Healing Sick Soils

Soil Lead Bioavailability in Risk Assessment and Remediation of Contaminated Soils

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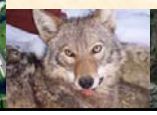
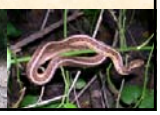




Environmental Science / Ecosystem Science
Terrestrial Wildlife and Ecology
mammals, avain (including migratory birds)
reptiles,
Soil Science (including soil ecology)
Carbon Management and Sequestration Center
Wetland Science / ecosystems
Olentangy River Wetland Research Park
Forest Ecosystems
Stream, Lake Ecosystems and Fisheries
Environmental Social Science

School of Environment and Natural Resources Soil Environmental Chemistry Program

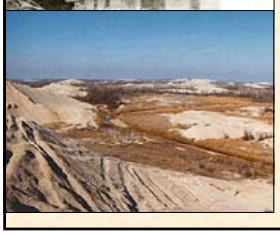
Research program
- Soil/Environmental contaminant chemistry; ecotoxicology
- Development and evaluation of remediation technologies of contaminated land
- Beneficial use of industrial by-products via land application
- Biogeochemical cycling of trace elements in soils

Today's Presentation

Pb Exposure (bioavailability) in Contaminated Soils

In situ soil remediation: Use of inexpensive soil amendments to remediate soils (reduce contaminant exposure / risk)

Sources of Trace Element Pollution



Mining and metal production

Sources of Trace Element Pollution

Energy production
Batteries

improper disposal

Leaded gasoline

Phased out in 1970s

50% deposited within 100 m of road

other 50% dispersed

Lead Paint

Pb mixed with paint until 1978

XRF testing

Effect of distance from the center of Baltimore on Pb concentration in garden soils (1983).

Distance	N	Mean	Med.	90%-ile	Max.	%>500
km		--------mg Pb/kg dry soil--------				
1-50	549	424	124	992	10900	20.9
1-4	90	1020	664	1810	10900	61.1
4-6	92	414	314	892	2700	26.1
6-10	127	419	153	690	7820	15.7
10-20	169	269	48	324	10600	8.3
20-50	71	53	14	94	730	2.8
US	3045	13	11	20	135	0.0

Pollution and Concentration (dose)

Paracelsus (1493- 1541) alchemist
"Father of Toxicology"

"All things are poison and nothing is without poison, only the dose permits something not to be poisonous."

"The dose makes the poison"

Contaminant only become toxic when it is concentrated

How much Pb does it take to make a soil sick?

Sick Soils Result Impair Human or Ecological Health

Fate and Transport are important to determine human and ecosystem **health risk**

Health Risk = pollution potential x **exposure** x **pollutant toxicity**

Blood Pb and Human Health

Hettiarachchi and Pierzynski 2004
Environmental Progress 23:78-93

Table 1. Blood lead levels associated with specific biological responses in children [31].

Blood lead level (μg/dL)	Effect
8	Subtle neurological impairment [78]
10	ALAD[1] inhibition
15–20	Erythrocyte protoporphyrin elevation
<25	Verbal IQ, mental development, physical size, and age at physical milestones such as first step, hearing thresholds, and postural sway [30]
40	Increased urinary ALA excretion, anemia coporporphyrin elevation
50–60	Cognitive (central nervous system) deficits [28]
50–60	Peripheral neuropathies
80–100 (acute levels)	Encephalopathic symptoms (also occur at lower PbB levels)

[1]δ-Aminolevulinic acid dehydratase.

Blood Pb and Human Health

Hettiarachchi and Pierzynski 2004
Environmental Progress 23:78-93

Table 2. Blood lead levels associated with specific biological changes in adults [31].

Blood lead level (μg/dL)	Effect
10	ALAD[1] inhibition
15	Erythrocyte protoporphyrin elevation
20–25	Chromosomal abnormalities
30	Toxicity to fetus
30–40	Reduced fertility (women)
	Altered spermatogenesis (men)
40–50	Anemia
40–60	Psychological, sensory, and behavioral changes
50	Impaired kidney function
50–60	Peripheral neuropathies
80–120 (acute levels)	Encephalopathic symptoms (also occur at lower PbB levels)

[1]δ-Aminolevulinic acid dehydratase.

