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In Situ Treatment of Soil Metals: Science to Experience (Part 2 of 2)

Sponsored by: U.S. EPA, Office of Superfund Remediation and Technology Innovation, Technology Innovation and Field Services Division

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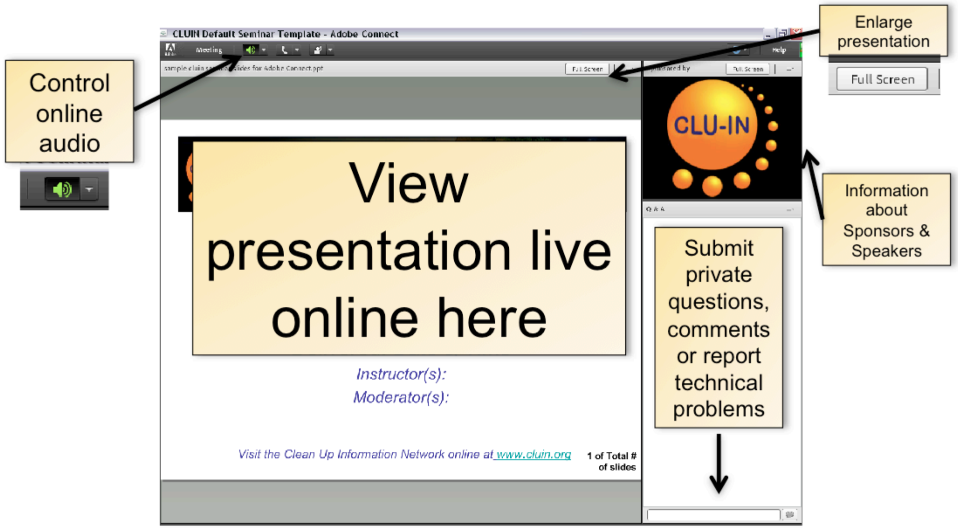
New online broadcast screenshot



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Mine Land Remediation
Considerations for Developing Performance Measures

Mark Sprenger
OSRTI – Environmental Response Team
December 19, 2012

Sustainability and Large Mining Sites: *Not* Business as Usual

- Size and scale of these sites can make traditional site assessment and cleanup approaches less sustainable and more costly.
- These approaches can also have long-term environmental and economic impacts for surrounding communities.
- Selection of CERCLA "protective remedies" and resulting performance measures play a key role.

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Sustainability and Large Mining Sites: Improving Outcomes

- Taking a second look at performance measures – alternatives to media concentration.
- Integrating future land use considerations.
- Bringing stakeholders to the table.
- Considering beneficial reuses of mining waste.

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Building on What We Already Do

- To effectively select alternate performance measures, think about site use.
- This is not new, we look at sites and we think about what remedy options are realistic.
- The performance measures need to be consistent with site use and meet the needs and expectations of the stakeholders.

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If we are going to approach things differently…

If we are going to turn this… **Into this…**

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We start by thinking about land use.

Note: currently residential land use is not an option, unless the contaminants do not pose a human health risk)

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We determine risk through a risk assessment.

Key considerations:

•What contaminant causes the current risk and which contaminants may cause risk if the land use changes?

•What information is needed to justify the risk reduction and meet the threshold criteria for protectiveness?

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Risk assessment = the tool to assess remedy performance.
Acceptable residual risk = successful remedy.

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The result is remediation.

The process is active.

It is not passive or monitored natural processes.

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Site Impacts

Sites can have soil loss…

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Waste Rock…

Tailings…

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Mine Drainage…

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Be Any Scale…

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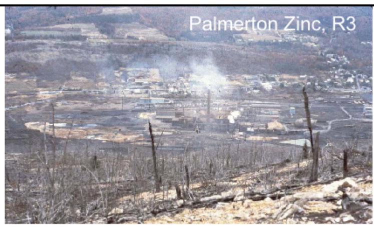
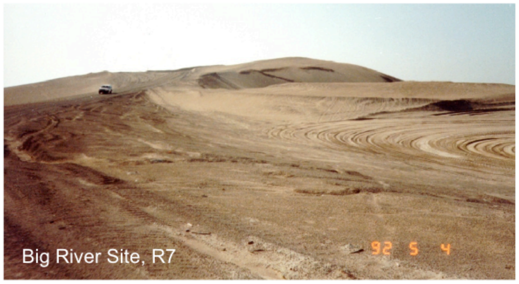
Releases can be:

- Atmospheric
- Water transport
- Erosion
- Placement
- Surface discharge





Contaminant Fate, Transport and Risks

Remedy options are informed by these impacts, site scale, chemical transport / fate and risks.

How do we do this?

We produce an ERA that identifies:

•Important contaminants of concern.

•The nature and extent of contamination.

•Contaminant's chemical form and fate and transport.

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ERA Considerations

1. Are the observed impacts and/or risks physical, agronomic or contaminant dominated?
2. What are the current chemical forms? Under what conditions will they change chemical form?
3. What contaminants (metals) are toxic and where and to what organisms (assessment endpoints)?
4. If contaminants move, will they expose different receptors?

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Observed Impacts and Chemical Form

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Chemical Fate/Transport

California Gulch entering the Upper Arkansas River, R8

Measuring ground water discharge at Palmerton Zinc, R3

Cadmium sulfide at Marathon Battery Site, R2

Assessment Endpoints

Cd through food chain

Pb through direct sediment ingestion

Cu or Zn through direct water exposure

Species of particular stakeholder concern

Establishing Performance Measures

- Risk reduction can be demonstrated through measures of toxicity and contaminant mobility – it is your performance measure.
- The risk assessment is the basis and baseline for the evaluation of the performance of the remedy.
- Community acceptability may remain an issue – stakeholder engagement and buy-in is key.

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What are the Performance Measures?

