Welcome to the CLU-IN Internet Seminar

Bioavailability-Based Remediation of Metals Using Soil Amendments: Considerations & Evaluation Techniques: Part 2

Sponsored by: U.S. EPA Office of Superfund Remediation and Technology Innovation

Delivered: August 31, 2011, 2:00 PM - 4:00 PM, EDT (18:00-20:00 GMT)

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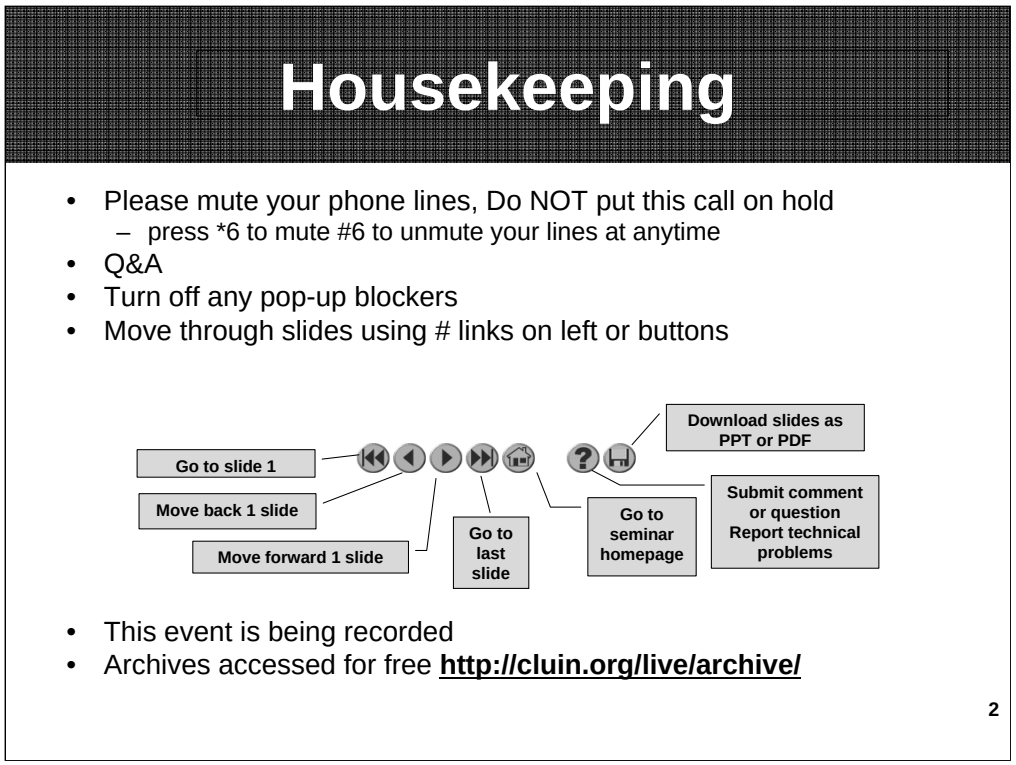
1

Visit the Clean Up Information Network online at www.cluin.org



Although I'm sure that some of you have these rules memorized from previous CLU-IN events, let's run through them quickly for our new participants.

Please mute your phone lines during the seminar to minimize disruption and background noise. If you do not have a mute button, press *6 to mute #6 to unmute your lines at anytime. Also, please do NOT put this call on hold as this may bring delightful, but unwanted background music over the lines and interupt the seminar.

You should note that throughout the seminar, we will ask for your feedback. You do not need to wait for Q&A breaks to ask questions or provide comments. To submit comments/questions and report technical problems, please use the ? Icon at the top of your screen. You can move forward/backward in the slides by using the single arrow buttons (left moves back 1 slide, right moves advances 1 slide). The double arrowed buttons will take you to 1st and last slides respectively. You may also advance to any slide using the numbered links that appear on the left side of your screen. The button with a house icon will take you back to main seminar page which displays our agenda, speaker information, links to the slides and additional resources. Lastly, the button with a computer disc can be used to download and save today's presentation materials.

With that, please move to slide 3.

Soil Metal(loid) Bioavailability in Risk Assessment and Remediation of Contaminated Upland Soils

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School of Environment and Natural Resources
Ohio State University

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USEPA NRMRL
Cincinnati, OH

USEPA Webinar
Bioavailability Part 2
August 31, 2011

3

School of Environment and Natural Resources
Soil Environmental Chemistry Program


Research program

- **Soil/Environmental contaminant chemistry; ecotoxicology**
- **Development and evaluation of remediation technologies of contaminated land**
- **Beneficial use of byproducts via land application**
- **Biogeochemical cycling of trace elements in soils**

Teaching

ENR 675 Environmental Fate and Impact of Pollutants in Soil and Water
ENR 660 Soil Chemical process and environmental quality
ENR 740 Field Soil Investigation of Soil Chemistry, Fertility, and Biology

4

National Risk Management Research Laboratory
USEPA

Research focus

- **Metal speciation in soils, sediments, water, and biological systems via advanced, molecular-level spectroscopic techniques**
- **Macroscopic kinetic and thermodynamic laboratory studies and field research to elucidate reaction mechanisms**
- **Evaluate fate, transport, reactivity, mobility, bioavailability, and toxicity of metals in the natural environment leading to effective and economic remediation/use strategies**

Collaborative research programs

- **Remediation of metal impacted soils and sediments**
- **Soil-metal bioavailability: Human impact and plant uptake**
- **Nanotechnology in the environment**
- **Waste management and beneficial re-use strategies**
- **Mineralogy and sorption mechanisms**

5

Today's Presentation

- **Important Soil Chemical Processes and Contaminant Bioavailability**
- **Using Soil Amendments to Manipulate Contaminant Chemistry**
- **Evaluation of Soil Amended Soils: Technology Performance Methods**
- **Limitations of Soil Amendment Technology**

6

Contamination of Upland Soils

Many contaminated upland soils at a variety of locations
Inorganic and organic chemical contaminants

Today focus on select metal(loid) contaminants with high frequency of contamination (Pb, As, Zn, Cd)

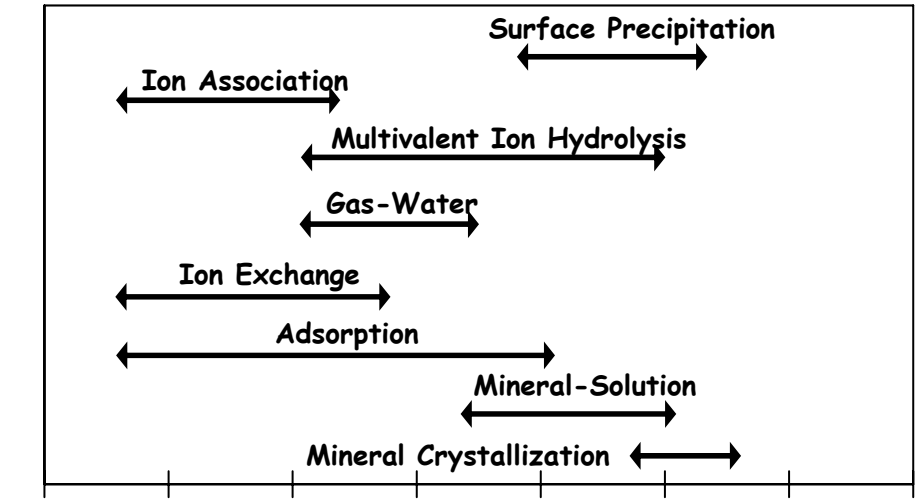
Great deal of research conducted on contaminated upland soils for Pb, Zn, Cd and As.

Historic smelter, mining wastes, Pb paint and automotive, pesticides, treated wood, etc.

7

Soil Chemical Processes and Contaminant Bioavailability

Time Scale of Metal Reactions in the Environment



msec sec min hr day mo yr mil

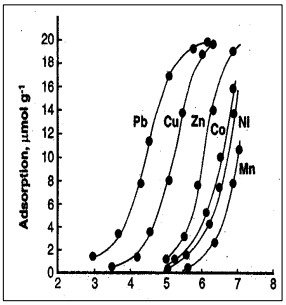
Time Scale

8

Adsorption of Heavy Metal Cations (Pb, Cd, Zn) by Fe, Mn, Al Oxides

Metal Cations

$$Fe\text{-}OH + M^{n+} = Fe\text{-}OM^{(n-1)} + H^{+}$$



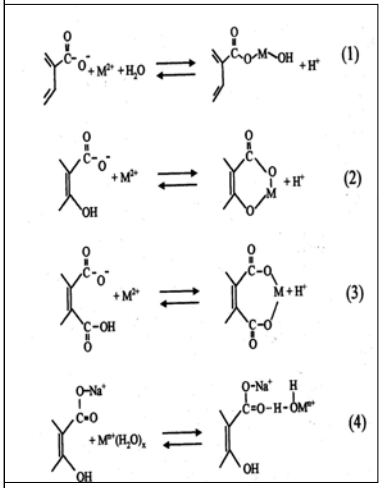
Soil pH

Adsorption greatly increases with pH!

Effective for Pb, Cu, Zn not as effective for Cd

9

Reaction of cationic metals natural organic matter (NOM)



from Senesi, 1992

type of ads depends on metal

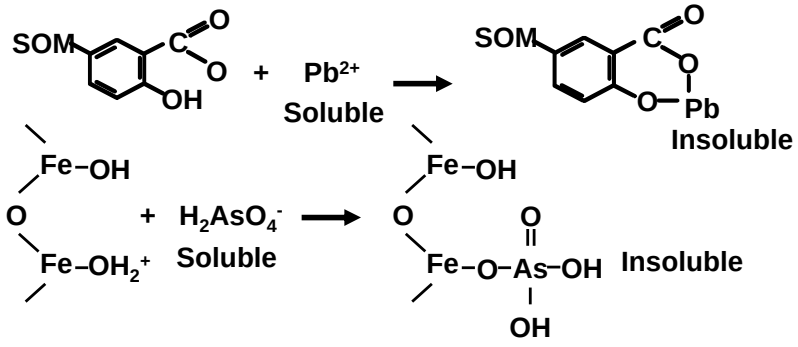
Cu, Pb strong affinity -- form strong covalent bonds; weaker for Zn, Cd

sorption capacity increases with pH

10

Soil Chemical Properties and Solid Phases Affect Contaminant Solubility

Surface Chemistry - Adsorption Reactions in Soil



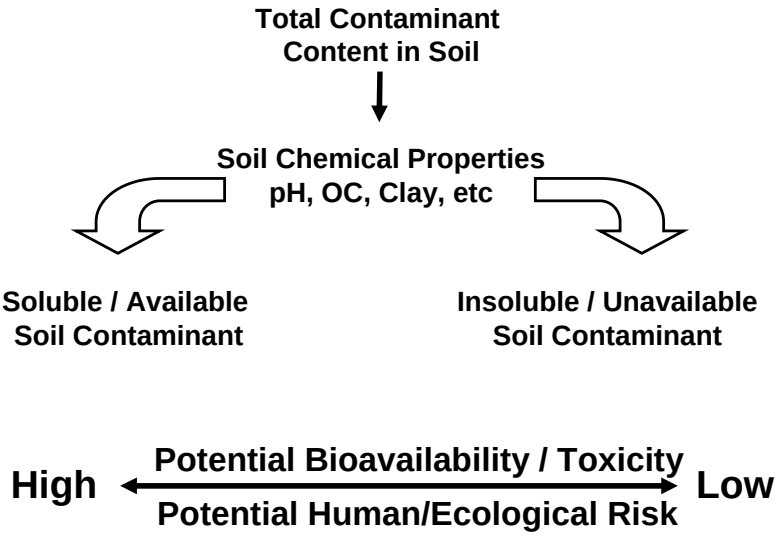
Precipitation Reactions in Soil

$$Ca_{10}(PO_4)_6(OH)_2 + xPb^{2+} \rightarrow Ca_{10-x}Pb_x(PO_4)_6(OH)_2 + xCa^{2+}$$

