United States
Environmental Protection
Agency

Immobilization Strategies for Pb & As

Kirk G. Scheckel, USEPA, Cincinnati, OH

Office of Research and Development
National Risk Management Research Laboratory, Land Remediation and Pollution Control Division, Waste Management Branch.

Acknowledgments

Bradley W. Miller
Karen D. Bradham (NERL)
David J. Thomas (NHEERL)

Dealing with High-Human Contact Soils

- Urban soils are challenging for remediation
  - Environmental
  - Economical
  - Social
- Most common recommendation is soil removal
- Costs often nullify the recommendation
- Residents continue to live in contaminated environments
- What alternatives are available?

United States
Environmental Protection
Agency

A Case for Soil-Metal Immobilization

- “in situ” [latin]: in a natural or original position
- in situ immobilization is the process of transforming a metal contaminant into a non-bioavailable, non-soluble, and non-transportable form in a soil matrix so that the soil is safer and does not warrant removal
- Numerous amending agents available, but in situ immobilization requires an understanding of soil chemistry so that maximum efficiency and effectiveness are achieved

A Case for Soil-Metal Immobilization

Advantages

- Minimal site disturbance
- Lower capital costs
- Sustainable/green initiatives
- High public acceptance
- Variety of amending agents

Disadvantages

- Contaminant is still in the soil
- Long term monitoring

Very successful in bench studies, field results are mixed.

A Case for Soil-Metal Immobilization

Lead (Pb)

Induce sulfate reduction in sediments to form galena (PbS)

~~Add molybdenum to soil to form wulfenite ($PbMoO_4$)~~

Add phosphate to soil to form pyromorphite ($Pb_5(PO_4)_3Cl$)

Arsenic (As)

Amendments with high iron, manganese, or aluminum

~~High pH soils may form calcium arsenates~~

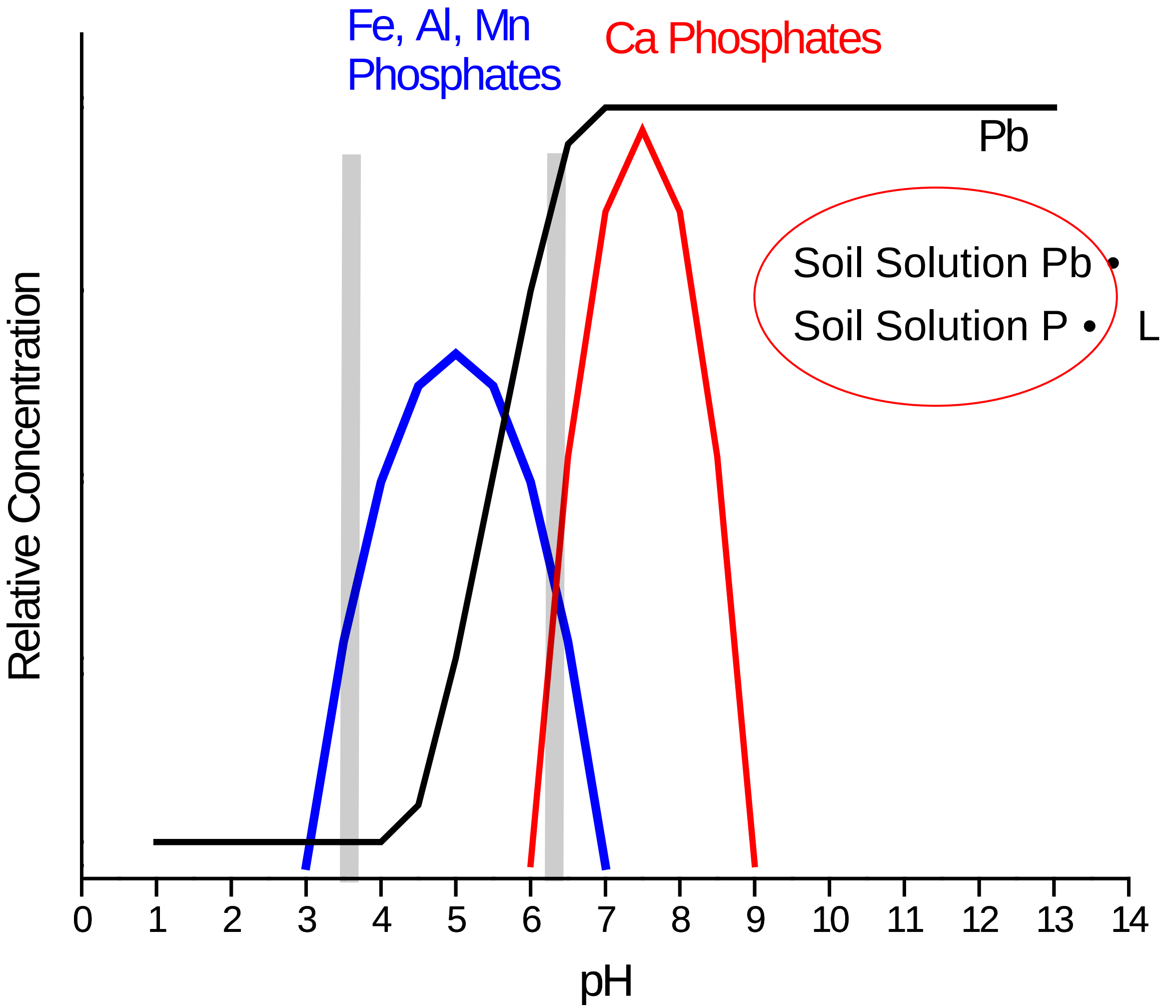
CREATIVE SCIENCE!

