

**EMERGING TECHNOLOGIES
FOR THE REMEDIATION OF METALS IN SOILS
INSITU STABILIZATION / INPLACE INACTIVATION**

-FINAL-

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EXECUTIVE SUMMARY

Inplace inactivation is a site stabilization technique in which amendments are applied to soils to alter the soil contaminant chemistry, making contaminants less soluble, less mobile, and less bioavailable. Inplace inactivation does not affect the total contaminant concentration, but reduces the risk of harm to a target organism (humans, animals, etc.) by reducing biological activity. The ITRC Metals in Soils Team identified these techniques as being applicable to some sites with soils contaminated with metals. This technology overview provides an introduction to inplace inactivation / insitu stabilization techniques and discusses several current approaches to implementation. The document outlines several case studies and identifies future research and development needs, as well as potential stakeholder and regulatory concerns. A preliminary cost discussion is included, as is an outline for a potential project workplan.

Membership on this work team was open to all ITRC members. Participants with expertise or interest in metals treatment technologies in their states elected to join the team and contributed consistently to the development of this work product. Members of the RTDF (Remediation Technologies Development Forum) IINERT technology team (In-Place Inactivation and Natural Ecological Restoration Technologies) also participated in this team and helped to provide an industry perspective. A representative from the U.S. Army Corps of Engineers and the Department of Energy actively participated on the team. Support was also provided by the United States Environmental Protection Agency and the Department of Defense. Input regarding public and community concerns for these technologies was provided by ITRC public stakeholder representatives.

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INPLACE INACTIVATION / INSITU STABILIZATION

1.0 INTRODUCTION

There is a growing need for the development of low cost, low input technologies that provide sufficient protection to human health and the environment. Many innovative remediation techniques currently being developed focus on exploiting or altering soil chemistry to either remove contaminants from the soil or to reduce their solubility and bioavailability. Some of the more promising innovative remediation alternatives include plant-based techniques such as phytoextraction and phytostabilization (i.e., inplace inactivation). In phytoextraction, the contaminant is gradually removed from the soil by plant uptake and harvesting (or, in the case of mercury, by volatilization). Conversely, inplace inactivation is a site stabilization technique in which amendments are applied to the soil to alter the soil contaminant chemistry, making the contaminant less soluble, less mobile, and less bioavailable. Inplace inactivation does not affect the total contaminant concentration, but reduces the risk of harm to a target organism (humans, animals, etc.) by reducing biological activity.

Inplace inactivation is based on fundamental soil chemistry, plant biology, agricultural practices, and experience with the restoration of drastically disturbed mine and roadside lands and construction sites. Both phytoextraction and inplace inactivation may be relatively simple, low cost, low input methods that could prove adaptable to a wide range of contaminated sites. The following text deals only with inplace inactivation, as phytoextraction is dealt with in a separate Metals in Soils ITRC “Emerging Technologies” document.

1.1 Background

Heavy metal contamination in soils is widespread in the U.S. and other parts of the world. Unlike organic compounds that can be destroyed, heavy metals can only be covered, buried, removed and recycled, moved to a safer location, or transformed into a less toxic form. The most common remedy for lead (Pb) contaminated soils, for example, has been to mix the soils with chemical binders such as portland cement and to relocate them to landfills, safely away from receptors. Portland cement works by increasing the particle size and imparting the resulting material with a high buffering capacity in the alkaline pH range. The large particles and alkaline pH buffering capacity that result from the stabilization process reduce the amount of contaminant that is extracted by laboratory leaching methods, including regulatory tests such as the Toxicity Characteristic Leaching Procedure (TCLP) and the Simulated Precipitation Leaching Procedure (SPLP)₁. Soil washing is another remedy in which soils are subjected to intense dry and wet processing to remove size and density fractions containing Pb. This process concentrates the contaminant in the water or fine particles, and leaves large particles relatively clean. The larger particles produced by the soil washing process can be reused as fill material. The water and fine particles in which the Pb resides must be further treated and the solids recycled or properly disposed.

The chemical form of heavy metals in soils is an important consideration in determining the hazard to human health and the environment. Some chemical forms of some heavy metals are very toxic.

For other forms, particularly certain naturally occurring forms, the toxicity can be lower. Nature itself provides hints for other solutions to remediate heavy metals in soils in addition to landfilling, covering, or washing. Populations living in or near natural Pb outcroppings often have lower blood and tissue Pb levels than populations living in areas where Pb paint is used. This occurs because many natural mineral forms of Pb have a low bioavailability. They do not dissolve in the human digestion system when ingested, but rather pass through unabsorbed without causing harm. From this and similar observations, scientists have postulated that if Pb contamination in soils could be converted to less toxic forms, it might be safe to leave in place.

One potential method of reducing the hazard of heavy metals in soils is by chemically and physically manipulating the soil to convert the forms of the contaminants from those of greater hazard (i.e., high water solubility, high mobility, high bioavailability) to those of lesser hazard. Inplace inactivation₂ has been recently coined to describe this process of chemically and physically inactivating contaminants, both in soil and other materials found at the earth's surface. Other names for this strategy include "phytostabilization," "agronomic stabilization," and "phytorestation." In this process, no actual reduction in pollutant concentration occurs. The risk reduction is provided by chemical and physical processes in the soil so that the soil can remain in place. Chemicals and materials that appear to be most promising for inplace inactivation include phosphates, mineral fertilizers, iron oxyhydroxides, other minerals, biosolids, and limestone. Conversion of Pb to less toxic forms has been demonstrated in soils amended with safe additives using common agricultural techniques_{3,4,5,6,7}.

To complement the use of soil amendments, a rich plant growth in treated areas will help hold the soils in place by preventing erosion, reducing rain impact and water infiltration, and providing an effective barrier against actual contact with soil. In some cases, plant roots may absorb contaminants to further prevent off site migration or leaching. Incorporating soil amendments and growing plants using existing agronomic techniques are more natural ways of restoring the ecology of a soil in comparison to many other remediation technologies. Importantly, this agriculturally-based technique should be less likely to impair the soil's potential for sustaining plant growth after treatment, and be relatively environmentally benign when compared to many conventional remediation practices.