Soluble — Insoluble

11

Soil Type (Properties) affects Contaminant Partitioning and Availability

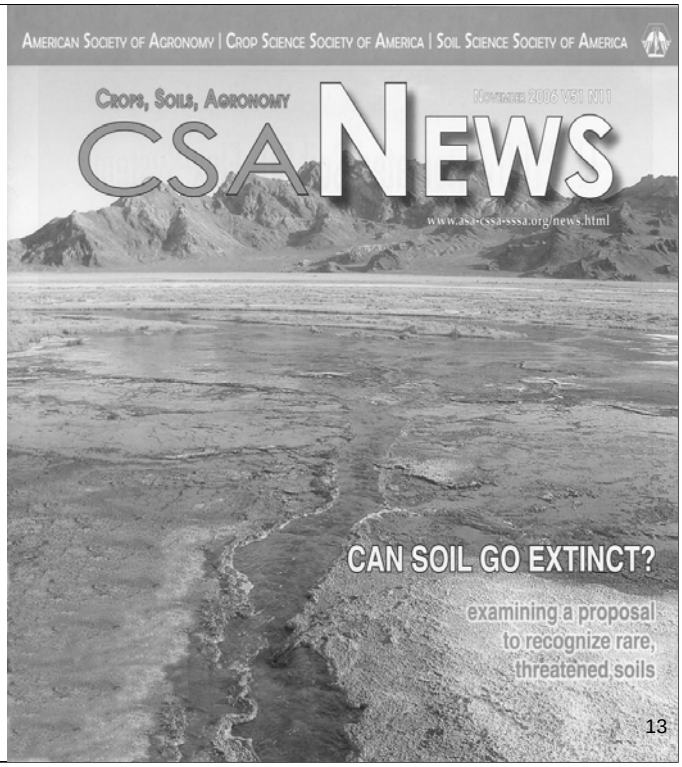


High ← Potential Bioavailability / Toxicity / Potential Human/Ecological Risk → Low

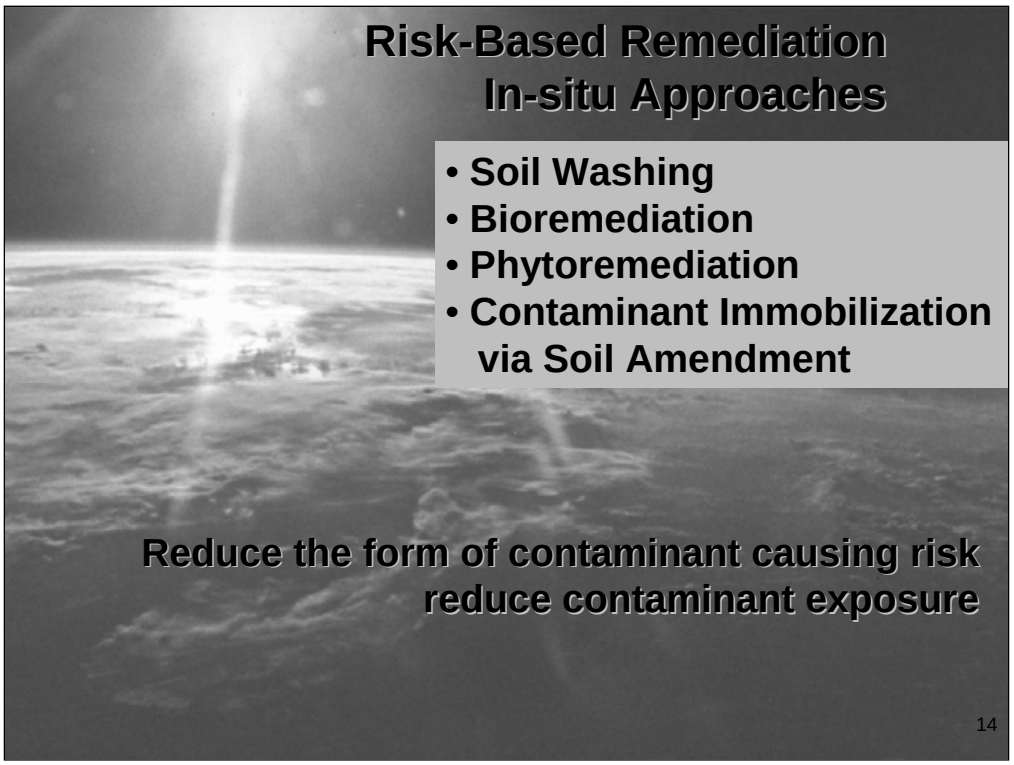
12

“It takes 500 yrs to form 1 inch of natural soil.”

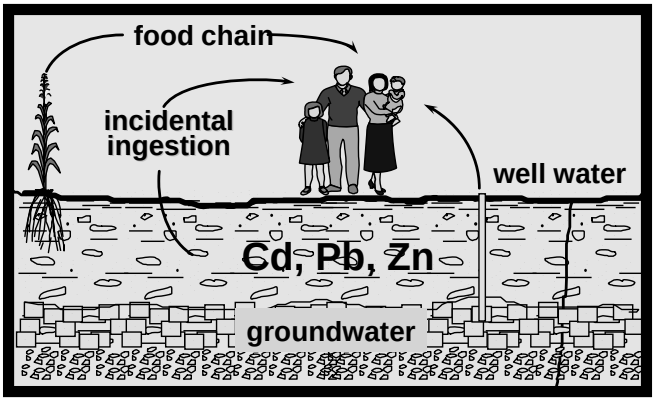
We should consider only removal of contaminated soil beyond repair



13


Risk-Based Remediation
In-situ Approaches
• Soil Washing
• Bioremediation
• Phytoremediation
• Contaminant Immobilization via Soil Amendment
Reduce the form of contaminant causing risk
reduce contaminant exposure
14

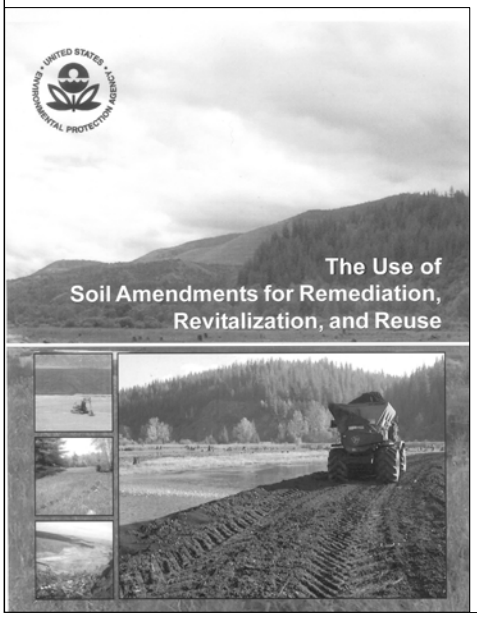
Using Soil Amendments to Manipulate Contaminant Chemistry and Reduce Bioavailability



Use soil chemistry and soil additives to reduce contaminant transmission and risk from phytoavailability, gastrointestinal availability, mobility in soil

15

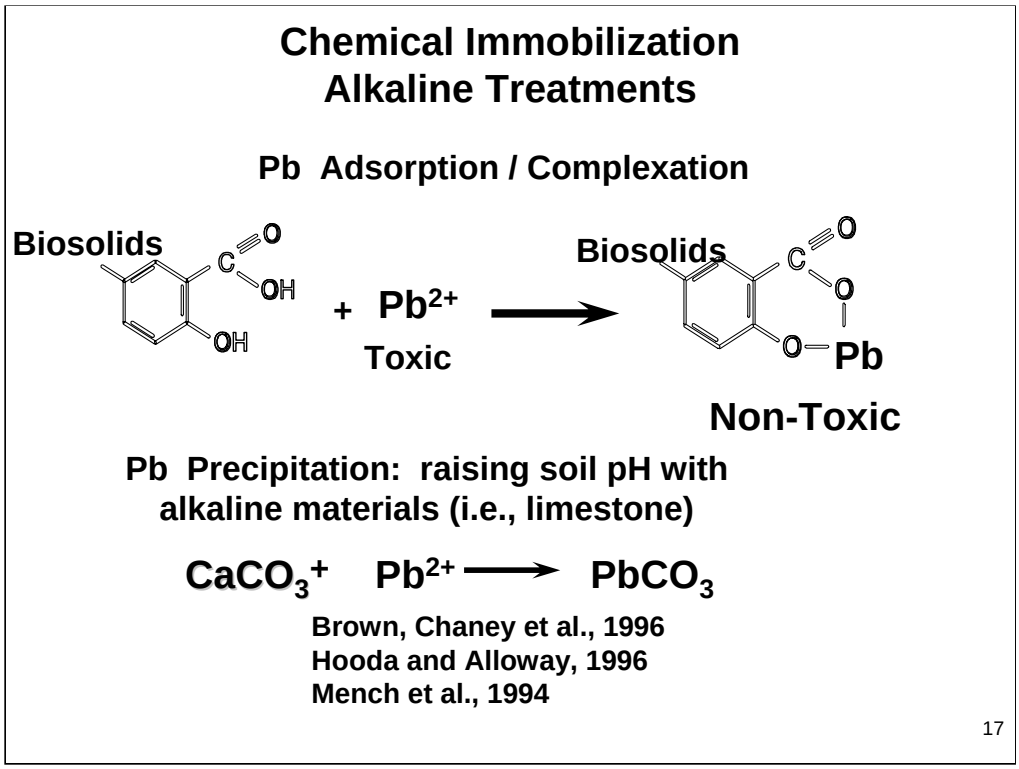
Soil Remediation and Ecological Restoration
cluin.org/ecotools



Soil Amendments

- **biosolids**
- **manures**
- **compost**
- **pulp sludges**
- **yard /wood waste**
- **lime**
- **wood ash**
- **coal combustion products**
- **sugar beet lime**
- **foundry sand**
- **steel slag**
- **FGD**
- **water treatment residuals**
- **etc**

16



In order to reduce the transfer of metals from the soil matrix, in-situ chemical immobilization processes may be used.

Chemical reactions such as sorption, precipitation, and complexation can be used to immobilize these metals with-in the soil matrix rendering them unavailable.

An example of this would be the addition of municipal biosolids (sewer sludge) to complex available lead rendering it unavailable

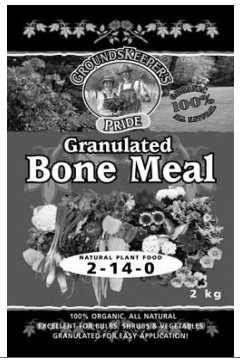
Another example is the precipitation of lead with the increase of the soil's pH.

