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Bioavailability-Based Remediation of Metals Using Soil Amendments: Considerations & Evaluation Techniques: Part 1

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

Delivered: June 22, 2011, 2:00 PM - 4:00 PM, EDT (18:00-20:00 GMT)

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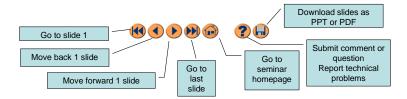
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With that, please move to slide 3.

Introduction to Bioavailability-Based Remediation of Metals Using Soil Amendments: Considerations & Evaluation Techniques: Part 1

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There are a large number of sites and large areas where "soils" have lost their functions. These include mining sites, but can include properties which have been impacted through other means.

The end result of the activities or impacts to these properties may be:

Loss of top soil;

Loss of soil functions;
loss of use options.

These may result from: Physical loss of soil; Loss of soil structure; Toxicity.







Because of the scale of the issues surrounding the remediation of these impacted lands there is a need to improve our ability to evaluate the risks which exist.

Exposure X Hazard = Risk

The exposure assessment is a critical element of the risk assessment; how do we evaluate/determine the site specific exposure?

Examples:

Human health risk assessments may do a market basket surveys;

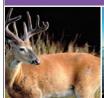
Ecological Risk assessments may conduct field collection of organisms and measures accumulation.

Both are trying to get at location/site specific bioavailability/bioaccessability the actual exposure.



EPA 120/R-07/001 | March 2007 www.epa.gov/osa

Framework for Metals Risk Assessment







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Environmental toxicology has also had a premise that the total concentration of a contaminant is not a good estimator of exposure. The metals framework outlines the issues and highlights that for metals chemical form is critical in determining the toxicity and the exposure.

We need to explore the available techniques for assessing exposure and hazard. We need to make sure we are applying the techniques correctly and interpreting the results correctly. The goal is to remediate the risks effectively; provide protective remedies.



- Soil Amendments
- Terrestrial Carbon Sequestration
- Plants and Revegetation
- Growing Gardens in Urban Soils
- Act Locally
- Organizations and Resources
- Land Revitalization Assistance
- Case Study Profiles





Since 1998, CLU-IN has presented Internet Seminars covering a wide variety of technical topics related to hazardous waste characterization, monitoring, and remediation. For each seminar topic, we have selected the highest-quality offering for placement in our archives.

- NARPM Presents...Ecological Revitalization: Turning Contaminated Properties into Community Assets: Archive of Mar 15, 2011 Seminar
- NARPM Presents...A Tale of Three Sites Supporting Reuse Throughout the Cleanup Process: Archive of Mar 10, 2011 Seminar
- Superfund Redevelopment Seminar Series: Archive of Sep 30, 2010 Seminar
- Identifying & Evaluating Ecosystem Services at Contaminated Sites Prior to Remediation: Archive of Aug 18, 2010 Seminar
- Green Remediation: Applying Strategies in the Field Session 1 of 3: Archive of Fall 2009 Seminars
- Ecological Revitalization Resources Available through EPA Parts 1 and 2: Archive of Dec 3 and 5, 2007 Seminars
- Ecological Revitalization Resources at Various Federal Agencies: Archive of Nov 27, 2007 Seminar
- Ecological Revitalization Case Studies The Atlas Tack Site and the Poudre River Site: Archive of Aug 2, 2007 Seminar
- Understanding and Reconstructing Soil Conditions at Remediation Sites: Archive of May 2, 2007 Seminar
- Revegetation and Restoration of an Oil Contaminated Wetland in Northern New Jersey: Archive of Dec 14, 2006 Seminar
- Jump-Starting Ecological Restoration Soil Health: Archive of Oct 5, 2006







http://www.cluin.org/ecotools

Ecological Revitalization Database

- · Entity responsible for cleanup
- Project Information
- · Project name · Site history and background
- Site use prior to revitalization
- Final use after revitalization The final use of the land after the revitalization process is complete (open space, ready-for-reuse, wildlife refuge, etc.).
- ready-for-reuse, wildlife refuge, etc.).

 Habitats created or restored Any habitats that are created or restored on an entire property or on a portion of a property through ecological revitalization (wetland, grassland, stream, etc.).

 50i amendments Any soil amendments that are used to aid in soil growth and health. Soil amendments are materials added to soils in order to make them suitable for sustaining plant life or development.

 Contaminated media type and concentration The contaminated media.

 Wetlast the concentration of the contaminant in each specific media.



Remediation technology – The technology used to remediate the contaminated media and site.

Remedy description

- Operations and maintenance (O&M) requirements O&M for the overall cleanup hipically includes inspection, sampling and analysis, routine maintenance and small reporting, as necessary. Any additional O&M requirements, including those specific to ecological revitalization activities, are listed.
- Long-term stewardship at the site Long-term stewardship as state voluntary cleanup programs and property
 owners have primary responsibility for carrying out maintenance of engineering controls and ICs for the long-term.
- Issues faced
 Solutions for issues faced Additional Information

References





Site-Specific Support

- Soil Amendments for Remediation & Reuse
- Site Reuse Planning
- Expert consultation
- Documentation
- Presentations
- Other?