1.2 Current Developments

Much of the research in inplace inactivation has involved Pb contaminated soils. Research has shown that raising the soil pH, increasing organic matter, adding metal oxyhydroxides, and increasing certain anions (especially phosphate) can decrease Pb mobility and lower the characteristic hazard (as measured using the TCLP) by an order of magnitude₈. Figure 1 on the following page shows the effects of amending soil with phosphate fertilizer, (KH_2PO_4) and iron oxyhydroxides (FeOOH - applied as Iron Rich, a co-product in the manufacturing of white pigment at the DuPont Co. Edgemore, DE, facility). The TCLP of untreated soils was well above the critical level of 5 mg Pb L^{-1} . The addition of phosphorus and FeOOH , however, significantly reduced the TCLP-extractable

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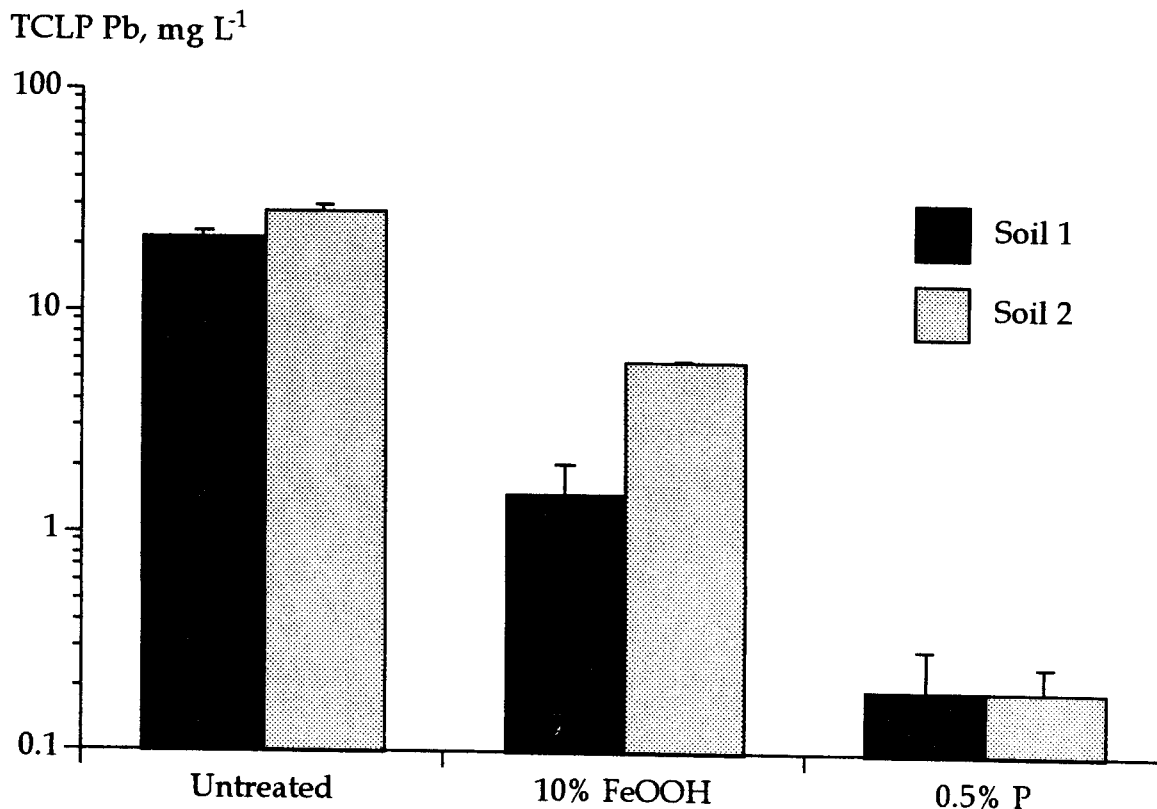


Figure 1-1. TCLP Pb from untreated soils 1 and 2 and after treating with 0.5% P and 10% FeOOH. Total Pb in soils 1 and 2 are 1200 and 2400 mg kg⁻¹, respectively. Please note that the y-axis is log-scaled in the figure (from reference 9).

A six-step sequential chemical extraction of these soils resulted in a fingerprint of the soil-Pb (Figure 2), which appears to give valuable information regarding the potential of Pb for leaching, plant-uptake, and mammalian bioavailability through soil ingestion. In the untreated soils the majority of the Pb was extracted in the first two fractions, which represent the more soluble or available forms of Pb. Application of amendments, particularly phosphorus and FeOOH, caused the Pb to shift from forms with high relative mobility and greatest potential hazard (fractions 1 and 2) to those with low or no relative mobility (fractions 3 to 6).