Earthworm (*Eisenia foetida*) Assays –
Survivorship & Biomass/Organism

Sample	Untreated		Treated	
	Survival (%)	Biomass (mg)	Survival (%)	Biomass (mg)
CL	0	NA	100.0	329.3
CO	0	NA	98.9	323.0
MB/ME	0/0	NA	90.0	372.0
RA/RB	0/0	NA	10.0*	280.3
Ref. A	-	-	98.7	244.0
Upst. Ref.	-	-	96.7	196.0
Lab Con.	100	not measured	100.0	258.6

*significantly < reference samples and/or control sample

Bioaccumulation Studies

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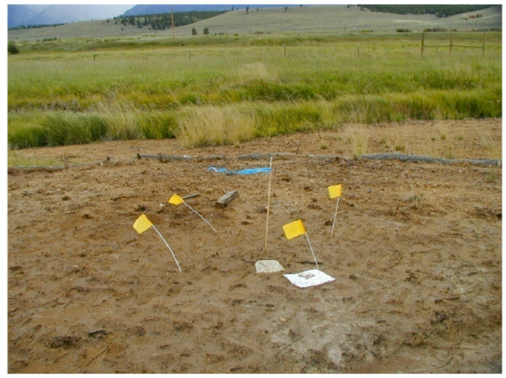
Plant Community and Health Studies, Biomass Production



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Biomass Production and Erosion Control

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Key Considerations

- Accumulation above background?
- Unacceptable risk? Is the remedy protective?
- Attractive nuisance?
- Stakeholder buy-in?

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Remember: future land use is a remedy selection criteria…

…and that means working with people.

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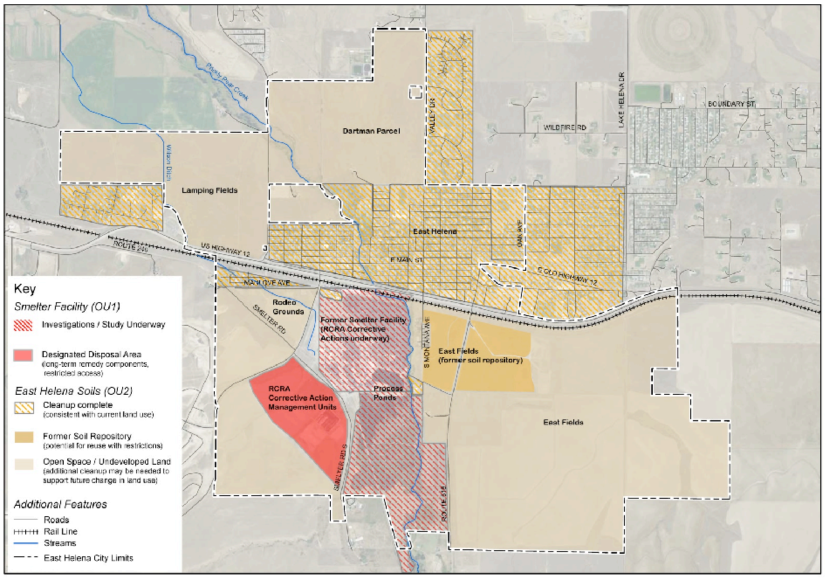
East Helena: Aligning Remedy and Future Land Use



Site Remedy Status Map
East Helena Smelter Site

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East Helena Reuse Planning Charrette

Stakeholders and technical experts participated in day-long working session to better coordinate remediation, local planning, institutional controls, and site reuse.

Charrette Outcomes

VISION FOR THE FUTURE

Guiding Principles

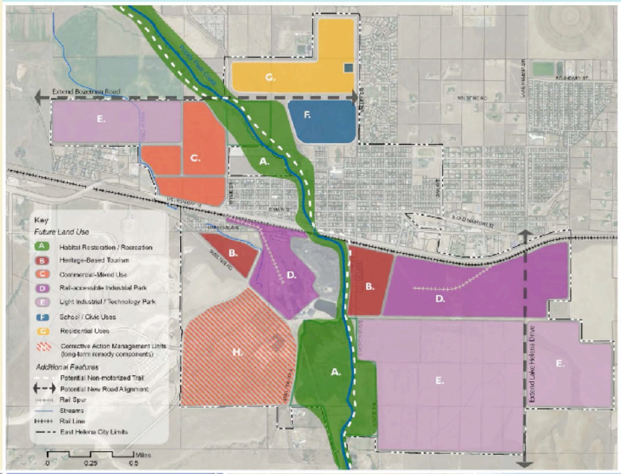
This concept plan integrates the key strategies developed during the community planning charrette. Sections on the following pages provide more detailed strategies and recommendations for each of the three focus areas: land use and development, cultural heritage, habitat and recreation.

Participants highlighted the following common themes and principles to guide a vision for the future:

- Jobs
- Livability
- Transportation
- Trails
- Creeks
- Connectivity
- Heritage

In addition, participants emphasized the need to facilitate redevelopment at key catalyst sites such as the Plant Manager's house, Lamping Fields, and parts of the East Fields and the desire to increase certainty in the development process.

Future Land Use Concepts



Focus Areas

Specific priorities are listed below for each focus area. More detailed strategies for each focus area are outlined in the following pages.

Land Use & Development Priorities

East Fields - Establish an industrial park as a catalyst for economic development.

Recreation & Heritage Corridor - Support recreation and heritage-based commerce at the Plant Manager's property and Prickly Pear Creek corridor.

Lamping Fields - Develop commercial retail and office or professional uses.

Dartman Parcel- Expand public, institutional and residential uses.

Cultural Heritage Priorities

Plant Manager's property - Preserve and restore the Plant Manager's property as a heritage museum and catalyst for community revitalization.

Heritage & Recreation - Extend heritage and recreational uses into surrounding area to support the reuse of the Plant Manager's property.

Habitat & Recreation Priorities

Regional Trail Network - Establish a regional trail network connecting East Helena to Helena, Lake Helena and Montana City.

Heritage & Recreation - Restore the Prickly Pear Creek riparian corridor through East Helena.