Chemical Immobilization
Phosphates / P Fertilizer

$$Ca_{10}(PO_4)_6(OH)_2 + xPb^{2+} \longrightarrow Ca_{10-x}Pb_x(PO_4)_6(OH)_2 + xCa^{2+}$$

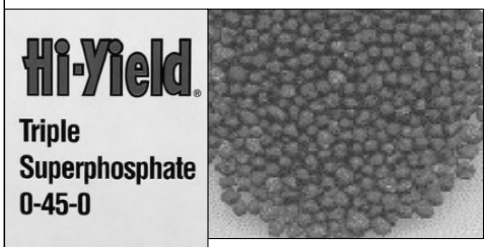
Hydroxyapatite + available Pb → **Lead pyromorphite**
Low bioavailability

Hydroxyapatite (Ma et al., 1995; Laperche et al., 1997)



18

Pb immobilization using water soluble phosphorus fertilizer calcium, ammonium or potassium phosphates



Hydroxyapatite (Ma et al., 1995; Laperche et al., 1997)

Soluble phosphates

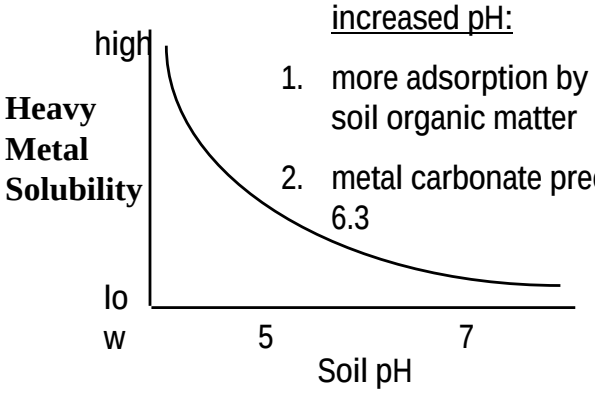
- **potassium phosphate (Pierzynski and Schwab, 1993)**
- **sodium phosphate (Mench et al., 1994)**
- **diammonium phosphate, DAP (McGowen et al., 2000)**

Soluble P Fertilizer reaction with Pb is Much Faster than Insoluble Phosphates (hydroxyapatite, bone meal)

19

Amendment Selection and Application
Pb, Cd, Zn

Pb, Zn, Cd (cationic metals) immobilization:
soil organic amendments, phosphates, Fe oxides, carbonates

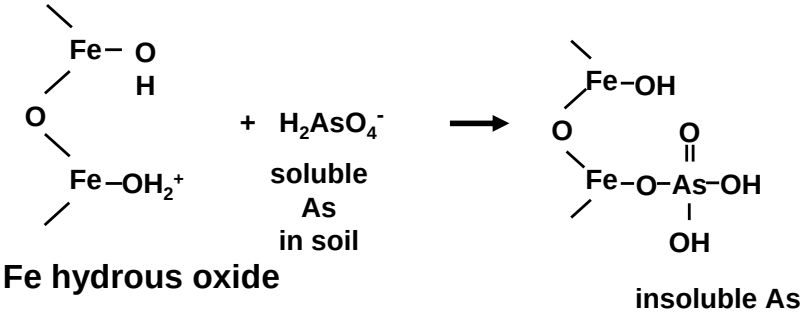


<u>metal cation solubility reduced with increased pH:</u>

1. more adsorption by soil oxides and soil organic matter
2. metal carbonate precipitation at pH > 6.3

20

Fe, Mn, Al oxides immobilize As(V) in Soil

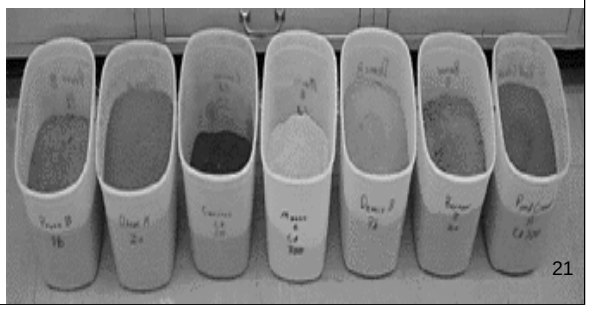


Fe hydrous oxide

insoluble As

Strong adsorption of arsenic: "insoluble arsenic sink-- not a source"

adsorption capacity:
Fe, Mn oxides > Al oxides



21

Assessing Metal Bioavailability in Soil Amended Contaminated Mining Soils

Is Very Costly and Ecologically Destructive Excavation and Soil Replacement Necessary?

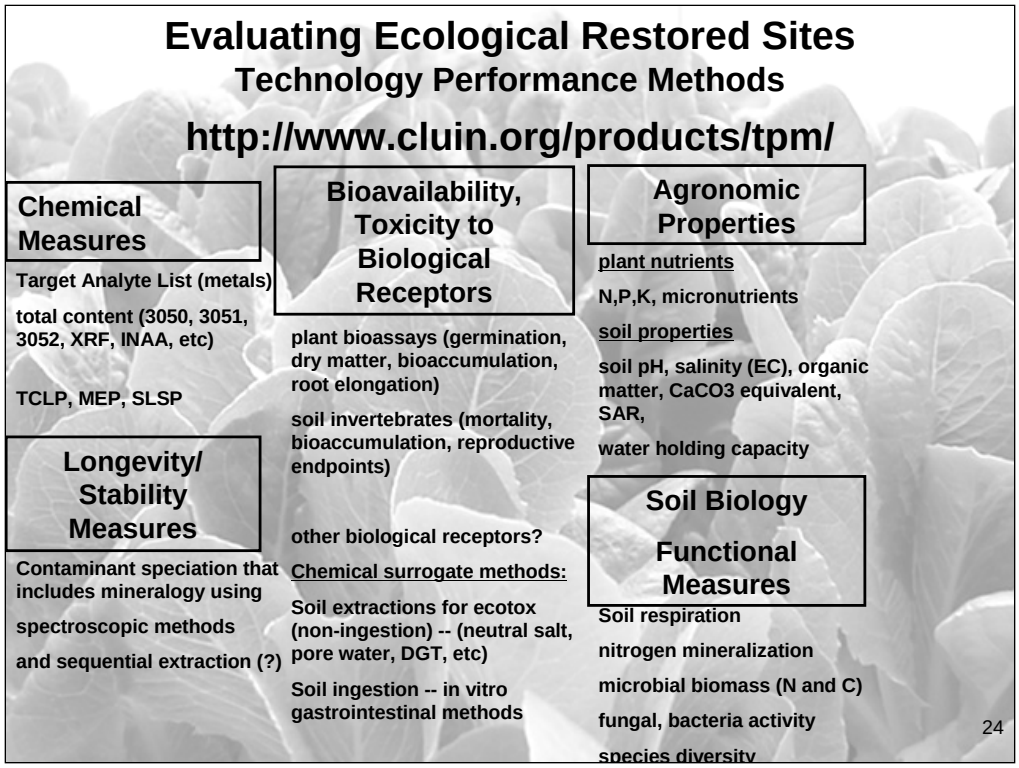
Accurate bioavailability-based risk assessment can inform Remedial Action Levels and prevent Destruction of Soil

22

Evaluating Ecological Restored Sites
Technology Performance Methods

http://www.cluin.org/products/tpm/

23


Evaluating Ecological Restored Sites
Technology Performance Methods
http://www.cluin.org/products/tpm/
Chemical Measures
Target Analyte List (metals)
total content (3050, 3051, 3052, XRF, INAA, etc)
TCLP, MEP, SLSP
Longevity/ Stability Measures
Contaminant speciation that includes mineralogy using
spectroscopic methods
and sequential extraction (?)
Bioavailability, Toxicity to Biological Receptors
plant bioassays (germination, dry matter, bioaccumulation, root elongation)
soil invertebrates (mortality, bioaccumulation, reproductive endpoints)
other biological receptors?
Chemical surrogate methods:
Soil extractions for ecotox (non-ingestion) -- (neutral salt, pore water, DGT, etc)
Soil ingestion -- in vitro gastrointestinal methods
Agronomic Properties
plant nutrients
N,P,K, micronutrients
soil properties
soil pH, salinity (EC), organic matter, CaCO3 equivalent, SAR,
water holding capacity
Soil Biology
Functional Measures
Soil respiration
nitrogen mineralization
microbial biomass (N and C)
fungal, bacteria activity
species diversity
24

Evaluation of In Situ Remediation Treatments

Assessment Methods are Exposure Pathway Based

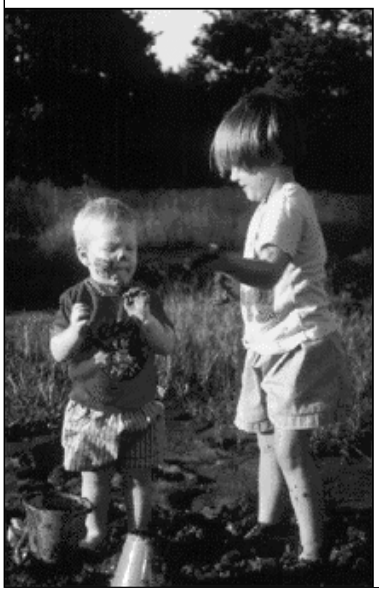
	Bioassay	In Vitro Methods
Food Chain	Plants	weak salt soil extraction
Soil Ingestion	Animal Models dosing trial	in vitro gastrointestinal simulation
Ecological Impact	Earthworms, mammals, others	correlated soil extraction

Soil Contaminant

In vitro methods MUST be correlated with appropriate animal / plant endpoints

25

Using Bioavailability to Assess Human Health Risk of the Soil Ingestion Pathway
How do we assess this risk?



<u>cancer risk</u> = CDI x SF
where CDI = chronic daily intake
SF = cancer slope factor
<u>non cancer risk</u>
Hazard Quotient = CDI ÷ RfD
where RfD = reference dose

Adjustments for Contaminant Relative Bioavailability (RBA), 0.0 to 1.0

$RfD_{adjusted} = RfD_{IRIS} \times RBA$
$SF_{adjusted} = SF_{IRIS} \times RBA$

Adjustment for small RBA will reduce exposure / risk associated with soil ingestion

26

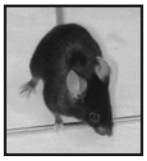
Measuring Bioavailability Using *In Vivo* Models

acceptable model for Pb, As, other

$25+K /soil

acceptable model

expensive ethical issues



inexpensive ($5K/soil)
recent developments
USEPA ORD RTP

Studies have reported RBA range widely for Pb and As (0.02 to 1.0)

27

In Vitro Gastrointestinal Methods

An Inexpensive, Fast, Accessible Alternative

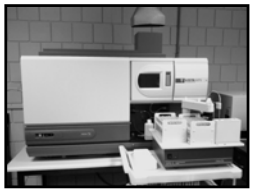
Simulated human gastrointestinal extraction

Bioaccessible metal = dissolved in gastric and/or intestinal solution; bioaccessible is a conservative measure of bioavailable metal

IVG extraction

OSU IVG

$$\%\ \text{IVBA} = \left(\frac{\text{In vitro dissolved metal}}{\text{Total soil metal}}\right)$$



metal analysis by ICP

28

U.S. EPA
Guidance for Evaluating the Oral Bioavailability of Metals in Soils for Use in Human Health Risk Assessment

OSWER 9285.7-80, May 2007

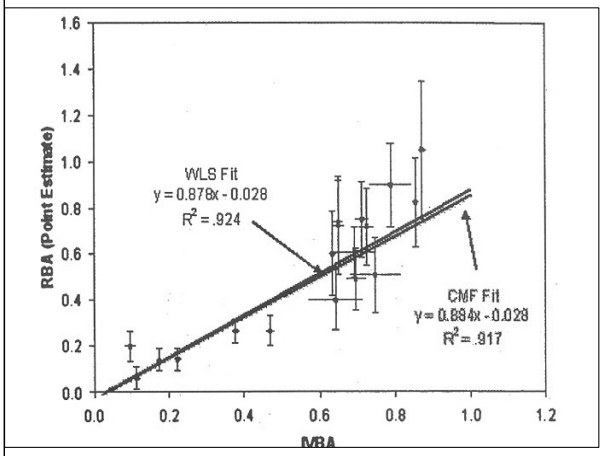
Recommended Criteria for Validation of Test Methods adapted from ICCVAM

"Data generated adequately measure or predict the toxic endpoint of interest and demonstrate a linkage between either the new test and effects in the target species."

In vitro gastrointestinal (IVG) method must be correlated with an acceptable *in vivo* model
IVG must be *predictive*

29

RBALP *in vitro* gastrointestinal method correlated with swine bioavailable Pb

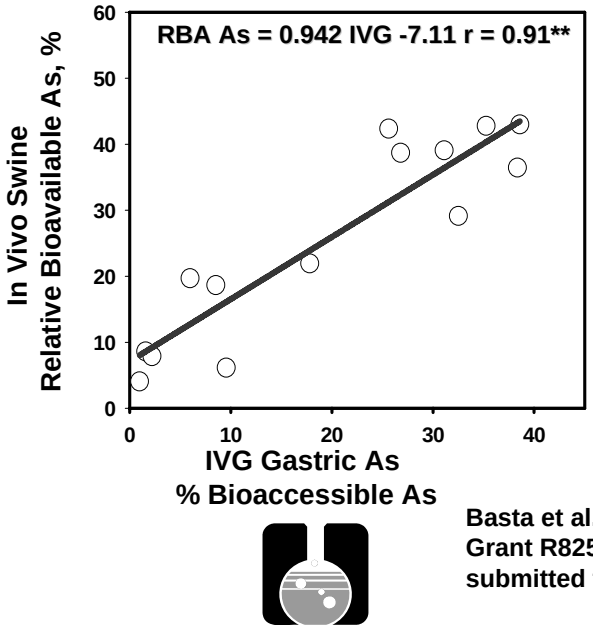


Drexler and Brattin. 2007. Human Ecol. Risk Assess. 13:383-401

U.S. EPA, Guidance for Evaluating the Oral Bioavailability of Metals in Soils for Use in Human Health Risk Assessment OSWER 9285.7-80, May 2007; RBALP IVG accepted for Pb, others under consideration for As.

