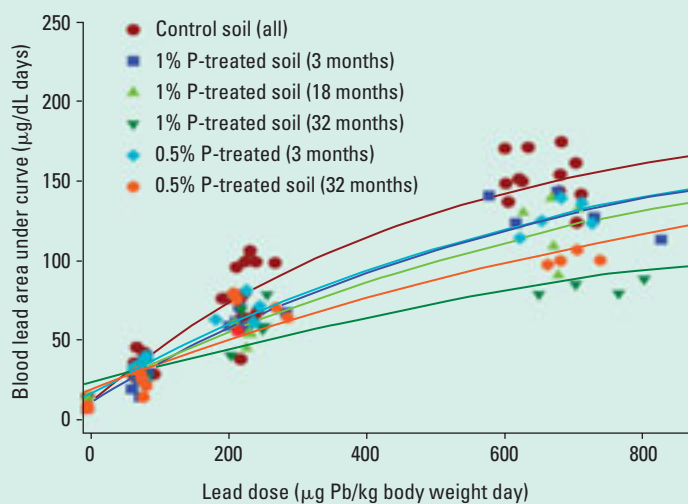
Results strongly support the mechanism of hydroxyapatite dissolution and reprecipitation of the phosphorus with lead as pyromorphite. The presence of common soil solution anions and cations had little impact on lead immobilization (37, 38). Further, environmentally relevant concentrations of other metals had no significant effect on lead immobilization by hydroxyapatite; in fact, hydroxyapatite may remove the metals (38). Also, pyromorphite formation from lead adsorbed on goethite ($\text{Fe}(\text{OH})_3$) (39) and primary lead minerals, including cerussite (PbCO_3) (40, 41), anglesite (PbSO_4) (42), litharge (PbO) (40), massicot (PbO) (40), and galena (PbS) (43), by addition of apatite have been reported. The completeness and kinetics of this transformation depend on the mineralogy of lead, the amount of apatite added, and the pH of the system. In soil systems, the changes in soluble lead levels and the identification of reaction products illustrate that the reaction can occur in contaminated soils (33). In all cases, hydroxyapatite dissolution followed by precipitation of hydroxypyromorphite, chloropyromorphite, or fluoropyromorphite was the primary process during the reaction, but lead adsorption by hydroxyapatite and cation substitution of lead for calcium on hydroxyapatite may also have occurred.

The speed with which the reaction between soluble lead and phosphorus takes place and the rate at which primary lead minerals, adsorbed lead, and soil lead are transformed to pyromorphite illustrate that the reaction is fast enough to occur during extraction procedures. Thus, using traditional soil chemical extraction procedures (e.g., sequential and *in vitro* bioaccessible extractions) can give an inaccurate assessment of the amount of transformation that has occurred (33, 44). Determining the mineral form of soil lead in these systems, particularly when they are

FIGURE 1

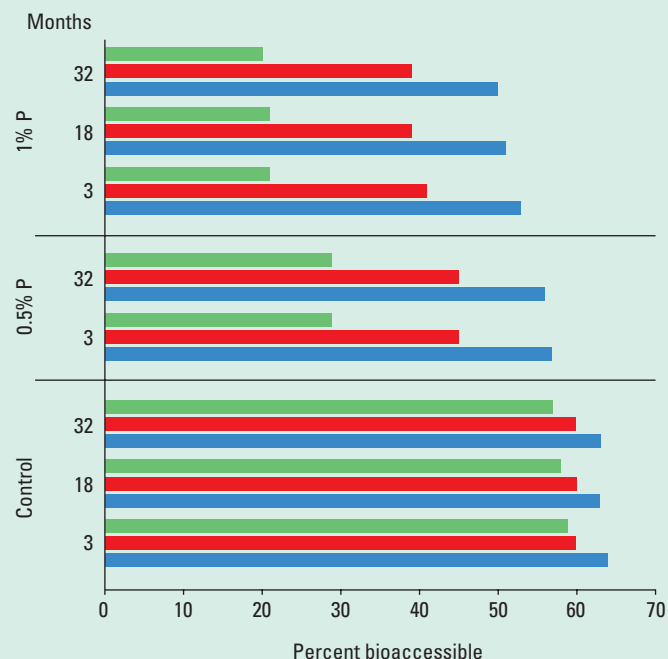
Swine blood lead response

Blood lead levels in swine after dosing with the contaminated soil treated with phosphorus were lower than blood lead levels in swine dosed with the contaminated soil, which proves that in situ treatment works.