Presentation Summary: *Looking Forward*

- Integrating future land use considerations.
- Bringing stakeholders to the table.
- Considering beneficial reuses of mining waste.
- Remedy protectiveness
- Taking a second look at performance measures – alternatives to media concentration.

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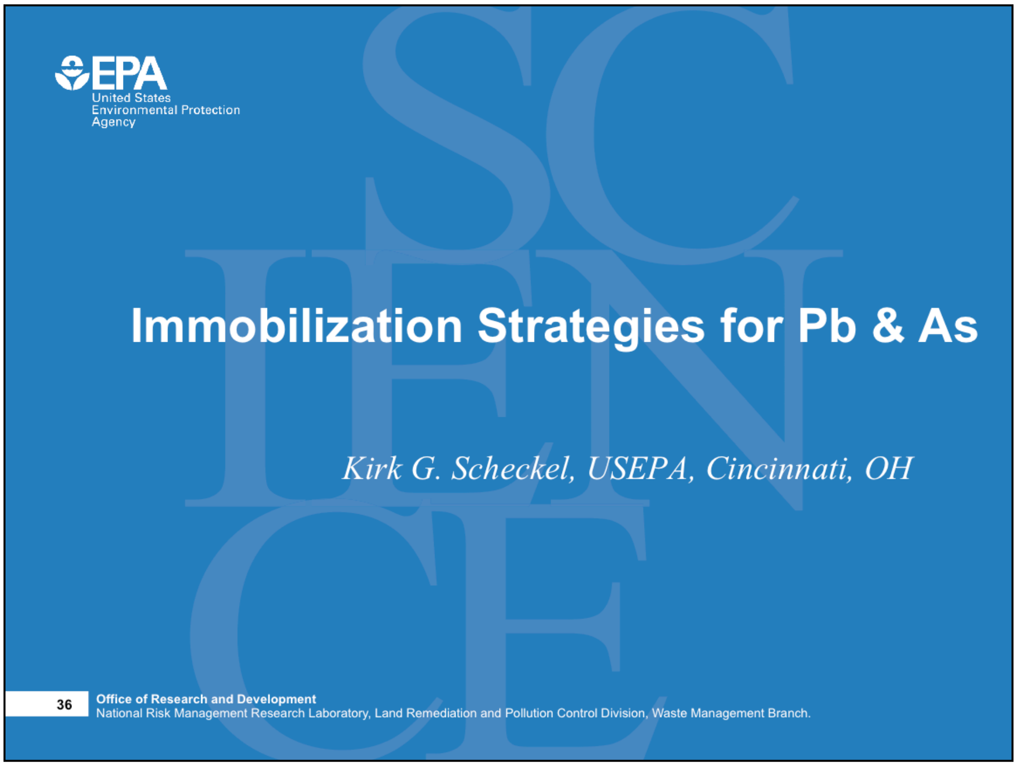
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Immobilization Strategies for Pb & As
Kirk G. Scheckel, USEPA, Cincinnati, OH
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Office of Research and Development
National Risk Management Research Laboratory, Land Remediation and Pollution Control Division, Waste Management Branch.

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Acknowledgments

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Karen D. Bradham (NERL)
David J. Thomas (NHEERL)

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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?

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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

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A Case for Soil-Metal Immobilization

Advantages	Disadvantages
Minimal site disturbance	Contaminant is still in the soil
Lower capital costs	Long term monitoring
Sustainable/green initiatives	
High public acceptance	
Variety of amending agents	

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

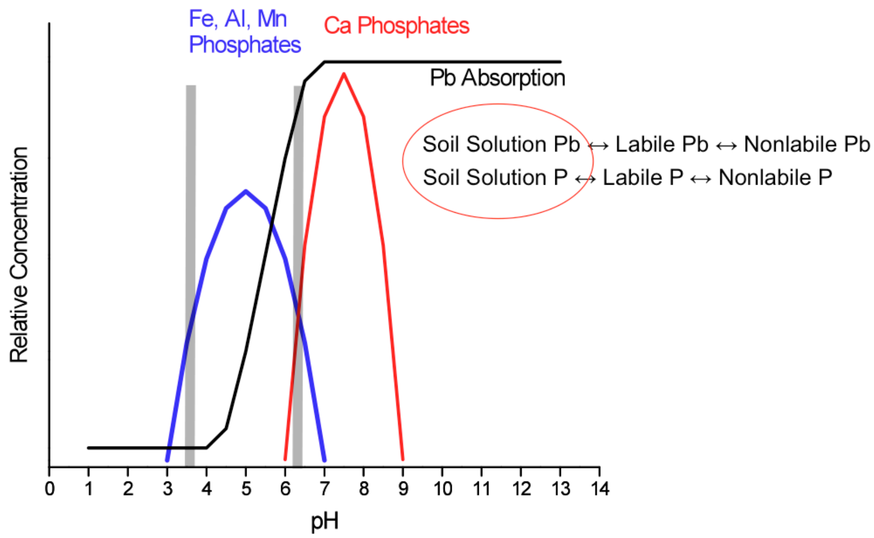
~~High pH soils may form calcium arsenates~~

Lead Immobilization

Soil-Pb + Orthophosphate → $Pb_5(PO_4)_3Cl$ [pyromorphite]

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



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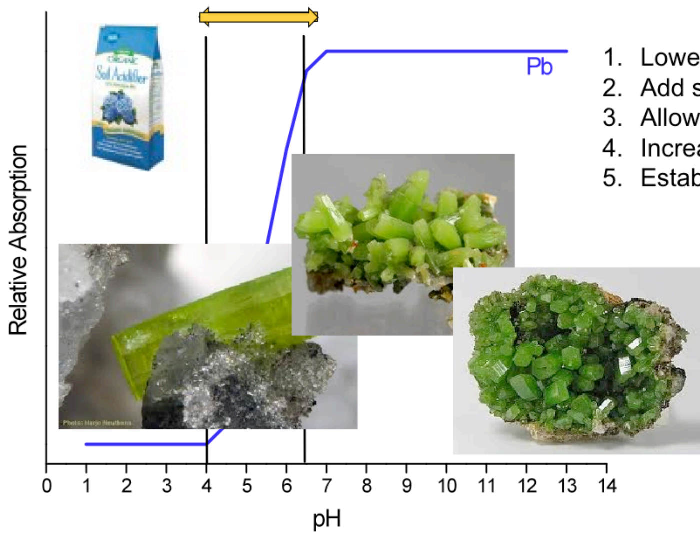
Lead Immobilization