Risk Assessment / Remedial Action

Soil excavation landfilling/ replacement usually based on total Pb (400+ ppm Pb) natural background Pb avg. about 22 ppm but can range from 5 to 250 ppm Pb

$200 to $600/ton

Soil Assessment Almost Always Based on Total Soil Pb

Strong acid digestion used to dissolve soil and release contaminants (U.S. EPA Method 3050, 3051, 3051A, 3052, etc)

Most of these contaminants are not bioavailable or mobile

Much of total may not pose risk

Total Contaminant Content is seldom an accurate predictor of risk

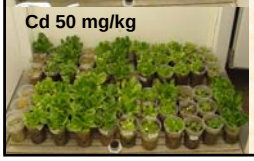
Total Content is a Poor Predictor for Soil Receptors (plants, soil invertebrates)

Soils Modifies Contaminant Bioavailability and Toxicity

21 soils (3 reps) all at the same contaminant level

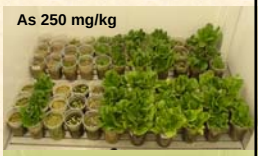
Uncontaminated Soils

Cd 50 mg/kg



U.S. EPA NCEA project

As 250 mg/kg



Pb, 2000 mg/kg

Soil Environmental Chemistry, Contaminant Bioavailability, and Toxicity

Soil / contaminant chemistry affects availability, contaminant transmission, and human and ecological risk

Bioavailability-Based Risk Assessment

Why Use Bioavailability?

Accurate bioavailability-based risk assessment prevents unnecessary Remedial Action Levels of Contaminated Soil

Is Very Costly Excavation and Soil Replacement Necessary?

How do we evaluate Bioavailability?

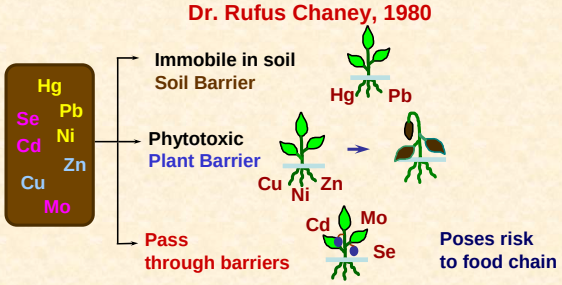
Assessment Methods are Exposure Pathway Based

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

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

Food Chain Contaminant Transmission and the Soil Plant Barrier Concept

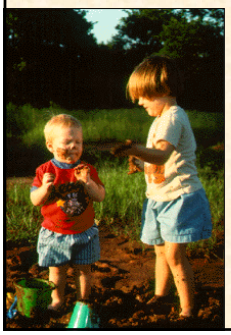
Dr. Rufus Chaney, 1980



Risk driver for food chain for Pb, As is often soil ingestion not plant food chain or invertebrates

Using Bioavailability to Assess Human Health Risk of the Soil Ingestion Pathway

How do we assess this risk?



cancer risk = CDI x SF
where CDI = chronic daily intake
SF = cancer slope factor

non cancer risk
Hazard Quotient = CDI ÷ RfD
where RfD = reference dose

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

$RfD_{adjusted} = RfD_{IRIS}$ x RBA
$SF_{adjusted} = SF_{IRIS}$ x RBA

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

Measuring Bioavailability Using *In Vivo* Models

accurate bioavailability

unlikely model

acceptable model for Pb, As, other bioavailability

acceptable model for bioavailability

expensive ethical issues

inexpensive recent developments USEPA ORD RTP

In Vitro Gastrointestinal Methods An Inexpensive Alternative

Sequential extraction, 37°C

Gastric phase
Intestinal phase

may also have saliva

may have several intestinal simulations for duodenum, jejunum, etc.