**FIGURE 2**

In vitro bioaccessible lead

Results show that 1% addition of phosphorus to contaminated soils at pH of 2.5 (green bars) reduced bioaccessibility of lead in soil. Red and blue bars represent results from pH of 2.0 and 1.5, respectively.



at nonsteady state, relies on nonaqueous separation or spectroscopic techniques.

Because the total concentration of lead in an intact soil system is often not enough for a traditional X-ray diffraction (XRD) to detect, enriched fractions are required for analysis. Additionally, scanning elec-

tron microscopy and energy-dispersive X-ray and X-ray adsorption fine structure (XAFS) analyses have been used to characterize the reaction product and forms of lead in contaminated soils (33, 44, 45).

Field studies. As it became apparent that soil lead mineralogy could easily be altered under laboratory conditions, NRMRL, in cooperation with DuPont Co., formed the In-Place Inactivation and Natural Ecological Restoration Technologies (IINERT) Soil-Metals Action Team to provide a forum to explore and develop in situ techniques. These techniques are outlined in the Supporting Information.

IINERT recognized the need to demonstrate a reduction in the bioavailability of lead in soil in a field setting, to identify the reason for a change in the bioavailability, and to determine the long-term stability of the change. The group established a field experiment to facilitate collaborative efforts and test the hypothesis that adding reactive materials to lead-contaminated soil will result in less hazardous lead forms. The soil composition at the Joplin site averaged 2400 mg Pb/kg soil (see Supporting Information for site characterization and experimental design). Treatments were installed during March 1997, and soil samples from plots treated with phosphoric acid were collected in June 1997, September 1998, and November 1999. Further sample collection is expected. Various collaborators will publish the data, but the following summarizes the interim results.

Results from IINERT

We worked with the swine model that EPA previously used to estimate site-specific oral soil lead bioavailability (31). The Supporting Information provides details. Because of cost and logistical considerations, the swine in vivo bioavailability assay was performed only on the phosphoric acid treatments.

We observed statistically significant reductions in blood lead in swine for the phosphorus-treated soil (Figure 1). Thus, the primary hypothesis that in situ field treatments reduce soil lead bioavailability is true. Rather than comparison to a lead acetate blood dose-response curve to determine relative bioavailability (31), we compared the response curves of the control soil and treated soil to determine the effectiveness of treatment. The percent reduction in soil lead bioavailability for the soil treated with 1% phosphorus was 29% for the 3-month sample and increased to 71% for the 32-month sample. The percent reduction in soil lead bioavailability for the 0.5% phosphorus treatment was 32% and 52% for the 3- and 32-month samples, respectively.

Rat in vivo bioavailability assays were performed on most treatments from the latter sampling. For comparison with the swine in vitro assay, only the phosphoric acid treatment (1% phosphorus at 3 months and 32 months and 0.5% phosphorus at 32 months) is presented. The blood lead of the animals dosed with the phosphorus-treated soil was not statistically different from the blood lead of the animals dosed with the control soil. However, using the methodology of Hettiarachchi et al. to analyze the plateau from response curves (46), the researchers showed that the data did exhibit a trend in the percent reductions in soil lead bioavailability, suggesting

that in situ treatments can be effective under field conditions, as shown in the Supporting Information.

At the 32-month sampling, there was a 40% decrease in response of the soil treated with 1% phosphorus and a 23% decrease in response with 0.5% phosphorus, compared with the control. The in vivo results for the rat and swine assays gave similar results for the 1% phosphorus treatment at the 3-month sampling, whereas the 32-month sampling of the rat in vivo bioavailability gave a smaller reduction than the swine in vivo bioavailability. Thus, the relationship between animals is less than perfect and requires a more robust data set for development. However, both animal assays led to the conclusion that in situ treatment can reduce soil lead bioavailability.

Following Maddaloni's methodology (47), Maddaloni and Graziano are conducting an adult human oral bioavailability study using a stable isotope analytical technique to measure adsorption in fasting human adults. Preliminary results for the 18-month 1% phosphoric acid and control soil study show that bioavailability was reduced 69% from an absolute bioavailability of 42% in control soil to 13% in soil treated with 1% phosphorus.