Bioavailability-Based Remediation of Soil Metals Using Soil Amendments: Considerations & Evaluation Techniques: Part 1

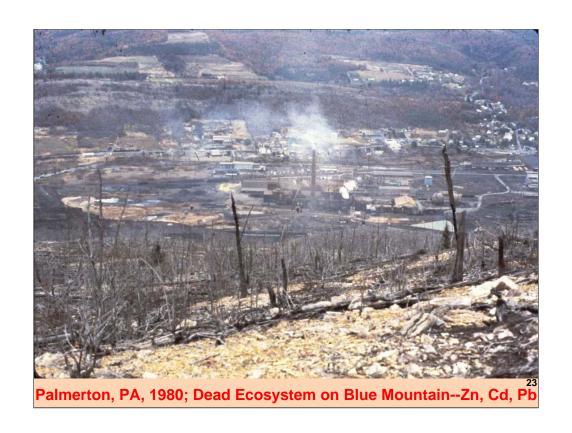
Rufus L. Chaney

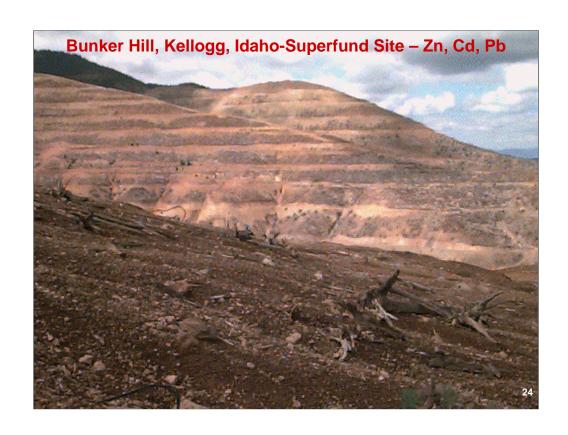
USDA-Agricultural Research Service
Environmental Management and Byproducts Utilization Lab
Beltsville, MD.

Webinar, June 22, 2011

The Problem:

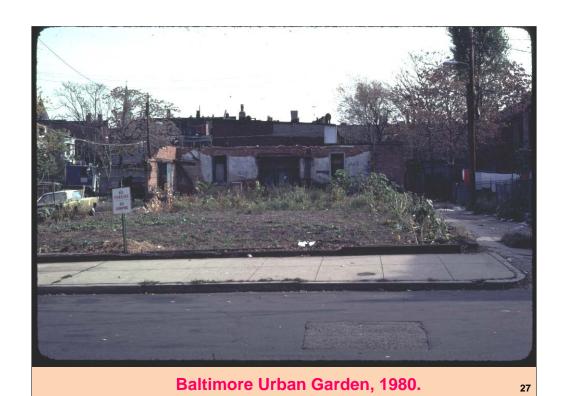
- Highly metal contaminated barren soils
 - -Mine wastes
 - -Smelter contamination
 - -Contaminated riverine or lake sediments on land
- Rich in phytotoxic elements
 - -Zn, Cu, Ni, Mn, Co.
- Risk thru soil ingestion Pb, As, F
- Risk thru food chain transfer Cd, Mo, Co
- May be highly acidic due to oxidation of sulfide
 - -Pyritic mine waste
 - -Natural soil acidity coupled with acidic rainfall
- Need: Reduce bioavailability of soil metal to remediate risks.











Revegetation/Remediation of Heavy Metal Contaminated Soils: Problems.

- Low soil pH or pH decline from pyrite oxidation.
 - Make site calcareous; balance Ca and Mg; Mn if needed.
 - Limestone with biodegradable organic matter aids leaching
- Nutrient Deficiencies, especially P and N.
 - High Pb soils need higher P addition to precipitate Pb.
 - Higher available soil P needed to maintain legumes.
 - No metal tolerant legumes to supply N to grasses
- Need more metal sorption by soil, Fe for grasses.
 - Grasses obtain Fe using secreted phytosiderophores (chelators), so higher soil Fe aids grasses metal resistance
- Low organic matter, lack of microbes--Zn Toxicity
 - Biosolids, manures and composts inexpensive source of Organic Matter and microbial inoculant.

Revegetation/Remediation of Heavy Metal Contaminated Soils: Solutions.

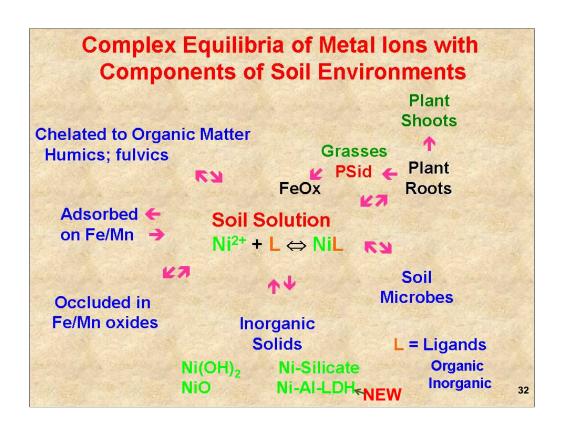
- Make Soil Calcareous Using By-Product Lime
 - -Increases metal adsorption and occlusion.
 - -Alleviates phytotoxicity of Zn, Cu, Ni, Cd, etc.
- Increase Metal Adsorption Capacity
 - —Include Fe, Mn hydrous oxides and phosphate.
 - -Provides persistent reduction in metal toxicity.
- Remediated Soil Must Support Legumes.
 - —High pH and soil P aids legume competition, alleviating need for annual N fertilization
- Food Chain Protection: Cd/Zn ratio; calcareous.
- Reduced bioavailability of soil Pb, As, Cd, etc. to animals with soil exposure at remediated site.
- Effective plant cover reduces soil ingestion.