Lead Immobilization

Soil-Pb + Orthophosphate ($H_2PO_4^{-1}$ or $H_1PO_4^{-2}$) • $Pb_5(PO_4)_3Cl$

Discovered in 1778 in Wales as green Pb ore by Thomas Pennant
Forms naturally through the reaction of galena oxidation in proximity of OM
Common corrosion control strategy in drinking water

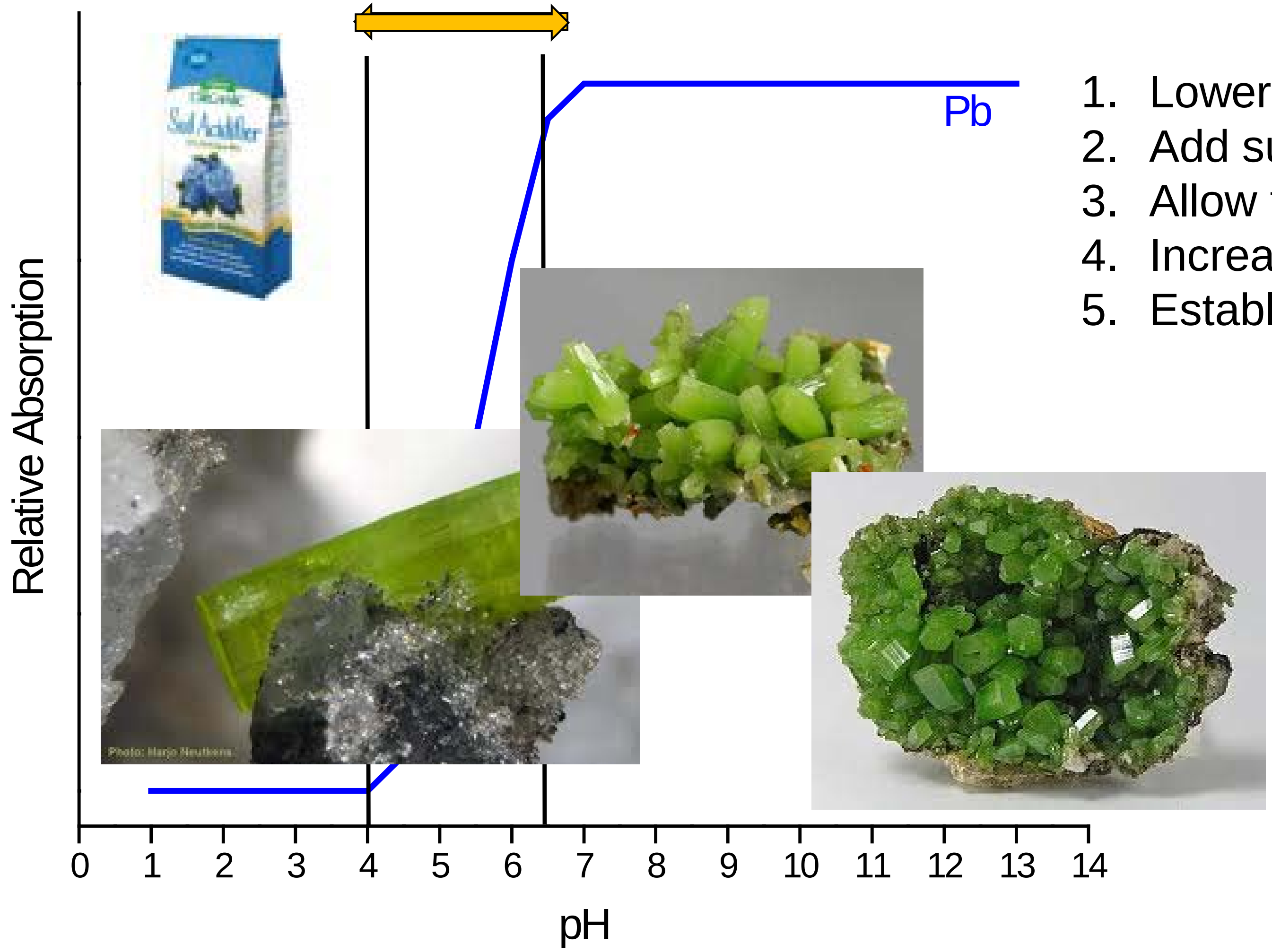