The human adult model provides a larger reduction in lead bioavailability measurement than either of the animal models. At the present time, sufficient numbers of samples have not been analyzed to develop the relationships between these various in vivo models. The complexity of the dissolution and precipitation reactions and the animal physiological processes involved ensures that a great deal of basic research will be required before a complete mechanistic understanding can be obtained. However, all animal models support the conclusion that reductions in bioavailability are possible by simple in situ treatments. The human model provides a measure of the greatest reduction in soil lead bioavailability, and the use of the animal model may provide a conservative estimate of reduction.

In addition to these in vivo animal models, in vitro chemical extractions devised to imitate the physiology of human and animal digestive tracts were evaluated. Ruby et al. (48) applied Miller et al.'s (49) and Reddy et al.'s (50) methods to soil lead, including evaluation of the role of enzymes, organic acids, and pH levels.

This methodology was refined and used on soil samples from a swine study conducted by EPA Region 8, which provided good correlations (26). To further verify and standardize the in vitro methodology, a solubility-bioavailability research consortium continues to work on these issues. They further simplified the methodology and found that an extraction pH of 1.5 or 2.0 (glycine-buffered HCl) relates well to the swine bioavailability measurements from EPA Region 8.

Soil samples from the IINERT field experiment were extracted at three pHs (1.5, 2.0, and 2.5) with this simplified in vitro methodology. Figure 2 shows the results from the samples for the phosphoric acid treatments at the three sampling times. The effect of treatment was more apparent as the pH of the extraction increased from 1.5 to 2.5; however, no effect of sampling time was observed. Thus, the in vitro ex-

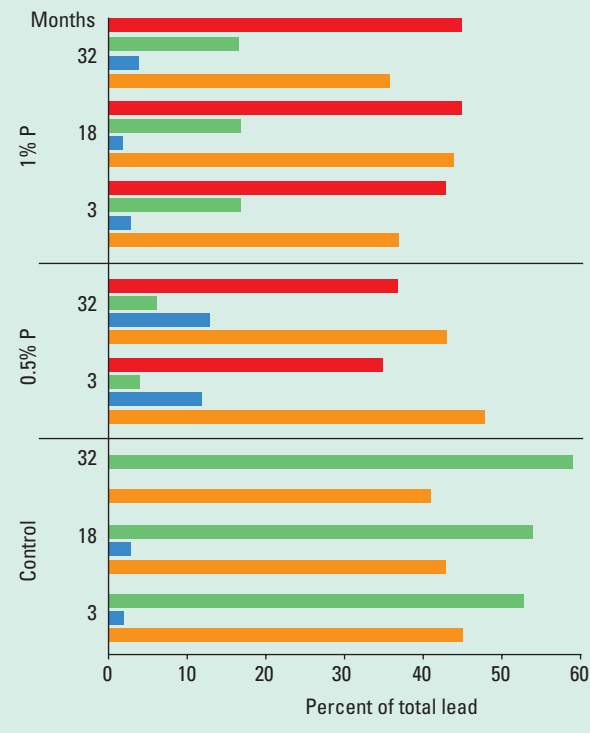
traction failed to predict the change observed in in vivo soil lead bioavailability associated with sampling time. The inability of an in vitro extraction technique to predict change in an amended system is similar to the inability of sequential extractions to measure changes in soil lead geochemical form in amended systems not at steady state (33, 44). Thus, extraction techniques may not be valid measures of changes in bioavailability associated with soil amendments. Rather, these values may only indicate directional changes and, possibly, what change in bioavailability may be obtained at steady state.

The issue of identification and quantification of lead species in the complex soil matrix remains a long-term research need and extends to other metals in soil systems. Results of XAFS and X-ray fluorescence microprobe analysis illustrate that the addition of phosphate resulted in increased pyromorphite in the soil samples from the Joplin site and thus provide a reason for the observed reductions in soil lead bioavailability (Figure 3).

FIGURE 3

Lead mineral forms in Joplin after treatment

The bioavailability of lead decreased because in situ phosphorus treatments converted the lead to various mineral forms. Red bars represent the pyromorphite percentage of total lead; green, lead sulfur; blue, lead carbonate; and orange, lead absorbed.