30

Correlation of OSU IVG method with the Young Swine *in vivo* model for soil arsenic



Basta et al. 2003.
Grant R825410 Final Report.
submitted to U.S. EPA ORD

31

In Vitro Gastro(intestinal) Methods Correlated with In vivo Pb, As, Cd Bioavailability

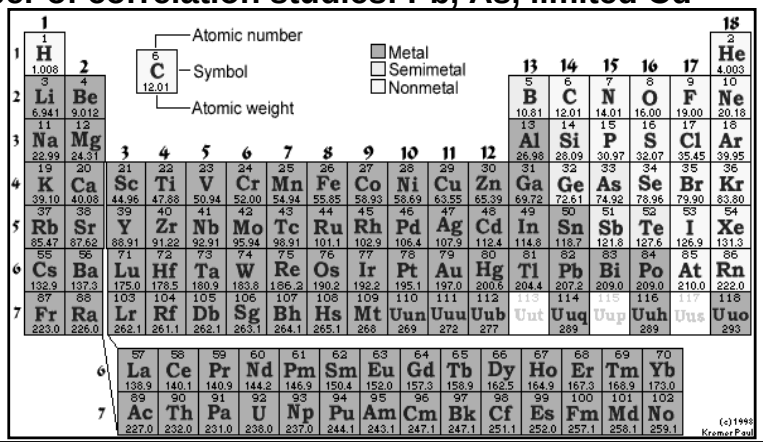
Bioaccessibility Method	Metal contaminants
RBALP	Pb
OSU IVG	As, Pb, Cd
UBM	As, Pb, Cd
SBRC	As, Pb, Cd

32

In Vitro Methods for Measuring Metal Bioavailability Method Validation Issues

How many metal(loid) soil contaminant can be evaluated?
<u>Only</u> in vitro methods corrected with acceptable animal models!

Number of correlation studies: Pb, As, limited Cd



33

Advances in Bioaccessibility Methodology to Determine Human and Ecological Bioavailability, Exposure, and Risk from Ingestion of Trace Element Contaminated Soil
11th ICOBTE Symposium 10
Firenze, Italia July 5 2011
http://www.icobte2011.com/

Co-Organizers:
Nick Basta, Ohio State University
Albert Juhasz, CERAR, University of South Australia
Ken Reimer, ESG, Royal Military College, Kingston, Canada
Joanna Wragg, British Geological Survey
Karen Bradham, NERL, U.S.EPA, Raleigh, NC

32 presentations (13 oral, 19 poster)

Proceedings will be published in a special issue of J. Environ. Health Science, Part A

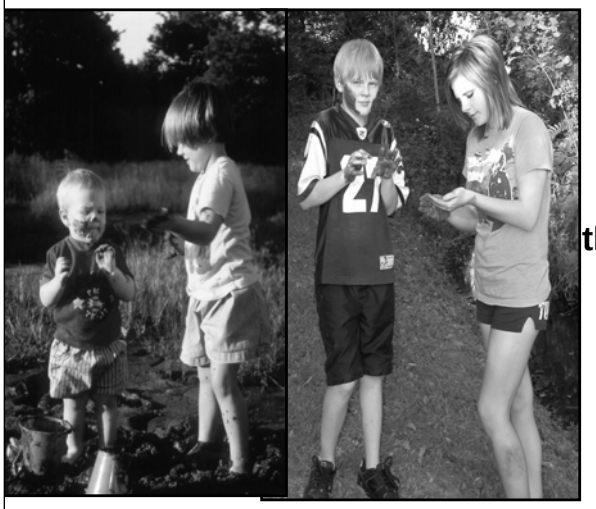
34

OSU Soil Environmental Chemistry
Metal Bioaccessibility Testing of Soil

We have a very active research program and we offer a variety of IVG soil tests to the public

35

OSU IVG Research and Service more active than ever after 10+ yr



the soil isn't contaminated

1997 **2007**

36

Case Studies
Tri-state Mining District

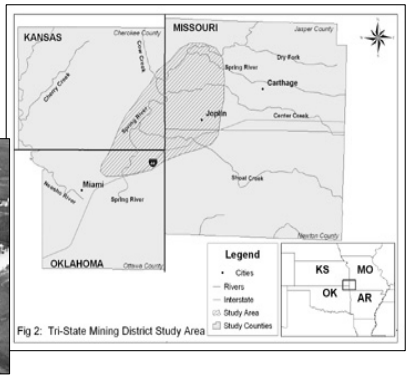


Fig 2: Tri-State Mining District Study Area

Tri-State Mining Region
Extensive Pb, Zn Mining
Smelting / Processing

Highest Child Blood Pb in US

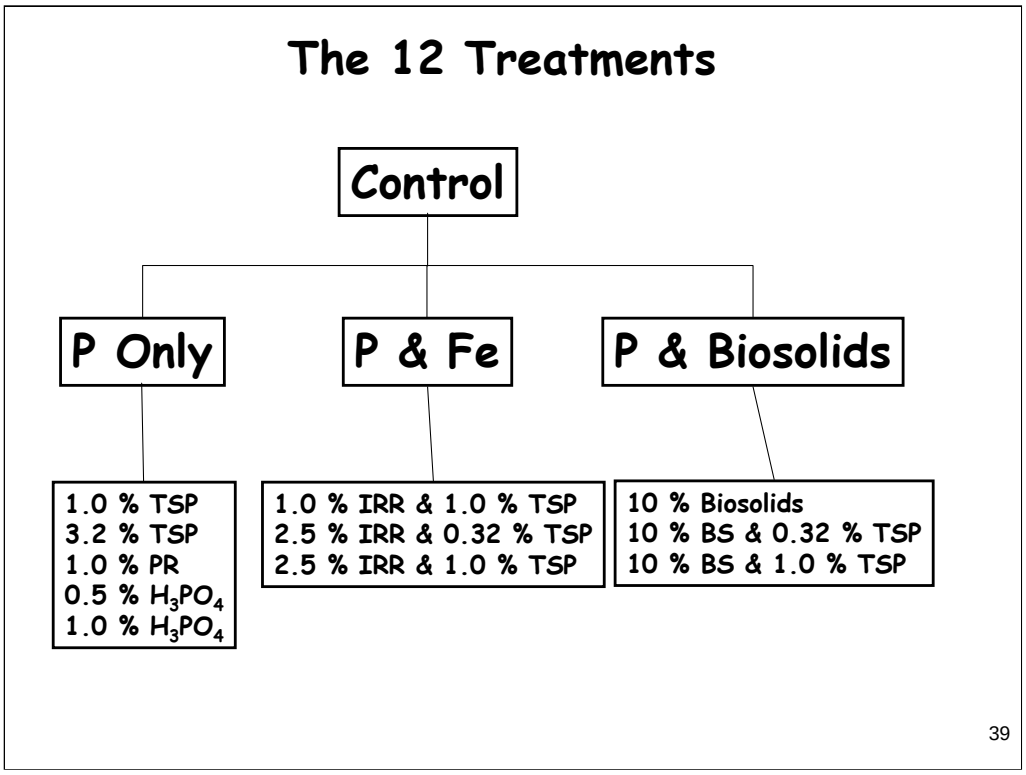
37

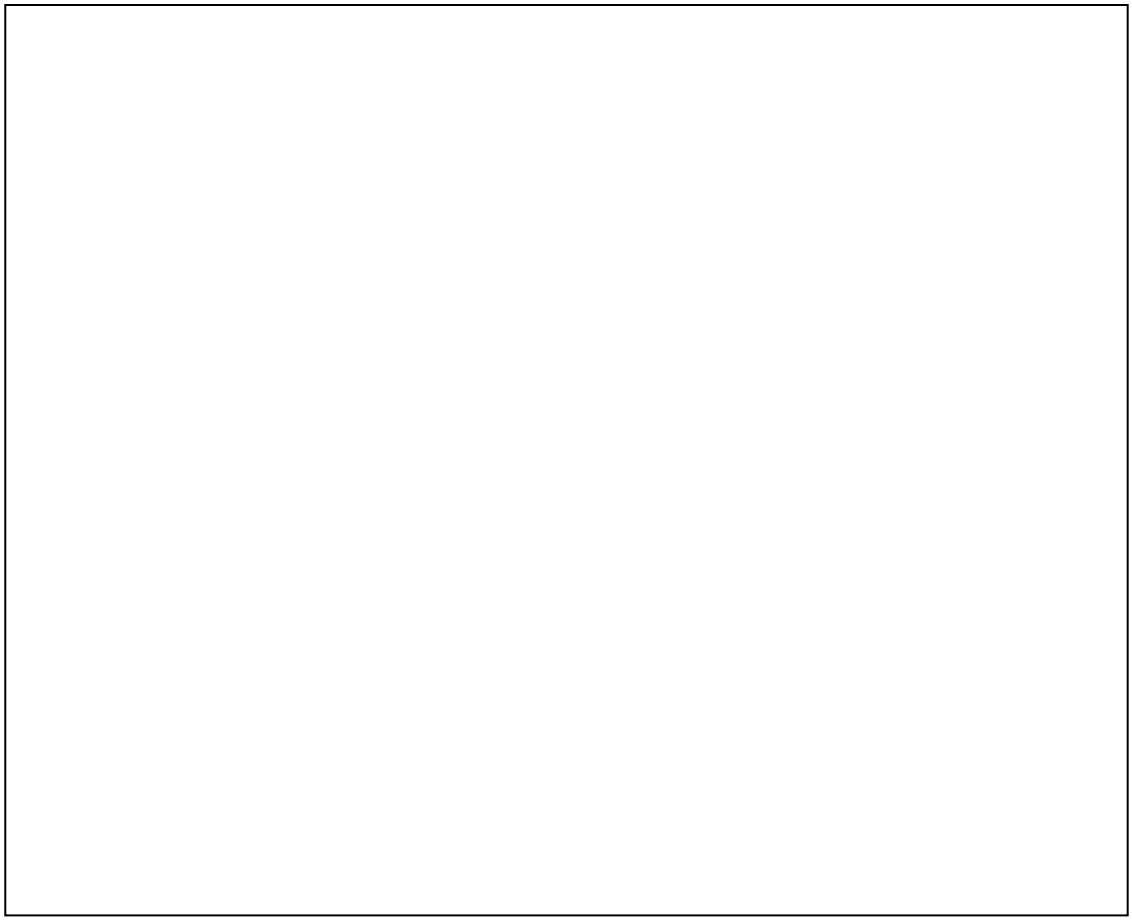
Remediation of Soil Pb at Joplin, Missouri

Remediation Technologies Development Forum (RTDF)
http://www.rtdf.org/public/iinert/default.htm