Using Logic in Immobilization



Soil Solution Pb • Labile Pb • Nonlabile Pb

Soil Solution P • Labile P • Nonlabile P

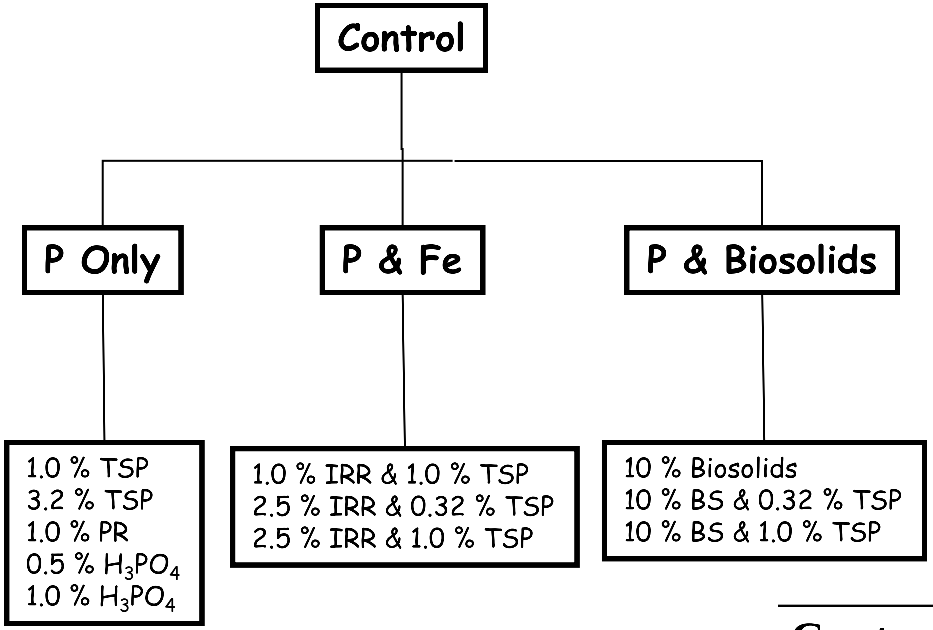
Lead Immobilization



1. Lower soil pH < 4
2. Add suitable P amendment
3. Allow time to react
4. Increase soil pH > 6
5. Establish vegetative cover