We conclude that in situ addition of phosphate to lead-contaminated soil under field conditions can alter the form of soil lead and its bioavailability and that it is possible to measure the bioavailability of soil lead using animal bioassays and simple chemical in vitro techniques. Thus, we proved that under field conditions, in situ soil treatments change the form of soil lead and its bioavailability. The apparent environ-

mental stability of the reaction products, along with the ready availability and low cost of phosphate, suggests that this approach has great merit for cost-effective in situ immobilization of lead in contaminated soils and wastes. However, the relationships between the various in vivo models, the various in vitro models, or an in vivo model and an in vitro model cannot be quantified at this time. Although a more robust data set may solve this problem, it's possible that the various measurements simply may not be related.

In situ soil treatments change the form of soil lead and its bioavailability.



Acknowledgments

EPA has not subjected this manuscript to internal policy review. Therefore, the results presented do not necessarily reflect agency policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. This information is a summary of the efforts of many people involved in the IINERT project, including C. Blum, S. Chillrud, J. Graziano, and N. Lolacona of Columbia University; T. Evans and J. Yang of the University of Missouri; D. Hill, K. Patterson, C. Veillon, and Q. Xue of USDA; and M. Ruby of Exponent. For more information on IINERT, visit www.rtdf.org.

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Note: Supporting Information is available on the Web at <http://pubs.acs.org/est>.

Supporting Information for *ES&T* A-page feature, “Reducing Children’s Risk from Soil Lead” by James A. Ryan, William R. Berti, Sally L. Brown, Stan W. Casteel, Rufus L. Chaney, Mark Doolan, Peter Grevatt, Judith Hallfrisch, Mark Maddaloni, Dave Mosby, and Kirk G. Scheckel.

BIOAVAILABILITY MEASUREMENTS

As used, bioavailability refers to absorption into systemic circulation ... consistent with use of the term in human health risk assessments and toxicological use of the term. Bioavailability can be expressed in absolute terms (absolute bioavailability) or relative terms (relative bioavailability). Absolute bioavailability (also referred to as oral adsorption fraction) is that fraction of the total amount of material in contact with a body portal-of-entry (gut, skin, lungs) that enters the central compartment (blood). Relative bioavailability is the ratio of the absolute bioavailability in a test material to the absolute bioavailability of a reference material. Relative bioavailability is important in risk assessment because we are often most interested in knowing the extent to which the absolute bioavailability of a metal increases or decreases in context with the exposure matrix (e.g., food vs water vs soil), or with the physical or chemical form(s) of the metal to which humans are exposed.

A related term, pertaining to bioavailability assessment, is bioaccessibility. This usually refers to a measure of the physiological solubility of the metal at the portal of entry into the body. Since solubilization is usually required for absorption across membranes, poorly soluble forms of metals, with low bioaccessibility, may also have low bioavailability. In certain circumstances, if solubility is the major determinant of absorption at the portal of entry,

bioaccessibility may be equivalent to bioavailability.

In the case of evaluation of lead bioavailability to children surrogate measurements must be used. This network of surrogate measures that are the most important surrogate measurements of lead bioavailability in children (or the fetus in a pregnant worker at industrial sites) are illustrated in Figure 1. At the bottom left of the diagram is the fundamental question: Is the soil harmful to a child? Immediately above is the question: Does ingesting the soil result in elevated lead levels in the child's blood and organs? Further up the diagram are questions of harm and elevated lead levels in the blood and tissues of lab animals used as surrogates. What is the relationship between blood lead elevation in laboratory animals and humans if each were fed the same soil? To the right of the diagram are physical and chemical soil measurements (e.g. soil metal speciation, *in vitro* extraction, total metal) that are being used as surrogates for lead bioavailability. If a soil is contaminated only with a lead compound of low solubility and its availability for chemical extraction is low, will accidental ingestion result in low or no elevations in blood lead to both animals and humans? At present, this lack of perfect relationships between bioavailability measurements in humans and animals as well as that between the *in vitro* surrogates and the animal or human measures requires collection of multiple kinds of observations (e.g., *in vivo* bioavailability, chemical speciation) to evaluate bioavailability. A change in a chemical surrogate (e.g., *in vitro* bioavailability, mineral species) measurement must be related to a change in an appropriate measure of *in vivo* lead bioavailability by an animal. Further, a change measured by *in vivo* lead bioavailability by an animal is of limited value without an understanding of the reason for the change.