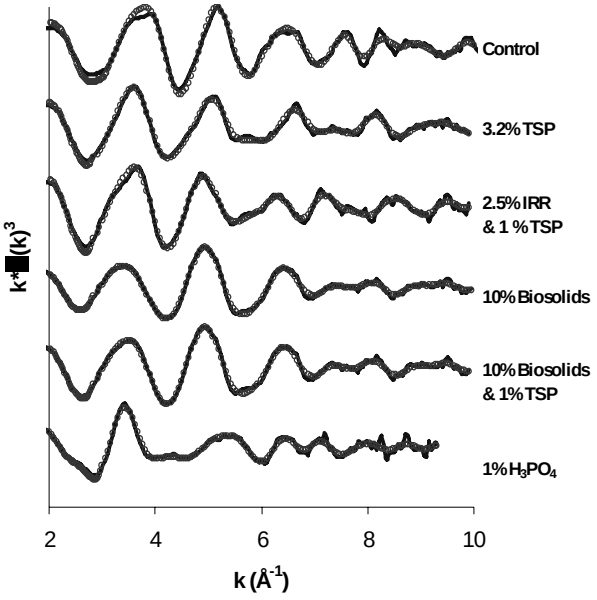
- **Reduction in soil Pb, Zn and Cd phytoavailability and phytotoxicity.**
- **Reduction of soil Pb bioavailability to mammals (rats, pigs, human adults).**
- **P-treated soil reduced bioavailability to humans from 42% to 13%**

38


The 12 Treatments
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
39



Chi Functions & LC Fits of Joplin Samples



40

Soil Lead Bioavailability Joplin 18 mo Sample

	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

41

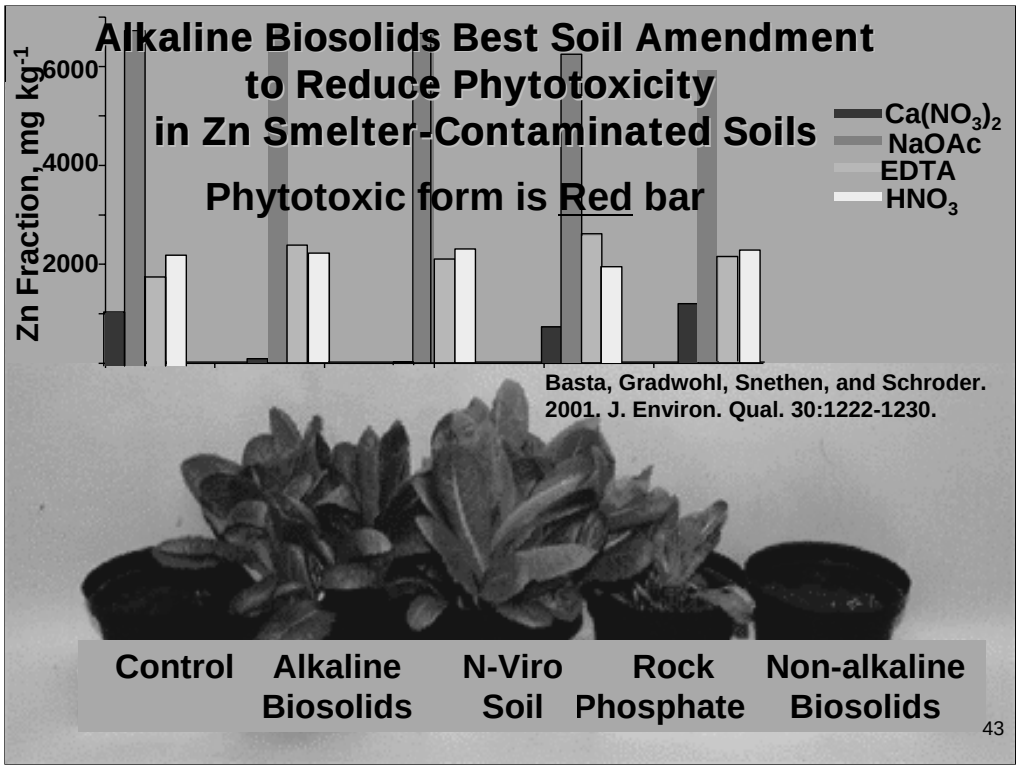
Contaminated Soil / Geomedia
Blackwell, Oklahoma

Waste mixed with soil

30% of children in area had excessive blood Pb

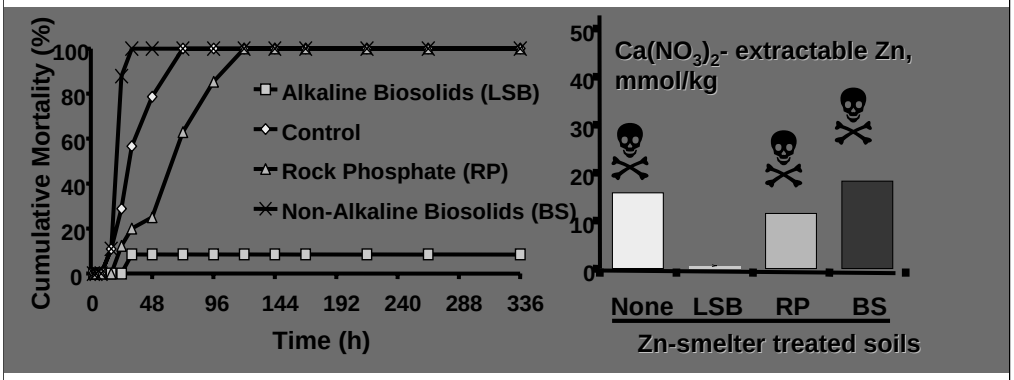
Contaminated "Soil"
69,000 mg/kg Zn!
5150 mg/kg Pb
1090 mg/kg Cd
152 mg/kg As

42


Alkaline Biosolids Best Soil Amendment
to Reduce Phytotoxicity
in Zn Smelter-Contaminated Soils
Phytotoxic form is Red bar
Zn Fraction, mg kg-1
6000
4000
2000
Ca(NO3)2
NaOAc
EDTA
HNO3
Basta, Gradwohl, Snethen, and Schroder.
2001. J. Environ. Qual. 30:1222-1230.
Control
Alkaline Biosolids
N-Viro Soil
Rock Phosphate
Non-alkaline Biosolids
43

Alkaline Biosolids Best Treatment To Reduce Zn Toxicity to Earthworms

Earthworm Toxicity Testing Zn, Pb, Cd Contaminated Smelter Soil

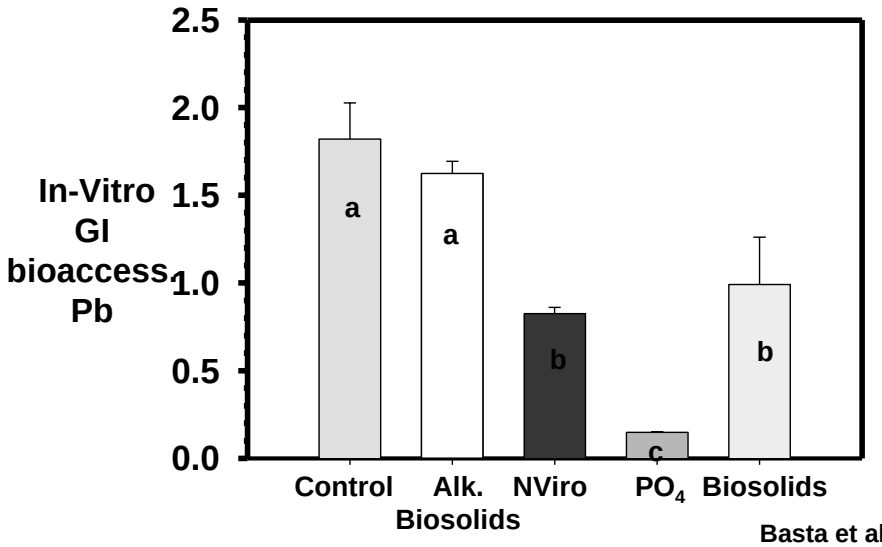


Condor, Lanno, and Basta. 2001. J. Environ. Qual. 30:1231-1237.

No toxicity to *Eisenia fetida* in alkaline biosolids treated soil !

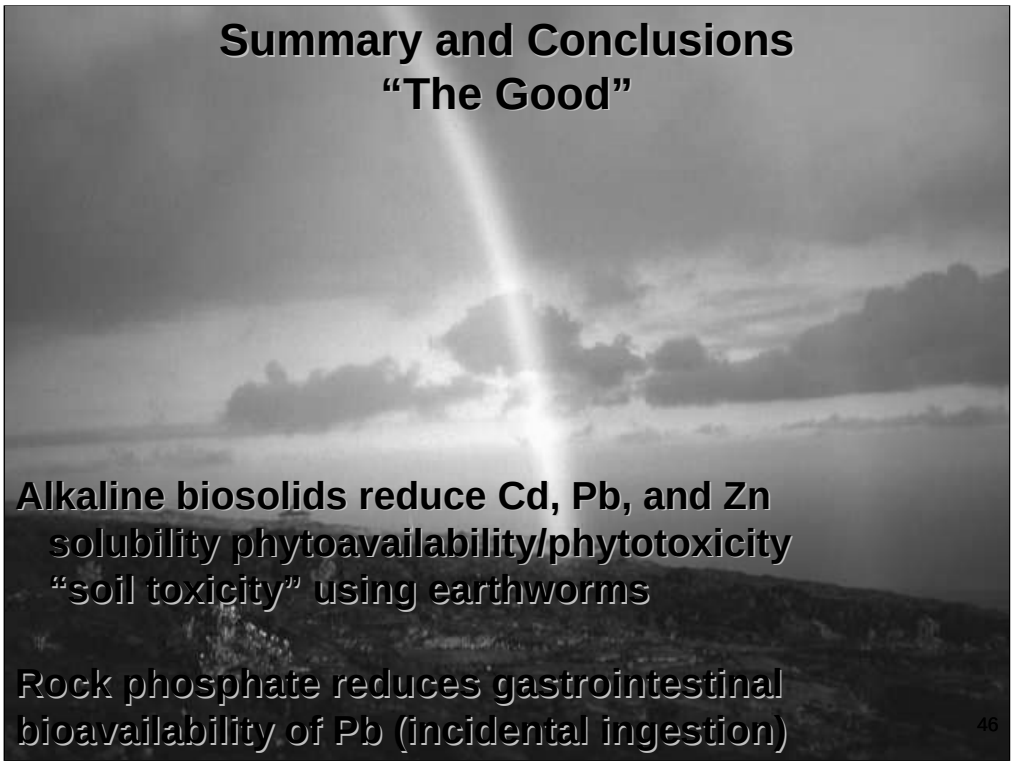
44

Phosphate was the Best Soil Amendment to Reduce Pb Soil Ingestion Risk NOT Alkaline Biosolids



45

Basta et al., 2001.
J. Environ. Qual. 30:1222-1230


Summary and Conclusions
"The Good"
Alkaline biosolids reduce Cd, Pb, and Zn
solubility phytoavailability/phytotoxicity
"soil toxicity" using earthworms
Rock phosphate reduces gastrointestinal
bioavailability of Pb (incidental ingestion)
46

Summary and Conclusions
"The Stinker"

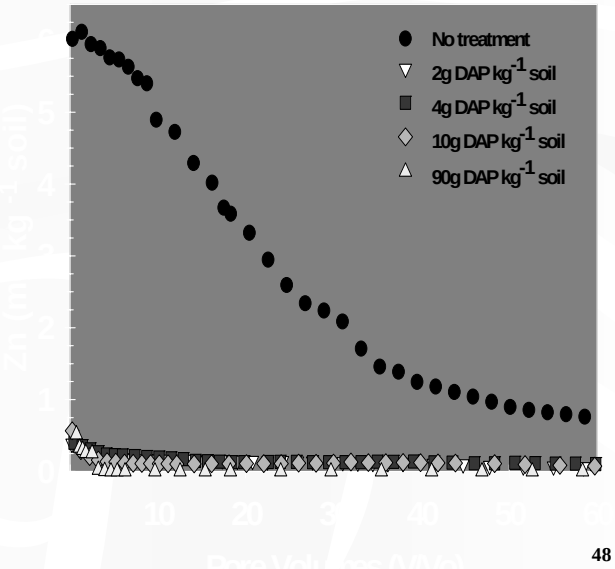
Alkaline biosolids did not reduce gastrointestinal bioaccessibility

Non-alkaline treatments did not decrease soil ecotoxicity

Rock phosphate had little effect on phytoavailability(esp. Cd, Zn)