Lead Immobilization – The Joplin Study

Reducing Children's Risk from Lead in Soil. J.A. Ryan, K.G. Scheckel, W.R. Berti, S.L. Brown, S.W. Casteel, R.L. Chaney, M. Doolan, P.Grevatt, J. Hallfrisch, M. Maddaloni, and D. Mosby. 2004. Environ. Sci. Technol., 38: 18A-24A.



Control

P Only

P & Fe

P & Biosolids

1.0 % TSP
3.2 % TSP
1.0 % PR
0.5 % H_3PO_4
1.0 % H_3PO_4

1.0 % IRR & 1.0 % TSP
2.5 % IRR & 0.32 % TSP
2.5 % IRR & 1.0 % TSP

10 % Biosolids
10 % BS & 0.32 % TSP
10 % BS & 1.0 % TSP

	Rat	Swine	In vitro	Human
Control	21.7	34.8	58 pH 2.5 60 pH 2.0 63 pH 1.5	42.2
Treated	7.2	21.6	21 pH 2.5 39 pH 2.0 51 pH 1.5	13.1

United States
Environmental Protection
Agency

Arsenic Immobilization

- Barber Orchard Superfund
  - Top 1’ removed and replaced with clean fill
  - Cost doubled and still have not found landfill
- Transformation of As???
  - Lead + P → Pyromorphite (Nriagu 1974, Ma *et al.* 1993, Scheckel and Ryan 2002)
  - As + Reactant→ New As Mineral
    - Scorodite ($Fe^{+3}AsO_4 \cdot 2(H_2O)$)
- Occlusion of As and Pb

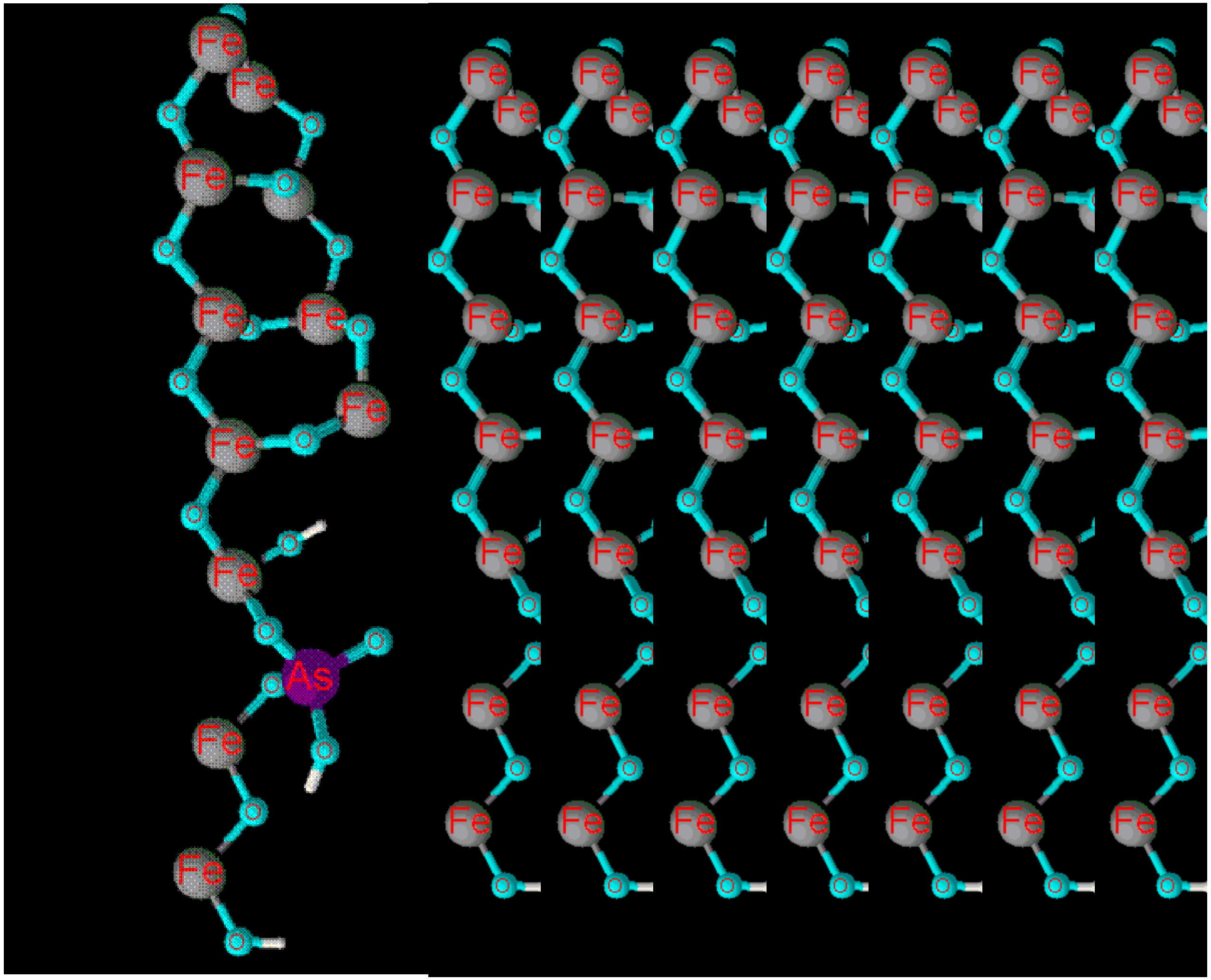
Pyromorphite
photo credit: www.minersoc.org