IINERT

The National Risk Management Research Laboratory (NRMRL) of the U.S. EPA and DuPont Co. formed the In-Place Inactivation and Natural Ecological Restoration Technologies (IINERT) Soil-Metals Action Team in November 1995 as part of the Remediation Technologies Development Forum (RTDF). EPA created the RTDF in 1992 to foster collaboration between the public and private sectors in developing innovative solutions to mutual problems of contaminated materials. The IINERT Soil-Metals Action Team includes representatives from industry and government who share an interest in further developing and validating in situ techniques as viable technologies for eliminating the hazardous metals in soils. Our purpose is to develop and demonstrate in-place inactivation and natural ecological restoration technologies that reduce and eliminate the risks of metals and metalloids in soil to human health and the environment and to achieve regulatory and public acceptance of these technologies. The goals of the group include the following:

- Understand the mechanisms by which these technologies work.
- Develop appropriate testing protocols and methodologies that illustrate the utility of these technologies.
- Improve predictive capabilities for these technologies.
- Facilitate validation of the effectiveness and persistence of these technologies.
- Prepare guidelines for effective implementation of these technologies.
- Gain scientific, public, and regulatory acceptance.

The IINERT Soil-Metals Action Team has developed the following hypotheses:

- Hypothesis 1: Surrogate relationships for lead availability can be identified and confirmed among *in vivo* studies (e.g., humans, pigs, and rats), *in vitro* studies, and chemical extractions. These relationships will lead to simple, fast, and less expensive tests and proofs of the technology.
 - Rat, weaning pig, primate, and human adult studies are equally useful for determining lead bioavailability in soils, which can be correlated to soil lead bioavailability in children or human adults.
 - Chemical extractions and *in vitro* tests can be identified that correlate well with the results of animal studies.

- Hypothesis 2: Good correlations exist between soil components (e.g., lead species, non-lead-containing components) and the soil lead hazard.
 - Soil constituents strongly adsorb, physically entrap, and/or precipitate lead, limiting the soil lead hazard.
 - The effect of soil components on the soil lead hazard can be determined from site- and soil-specific information.

- Hypothesis 3: Engineered addition of materials to lead-contaminated soils will induce the formation of less hazardous lead forms, providing a practical approach to in-place inactivation.
 - Soil lead inactivation approaches are sufficiently robust to overcome variability from site to site and within a single site.
 - Soil lead inactivation approaches will provide a long-term reduction in the soil

lead hazard.

- Hypothesis 4: The research and development of IINERT for soil lead extends to other soil contaminants as well (Zinc, Cadmium, Chromium, Nickel, Arsenic, Copper, Selenium, petroleum hydrocarbons, etc.).

Joplin site

The 42 × 47-m site is surrounded by a chain-link fence in a residential environment near a lead smelter, which operated from the 1880s until the late 1960s. Smelter emission was the primary source of lead contamination to the site. The soil lead concentration at the site is variable, ranging from 270 to 7100 mg Pb/kg with 25th and 75th percentile value of 1160 and 3320 mg Pb/kg, respectively, and average and median values of 2400 and 2100 mg Pb/kg, respectively.

Preliminary analysis of the bulk samples indicated that the primary forms of soil lead were sulfate, sulfide, carbonate, and oxide. The soil had a neutral pH (6.9–7.2), organic carbon content of 4.6–5.6 %, a cation exchange capacity of 27.2–32.2 meq/100 g soil, and a Bray extractable phosphorus of 12–39 mg P/kg soil.