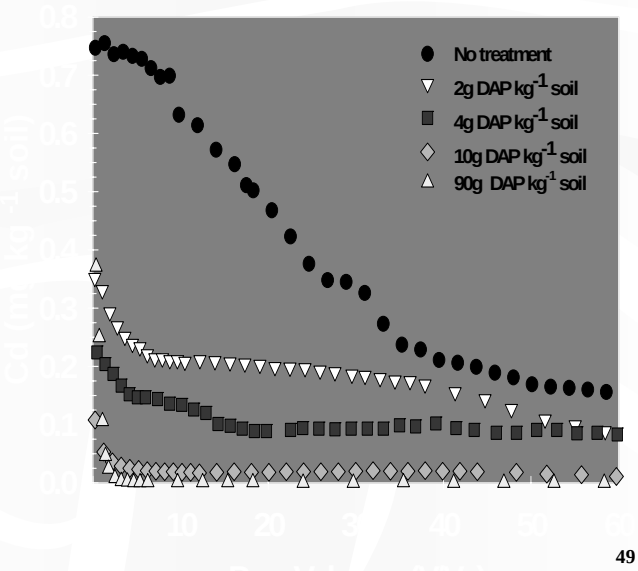
Soluble phosphates may be useful to reduce Cd, Zn, and Pb solubility and bioavailability 47

Using DAP Fertilizer to Immobilize Pb, Cd, Zn
Zinc Elution (Mobility)



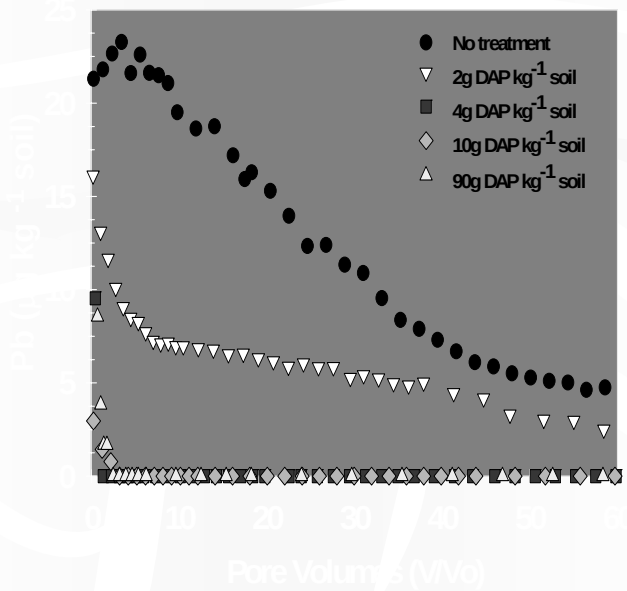
48

Using DAP Fertilizer to Immobilize Pb, Cd, Zn
Cadmium Elution (Mobility)



49

Using DAP Fertilizer to Immobilize Pb, Cd, Zn
Lead Elution (Mobility)



50

Soil Remediation in Picher, OK using Byproducts

Univ. of Washington, USEPA ERT, OSU

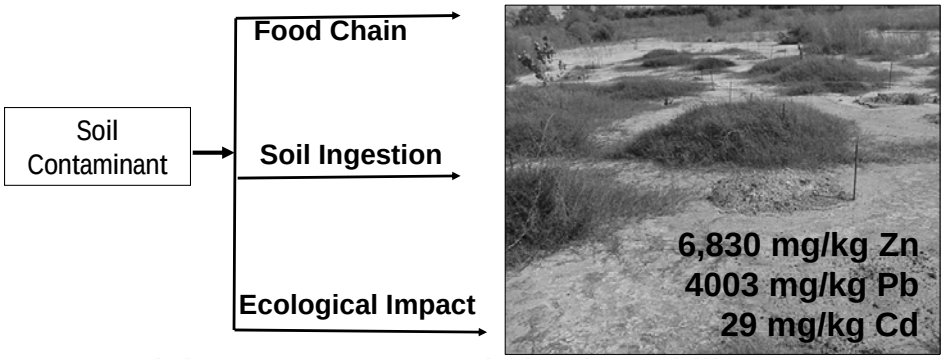
<u>72 plots on Pb, Zn, Cd contaminated land</u>
combinations of:
Alkaline Biosolids
Biosolids Compost
Commercial phosphorus fertilizer
Drinking water residuals

Seeded with Bermudagrass

51

Best Amendment to Reduce Pb, Zn, Cd Bioavailability / Mobility

Biosolids + Phosphorus Combination

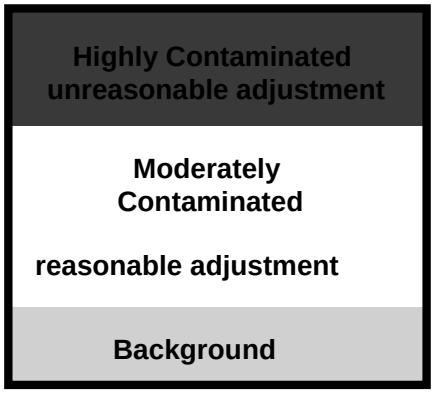


High Rate of DAP needed to immobilize Zn
salinity prevented emergence yr 1 but ok yr 2

Brown, S.L., H. Compton, and N.T. Basta. 2007.
Field Test of *In Situ* Soil Amendments at the Tar Creek National Priorities List Superfund Site
J. Environ. Qual. 36:1627-1634.

52

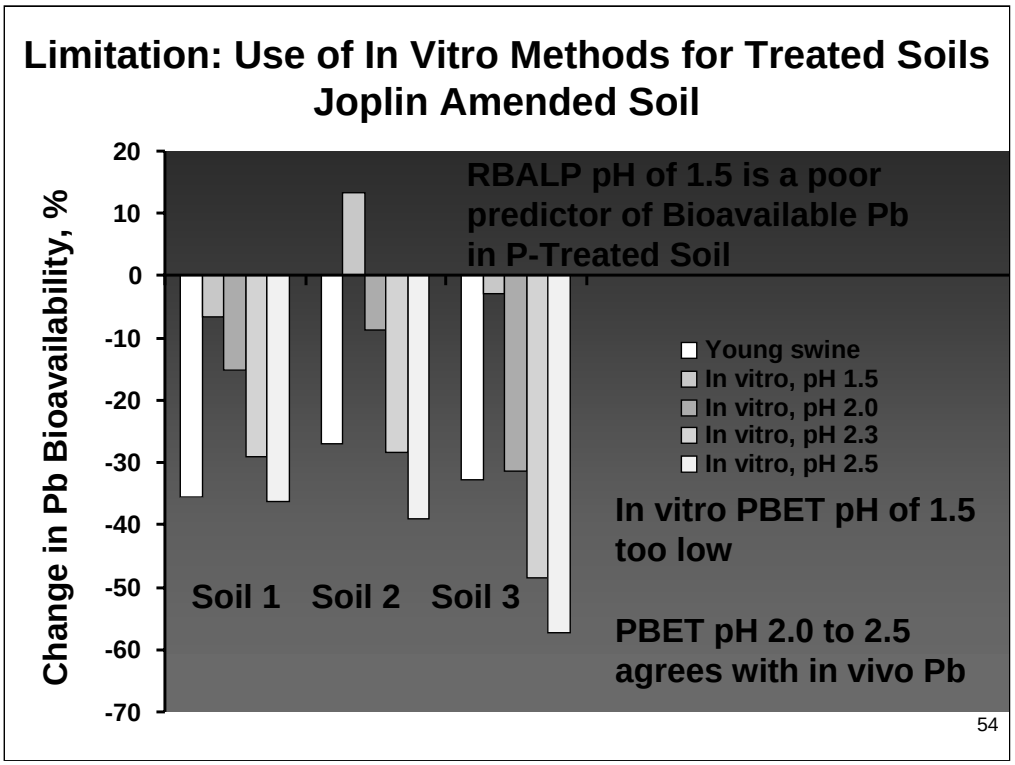
Limitations of Soil Amendment Treatments
Contaminant Concentration in Soil / Solid Waste
when will bioavailability adjustments be made?



High level: 4,000+ mg/kg total Pb
Bioavailability has to be very very low
unreasonable adjustment

Moderate level:
below 4,000 mg/kg Pb?
not percent level of Zn or Pb
moderate bioavailability so
reasonable adjustment

53


Limitation: Use of In Vitro Methods for Treated Soils
Joplin Amended Soil
Change in Pb Bioavailability, %
20
10
0
-10
-20
-30
-40
-50
-60
-70
RBALP pH of 1.5 is a poor predictor of Bioavailable Pb in P-Treated Soil
Young swine
In vitro, pH 1.5
In vitro, pH 2.0
In vitro, pH 2.3
In vitro, pH 2.5
Soil 1
Soil 2
Soil 3
In vitro PBET pH of 1.5 too low
PBET pH 2.0 to 2.5 agrees with in vivo Pb
54

Decreasing Toxic Metal Bioavailability with Various Soil Amendment Strategies

CU-1350

Philip M. Jardine
Jack C. Parker
Oak Ridge National Laboratory

Mark O. Barnett
Auburn University

Scott E. Fendorf
Stanford University

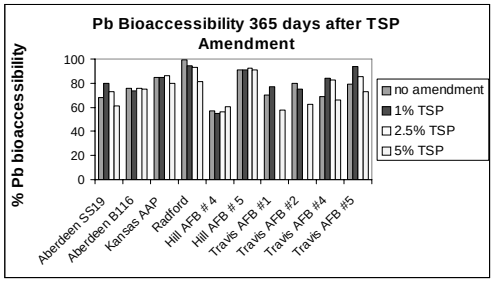
Melanie Stewart
University of Tennessee

55

In vitro extraction pH makes all the difference in evaluating P Treatments Pb soils

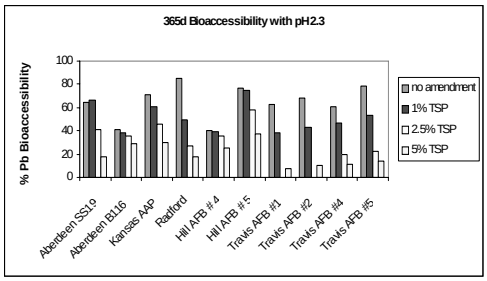
Phosphate treated Pb contaminated DoD soils

RBALP, gastric extraction pH 1.5



P Treatment had little effect on Bio Pb

RBALP, gastric extraction pH 2.3

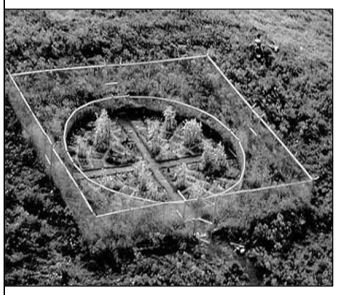


P Treatment greatly reduced Bio Pb

Does P Treatment work or not !!
What does the animal model say?
Which in vitro pH agrees with the real bioavailability of the animal model?

56

Mel Chin, conceptual artist



Revival field

Dr. Rufus Chaney and Mel Chin

soil treatments and hyperaccumulating plants where “contaminated soil is restored into rich earth, capable of sustaining a diverse ecosystem.”

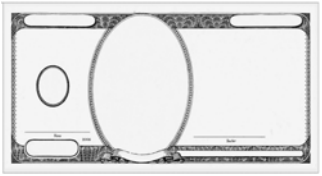
New Orleans Fundred Project:
Soil Remediation Using Phosphate-based Amendments

"Phosphate loves lead," said Chin.
"It's like this chemical sex that occurs.”