Tailor-Made Mixtures For Remediation of Metal Toxic Soils

- Mix Composts, Biosolids and Byproducts to Complement benefits or improve metal sorption:
 - **—APL** Biosolids and composts
 - -Composts of Yard Debris or pre-separated MSW.
 - -Agricultural Organic Byproducts
 - Manures; crop residues; food processing byproducts
 - -Fe, Mn, Silicate Byproducts from industry.
 - -Coal Combustion Byproducts, FGDB, Ash.
 - -Drinking Water Treatment Residues
 - —Limestone equivalent byproducts.
 - Wood ash; waste lime; sugarbeet lime; fly ash; etc.

Tailor-Made Biosolids Mixtures For Beneficial Use and Remediation

- Apply mixture of limestone equivalent, metal adsorbent, organic soil amendment, and fertilizer value to correct all risks/problems of the contaminated soils:
 - -Zn or Ni Phytotoxicity; make soil calcareous.
 - -Food-chain risks from Cd prevented by Zn.
 - —Soil ingestion risk from soil Pb, As, etc.
 - —N fixation by legumes made possible.
 - Leaching of limestone equivalent corrects surface and subsurface soil metal phytotoxicity.
- One treatment for comprehensive remediation.



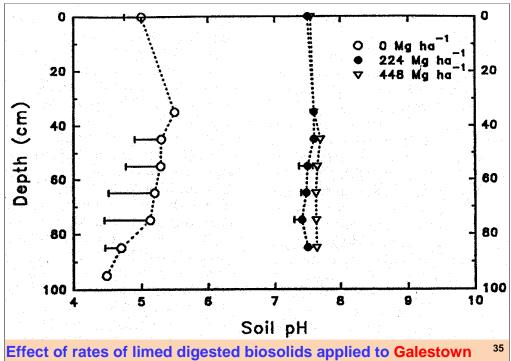
SOIL-PLANT BARRIER

Processes in soils or plants which prevent excessive food-chain transfer of elements

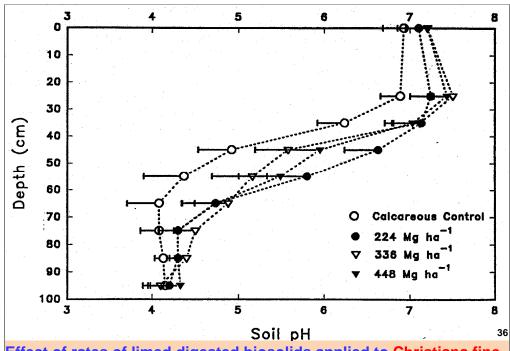
- Insolubility or adsorption in soil or plants roots:
 - -Cr, Pb, Fe, Hg, Sn, Au, Ag, Zr, Al, Ce, Ti, etc.
- Phytotoxicity limits plant yield at levels which are not toxic for lifetime consumption by livestock:
 - -Zn, Cu, Ni, As, Mn, B, F, etc.
- Exceptions to Soil-Plant Barrier:
 - —Cd, Se possible risk to humans
 - —Mo, Se, Co possible risk to livestock
- Barrier can be circumvented by direct ingestion of surface soils.
 - —Pb, As, F, Hg, Fe may comprise risk if high on surface.

Difficulties in Raising Soil pH

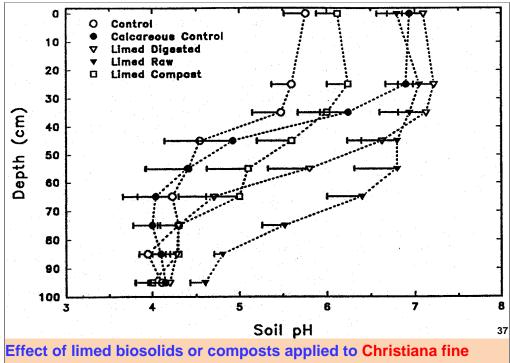
- Agricultural limestone can only react with soil acidity very near the limestone articles.
 - -Diffusion of Ca²⁺ and H⁺ only short (mm) distances.
- Need to raise pH of contaminated soil depth using mixing or alternatives.
- We found that mixing limestone equivalent with biodegradable organic matter formed alkaline leachable mixture.
 - —Ca-organic acid complexes can readily leach.
 - Oxidation of the organic acid essentially leaves a residue of highly reactive CaCO₃ at depth.
 - The greater the rate of biodegradation of the applied organic matter, the greater the leaching of CaCO₃.
 - —Finer lime materials more reactive.



Effect of rates of limed digested biosolids applied to Galestown loamy sand in 1976 on pH at soil depths in 1992 (Brown et al., 1997).



Effect of rates of limed digested biosolids applied to Christiana fine sandy loam in 1976 on pH at soil depths in 1992 (Brown et al., 1997).



sandy loam in 1976 on pH at soil depths in 1992 (Brown et al., 1997).

Effect of Biosolids Processing Technology in Reducing Soil-Pb Bioavailability.