Evaluating *In Vitro* Gastrointestinal Methods

proportional to ?
or
approximately equal to ?

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

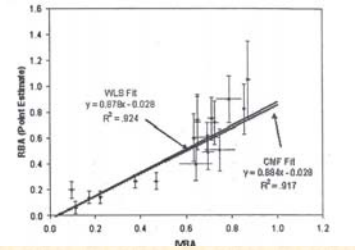
OSWER 9285.7-80, May 2007

Recommended Criteria for Validation of Test Methods adapted from ICCVAM

Ad Hoc Coordinating Committee
National Institute of Environmental Health Sciences
Research Triangle Park, N.C.

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

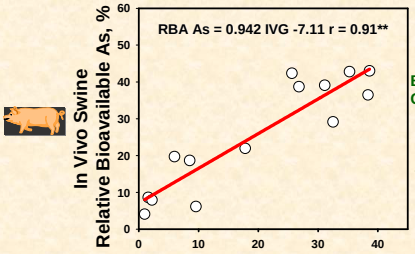
RBALP *in vitro* gastrointestinal method correlated with swine bioavailable Pb



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 Pb and As.

OSU IVG method correlated with bioavailable As (swine)

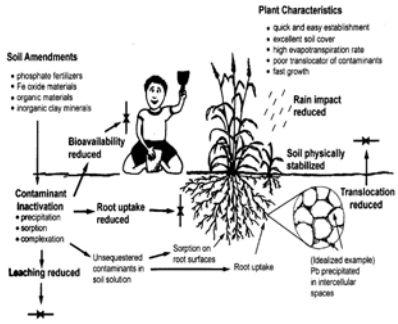


Basta et al. 2003.
Grant R825410 Final Report.

Basta et al., 2007. J. Environ. Health Sci. Part A 42:1275-1181

In-Place Inactivation and Natural Ecological Restoration Technologies (IINERT)

Healing Sick Soils



Soil Remediation by *in situ* Soil Amendments

Healing Sick Soils

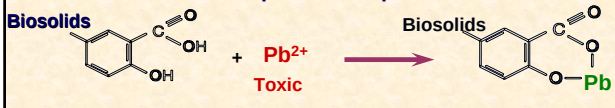
Treat soil to reduce contaminant solubility/availability to ecological and human receptors

- adjust soil pH
- increase clay/oxide content
- add organic matter, etc.

In Situ Chemical Immobilization of Pb

Chemical Immobilization Alkaline Treatments

Pb Adsorption / Complexation



Pb Precipitation: raising soil pH with alkaline materials (i.e., limestone)

$CaCO_3 + Pb^{2+} \rightarrow PbCO_3$

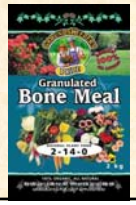
Chemical Immobilization Phosphates / P Fertilizer

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

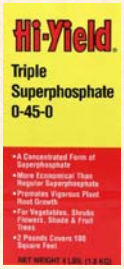
Hydroxyapatite + available Pb

Lead pyromorphite
Low bioavailability

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



Pb immobilization using phosphorus fertilizer calcium or ammonium phosphates



Soluble phosphate fertilizers
Basta and McGowen, 2004; McGowen et al., 2000; others

Poultry Litter
An excellent source of phosphorus fertilizer calcium phosphate

Monogastric animals don't metabolize organic P in grain
Mineral P supplements for chickens

Ca Phosphates – very soluble
>90% soluble phosphate in manure
high soluble P in waste

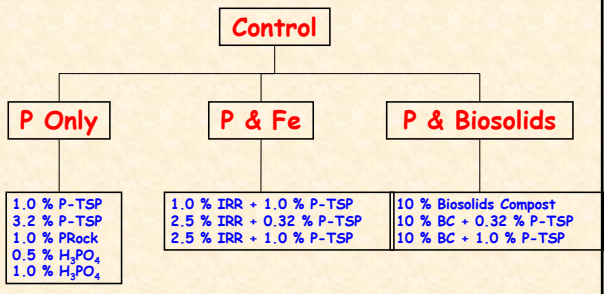
Remediation of Soil Pb at Joplin, Missouri