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

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Lead Immobilization – The Joplin Study

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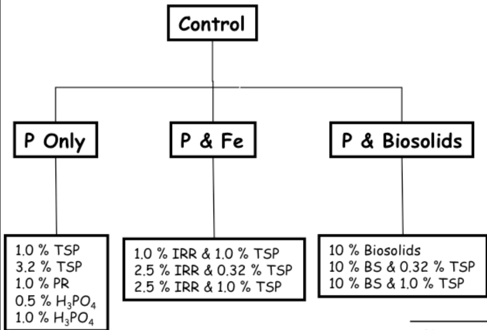
Reducing Children's Risk from Lead in Soil. J.A. Ryan, K.G. Scheckel, W.R. Berti, S.L. Brown, S.W. Casteel, R.L. Chaney, M. Doolan, P.Grevatt, J. Hallfrisch, M. Maddaloni, and D. Mosby. 2004. Environ. Sci. Technol., 38: 18A-24A.



	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

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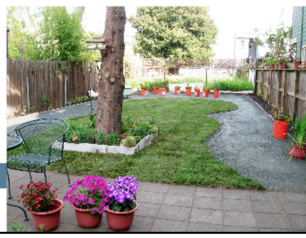
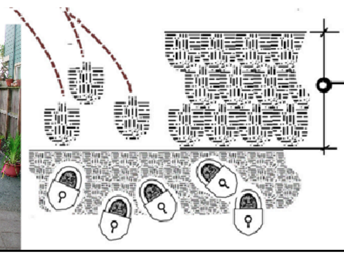
West Oakland Lead Project

A community-engaged remediation to protect children's health

A grander vision for the project beyond just remediating the residential soils that involved:

1) educating residents on the harm of Pb in homes and safe methods for urban gardening (i.e., raised beds),
2) utilizing a sustainable phosphate source as Apatite II, which is simply ground fish bone products as a beneficial waste re-use scenario, for the Pb immobilization,
3) establishing a worker training program to employ local out of work residents to assist with the TLC process through health and safety training, landscaping instruction, and mechanical equipment operation,
4) dust suppression through green covers of lawns, vacant lots, and easements, and
5) prevention of Pb exposure through the Rebuilding Together Oakland, the City of Oakland Redevelopment Program and Residential Lending Section, and the Alameda County Lead Poisoning Prevention Program to address old peeling lead-based paint on the exterior of homes.





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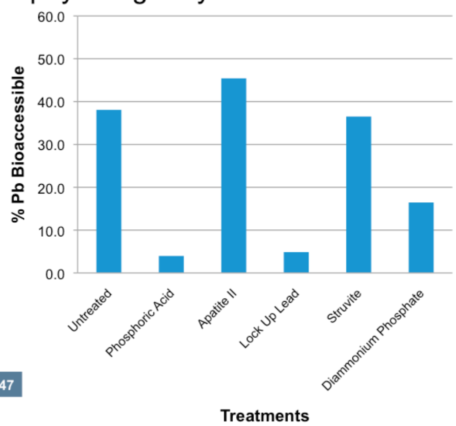
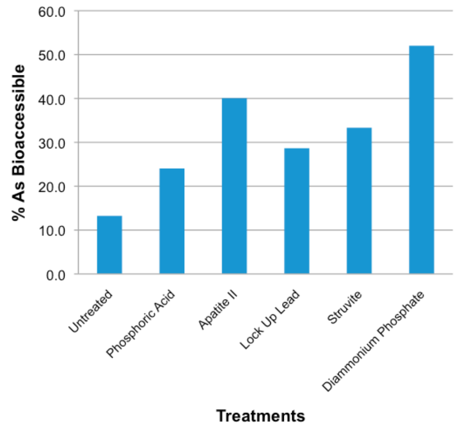
Lead Immobilization in the Presence of Other Contaminants

- Many sites are co-contaminated with other elements such as arsenic, zinc, cadmium, and chromium.
- Arsenate (As^{5+}) is the common form of arsenic in soils
- Phosphate and arsenate have similar behaviors geochemically and physiologically





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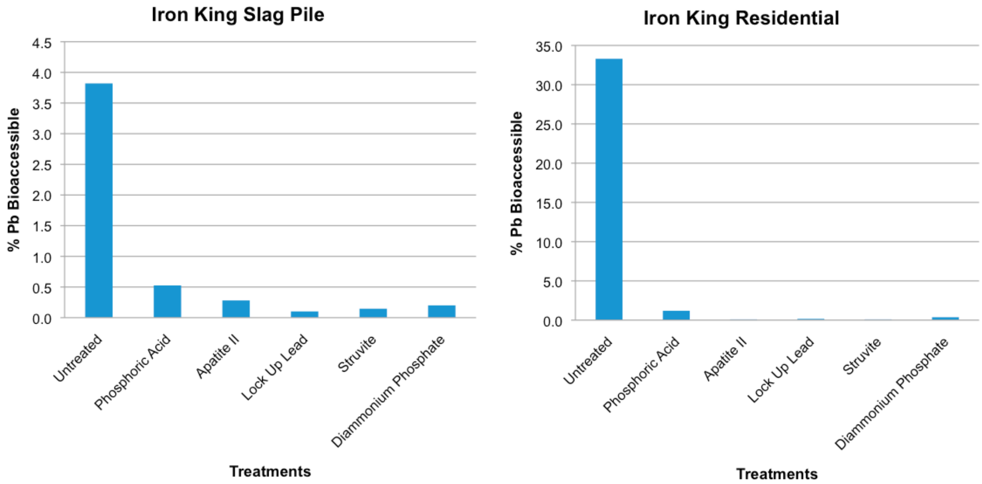
Lead Immobilization in the Presence of Other Contaminants