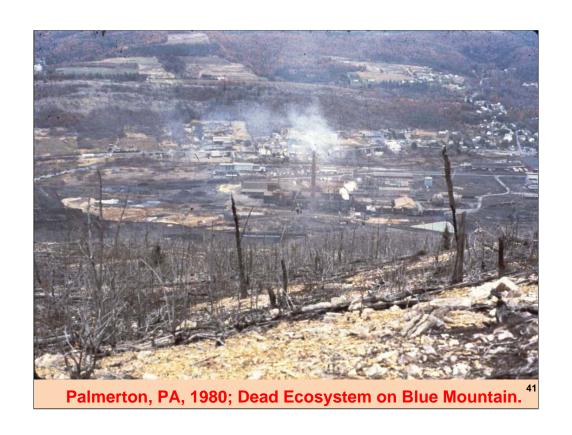
- Conducted by Brown, Xue, Hallfrisch and Chaney/WERF.
- Baltimore urban soil = 2135 mg Pb/kg
- Mixed biosolids products at 10% dry weight (224 t/ha) or equivalent added biosolids matrix.
 - —Incubated moist for 30 days; dried; mixed.
- Added 5% soil to purified rat diet for 35 day feeding period -- simulates pica soil ingestion levels.
 - —Measured Pb in blood, bone, kidney, etc.
 - —Compare to Pb-acetate (soluble; 100% bioavailable); interpolate Pb-acetate which gives equal tissue Pb concentration as soils.

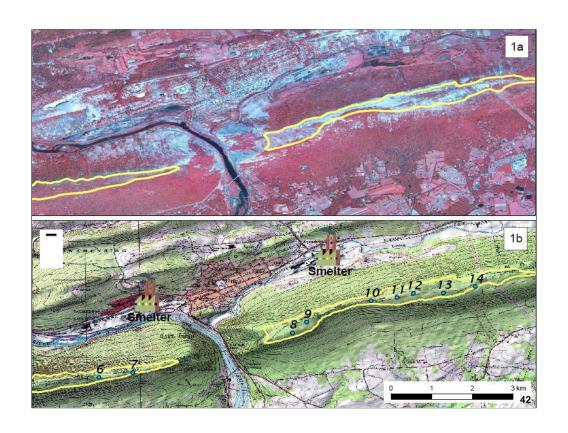
Effect of Biosolids Processing Technology in Reducing Soil-Pb Bioavailability.

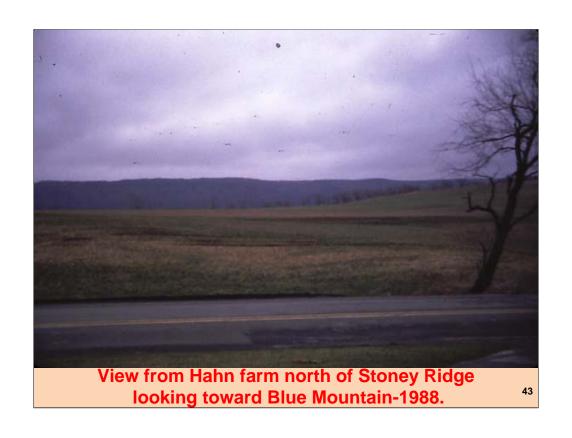
Treatment 5	Soil Pb	Diet Pb	Bone-Pb
		mg/kg dry we	eight
Unamended	2135	125.3 a	144.6 a
Syracuse Raw	2099	82.4 cd	87.5 b-e
Syracuse Pellet.	2034	84.3 cd	86.7 cde
Syracuse Comp.	1768	116.7 ab	104.5 bc
Orgro-Baltimore	2576	100.6 b	73.3 de
Compro-DC	2309	99.2 b	81.8 cde
			39

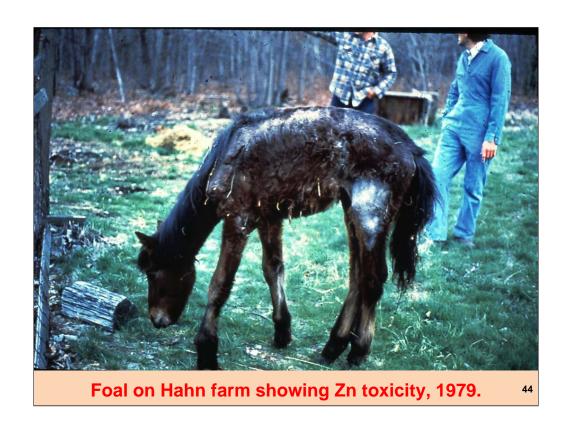
Bioavailability of Cadmium in Biosolids-Fertilized Swiss Chard Fed at 28% of Diet to Guinea Pigs for 80 Days (Chaney et al., 1978)

Treatment	Rate	Soil	Soil	Ch	ard	Kidney	Liver
		Cd	рН	Cd	Zn	Cd	Cd
	t/ha	t/ha mg/kg		mg/kg dry		mg/kg dry	
Control	0	0.04	6.0	0.5	70	14.9 a	3.1 a
Biosolid-1	56	0.32	5.7	1.5	950	14.5 a	2.7 a
Biosolid-2	112	0.94	5.5	2.7	580	14.5 a	2.7 a
Biosolid-3	224	0.89	6.6	1.4	257	15.8 <mark>a</mark>	3.6 a





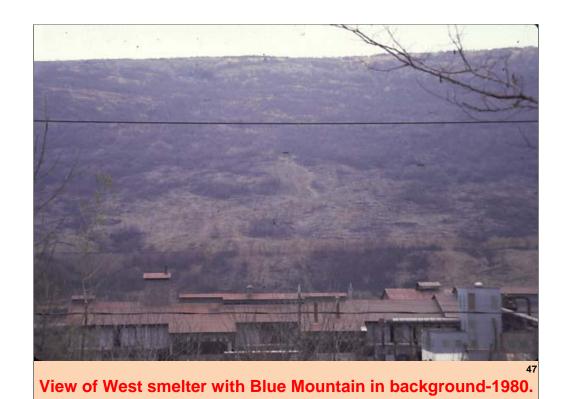


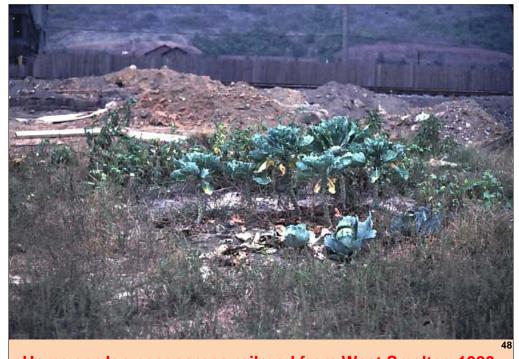






Palmerton, PA, 1980; because lawn grasses died from Zn, many residents covered their lawns with stones or mulch.⁴⁶