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

In-place Inactivation & Natural Ecological Restoration Technologies (IINERT)

Overall Goal
Field Amendments:
Engineered addition of materials to Pb-contaminated soils will induce the formation of less hazardous Pb forms, providing a practical approach to in-place inactivation and reduce Pb bioavailability and risk

The 12 Field Amendments at Joplin



Joplin Soil Feeding Test Clinical Protocol

- Human volunteers with Pb isotope ratio different from that of the test soils.
- Screening and physical exam.
- Obtain informed consent.
- Three day clinic admission.
- Subject dosed at 250 µg Pb/70 kg BW using soil <250 µm in gelatin capsules.
- Collect blood and urine samples.
- Analyze isotope ratios using ICP-MS.
  - QA/QC on all samples; chain of custody handling.
- Standardized meals

Phosphate Amendment Reduced Soil Pb Bioavailability to Humans

Joplin Soils -- Results

Group	Age	Weight	Pb Dose	Soil Dose	Bioavailability
	yr	kg	µg	mg	%, Absolute
Untreated	29.6	62.2	238	45.7	42.2 (26.3-51.7)
P-Treated	34.5	72.2	261	61.5	13.1 (10.5-15.8)

Graziano et al., 2001; unpublished.

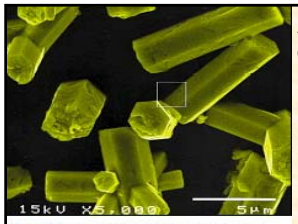


Figure 3. Pyromorphite crystals. Phosphorus from a hydroxyapatite additive can immobilize soil-based lead into this stable compound and make it less bioavailable.

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

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

Hydroxyapatite + available Pb $\longrightarrow$ Lead pyromorphite
Low bioavailability

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

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."

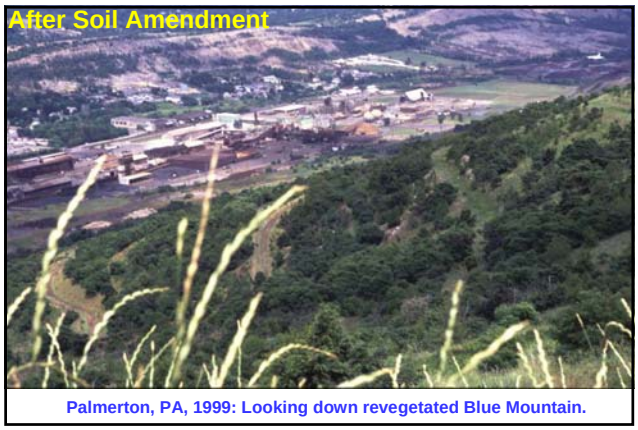
New Orleans Fundred Project:
Soil Remediation Using Phosphate-based Amendments

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

Palmerton, PA, Dead Ecosystem on Blue Mountain.

Palmerton, PA, 1980; because lawn grasses died from Zn, many residents covered their lawns with stones or mulch.

Zn-toxic pony near Palmerton in 1979.



Palmerton, PA, 1999: Looking down revegetated Blue Mountain.

Soil Remediation in Picher, OK using Byproducts
Univ. of Washington, USEPA ERT, OSU

<u>72 plots on Pb, Zn, Cd contaminated land</u>
Alkaline Biosolids
Biosolids Compost
Commercial phosphorus fertilizer
Al-Drinking water residuals
Fe-Drinking water residuals

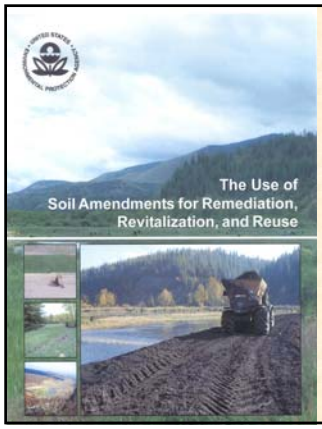
Seeded with Bermudagrass

Soil Remediation in Picher, OK using Byproducts
Univ. of Washington, USEPA ERT, OSU