The researchers installed treatments in March 1997, using a completely randomized design with four replicates. A high-density polyethylene membrane was placed around the perimeter of each of the 2 × 4-m plots to reduce the potential of interplot contamination. In addition to the phosphate treatment, other materials that have been reported to reduce bioavailability were included as treatments:

- 1) Control (100 kg ha⁻¹ (Nitrogen, Phosphorus, Potassium))
- 2) 1% P as triple super phosphate (TSP)

- 3) 3.2% P as TSP
- 4) 1% Fe as “iron rich” (an industrial byproduct of making TiO₂) + 1% P as TSP
- 5) 2.5% Fe as “iron rich” + 0.32% P as TSP
- 6) 2.5% Fe as “iron rich” + 1% P as TSP
- 7) 1% P as rock phosphate
- 8) Biosolids compost at 10%
- 9) Biosolids compost at 10% + 0.32% P as TSP
- 10) Biosolids compost at 10% + 1% P as TSP
- 11) 0.5% P as phosphoric acid + 0.05% KCl
- 12) 1% P as phosphoric acid + 0.05% KCl

Amendments were weighed and hand-applied on a per-plot basis to the tilled soil. After amendment, plots were well mixed with a rototiller and covered with a commercial landscape fabric to limit erosion. In May, the fabric was removed, and lime (Ca(OH)₂) (71% purity) was added and rototilled into each plot to bring the pH back to 7. The plots were then hand-seeded with Kentucky 31 tall fescue (*Festuca elatior* cv.). For the phosphoric acid treatments, liquid fertilizer-grade phosphoric acid and fertilizer-grade potassium chloride (KCl) were surface-applied and rototilled. Lime (Ca(OH)₂) was applied 10 days later and hand-raked to incorporate to a depth of 10 cm; 30 days later, the plots were seeded.

Soil samples from the phosphoric acid-treated plots were collected in June 1997, September 1998, and November 1999. Further sample collection is anticipated. Composite samples from each of the four replications were mixed and sieved. The sample with <250 μm size fraction was

used for in vivo (rat, swine, and human) bioavailability and in vitro bioaccessibility analysis as well as analysis for mineral form forms of lead. This size fraction was used to represent the particle size of the material that adheres to children's hands and thus is most likely ingested.

Swine bioavailability

Soil (3 dosage rates) was placed in approximately 5 g of moistened food fed by hand, twice daily, 2 h before feeding, to simulate a fasting condition. Five replicate pigs were used for each dosage rate. After 15 days, liver, kidney, and right femur tissue samples were collected.

Response curves for blood lead (area under the curve from blood samples collected (on days -4, 0, 1, 2, 3, 5, 7, 9, 12, and 15) during the 15-day dosing experiment) and lead dosing level (0, 75, 225, and 625 $\mu\text{g Pb (kg body weight}\cdot\text{day)}^{-1}$) were fitted with a nonlinear curve ($y = a + b(1 - \exp^{-cX})$) where X is dosing. EPA used this swine model to estimate site-specific soil lead bioavailability (*I*). To determine the effectiveness of treatment, we compared the response curves of the control soil and treated soil rather than a comparison to a lead acetate (PbOAc) blood dose-response curve as reported in (*I*). The reductions in soil lead bioavailability were calculated by dividing the difference in the rate of curvature for the blood lead dose-response curve from the phosphoric acid-treated soil and the rate of curvature for the blood lead dose-response curve from the control soil by the rate of curvature for blood lead dose-response curve from the control soil. For additional information on the swine model and its use by EPA Region 8 to evaluate site-specific lead bioavailability, see

<http://www.epa.gov/region08/superfund/risksf/risksf.html>

Rat bioavailability

Seven replicate rats were used for each dosage rate. The soil was mixed in the diet to provide 0, 25, 50, and 75 mg Pb/ kg food. The basal diet consisted of 950 g fiber-free rat feed (AIN93G Purina Test Diet™) and 50 g inert material (silica sand (<250 μm) + soil (<250 μm) or PbOAc) to give the desired lead dose. After 32 days, blood, liver, kidney, and right femur tissue samples were collected. The blood lead response curves were developed from the blood samples collected at the end of the exposure period for the four dosing levels (0, 25, 50, and 75 mg Pb/kg of food) and fitted with a nonlinear curve ($y = a + b(1 - \exp^{-cX})$). The reduction in soil lead bioavailability was calculated by dividing the difference in the plateau value of the blood lead dose–response curve from the phosphoric acid-treated soil and the plateau value of the blood lead from the control soil dose–response curve by the plateau value of the blood lead from the control soil dose–response curve, similar to the technique used by Hettiarachchi et al. (2). In the rat feeding experiments, no statistically significant effect could be attributed to treatment or time; however, the data in Figure 2 exhibit a trend which illustrating in situ treatments can be effective under field conditions.