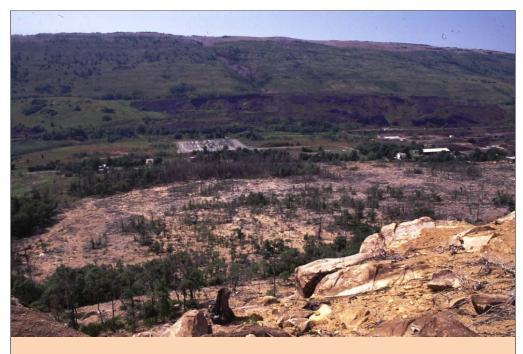




Home garden near across railroad from West Smelter, 1980.



Chlorotic radishes (Zn phytotoxicity) - Palmerton garden, 1980.



View from Stoney Ridge toward Blue Mountain, 2000. $_{50}$



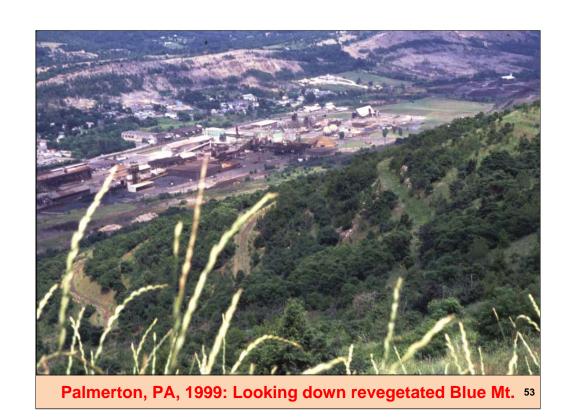
Palmerton, PA, 1990: Oyler's First Test Plot Using Biosolids + ⁵ FlyAsh + Limestone, with 'Merlin' Red Fescue; adjacent control.

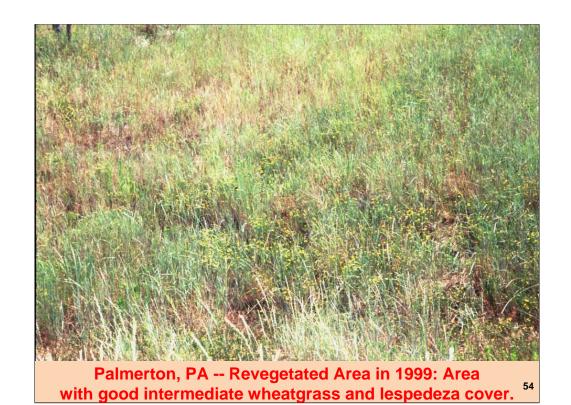
Characteristics of the Blue Mountain North Slope Soils Sampled in bulk in 1998 for *Thlaspi* studies.

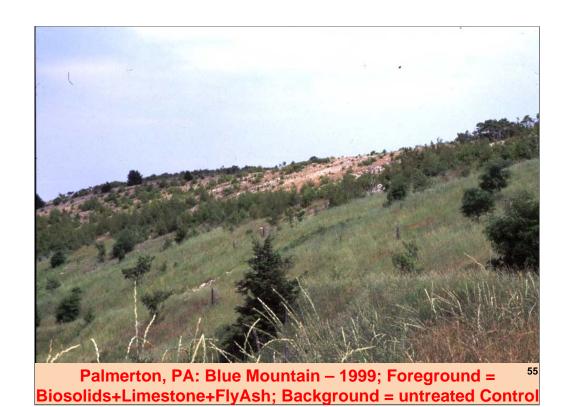
mg/kg DW

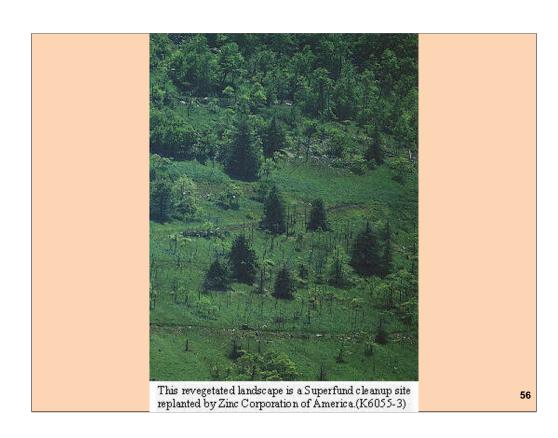
44,100 Zn 25,500 Fe 8,920 Mn 863 Cd

pH 6.25











Palmerton, PA 1999; Untreated area adjacent to revegetated area of Blue Mountain, with John Oyler and Tom Stuczynski. 57

Mean total Zn, Cd and Pb, and DTPA-extractable Zn and Cd (at 100 mL extractant/2 g soil) in Palmerton "Revival Field" Test Plots Comparing Traditional and Biosolids Compost Remediation Treatments (Li et al., 2000).