Scorodite
photo credit: www.minersoc.org

Gravity fed irrigation in stream and trough for pesticide

Soil collected from terraced orchard row .

As Occlusion Treatment

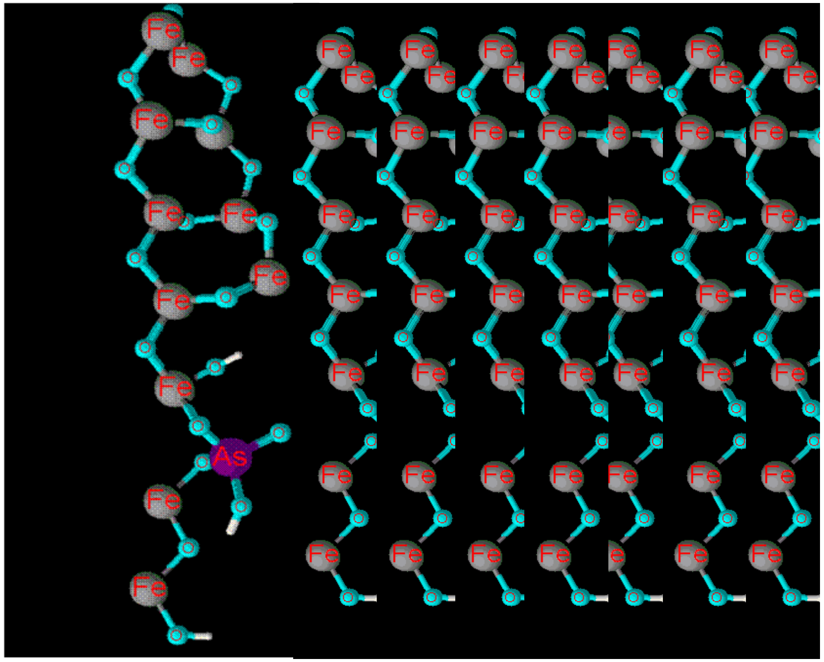


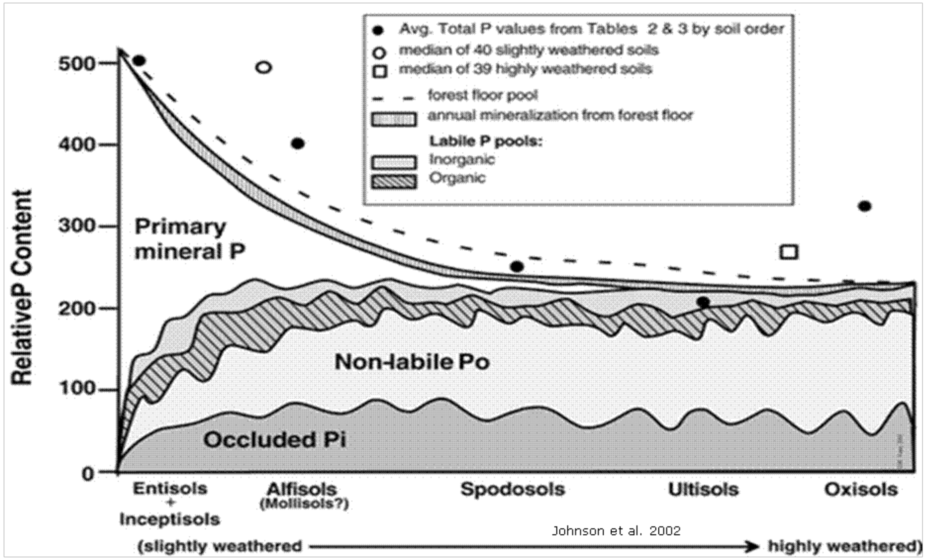
$$\mathrm{FeNO_3\ (L) + KOH\ (L) \rightarrow Ferrihydrite\ (s)}$$

EPA
United States
Environmental Protection
Agency

As Occlusion Treatment

- Benefits of *In Situ* Occlusion Treatment
  - Green Chemistry
    - Iron Nitrate and Potassium Hydroxide
    - By Products of Chemical Reaction
      - Phosphorus, Potassium, and Nitrogen (Macronutrients)
      - Iron Micronutrient and Benign.
      - Calcium to improve soil tilth and cation exchange capacity.
  - Beneficial Reuse of Nanowaste (Iron Welding fumes)
  - New co-precipitated As-Fe mineral stable over the long-term??? (Ford 2002)
  - Low cost
- Occluded P (and As?) in soils around the world
- Study Plan
  - Bench Scale Study Spring 2012
  - Greenhouse Scale Fall 2012
    - In Vitro Extractions
    - Chinese Brake Fern
    - In Vivo animal study





Johnson et al. 2002

Immobilization Requirements: Getting Started

If in situ immobilization is going to work for contaminated soils, the metal must be put into a form which is highly insoluble over a large pH range including that found in the stomach after ingestion

- Which amending agent to use?
- Application rate?
- Understand the soil matrix characteristics
  - pH, oxide concentrations, water capacity
- Time is important

Recommend bench/greenhouse pot studies followed by simple extraction tests

Immobilization Requirements: Verifying Results

If in situ immobilization is going to work for contaminated soils, the metal must be put into a form which is highly insoluble over a large pH range including that found in the stomach after ingestion

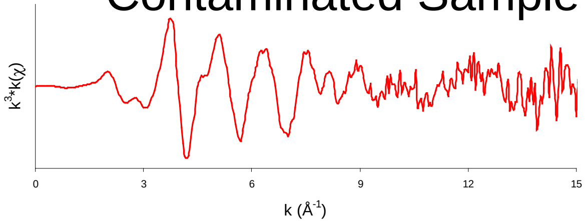
1. Identify and quantify a change in speciation
2. Demonstrate a significant reduction in bioavailability