References:

- (1) Casteel, S. W.; et al. *Fundam. Appl. Toxicol.* **1997**, *36*, 177–187.
- (2) Hettiarachchi, G. M.; et al. *J. Environ. Qual.* **2003**, *32*, 1335-1345.

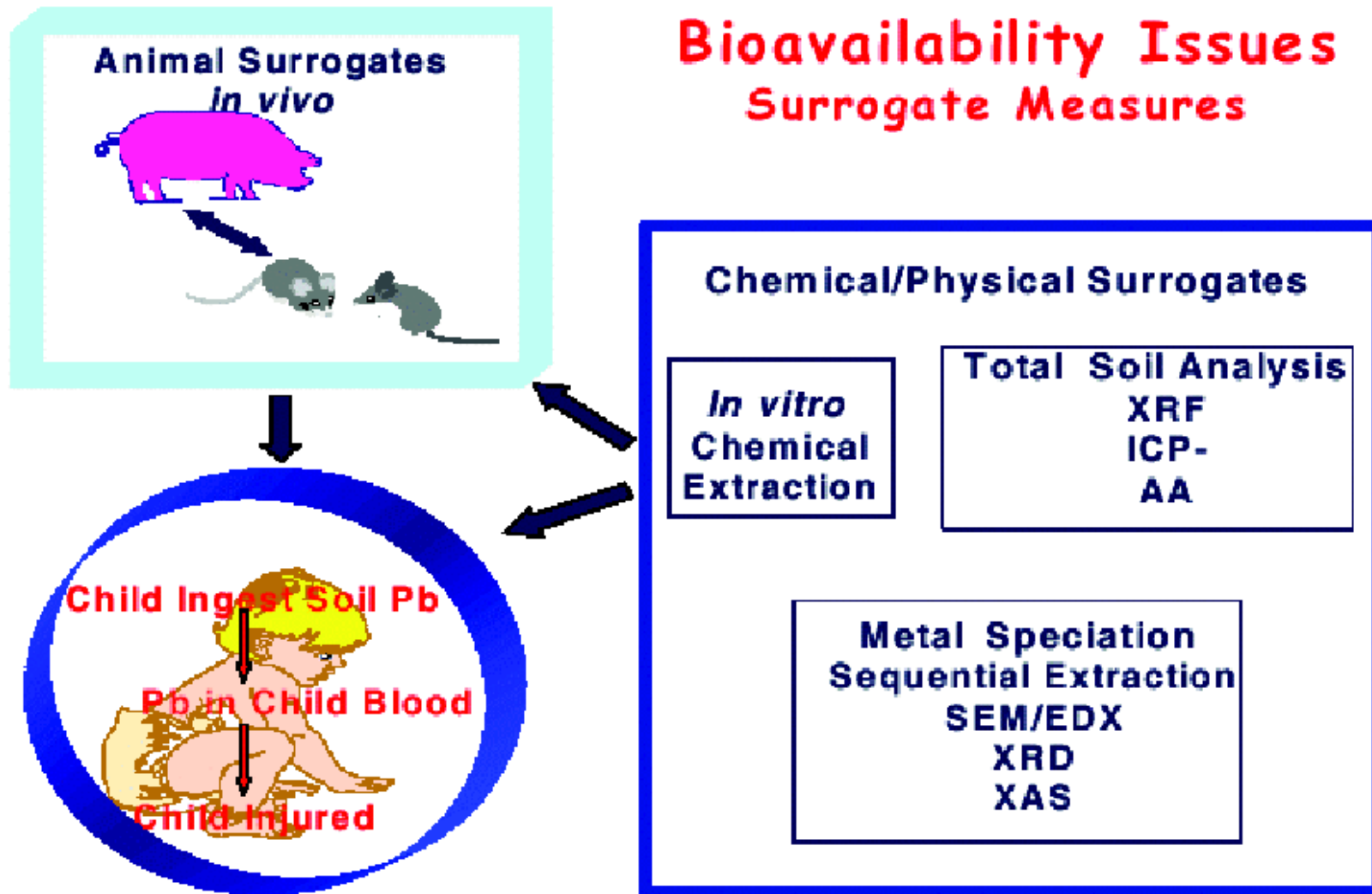