Soil Remediation and Ecological Restoration

"Ecological Revitalization" of Contaminated Superfund Sites

http://www.cluin.org/ecotools/



Ecological Restoration 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

Evaluating Ecological Restored Sites Technology Performance Methods

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

TPM for Amended Soils

Chemical Measures

Target Analyte List (metals)

total content (3050, 3051, 3052, XRF, INAA, etc)

extractable: 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

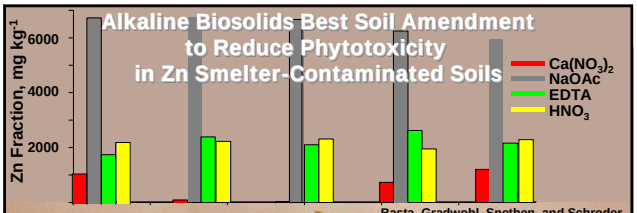
Important Risk Pathways to Assess

Human Receptors: Exposure and Risk
Soil Ingestion -- Oral Bioavailability

Remediated Site

Ecological Receptors:
U.S. EPA Ecological Risk Framework
Plants and Soil Invertebrates

Alkaline Biosolids Best Soil Amendment to Reduce Phytotoxicity in Zn Smelter-Contaminated Soils



Basta, Gradwohl, Snethen, and Schroder. 2001. J. Environ. Qual. 30:1222-1230.

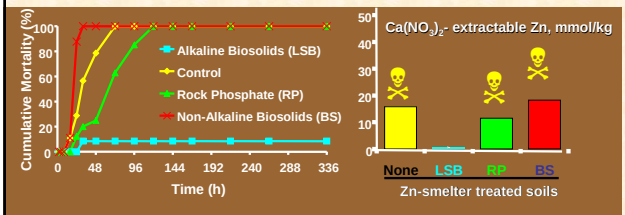
Control | Alkaline Biosolids | N-Viro Soil | Rock Phosphate | Non-alkaline Biosolids

Lab test organisms

- Earthworms *Eisenia andrei*
- 28-day reproduction bioassay
- 56-day bioaccumulation assay

Alkaline Biosolids Best Treatment To Reduce Zn Toxicity to Earthworms

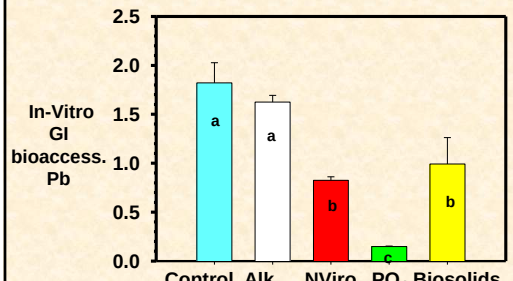
Earthworm Toxicity Testing
Zn, Pb, Cd Contaminated Smelter Soil



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

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

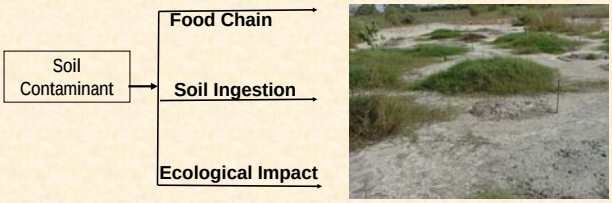
Phosphate the Best to Reduce Pb Soil Ingestion Risk NOT Alkaline Biosolids



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

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

Biosolids + Phosphorus Combination



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.

In situ immobilization of Pb in soils

Hettiarachchi and Pierzynski 2004
Environmental Progress 23:78-93

Table 4. Estimated economic analysis of selected remediation alternative for a 1-hectare Pb-contaminated site.[1]

Alternative	Net present cost (USD)
Site decontamination	
Solidification and stabilization	
off-site	1,600,000
Soil washing	790,000
Phytoextraction	279,000
Site stabilization	
Asphalt capping (parking lot)	160,000
Soil capping	130,000
In situ stabilization[2]	60,000

So Why Aren't We Using Immobilization Methods?