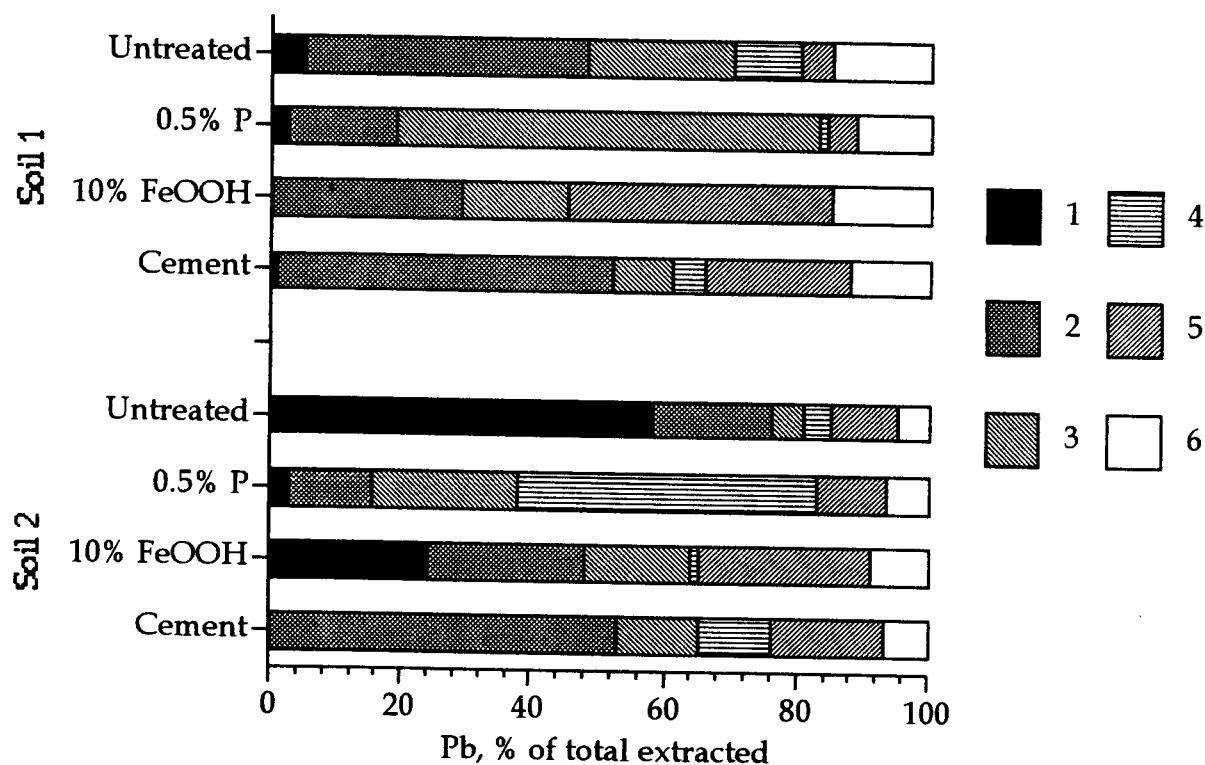


Figure 1-2. Sequential chemical extraction of Pb from untreated soils 1 and 2 and after treating with 0.5% P, 10% FeOOH, and portland cement. Fraction number: 1 = exchangeable, 2 = carbonates, 3 = Mn oxides, 4 = organic, 5 = Fe oxides, 6 = residual (from reference 9).

blood stream, which is referred to as *bioavailability*. *Absolute bioavailability* is the fraction of the total dose (i.e., amount of soil Pb ingested) that is absorbed into the bloodstream. The absolute bioavailability of Pb in ingested food and water is currently set by the U.S.EPA at 50 %, while the value for Pb in ingested soil is 30 %. *Relative bioavailability* is the ratio of absolute bioavailability of a compound in a dose to its absolute bioavailability in a reference dose (e.g., the bioavailability of lead in soil relative to lead in food or water would be 60 %).

Like contaminant solubility and mobility, bioavailability can also be reduced through the application of certain materials to soils. Preliminary results of a swine soil-dosing study at the University of Missouri (Drs. Stan Casteel and Robert Blanchar, personal communications) and a Sprague-Dawley rat dosing study at the U.S. Department of Agriculture-Agricultural Research Service (USDA-ARS) (Dr. Sally Brown and Rufus Chaney, personal communications) indicate a significant reduction in soil Pb bioavailability as a result of adding phosphorus alone or in combination with FeOOH to a soil from Joplin, MO (total soil-Pb about 4000 mg kg⁻¹). In both studies, treatments were applied to the soils in laboratory studies. Experiments to determine the changes in Pb bioavailability of soils treated in the field are ongoing and results are expected in the fall of 1997.

1.3 Measuring Bioavailability for Determining Risk

Animal dosing studies, such as the swine and rat studies reported above, are the method of choice when measuring bioavailability. As a test method to evaluate bioavailability for use in risk assessment and developing remediation alternatives, however, they may have limited value. Animal dosing studies are expensive, complex, time consuming, and may create ethical concerns¹⁰. The Physiologically-Based Extraction Test (PBET)₁₁ is a quick chemical extraction that is being developed to serve as an alternative to animal studies. It has been used to determine the bioaccessibility of Pb, As, and other soil contaminants. Bioaccessibility, as used here, is defined as the solubility of soil-Pb in the simulated stomach solution of the PBET relative to the total Pb in the soil. Soil-Pb bioaccessibility determined in this way has been shown to be well correlated with soil-Pb bioavailability using a Sprague-Dawley rat model₄ and a swine model₉ ($R^2 = 0.88$, Figure 3). An interesting feature of Figure 3 is the wide range of soil-Pb bioavailabilities measured in the two animal models on two different sets of soil. In the swine model, for example, relative bioavailability (RBA) of Pb ranged from 1 to 87%, or less than 1 to 44% Pb absolute bioavailability (ABA). The overall average for Pb RBA in the swine model for the 15 soils was 53%¹¹, or 27% Pb ABA, which compares well to the EPA default Pb ABA of 30%.

Soil-As bioaccessibility has also been shown to correlate well with soil-As bioavailability using a *Cynomolgus* monkey model₄, a rabbit model₄, and a swine model₁₀ ($R^2 = 0.54$ overall, $n = 10$; $R^2 = 0.75$ for swine model data only, $n = 7$; Figure 4). The correlations between in vitro and in vivo studies for As are not as good as those demonstrated for Pb. However, both of these comparisons indicate that a simple soil test for As, Pb, and perhaps other soil contaminants may be valuable for