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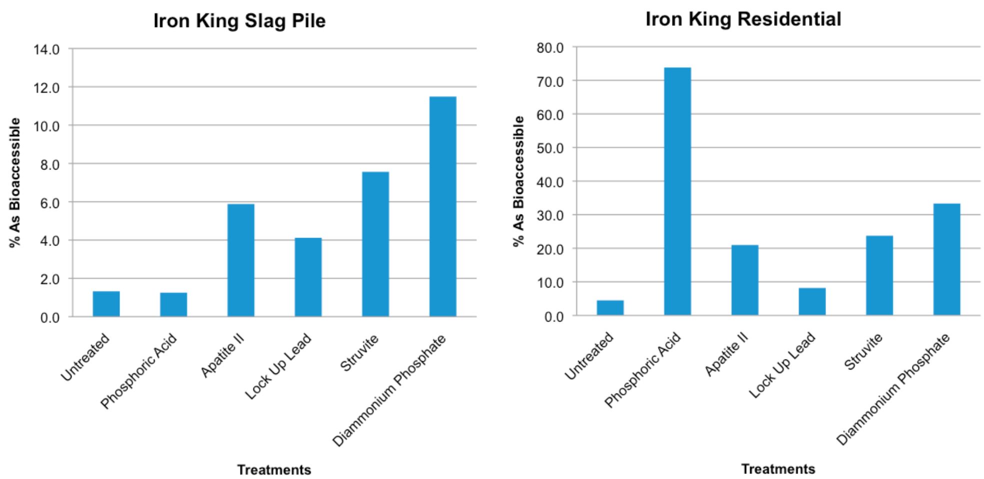
Lead Immobilization in the Presence of Other Contaminants



Arsenic Immobilization

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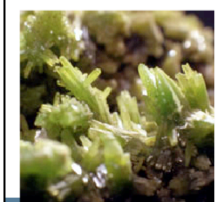
- Barber Orchard Superfund
  - Top 1’ removed and replaced with clean fill
  - Cost doubled and still have not found landfill
- Transformation of As???
  - Lead + P → Pyromorphite (Nriagu 1974, Ma *et al.* 1993, Scheckel and Ryan 2002)
  - As + Reactant→ New As Mineral
    - Scorodite ($Fe^{+3}AsO_4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

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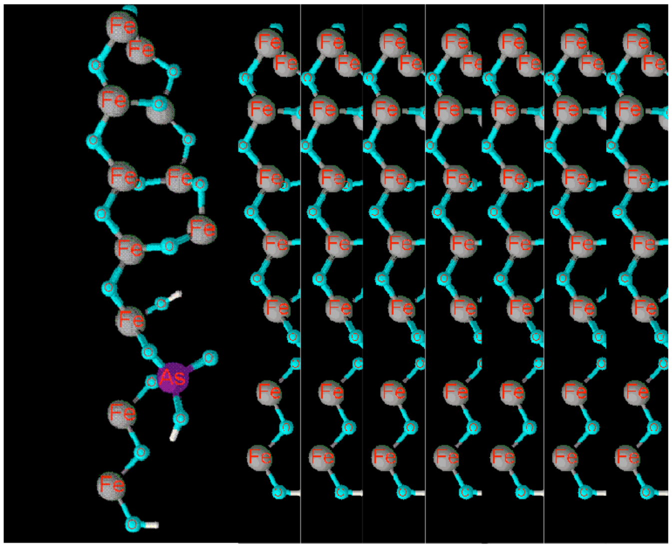
As Occlusion Treatment



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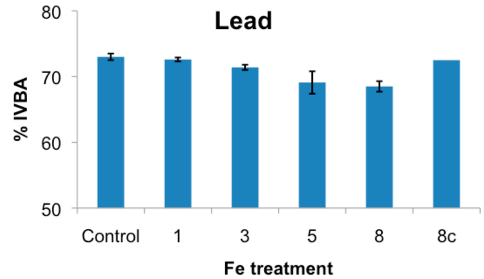
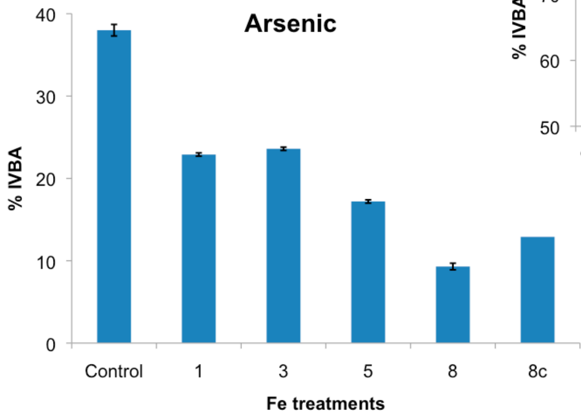
$Fe(NO_3)_2$ (L) + KOH (L) → Ferrihydrite (s)

As Occlusion Treatment



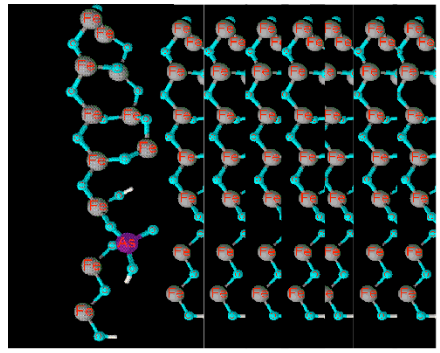


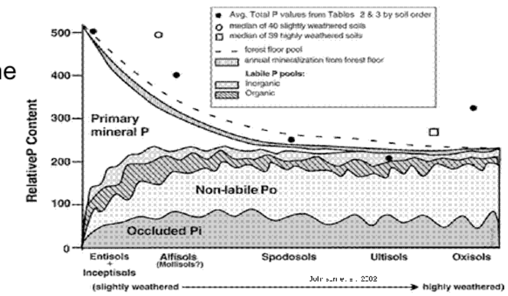
<u>Co-contaminated Soils:</u>

1. Fe treatment - As
2. P treatment - Pb

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
  - Greenhouse Scale
    - In Vitro Extractions
    - Chinese Brake Fern
    - In Vivo animal study