57

Fundred and Paydirt Projects

Operation Paydirt/Fundred Dollar Bill Project **is a national, artist-driven, multidisciplinary project with a critical mission: to support a solution to lead-contaminated soil in urban communities and to help end this form of childhood lead poisoning.**



Jim Wilson/The New York Times

58

Fundred and Paydirt Projects
West Oakland Residential Lead Project

Pb concentrations up to 2700 ppm: average 843 ppm; 80% above 400 ppm

Community buy-in and support

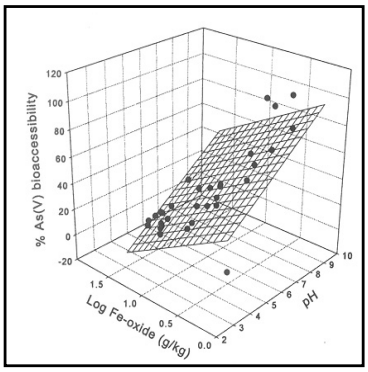
Fish bone (Apatite II) application

High unemployment, toxic environment – one solution

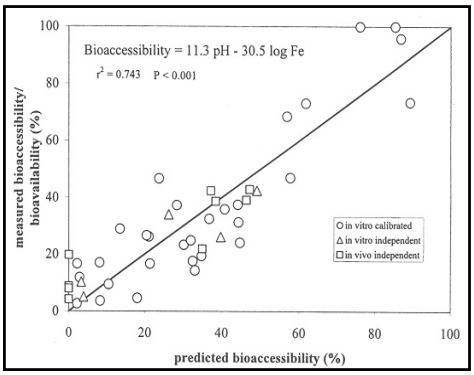
Promote the technology: NYT, Facebook, Jean Michel Cousteau documentary

59

Bioaccessible As inversely related to Reactive Soil Fe
Arsenic Loves Fe Oxide



Yang et al. 2002



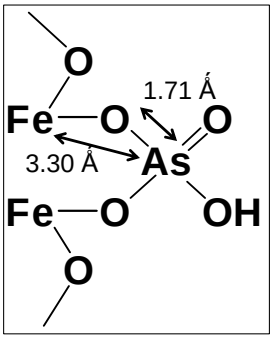
Soil reactive Fe and pH predict As Bioavailability (Δ) and Bioaccessibility (O)

Yang, Barnett, Jardine, Basta, and Casteel. 2002. Environ. Sci. Technol. 36:4562-4569

similar findings reported by Juhasz et al. 2007. Chemosphere 69:961-966.

60

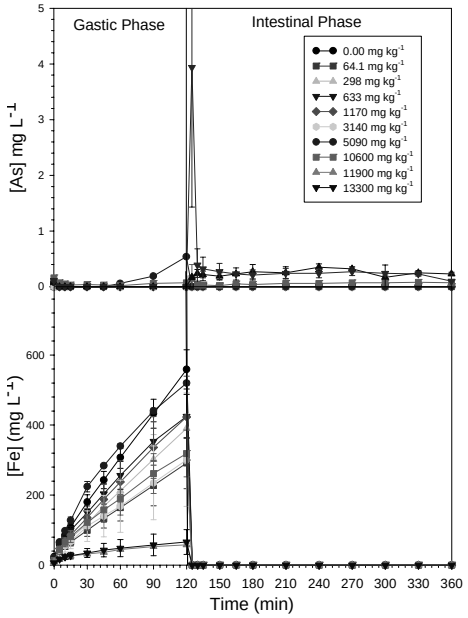
Reduced Bioaccessibility of Arsenic Sorbed to Ferrihydrite



Soil Ingestion

Bioaccessible As

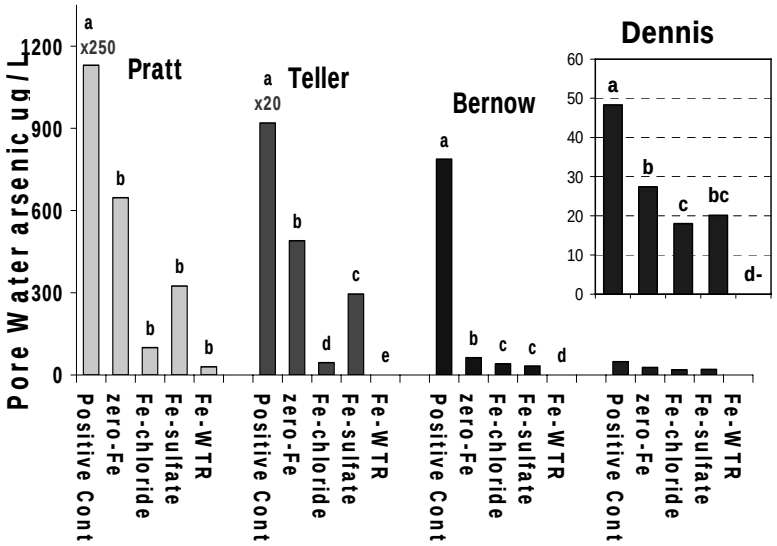
Dissolved Fe



Beak, Basta, Scheckel, Traina. 2006. Environ. Sci. Technol. 40:1364-1370

61

Fe Treatments Reduced Pore Water Arsenic
250 mg/kg As in All soils



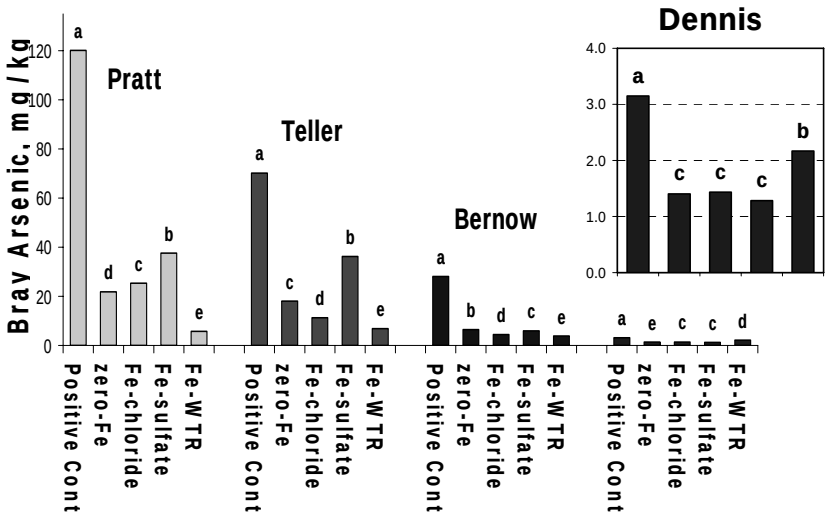
Reduction WTR > rest, due to amorphous Fe

Armstrong 2003. PhD dissertation

62

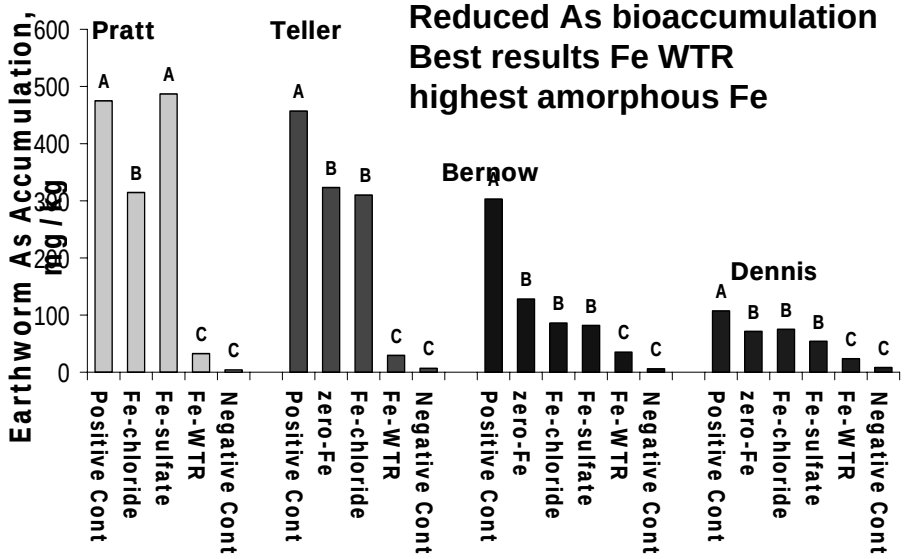
Treatments Reduced "Phytoavailable" Arsenic

arsenic extracted by Bray 1



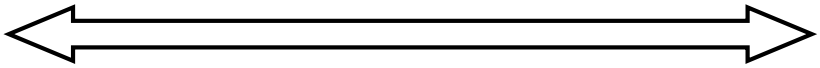
63

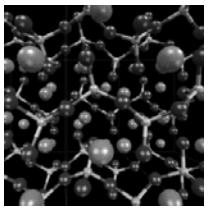
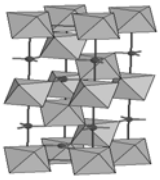
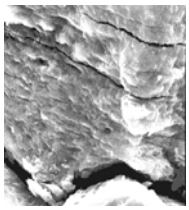
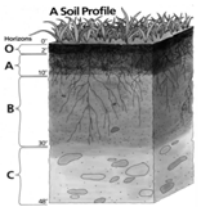
Arsenic Bioaccumulation in Earthworm



64

Important to Evaluate In-Situ Mechanisms



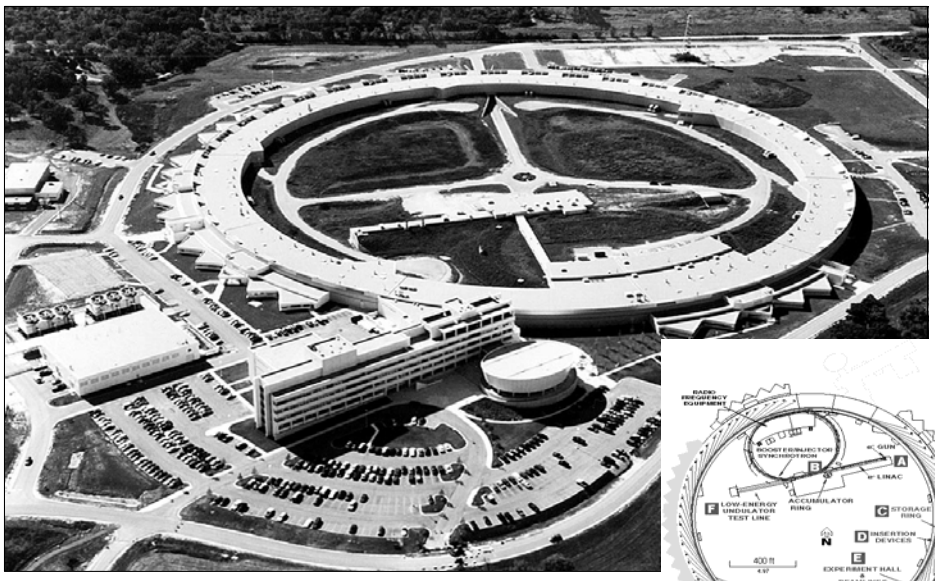
Atomic	Molecular	Microscopic	Macroscopic	Field
				
• XRF • XPS • XAS *Requires synchrotron radiation.*	• XRD • TGA • FTIR • DRS	• Enhanced Visual Analysis: 1. SEM 2. TEM 3. AFM	• Field Plots • Equilibrium Studies • Kinetic Studies • Extractions	• Visual/ Intuitive Insight • Field Plots

Adaptation of Bertsch and Hunter, 1996.

65

Advanced Photon Source

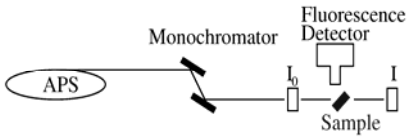
(Argonne National Laboratory, Argonne, IL)

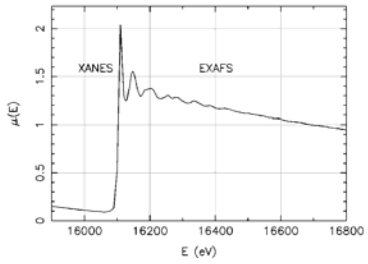


66

X-ray Absorption Spectroscopy

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





Element Specific: Elements with Z>20 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.