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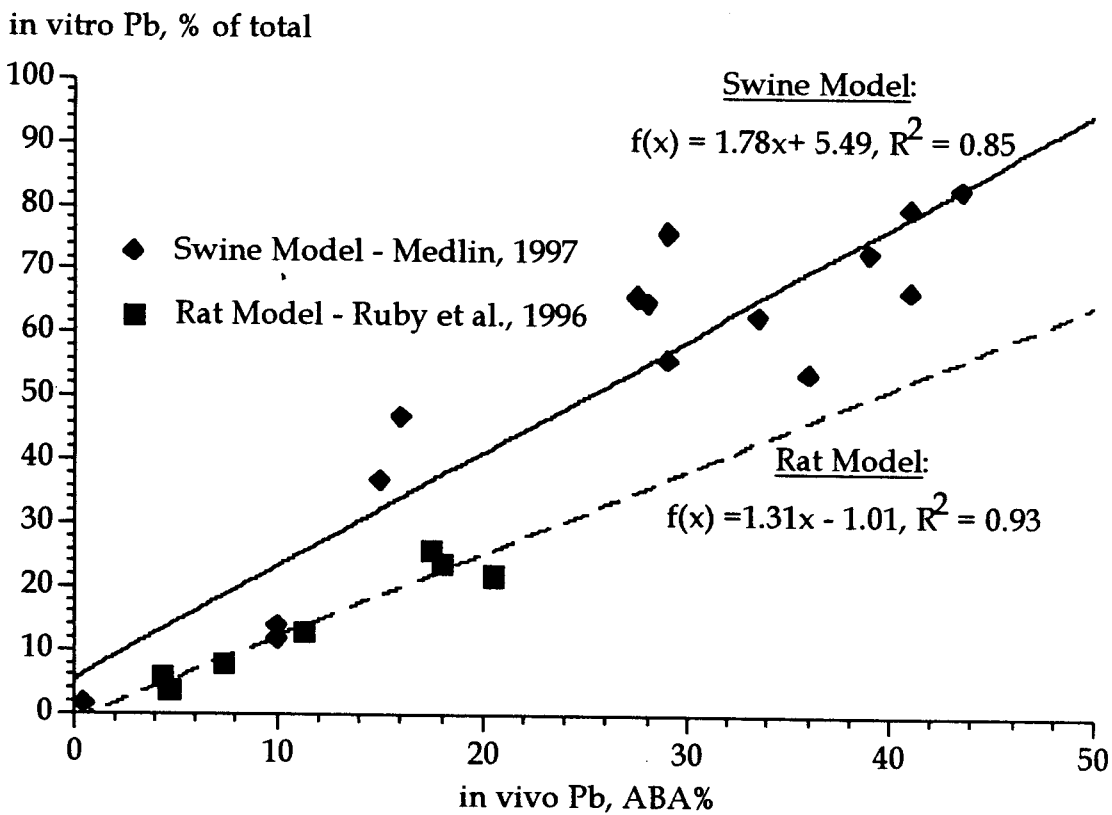


Figure 1-3 *In vitro* relative Pb bioaccessibility measured using the PBET procedure at pH 1.5 vs. EPA swine model blood-Pb relative bioavailability (RBA) (diamonds; from reference 12) and *in vitro* relative Pb bioaccessibility measured using the PBET procedure at pH 2.5 vs. Sprague-Dawley rat model blood-Pb RBA (squares; from reference 11).

The Solubility/Bioavailability Research Consortium (SBRC) is working to develop and validate methods such as the PBET to determine the bioavailability of hazardous substances in contaminated soils¹⁰. The consortium is a collaborative effort among academics, consultants, regulators, and the regulated community. The initial research of the consortium will focus on Pb and As for the purpose of refining human exposure estimates. Other inorganic constituents, such as beryllium, cadmium, chromium, and mercury, will be considered for methods development and validation once tests for Pb and As have been established.

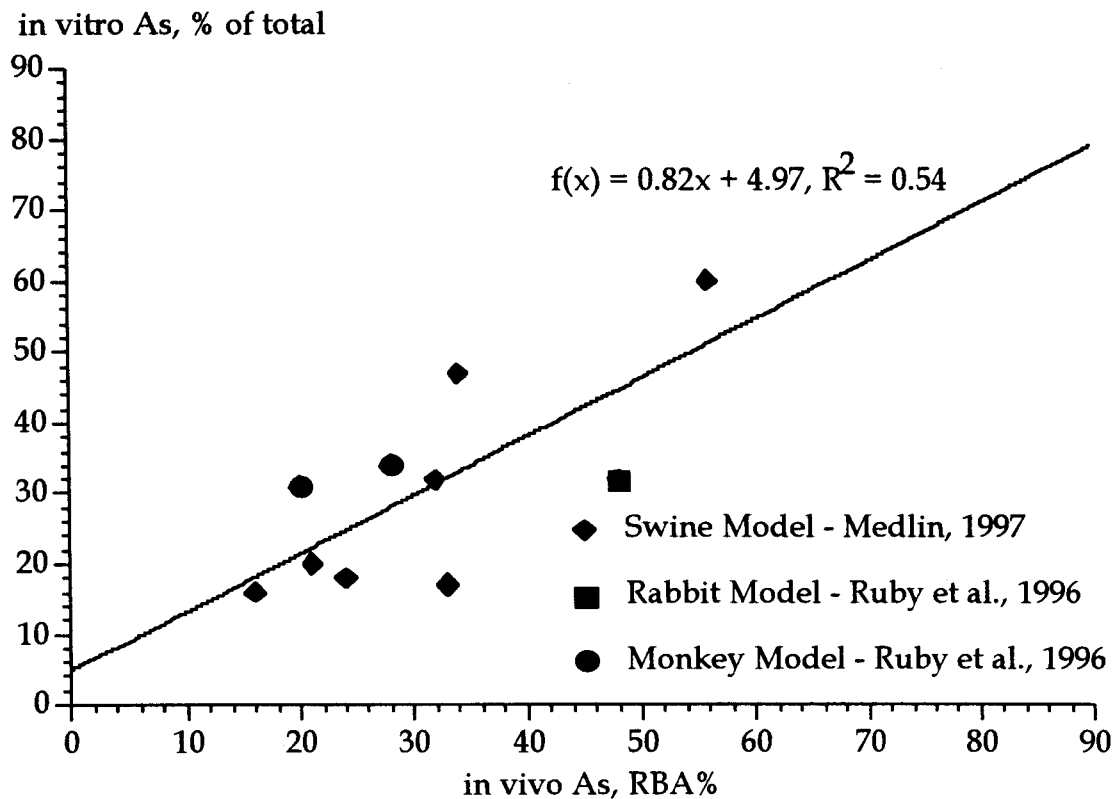


Figure 1-4 *In vitro* relative As bioaccessibility measured using the PBET procedure at pH 1.5 vs. EPA swine model blood-As RBA (diamonds; from reference 12) and *in vitro* relative Pb bioavailability measured using the PBET procedure at pH 2.5 vs. rabbit (squares) and *Cynomolgus* monkey model (circles) blood-Pb RBA (squares; from reference 11).