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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

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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

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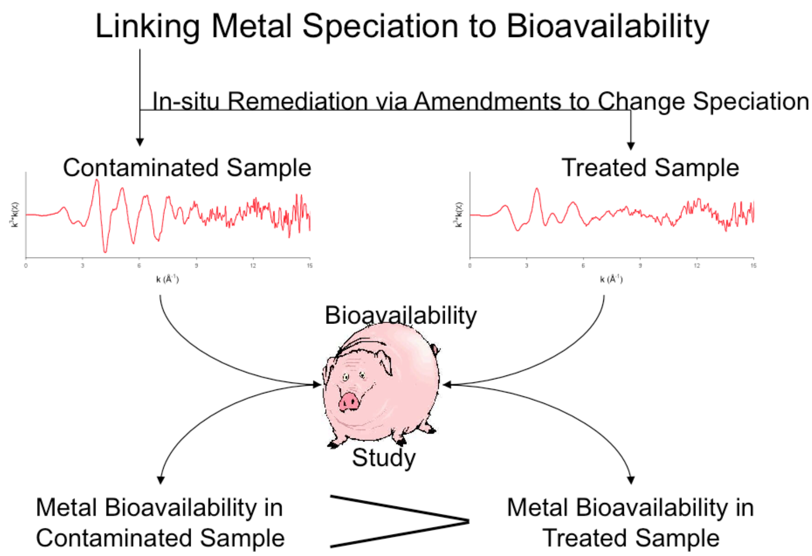
Immobilization Requirements: Verifying Results



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Advanced Photon Source

(Argonne National Laboratory, Argonne, IL)

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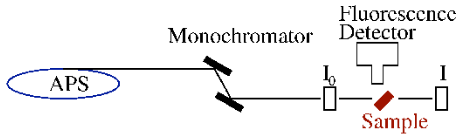
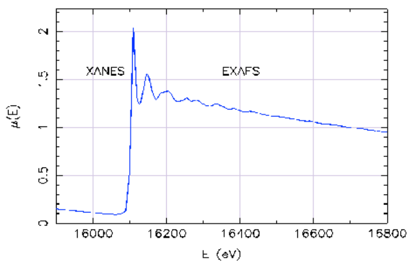
X-ray Absorption Spectroscopy

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.

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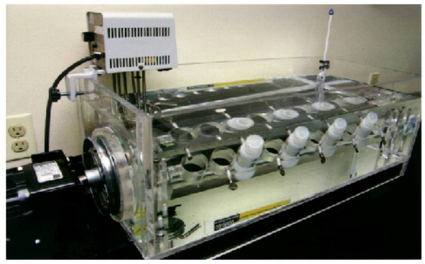
Bioavailable and Bioaccessible



- 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
  - Gastric Phase
  - Intestinal Phase
  - IVBA (%) = [in vitro extractable (mg kg^{-1})/total contaminant (mg kg^{-1})]*100

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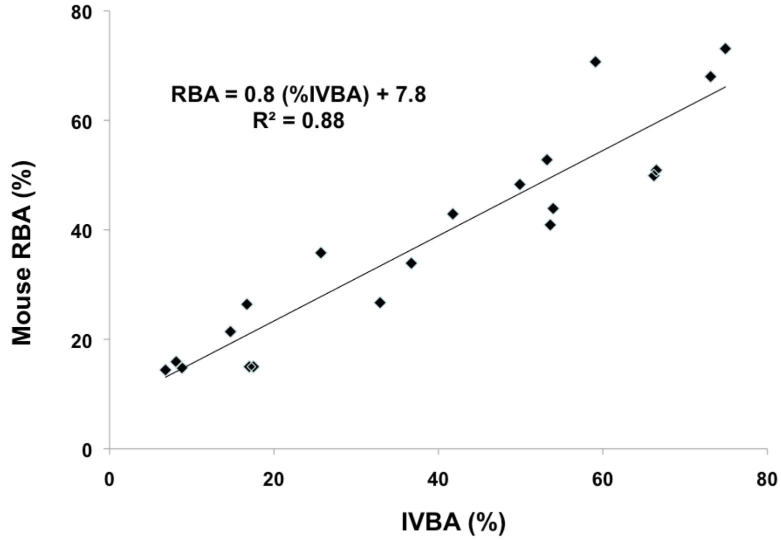
Prediction of Bioavailability for Risk Assessment



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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

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Immobilization Strategies for Pb & As

Kirk G. Scheckel, USEPA, Cincinnati, OH

Carpenter Snow Creek and Barker Hughesville Mining Districts Superfund Sites

Cascade/Judith Basin Counties, Montana

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- Mines yielded primarily silver, lead, and zinc
- Became Superfund sites in 2001
- Approximately 50 abandoned mines identified