Longevity of Treatment Effectiveness
Public policy

How Long Will Remediation Treatments Last?

What is the "stability" of chemical immobilization products?

Will the immobilized contaminant remain unavailable?

Depends on
- **molecular environment of immobilized contaminant**
- **the chemical process(es) governing contaminant availability**

How long is Pb Immobilized?

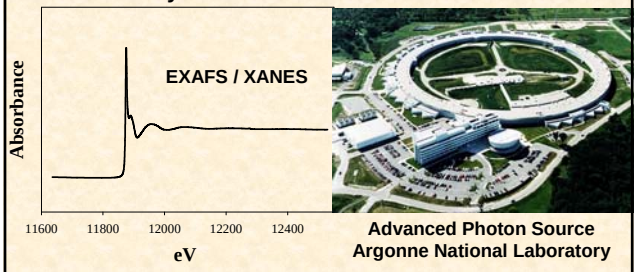
What is the long-term availability of immobilized Pb?
Consider the following three possible reaction products

"stability": Short → Long

- **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

Chemical Speciation of Immobilized Pb Synchrotron Radiation Studies



Advanced Photon Source
Argonne National Laboratory

Spectroscopy used to identify the environment and form of the soil contaminant
Dr. Kirk Scheckel, USEPA, Cincinnati (Adjunct faculty at OSU)

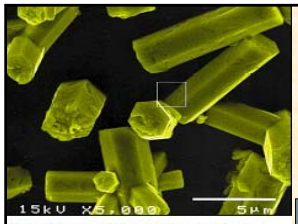


Figure 3. Pyromorphite crystals. Phosphorus from a hydroxyapatite additive can immobilize soil-based lead into this stable compound and make it less bioavailable.

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

Public Policy

Use of risk-based endpoint criteria
bioavailable, soluble forms (not total content)
criteria affects all in-situ remediation methods

Public acceptance?
contaminant removal (no risk)
vs.
reduced availability (acceptable risk)

Acceptable Risk in Oklahoma?

F5 tornado in Oklahoma
0.5 to 1 mile wide for 100 miles (4.5 hr)
May 3, 1999

Summary

- **Contaminant bioavailability (soil ingestion) should be considered in risk assessment of contaminated Pb soils**
- **In situ immobilization is a proven technology BUT MUST BE APPLIED CAREFULLY (i.e., based on solid science)**
- **Successful soil amendment(s) depends on contaminants (Pb, etc) and risk-based exposure pathways**
- **Phosphate loves Pb**

Approaches for Evaluating Byproducts for Beneficial Use in Soil Applications

Using Byproducts as a Soil Cap / Barrier for Ecosystem Restoration

E.A. Dayton and N.T. Basta

School of Environment and Natural Resources

Ohio State University

Industrial Non-Hazardous Waste
7.6 billion tons

Municipal and Industrial Sludge

Dredge
several 100 million yards

Animal Manure
500 million tons

Remediation of Contaminated Sites

Superfund National Priorities List Sites: 1,498

Brownfields: 450,000

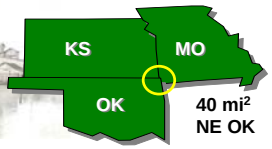
Military Bases: 204 currently undergoing cleanup

Abandoned Mine Lands: 10,200 BLM sites
> 80,000 total

EPA Draft ROE, 2003

Manufactured Soil Needs

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



40 mi²
NE OK

Manufactured Soil Need

Acre Furrow Slice
1 Acre of Soil 6.5 in deep = 1,000 tons

40 mi² X 640 A/mi² X1,000tons/A =

25.6 Million Tons

Non-Hazardous Byproducts Are Needed for Site Restoration

Inconceivable to use natural soils

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

Thank you for your attention
More information? Please contact:

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