The hazard presented by Pb at a residential site is often determined for young children (7 and younger) using the Integrated Exposure and Uptake Biokinetic model (IEUBK)^{11,12}. This model considers several parameters, such as a child's nutritional status, exposure frequency and rate, and Pb bioavailability, to predict the percentage of children in an exposed population who may have a blood Pb level greater than $10 \mu\text{g dL}^{-1}$. Children with blood Pb levels above this value are considered to be at risk of suffering Pb-related health problems. The IEUBK model uses a default value of 30% (relative to Pb acetate in soil) for soil-Pb bioavailability. This may, however, greatly overestimate or underestimate Pb bioavailability for a given site. A change in the default value of Pb bioavailability in the IEUBK model may change the percentage of children with blood Pb levels above $10 \mu\text{g dL}^{-1}$ (Figure 4). It is generally accepted that no more than 5% of the exposed children will have blood Pb levels above the critical level, as predicted by the IEUBK model. For a soil with $2000 \text{ mg Pb kg}^{-1}$ and a Pb bioavailability of 30%, the IEUBK predicts that over 50% of the exposed children will be above the critical blood Pb level.

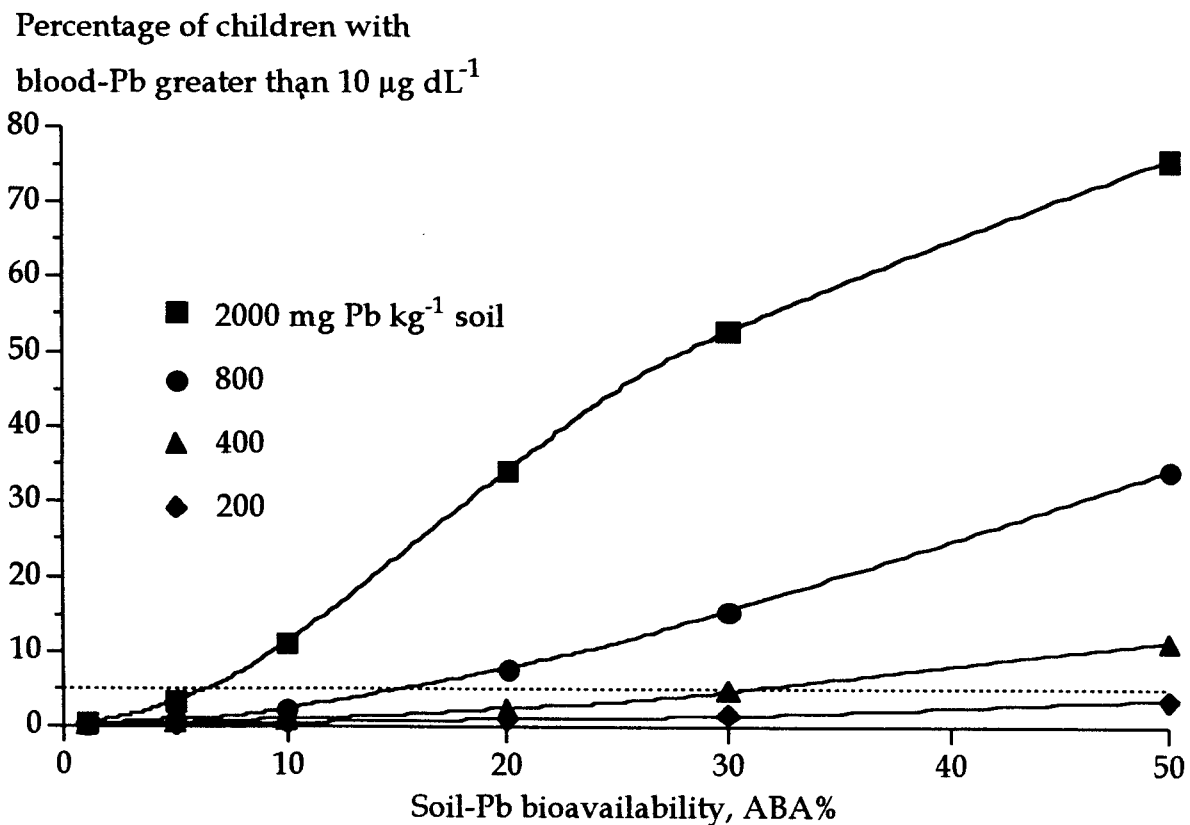


Figure 1-5 Influence of soil-Pb bioavailability on the percentage of children with blood-Pb levels above $10 \mu\text{g dL}^{-1}$, as determined using the IEUBK model^{2,9}.

If Pb were closer to 50% bioavailability, the percent of children at risk may approach 80% of the population. When the Pb bioavailability is 10%, or is reduced to 10% by inplace inactivation, the percent of children who are at risk from soil Pb may be only about 10%. While this hypothetical scenario still exceeds the U.S. acceptable limit for the percent of children above the critical blood Pb level, it indicates that default assumptions on Pb bioavailability may yield incorrect predictions concerning children at risk at a given site.