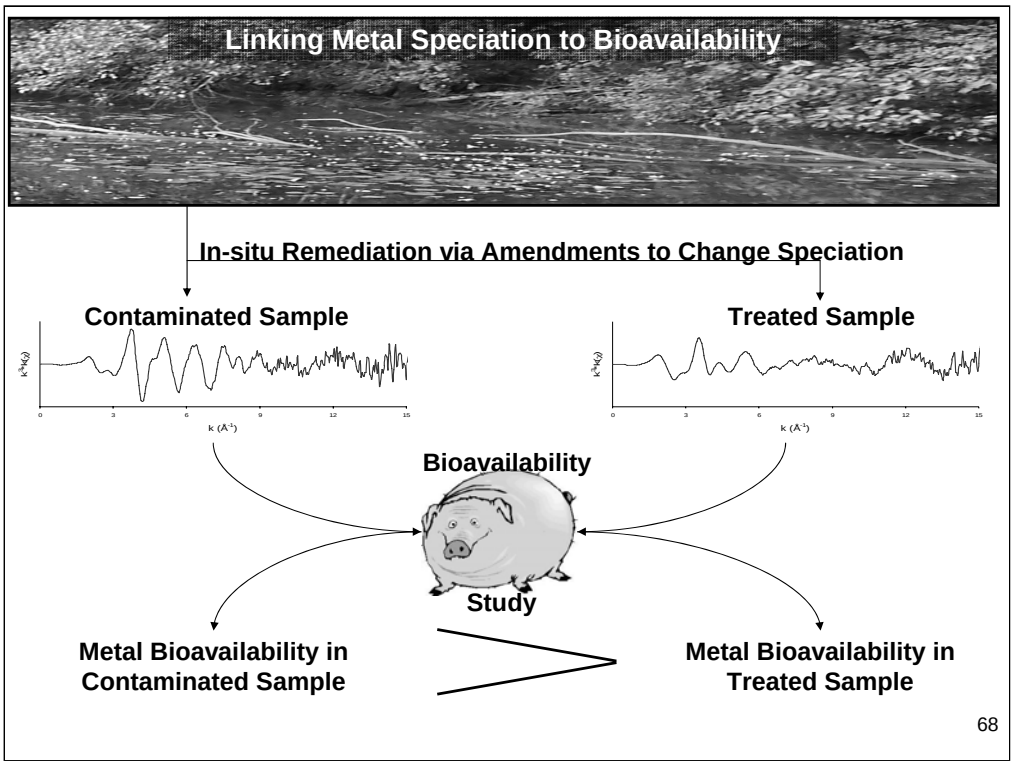
Natural Samples: samples can be in solution, liquids, amorphous solids, soils, aggregates, plant roots, surfaces, etc.

Small Spot Size: XANES and EXAFS measurements can be made on samples down to ~1 micron in size.

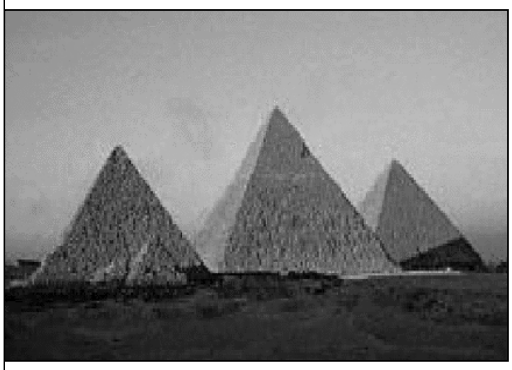
XANES = X-ray Absorption Near-Edge Spectroscopy

EXAFS = Extended X-ray Absorption Fine-Structure

67


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
68

How Long Will Remediation Treatments Last?



What is the "stability" of chemical immobilization products?

Will the immobilized contaminant remain unavailable?

Depends on

- **the "chemical speciation" of the immobilized contaminant**
- **the biogeochemical process(es) governing the immobilized contaminant solubility and availability**

69

What is the long-term availability of immobilized Pb? Consider the following three possible reaction products

- Specific adsorption of Pb by -SH groups of SOM
- Specific adsorption of Pb to amorphorus Fe oxide surfaces
- Formation of lead pyromorphite surface precipitate

Three very different chemical mechanisms controlling short- and long-term Pb availability

70

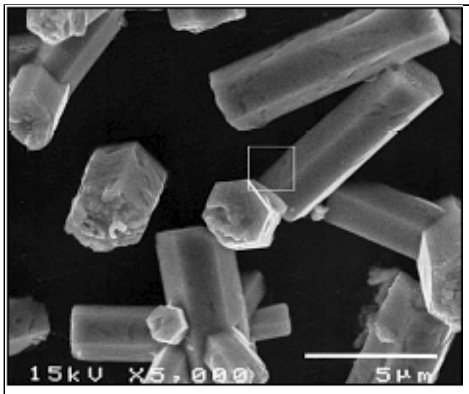


Figure 3. Pyromorphite crystals. Phosphorus from a hydroxyapatite additive can immobilize soil-based lead into this stable compound and make it less bioavailable.

A Mechanistic Understanding of the Reduction in Pb Bioavailability is Very Important

Pb Pyromorphite is Stable Remediation Treatment Will Last Scheckel and Ryan (2002)

$$Ca_{10}(PO_4)_6(OH)_2 + xPb^{2+} \longrightarrow Ca_{10-x}Pb_x(PO_4)_6(OH)_2 + xCa^{2+}$$

Hydroxyapatite + available Pb → **Lead pyromorphite Low bioavailability**

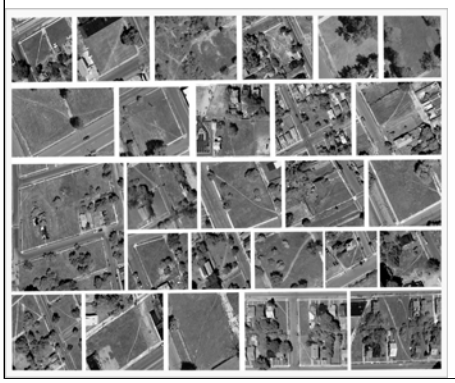
71

Reuse of Vacant Land Soil in Metropolitan Areas

Cleveland

<u>Urban agriculture/gardening</u>
improve the availability of healthy, fresh foods, improve nutrition and health of residents

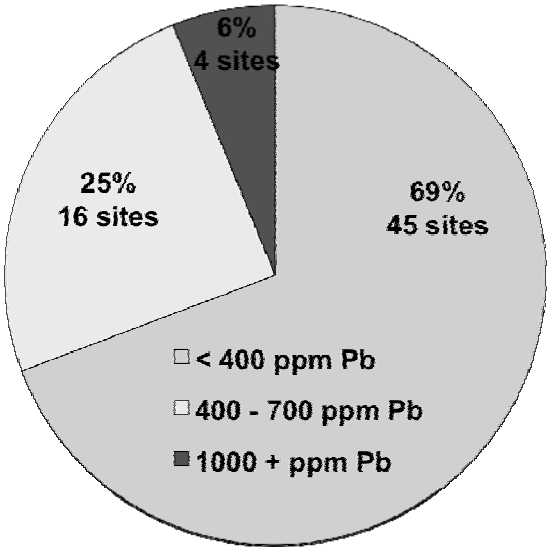
Community gardens improve the quality of life and social fabric of city neighborhoods



Rural Detroit

Total Soil Pb in Vacant Lots in Cleveland

60 soils from OSU extension from urban sites in Cleveland can they be used for food production?

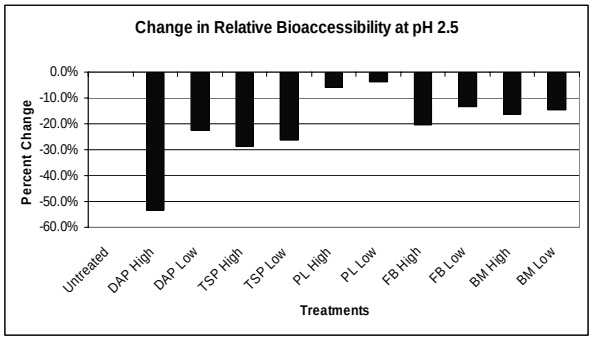


Soils above 400 mg/kg Pb are excellent candidates for remediation via soil amendment

73

Remediation of Pb in Urban Soil with P Soil Amendments

Community Garden soil (800 mg/kg Pb)
Treatments:
DAP, TSP, poultry litter, fishbone, bone meal
low rate (0.15% P:soil), 14:1 P:Pb mole ratio
high rate (0.5% P:soil), 47:1 P:Pb mole ratio
incubated 3 months



Reduction in bio Pb:
Soluble P >> insoluble P

soil Pb reacts quickly with soluble P not insoluble P

74

Soil Amendment Application Rate and Reaction

Lead Pyromorphite: $Pb_5(PO_4)_3X$; where X = Cl, OH, Br, F

5:3 Pb:P molar ratio

theoretically 3 moles of P will immobilize 5 moles of Pb only possibly if both Pb and P are dissolved in a stirred solution in a beaker in a chemistry laboratory

Non- mixed soil system with SOLID Pb and maybe solid P going to take much more P amend and time!

we applied an excess of 78x P to soil and still did not >50% reaction with soil Pb

APPLY EXCESS AMENDMENT IN SOILS
The soil system is not "optimized" for Pb reaction with P

75

Restoration / Remediation / Restoration of Degraded Soils by using Soil Amendments

Objective is to restore / optimize soil function(s) by adding soil amendments

- **improve soil physical properties (aeration / infiltration)**
- **reduce soil bulk density**
- **improve plant nutrient availability / cycling**
- **adjust soil pH**
- **reduce contaminant content / bioavailability**
- **improve soil community structure/function (microbes, etc)**
- **store carbon**

76

Poultry Litter
an excellent source of organic matter
and some phosphorus

77

Organic Soil Amendments
US Compost Council
Certified Vegetative Compost

78

Class A Biosolids and Biosolids Compost

60+% organic matter
contains sorbents (Fe oxides)
contains some phosphorus

79

Restoration of Urban Degraded Land
Pb / Zn Smelter Contaminated Land

Palmerton, PA. 1980; Dead Ecosystem on Blue Mountain[80]

Restoration of Blue Mountain in Palmerton Using Soil-Biosolids Blends

Palmerton, PA.
Looking down revegetated Blue Mountain

Organic Amendments are excellent choices for soil restoration

81

Take Home Message

- **In situ remediation is based on biogeochemical processes. Successful soil amendment(s) depends on (1) contaminant of concern and (2) reactivity of soil amendment, and (3) risk-based exposure pathways of concern**
- **Apply excess soil amendment to ensure reaction. System may have to be "optimized" to achieve contaminant immobilization**
- **Exposure pathway based Technology Performance Measures must be used to evaluate soil treatment. Don't forget soil quality measures and organic amendments. Spectroscopic studies are essential to ensure stability (i.e. permanence) or stabilization**
- **Phosphorus loves Pb; Iron loves arsenic**

82

Thank you for your attention
More information? Please contact:

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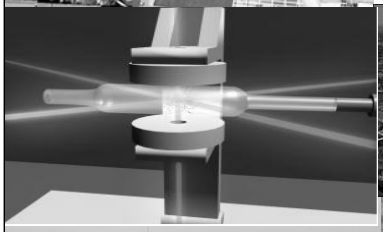
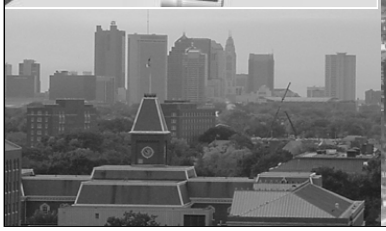
Kirk Scheckel,
scheckel.Kirk@epamail.epa.gov
Rufus Chaney, Rufus.Chaney@ars.usda.gov

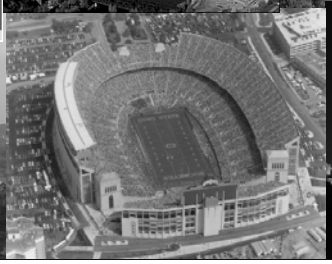
THE OHIO STATE UNIVERSITY

USDA United States Department Of Agriculture Agricultural Research Service ars



Kottman Hall





Resources & Feedback

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84