Treatment		Total			DTPA-Extractable		
	Zn	Cd	Pb	Zn	Cd		
mg kg ⁻¹							
Control	14900 a†	164. a	687. a	4940. a	83.1 a		
Limestone	15700 a	161. a	680. a	4980. a	82.9 a		
Compost	16000 a	170. a	767. a	4550. a	69.1 b		

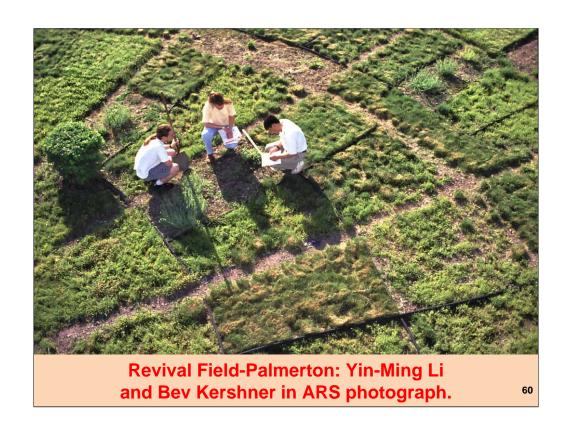
†Treatment means followed by the same letter are not significantly different at the 5% level (Duncan-Waller-test).

Use of DTPA-TEA extraction required using 5 g/50 mL rather than 10 g/20 mL because high soil metals saturated DTPA chelation capacity.

Mean pH, Sr-extractable metals, pH, organic matter and oxalate Extractable Fe and Mn in Palmerton "Revival Field" Plots comparing remediation using traditional or biosolids compost methods; plots Installed in 1993, last sampled in 1998 (Li et al., 2000).

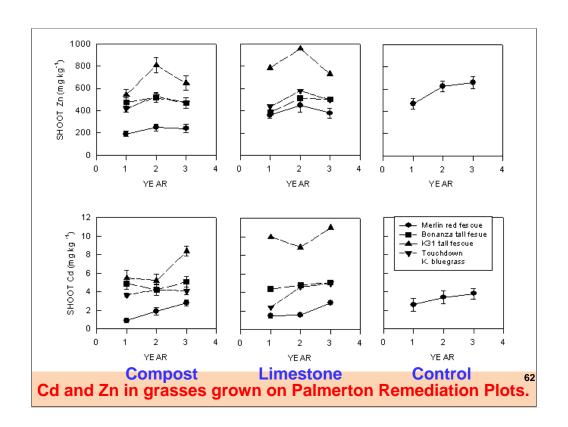
Treatment	Sr(NO ₃) Zn	₂ -Extr. Cd	рН	Organic Matter		e-Extr. Mn	
mg kg ⁻¹				%	g kg ⁻¹		
Control Limestone Compost	195. a 156. a 4.8 b	1.99 a 1.65 a 0.033 b	5.9 6.5 7.2		5.74 a 5.61 a 16.7 b	2.12 1.92 2.44	

†Treatment means followed by the same letter are not significantly different at the 5% level (Waller-Duncan test.)





Palmerton, PA, Revival Field, Year-3: Grasses thrive only on Alkaline Biosolids Compost Treatment (Cooperator Bev Kershner). 61









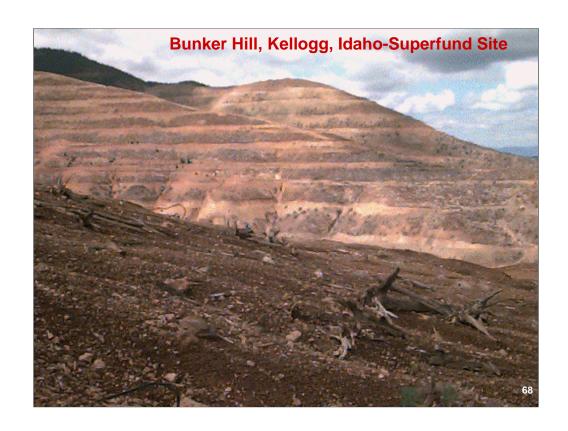
Sassafras growing on south face of Blue Mountain near Palmerton, PA., 6-21-2006 Leaves show severe interveinal chlorosis expected from Zn phytotoxicity. 65

Why Use High Quality Tailor-Made Biosolids Mixtures in Remediation of Soil Metals?

- Fe and phosphate in biosolids increase metal "specific adsorption ability of the soil, reducing metal phytoavailability.
 - Can remediate Zn phytotoxicity and food chain Cd risk.
 - Can reduce soil Pb bioavailability/form Pb pyromorphite
- Combining limestone equivalent and biodegradable organic matter causes alkalinity to leach down soil profile.
 - Corrects subsoil acidity and metal phytotoxicity/leachability
- With pH buffered by applied limestone equivalent, metal adsorption is maximized, and occlusion promoted.
 - Some metals are occluded in crystalline Fe oxides, Mn oxides.
- Organic matter and balanced nutrient supply supports crops!
- Tailor-Made Remediation Mixtures can immediately inactivate metals, provide microbial inoculum, add energy and nutrients.
- Cost savings; public benefit.

What Does it Take To Develop Local Tailor-Made Remediation Products?

- Risk assessment and value information from evaluation of field studies of product utilization.
- Courageous agencies and businesspersons who will seek out such combinations of biosolids, byproducts, and valuable commercial uses of the products.
- Organized valid risk assessment information on:
 - Phytoavailability of applied and soil elements in field.
 - Bioavailability of soil and crop elements
- Improved risk communication, and honest risk assessments. Examples from Cd food-chain risk, soil Pb and As risk, and phytotoxicity risks from biosolids show massive errors of conservative assumptions.