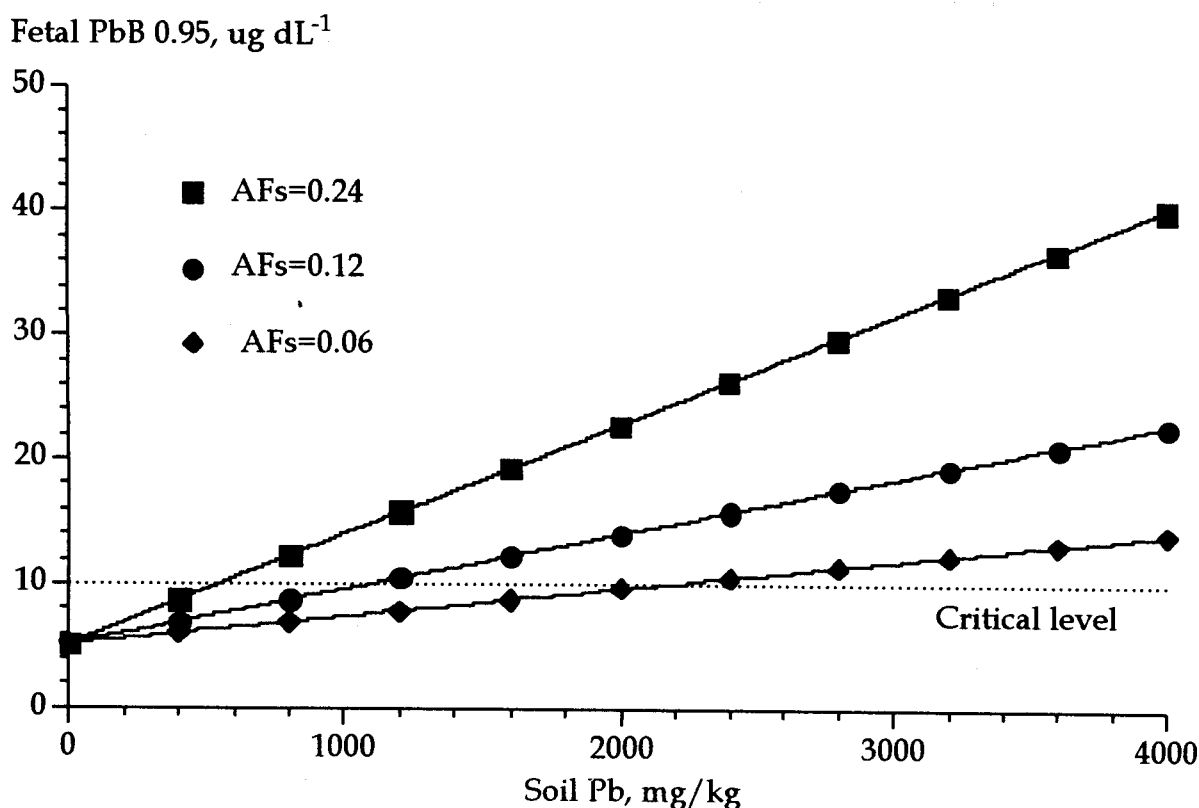


Figure 1-6 Potential influence of soil-Pb bioavailability (AFs) on fetal blood-Pb (PbB) concentrations in response to pregnant females exposed to total soil-Pb concentrations, as determined using the risk estimation algorithm from Technical Review Workgroup for Lead₁₆. The critical level is the PbB concentration that results in a risk of Pb poisoning to the fetus.

and evaluation of an integrated exposure biokinetic model for adults.

1.4 General Inplace Inactivation Advantages and Limitations

Any site to which conventional remediation techniques can be applied is a candidate for inplace inactivation. Compared to the equipment needed for many conventional remediation practices, the supplementary equipment needed for inplace inactivation (e.g., basic farming equipment) is easier to transport to remote sites. Debris surrounding a site may impose limitations regarding the use of farming implements. However, the utilization of downsized equipment, soil amendments, hydroseeding, and transplanting may alleviate these concerns. In general, inplace inactivation may be less expensive and create fewer operational hazards than more conventional remedial methods. Plant uptake and hazards to humans or animals who may consume the plants may be greatly reduced with inplace inactivation. Plants may sequester pollutants in their roots without translocating them to aboveground material. In these cases, additional degrees of inactivation are established. Because inactivation processes are generally inexpensive and easy to implement, they may also serve as interim measures for reducing risk prior to subsequent phytoremediation or remediation by other techniques.

2.0 APPROACHES TO INPLACE INACTIVATION TECHNOLOGIES

2.1 Capital and Operating Costs

Specific capitalization costs are difficult to determine but farming operation costs are relatively low. Equipment for farming operations (e.g., fertilizing, plowing, etc.) is generally readily available. It appears that overall remedial costs would be substantially lower than those associated with traditional methods.

2.2 Site-specific Requirements

Inplace inactivation is not a panacea for contaminated soil. Plants are living organisms with constraints (e.g., soil pH, soil texture, ionic balance, nutrient availability, climate, pests and disease) that are often in conflict with the nature of the pollutant and/or the industrial setting. However, soil initially hostile to plants can be converted to reasonable growth media with proper amendments by soil and plant scientists.

2.3 Chemical Requirements

Soil amendments including phosphates, other plant nutrients, lime, ash, and metal (Fe/Mn) oxyhydroxides are all useful in stabilizing metals and may be applied prior to planting.

2.4 Physical/Hydrogeologic Requirements

Vegetation requires that the soil be friable enough to allow plant roots to take hold. Plants also have certain pH and nutrient requirements and require sufficient water, air, and sunlight.

2.5 Contaminant Partitioning and Transport

Soil amendments may be used to stabilize many metals. In certain precipitated forms, many metals are essentially non-leachable and pass leachate and TCLP testing protocols.

2.6 Time Requirements

Most of the stabilization techniques mentioned above occur rapidly. Plant vegetative covers used to decrease erosion may require more time (e.g., 1 to 3 growing seasons). The establishment of a vegetative cover depends on the plant, climate, and soil. However, techniques (e.g., the use of fast-growing grasses, mulch, and landscape fabric) are available to prevent erosion until full plant cover is established. Permanent establishment of selected plant species may be delayed because of seasonal changes in growth rates or sub-optimum climatic conditions, particularly in the late fall and winter. Plant establishment during summer months may require irrigation.

2.7 Site Assessment

The more the site resembles a farmer's field, the less expensive and more easily applied this technology will be. Plants can, however, be planted in a wide variety of unfavorable conditions using technologies such as hydroseeding. Abandoned buildings and lots (even in more polluted areas) are often quickly covered with weeds and scrub trees. These requirements, except for the time of year and short-term weather conditions, may be less rigorous than other remediation technology requirements.

In general, knowing the type and extent of contamination at a site plays a crucial role in:

- Assessing the feasibility of inplace inactivation
- Determining the proper type and amount of soil amendments to be added
- Selecting the proper plant species to be used

Plows have been designed to have a maximum plowing depth of up to 3 feet. Soil auguring equipment is also available that can deliver and mix materials to a depth of 100 feet or greater.

2.8 Soil Biogeochemistry

For inplace inactivation, soil amendments are selected based on their ability to stabilize the pollutants.