Immobilization Requirements: Verifying Results

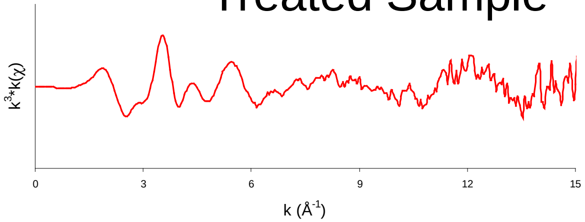
Linking Metal Speciation to Bioavailability

In-situ Remediation via Amendments to Change Speciation

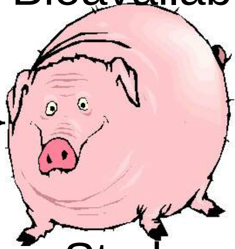
Contaminated Sample



Treated Sample



Bioavailability



Study

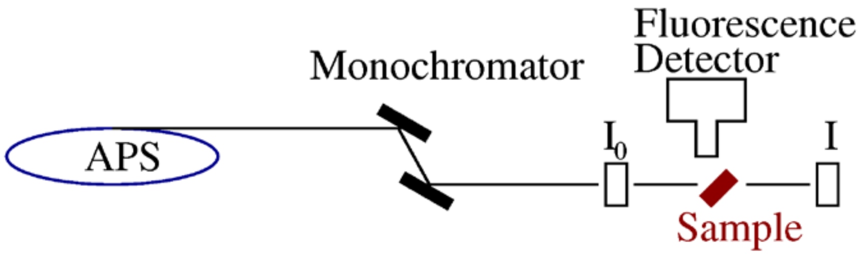
Metal Bioavailability in Contaminated Sample > Metal Bioavailability in Treated Sample

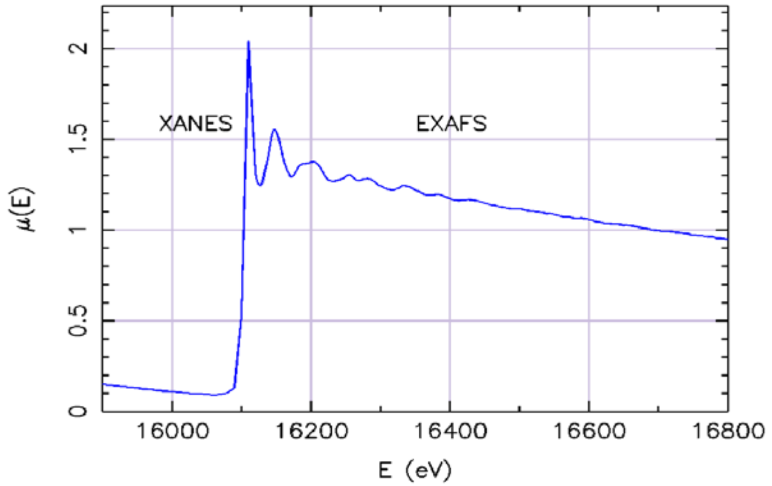
Advanced Photon Source

(Argonne National Laboratory, Argonne, IL)

X-ray Absorption Spectroscopy

X-ray Absorption Spectroscopy: Measure energy-dependence of the x-ray absorption coefficient μ(E) [either log(I_0 /I) or (I_f / I_0)] of a core-level of a selected element





XANES = X-ray Absorption Near-Edge Spectroscopy

EXAFS = Extended X-ray Absorption Fine-Structure

Element Specific: Elements with Z>13 can be examined.

Valence Probe: XANES gives chemical state and formal valence of selected element.