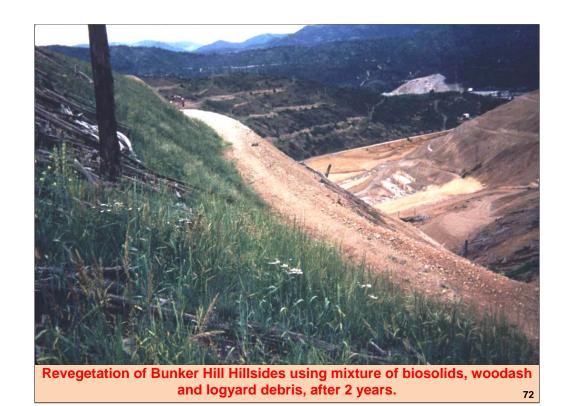






Aerospreader Applying Biosolids-Wood Ash Mixture at Bunker Hill 70





Remediation of Page Swamp

- The Page Swamp is a wetland constructed in a Pb-Zn-Cd mining waste storage pile near Kellogg, ID.
- In cooperation with US-EPA Superfund ERT, Henry and Brown of Univ. Washington, Chaney et al. tested application of organic amendment plus alkaline byproducts to remediate the highly contaminated site soils.
- Before treatment, the site lacked vegetation even when flooded. Further, the acidity allowed soil metals to inhibit soil microbes so that flooded soil did not become sufficiently reducing to form PbS.
- Application of the composted biosolids plus wood ash mixture prevented toxicity to microbes or plants, soil became highly reducing and PbS was formed
 - Formation of PbS reduces risk to birds which ingest sediments.
 - Vegetation was low in metals and safe for wildlife consumption.

′3







Page Swamp remediated area in next season after reactions
Of soil amendments and natural plant colonization.

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Design of Experiment to Test Remediation (Phytostabilization) of Ni-Phytotoxic Soil With Limestone and Fertilizers For Crops Which Differ in Susceptibility to Ni.

Plant species tested

Poaceae Dicots

Corn Wheat Radish Tomato

Barley Ryegrass Bean Soybean
Oat Redbeet Swiss Chard

Three limestone rates

0. - Control

2.54 Mg ha⁻¹ - Limed soil (pH 6.0)

50. Mg ha⁻¹ - Calcareous soil (pH 7.7)

Lime=powdered reagent grade CaCO₃ + MgCO₃ (4.8 : 1 w/w) ⁷⁷

Experimental Design-2

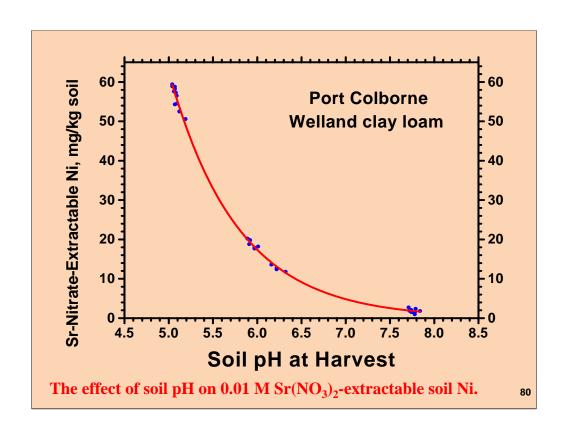
Mn rates – Applied as MnSO₄•H₂O to prevent Mn deficiency seen on Port Colborne Soils if limed.

Control - 20 kg ha⁻¹ Limed soil - 50 kg ha⁻¹ Calcareous soil - 100 kg ha⁻¹

- Plants grown for 42 days
- Ni in plant tissue determined by AAS after ashing and digestion in HNO₃/HCl.
- Soil pH measured in 1:2 v/v water slurry-Harvest
- Soil Ni extracted with 0.01 M Sr(NO₃)₂.
 - 10g soil:40 mL solution (Helmke, Corey et al.).;
 - Shaken for 2 hr, filtered; analysis by AAS.

Properties of Welland Clay Loam Soil (from Port Colborne, Ontario, Canada, Used in Nickel Phytotoxicity Remediation Tests.

Measurement	Welland	
Total Ni, mg/kg	2900	
DTPA-Ni, mg/kg	634	
Sr(NO ₃) ₂ -Ni, mg/kg	57	
Initial pH	5.2	
		79





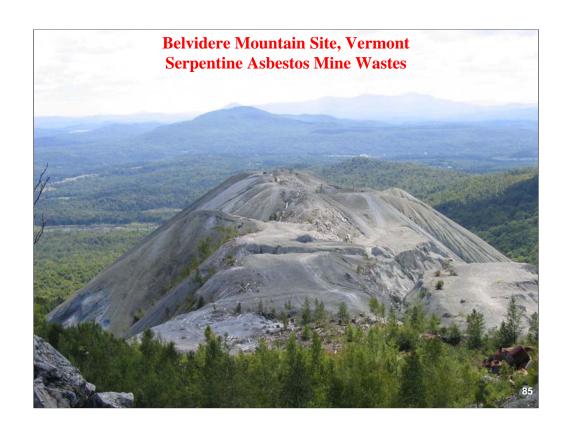


The Vermont Asbestos Group Site Near Eden/Lowell/Stowe, VT.