Plant species are selected based on their ability to tolerate site conditions and maximize plant growth and ground cover. Soil amendments, including lime and inorganic and organic materials, may be applied to maximize the inactivation process.

2.9 Geologic Properties

This technology requires the soil to be of a type and form that can support plant life, either in its current state or with traditional agricultural amendments that make the soil productive. Information on the productivity of the soil and amendments necessary to optimize its productivity can be obtained with the help of the US Department of Agriculture, Natural Resource Conservation Service (formerly the Soil Conservation Service). The Natural Resource Conservation Service can also help with selecting the appropriate plant material for stabilization.

The hydrologic properties of the site should support plant growth. Barriers to prevent the off-site migration of any runoff or drainage may be required in some instances. The underlying aquifer is of less importance in the inplace inactivation of metals and fairly immobile organics. In general, as the water solubility of the target pollutants increases, the concern for the quality, quantity, final disposition, and fate of the underlying water also increases.

3.0 RESEARCH AND DEVELOPMENT - FUTURE NEEDS

Several areas of research and development have been identified by the Inplace Inactivation and Natural Ecological Restoration (IINERT) Action Team, which is part of the U.S. EPA Remediation Technologies Development Forum (RTDF):

- A more thorough understanding of the factors that control soil-metal bioavailability to humans, which should include the biological, chemical, and physical factors that affect bioavailability.
- Develop and validate simple techniques that can be used to assess soil-metal bioavailability to humans. These simple techniques should be well correlated to appropriate human or animal (e.g., pigs and rats) model surrogates.
- Develop correlations between soil components (i.e., metal species, non metal-containing components) and the soil-metal bioavailability that determine the short and long-term stabilities of soil-metal components.
- Develop treatment technologies and processes for the additions of materials to metal contaminated soils that induce the formation of less bioavailable metal forms, providing a practical approach to inplace inactivation.
- Develop and validate simple techniques that can be used to evaluate environmental hazards for both soil contaminants and for various remediation options.

4.0 CASE STUDIES AND RESULTS

Inplace inactivation is a nascent technology, but it has a sound technical basis. It has the potential to develop into a viable remediation option in cases where pollutants are relatively non-leachable and pose little eminent risk to human health or the environment.

Inplace inactivation is currently being used to remediate zinc-, lead-, and nickel-contaminated soil at a Superfund site in Palmerton, Pennsylvania. Metal stabilization has recently been accepted in a Record of Decision (ROD). Soil parameters that can be altered significantly by vegetation management have a dramatic effect on the regulatory status of the soil as measured by the TCLP.

Inplace inactivation is also undergoing initial field trials in Joplin, MO. This area was the site of Pb and Zn mining and smelting activities in the earlier part of the century. These operations elevated soil Pb levels across much of the county (about 6500 ha). Soil Pb levels in the area vary considerably, ranging approximately from 1111 to 5350 mg kg⁻¹ at a depth of 1 to 8 cm, and 1998 to 4824 mg kg⁻¹ at a depth of 8 to 15 cm. At residential homes with the most severe Pb contamination or where the blood Pb level in children indicates a health risk, the contaminated soil around the homes has been excavated and replaced. This plan of remediation will continue house by house until the property surrounding approximately 2500 homes at risk is remediated. The Joplin workgroup plans to demonstrate inplace inactivation practices that could be implemented easily, including some practices that could be accomplished by the homeowners themselves so that they can take steps to protect the health of their families at least until the contaminated soil around their homes can be replaced. It is hoped that this demonstration will also raise public and regulatory support for phytoremediation of other contaminated sites.

In early 1997, the IINERT workgroup installed a field validation study at Joplin to evaluate the effectiveness of amendments including phosphate fertilizers (triple super phosphate), phosphoric acid, high-Fe byproducts Compro7 and Iron Rich to reduce Pb bioavailability. Extensive preliminary research to characterize the sites and select treatments was performed prior to field implementation, and the first round of sampling and testing of the field plots has been conducted with results pending. This study is conducted by a workgroup gathered from three parties, the IINERT Team under the US EPA RTDF, the U.S. Department of Agriculture (USDA), and the Missouri Department of Natural Resources (MDNR).

5.0 REGULATORY AND STAKEHOLDER ISSUES

Several areas of concerns regarding this technology include those identified as research needs, as well as longevity of treatments, assessing bioavailability, the level of current understanding of Pb exposure

and bioavailability as captured in IEUBK, restrictions on land use, costs of implementing the technology, mitigating dust from tillage operations, eliminating any potential environmental effects of materials added, and reclamation / revegetation work vs. inplace inactivation. Due to the innovative nature of the technology, regulators and other stakeholders will continue to have questions and concerns until these areas are addressed.

6.0 COST

An economic analysis comparing inplace inactivation techniques to some currently practiced remediation techniques shows that inactivation techniques are considerably less expensive than their current counterparts. Phytoextraction is compared to two currently practiced site stabilization techniques, solidification and stabilization off-site, and soil washing by particle separation. Both of these techniques involve the excavation of the soil to 30 cm, stabilization of the contaminated soil with cement, and final placement in a hazardous waste landfill. In soil washing, however, the fine material is separated and landfilled instead of the whole soil. Inplace inactivation, or phytostabilization, is compared to common site stabilization practices including asphalt and soil capping. In these techniques, a layer of either asphalt or uncontaminated soil is placed over the contaminated area to prevent environmental exposure of the contaminants and restrict water infiltration into the contaminated profile.

Of the site decontamination techniques, solidification and stabilization off-site is the most expensive, with costs exceeding \$1.5 million per hectare excavated to a depth of 30 cm. This technique remediates a site in one year, but requires expensive landfill space and does not include extensive restoration of the site. Soil washing to remove the fine soil fractions is the second most expensive decontamination technique (\$790,000 per hectare to 30 cm). The least expensive decontamination alternative is phytoextraction to remediate the site to a level acceptable for residential land use (from 1.4% Pb (w/w) to 0.4% Pb (w/w)). In this scenario, plants produce 40 tons of biomass per hectare each year, and contain 1% Pb (w/w). Chelates (Na_4EDTA) are applied to assist Pb removal. With these parameters, phytoextraction requires 10 years to remediate the site, and costs approximately \$260,000 ha^{-1} .