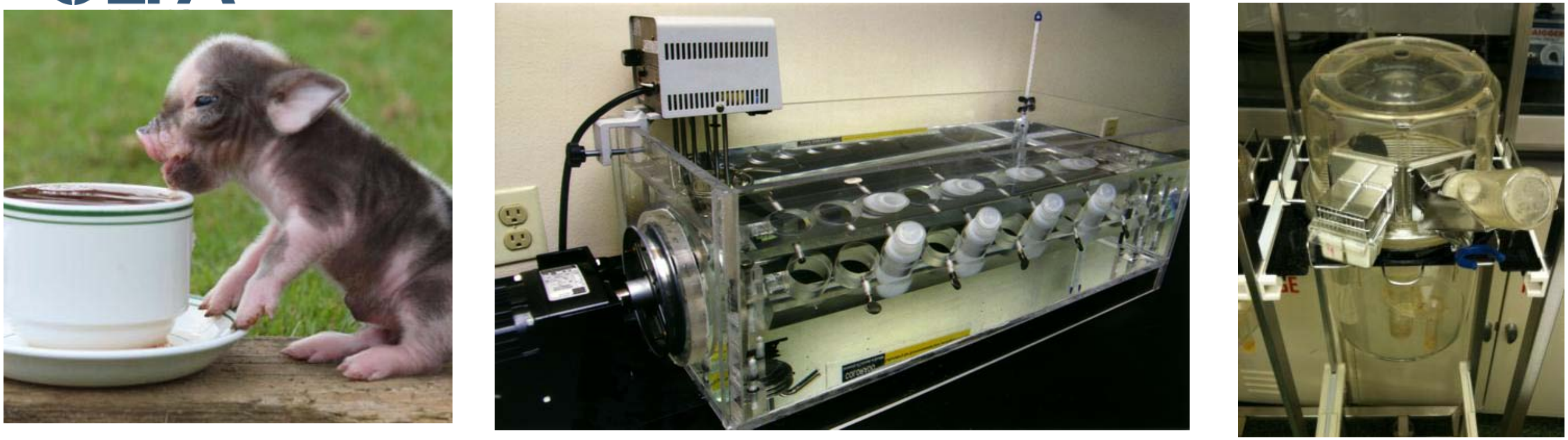
Local Structure Probe: EXAFS gives atomic species, distance, and number of near-neighbor atoms around a selected element.

Low Concentration: concentrations down to 1 ppm for XANES, 10 ppm for EXAFS.

Natural Samples: samples can be in solution, liquids, amorphous solids, soils, aggregates, plant roots, surfaces, etc.

Small Spot Size: XANES and EXAFS measurements can be made on samples down to ~100s nanometers in size.

Bioavailable and Bioaccessible



- In vivo studies (Casteel et al. 1997; Freeman at al. 1995; Nagar et al. 2009; Pascoe et al. 1994; Rees et al. 2009; Roberts et al. 2002)
  - Separate recovery of urine and feces
- Relative bioavailability (RBA)
  - Ratio of the ABA in soil to the ABA in a diet containing sodium arsenate
  - % RBA = [ABA for As in a specific diet/ABA of As in sodium arsenate]*100
- In Vitro Studies performed 37° C (Solubility Bioavailability Research Consortium)
  - Gastric Phase – 1% Pepsin, 0.15 M NaCl, pH 1.5
  - Intestinal Phase Extractions Bile Pancreatin pH 5.5
- IVBA (%) = [in vitro extractable (mg kg^{-1})/total contaminant (mg kg^{-1})]*100

Summary

- Pb immobilization has been successfully demonstrated in soils
- Important to confirm the formation of Pb-phosphates
- in-vitro and in-vivo results provide evidence of reduced bioavailability

Other issues to consider:

1. effects on Pb mobility in soil, including plant uptake;
2. co-contaminant mobility and bioavailability;
3. duration of efficacy and requirements for repeated amendments;
4. relative expense of alternative methods (e.g., excavation, barrier, institutional controls);
5. potential hazard and regulatory concerns associated with increased loading of phosphate to the local environment (e.g., watershed); and
6. education and acceptance of the community regarding efficacy and what it means in terms of Pb health risk

Summary

- As immobilization has limited studies
- Important to confirm the speciation changes
- There is yet to be an in-vivo study on As treated soils to demonstrate a reduction in As bioavailability
- Will in-vitro tests for As show artifacts found in Pb in-vitro studies?

Procedure with caution and common sense

United States
Environmental Protection
Agency

Immobilization Strategies for Pb & As

Kirk G. Scheckel, USEPA, Cincinnati, OH