- Has been barren since about 1950. Potential dispersal of asbestos from the barren ground rock presents an environmental risk.
- Rock is serpentinite, rich in Ni, Cr, Co, and Mg silicate. Deficient in many plant nutrients.
- Extremely infertile; Mg phytotoxic=Ca deficient.
- Not Ni, Co or Cr phytotoxic due to high pH (>8.0)
 which is caused by presence of Mg-silicate.
- Alternative to in situ phytostabilization would be covering mine waste with 12-24 inches of topsoil!

Severe Infertility and Lack of Soil Properties Prevent Plant Survival

- Serpentine soils are Mg phytotoxic due to very low Ca:Mg ratio of this type of rock.
- N, P, K, and trace elements are also deficient.
- Serpentine soils are normally severely Ca and P deficient for all but serpentine ecology plants.
- Because site has high slopes, goal was to use surface applied amendment mixture to achieve revegetation at low cost.
- Designed experiment to evaluate surface applied compost plus Ca and NPK fertilizers.

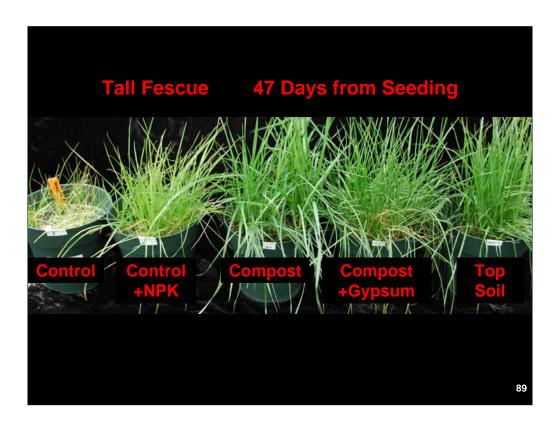




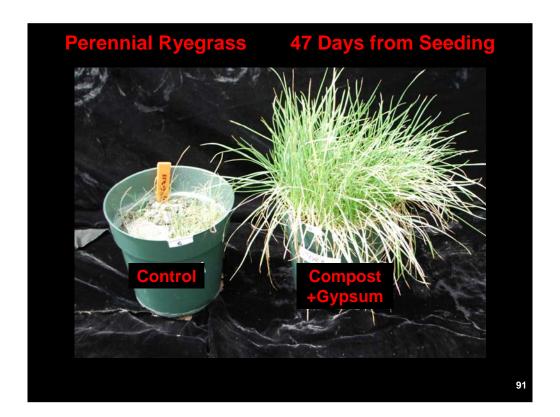


Treatments Tested:

- Surface Applied Soil Amendments:
 - -Control
 - —NPK Fertilizer (normal roadside revegetation)
 - -Compost + NPK
 - -Compost + NPK + Gypsum(=CaSO₄)
 - Topsoil + NPK
- Plant Species Tested:
 - -Kentucky bluegrass
 - —Perennial ryegrass
 - -Tall Fescue
 - -Alsike Clover

















Preparing mixture of COMPOST (manure and yard debris), mined gypsum, NPK fertilizer plus limestone



August 24, 2011: Applying the compost mixtures to test plots; compost was raked even, then seeded with crop mix. 97







How Did We Achieve Success on VAG Site?

- Evaluated composition of soil for metals, pH, and nutrients before plant testing.
- Recognized severe Ca and P infertility of serpentine rock derived soil materials.
- Tested treatments and plant species on site soil in greenhouse.
- Amendment mixture included all nutrients needed for plant growth in compost.
- Added limestone to prevent acidification of compost layer over time with N-fixation.
- Included gypsum to add Ca to sub-surface soil. 101

Summary

- Risk Assessment of contaminated soil:
 - -Soil-Plant Barrier.
 - -Phytoavailability related to soluble metal level.
 - Affected by pH, sorbents (Fe, Mn, OM) and competition.
 - Bioavailability of metals in ingested soil requires test correlated with bioavailability to animals.
 - Important risk for Pb, As, F, and some others.
- In situ remediation using byproducts to reduce phytoavailability, bioavailability and improve agronomy.
 - -Alkalinity to reduce metal solubility.
 - —Organic matter/N to improve fertility.
 - —Diverse microbial inoculum.
 - -Support growth of perennial grasses and legumes.

What Does it Take To Develop Local Tailor-Made Remediation Products?

- Risk assessment and value information from evaluation of field studies of product utilization.
- Courageous agencies and businesspersons who will seek out such combinations of biosolids, byproducts, and valuable commercial uses of the products.
- Organized valid risk assessment information on:
 - Phytoavailability of applied and soil elements in field.
 - Bioavailability of soil and crop elements
- Improved risk communication, and honest risk assessments. Examples from Cd food-chain risk, soil Pb and As risk, and phytotoxicity risks from biosolids show massive errors of conservative assumptions.

Summary

- One Shot Remediation of Metal Toxic Soils:
 - —For Zn, Cu, Ni rich acidic soils causing phytotoxicity.
 - -Make contaminated soil depth calcareous
 - Provide enough P, K, and other nutrients to support diverse vegetation, and enough organic-N to achieve stable ecosystem which includes legumes.
 - For Pb or As co-contaminated soils have to reduce bioavailability of Pb or As in ingested soil.
 - Phosphate and composts can reduce soil Pb bioavailability.
 - Iron oxides can reduce soil As bioavailability
 - —With normal <1:100 Cd:Zn ratio, Zn limits plant growth before Cd accumulated in plants is a risk to foods.
 - —If slope of the site is to high for tillage, can combine biodegradable amendments with alkaline organic amendments and surface apply; allow rainfall to leach soluble alkalinity into soil profile.

Resources & Feedback

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