Site stabilization techniques generally are less expensive than decontamination techniques. Of the site stabilization techniques considered in this comparison, asphalt capping is the most expensive, costing \$160,000. Asphalt capping effectively prohibits contact of the soil with the environment but limits future land use to parking lots or similar functions. A less expensive yet similar technique involves soil capping with a 60 cm thick layer of uncontaminated soil covering the contaminated area. Vegetation is established to stabilize the soil cap. The cost per hectare for soil capping is approximately \$140,000. Compared to these two stabilization techniques, inplace inactivation is an economically attractive alternative, costing approximately US\$53,000 per hectare. In this scenario,

inplace inactivation includes site preparation, plowing, application of amendments to inactivate Pb, lime and fertilizer application, planting and mowing (4 times per year). Soil amendments to inactivate soil Pb include 90 ton ha⁻¹ triple super phosphate fertilizer, and about 400 ton ha⁻¹ Iron Rich, a byproduct from TiO₂ production containing 50-60% hydrous iron oxides by weight. All site stabilization techniques require some annual maintenance, such as asphalt patching or repairs, mowing or re-seeding.

When compared to commonly practiced remediation techniques, phytoextraction and inplace inactivation are the least expensive alternatives for their respective approaches. Phytoextraction is more expensive than inplace inactivation, and often takes longer to remediate a site. However, the greater time requirements and larger cost of this technique may in some cases be displaced by the benefit from added land value in removing the Pb from the site. In addition to the attractive low cost of both phytoremediation techniques, these techniques may also be less invasive and more quickly promote the restoration of a healthy ecosystem.

7.0 A TYPICAL WORK PLAN

The following outlines areas which should be considered when formulating a workplan for inplace activation.

Material and Equipment Requirements

Materials may include inorganic and organic plant nutrients, organic matter, liming materials, pesticides, and appropriate plant species and materials. The following equipment may be required: tractors, plows, cultivators, planters, tractor-mounted spray rigs, and irrigation equipment.

General Process Operation and Monitoring

Plant and soil samples can be obtained on a regular basis to assess remediation progress. Monitoring may also include air sampling, water-quality runoff monitoring, groundwater monitoring, and vadose zone water quality monitoring.

Documentation Requirements

Documentation requirements for inplace inactivation are similar to current remediation technologies. Since fewer personnel may be involved and the contaminated material may never leave the site except for sampling, documentation requirements may be less.

8.0 CONCLUSIONS

Reducing metal availability and maximizing plant growth through in-place inactivation may prove to be an effective method of insitu soil-metal remediation for industrial, urban, smelting, 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.

9.0 REFERENCES

- ¹ U.S. Environmental Protection Agency. 1995. Test methods for evaluating solid waste: Physical/chemical methods 3rd ed -4 vols. Proposed update EPA 530/SW-846 chapt. 6.
- ² US Environmental Protection Agency. 1996. IINERT Soil-Metals Action Team. Research and Development. Solid Waste and Emergency Response. EPA 542-F-96-101D.
- ³ Berti, W.R., and S.D. Cunningham. 1994. Remediating soil with green plants. In: Cothorn, C.R., (ed.) Trace substances, environment and health. Science Reviews: Northwood. 43-51.
- ⁴ Rabinowitz, M.B. 1993. Modifying soil lead bioavailability by phosphate addition. Bull Environ Contam. 51:438-444.
- ⁵ Ruby, M.V., A. Davis, and A. Nicholson. 1994. *In situ* formation of lead phosphates in soils as a method to immobilize lead. Environ Sci Technol. 28:646-654.
- ⁶ Mench, M.J., V.L. Didier, M. L`ffler, A. Gomez, and P. Masson. 1994. A mimicked in-situ remediation study of metal-contaminated soils, with emphasis on cadmium and lead. J Environ Qual. 23:58-63.
- ⁷ Ma, Q.Y., Logan, T.J., Traina, S.J. 1995. Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. Environ. Sci. Tech. 29: 1118-1126.
- ⁸ Berti, W.R., and S.D. Cunningham. 1997. Inplace inactivation of soil-Pb in Pb contaminated soils. Environ. Sci. Technol. 31:1359-1364.
- ⁹ Medlin, E.A. 1997. An in vitro method for estimating the relative bioavailability of lead in humans. MS thesis. University of Colorado, Boulder (Dissertation Abstact 97).

¹⁰ Ruby, M.V., C. Weis, S. Christensen, G. Post, B. Brattin, J. Drexler, B. Chappell, A. Ramaswami, W.R. Berti, R. Jensen, M. Carpenter, and D. Edwards. 1997. Solubility/bioavailability research consortium: Statement of purpose. PTI, Inc., Boulder, CO.

¹¹ U.S. Environmental Protection Agency. 1996. Recommendations of the technical review workgroup for lead for an interim approach to assessing risks associated with adult exposures to lead in soil. Adult Lead Risk Assessment Committee, Technical Review Workgroup for Lead. New York.

APPENDIX A

Acronyms

ACRONYMS

ABA	Absolute Bioavailability
As	Chemical symbol for Arsenic
DE	Delaware
IEUBK	Integrated Exposure and Uptake Biokinetic Model
IINERT	In-Place Inactivation and Natural Ecological Restoration Technologies
ITRC	Interstate Technology and Regulatory Cooperation Working Group
MDNR	Missouri Department of Natural Resources
mg/kg	milligrams per kilogram
MO	Missouri
P	Chemical symbol for the element Phosphorus
Pb	Chemical symbol for the element Lead
PBET	Physiologically-Based Extraction Test
RTDF	Remediation Technologies Development Forum
SBRC	Solubility/Bioavailability Research Consortium
SPLP	Simulated Precipitation Leaching Procedure
TCLP	Toxicity Characteristic Leaching Procedure
USDA-ARS	United States Department of Agriculture - Agricultural Research Service
USEPA	United States Environmental Protection Agency

APPENDIX B

ITRC Work Team Contacts
ITRC Fact Sheet
Product Information
User Survey

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