Streamside Investigation

Almost 2000 field measurements taken

Samples taken at the surface and in test pits

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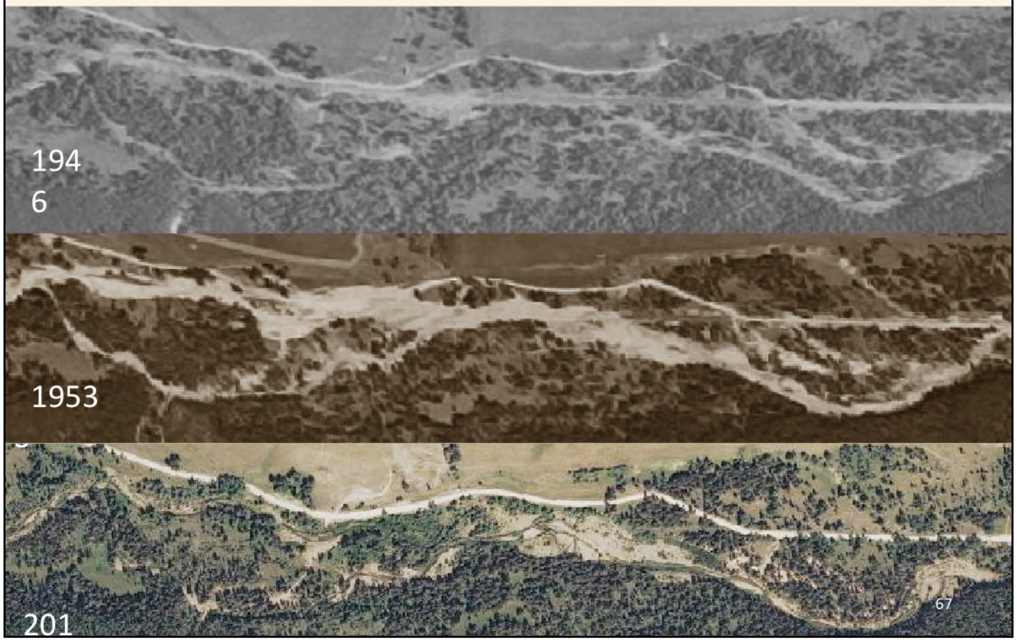
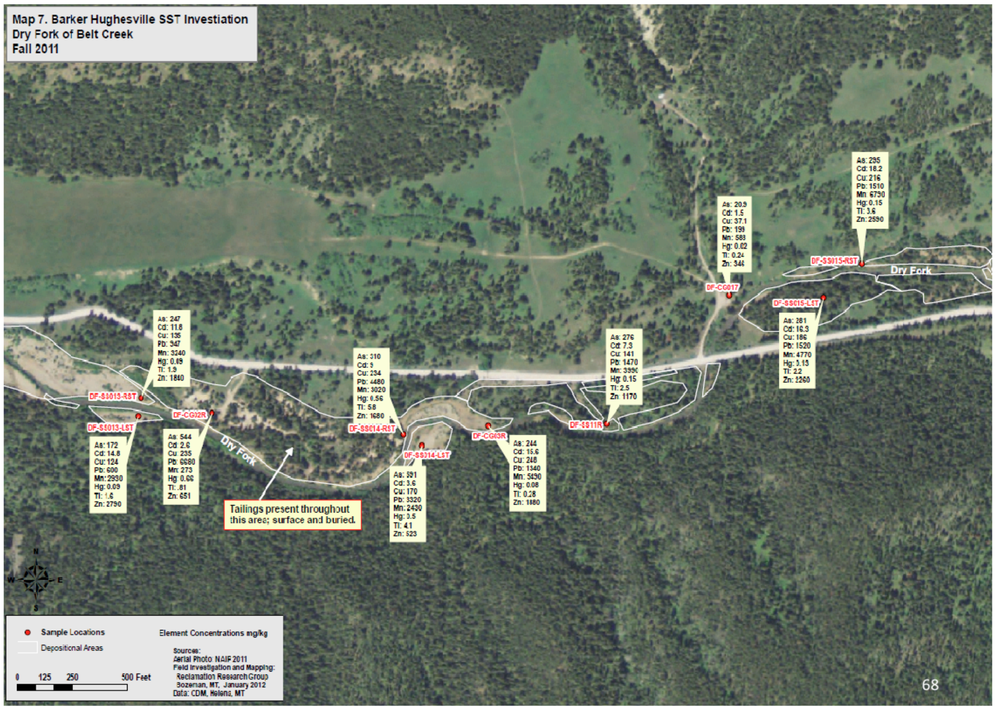
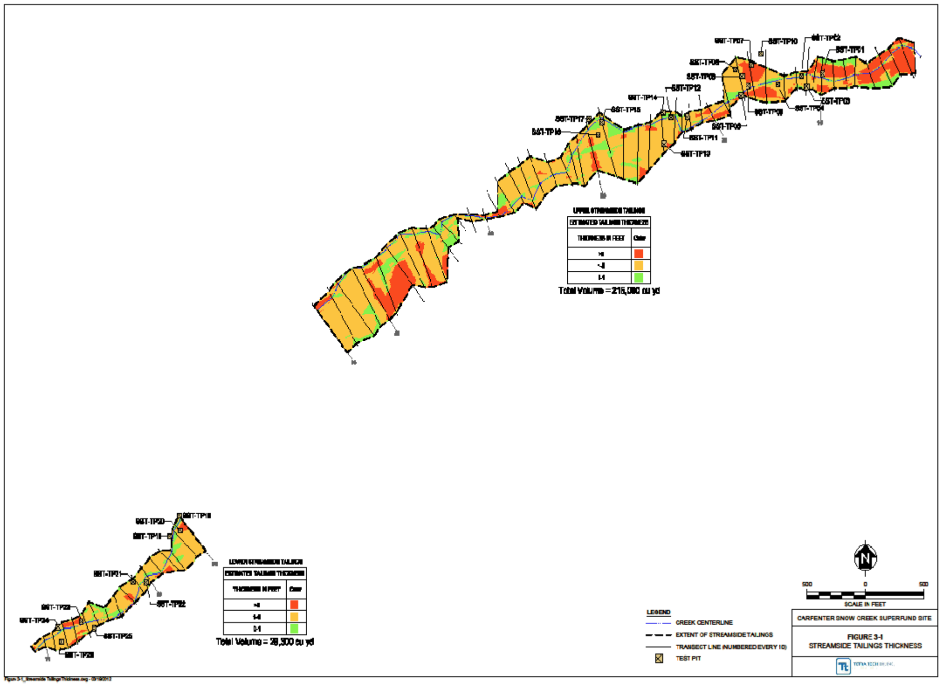
Streamside Investigation