Figure 1. Fundamental issues addressed by IINERT

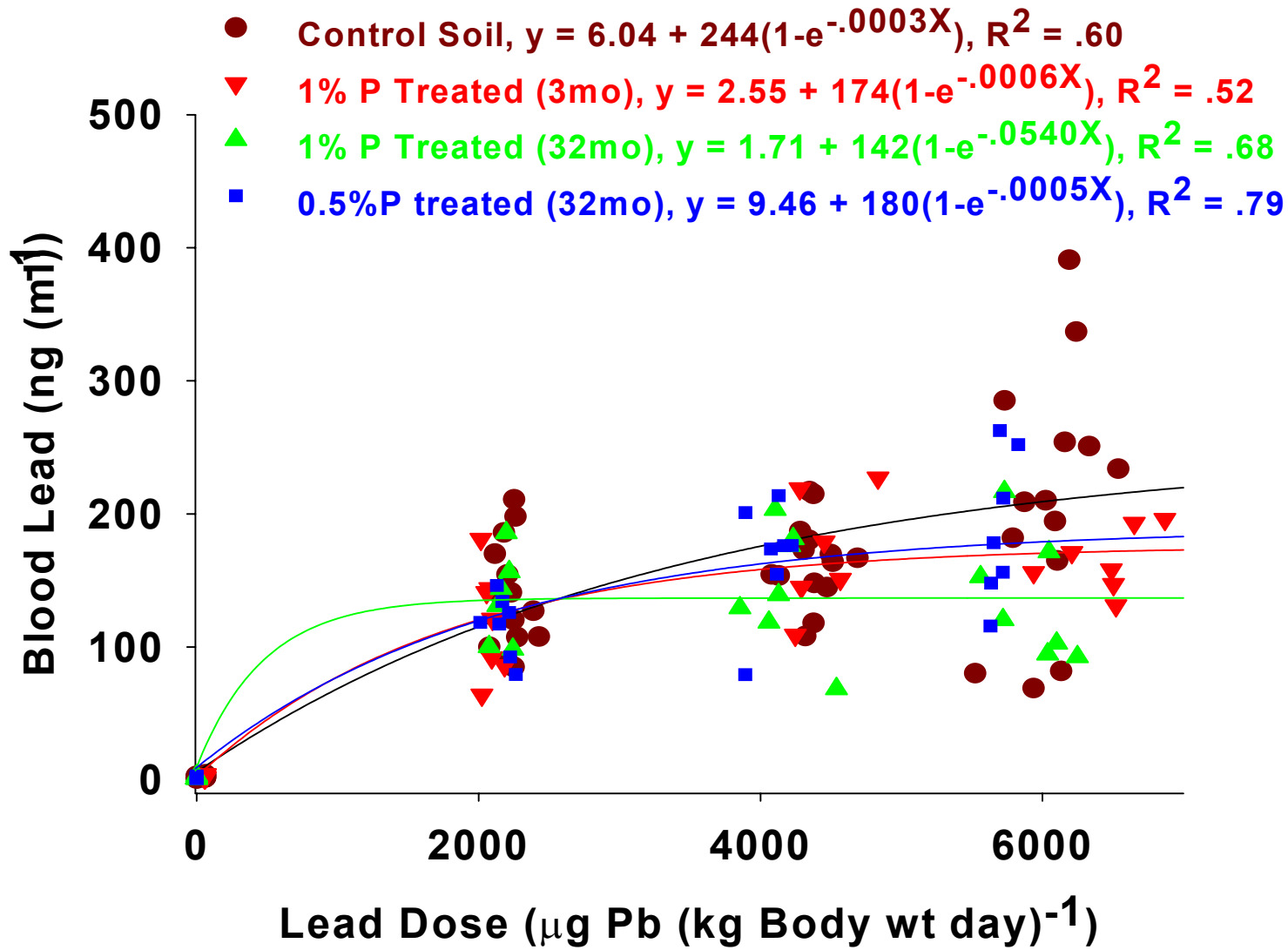


Figure 2. Rat blood lead response as a function of in situ phosphorus treatment and time after treatment of a lead-contaminated soil.