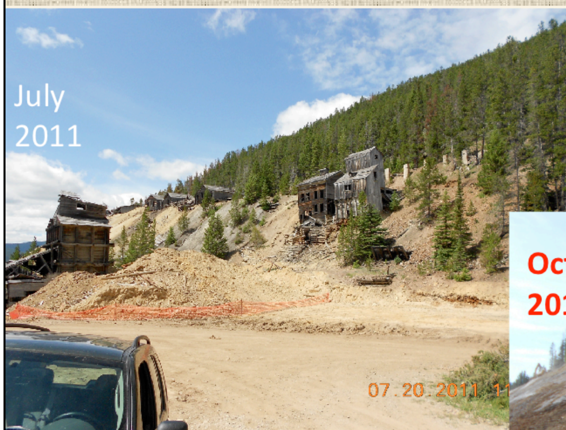


Map 7. Barker Hughesville SST Investiation
Dry Fork of Belt Creek
Fall 2011
DF-SS013-RST
As: 247 Cd: 11.8 Cu: 135 Pb: 947 Mn: 3240 Hg: 0.09 Tl: 1.9 Zn: 1840
DF-SS013-LST
As: 172 Cd: 14.8 Cu: 124 Pb: 600 Mn: 2930 Hg: 0.09 Tl: 1.6 Zn: 2790
DF-CG02R
As: 544 Cd: 2.6 Cu: 235 Pb: 6680 Mn: 273 Hg: 0.66 Tl: .81 Zn: 651
Dry Fork
Tailings present throughout this area; surface and buried.
DF-SS014-RST
As: 310 Cd: 9 Cu: 234 Pb: 4480 Mn: 3020 Hg: 0.56 Tl: 5.8 Zn: 1680
DF-SS014-LST
As: 591 Cd: 3.6 Cu: 170 Pb: 3320 Mn: 2430 Hg: 0.5 Tl: 4.1 Zn: 523
DF-CG03R
As: 244 Cd: 15.6 Cu: 248 Pb: 1340 Mn: 5490 Hg: 0.08 Tl: 0.28 Zn: 1880
DF-SS11R
As: 276 Cd: 7.3 Cu: 141 Pb: 1470 Mn: 3990 Hg: 0.15 Tl: 2.5 Zn: 1170
DF-CG017
As: 20.9 Cd: 1.5 Cu: 37.1 Pb: 199 Mn: 583 Hg: 0.02 Tl: 0.24 Zn: 346
DF-SS015-RST
As: 295 Cd: 18.2 Cu: 216 Pb: 1510 Mn: 6790 Hg: 0.15 Tl: 3.6 Zn: 2590
Dry Fork
DF-SS015-LST
As: 261 Cd: 16.3 Cu: 186 Pb: 1520 Mn: 4770 Hg: 3.13 Tl: 2.2 Zn: 2260
N
W
E
S
Sample Locations
Depositional Areas
Element Concentrations mg/kg
Sources:
Aerial Photo: NAIP 2011
Field Investigation and Mapping:
Reclamation Research Group
Bozeman, MT, January 2012
Data: CDM, Helena, MT
0 125 250 500 Feet


SST-TP15
SST-TP17
SST-TP16
Total Volume = 28,300 cu yd
500
0
500
SCALE IN FEET
LEGEND
CREEK CENTERLINE
EXTENT OF STREAMSIDE TAILINGS
TRANSECT LINE (NUMBERED EVERY 10)
TEST PIT
CARPENTER SNOW CREEK SUPERFUND SITE
FIGURE 3-1
STREAMSIDE TAILINGS THICKNESS

Block P Mine Cleanup

- Almost 240,000 cubic yards of overburden excavated and placed in a nearby repository



Abandoned Mine Surveys

Completed the evaluation of all known abandoned mines at both sites

Soil, sediment & water samples collected and physical & chemical hazards assessed;

Estimated volumes determined

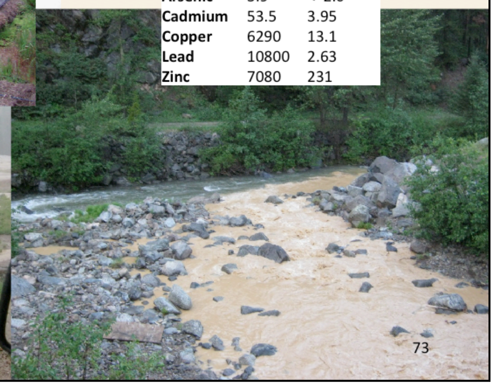
Geochemical analyses conducted

Interim Measures

Construct wetlands to passively treat mine water at three locations

Construct water diversions to route clean water around contaminated areas at several locations

C103	Total ppb	Dissolved ppb
Arsenic	3.9	< 2.0
Cadmium	53.5	3.95
Copper	6290	13.1
Lead	10800	2.63
Zinc	7080	231



http://www.cluin.org/ecotools

- EPA Presentations
- Principles for Ecological Land Reuse
- Soil Amendments
- Terrestrial Carbon Sequestration
- Plants and Revegetation
- Urban Gardens
- Act Locally
- Organizations and Resources
- Land Revitalization Assistance
- Case Study Profiles

New Ways to stay connected!

- Follow CLU-IN on Facebook, LinkedIn, or Twitter

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https://twitter.com/#!/EPACleanUpTech

http://www.linkedin.com/groups/Clean-Up-Information-Network-CLUIN-4405740

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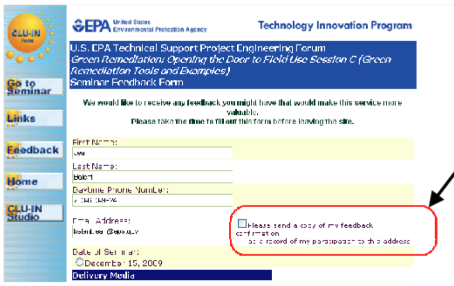
Resources & Feedback

- To view a complete list of resources for this seminar, please visit the [Additional Resources]
- Please complete the [Feedback Form] to help ensure events like this are offered in the future



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