The Effect of Soil Properties on Toxic Metal Bioavailability: Field Scale Validation to Support Regulatory Acceptance

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Background

- Project funded by ESTCP for FY05 – FY07
- Capitalizing on previous research by taking two completed SERDP projects to the demonstration phase
  - CU-1166 Quantifying the Bioavailability of Toxic Metals in Soils (Barnett, Fendorf, Jardine)
  - CU-1210 Determining the Bioavailability, Toxicity, and Bioaccumulation of Organic Chemicals and Metals for the Development of Eco-SSLs (Basta, Chekai, Kuperman, Lanno)

Problem Statement

- **Toxic metals As(III/V), Cr(III/VI), Cd, and Pb exist at thousands of DoD sites**
- **By default As, Cr, and Cd are assumed to be 100% bioavailable in human health and ecological risk assessments**
- **Need to be able to determine appropriateness of:**
  - In vivo studies
  - Excavation/Removal
  - Soil stabilization technologies

Problem Statement

- Metal sequestering properties of soil can significantly lower or alter the bioavailability and risk to human and ecological receptors

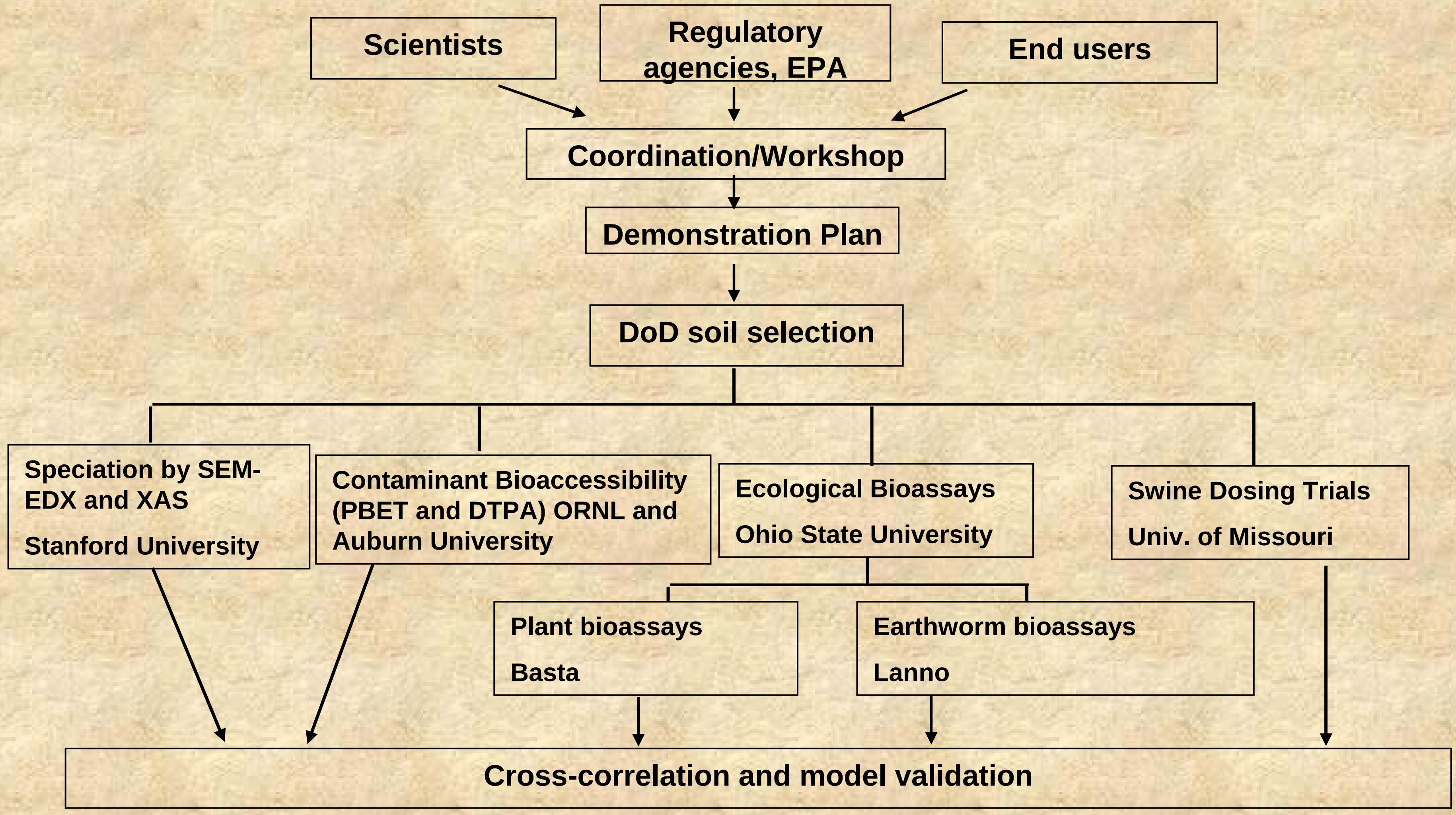
- *In vitro* bioaccessibility, *in vivo* swine metal bioavailability, and molecular-level metal speciation studies all suggest that key soil properties control metal bioavailability

- Models to help predict metal bioavailability and toxicity can be developed based upon these key soil properties

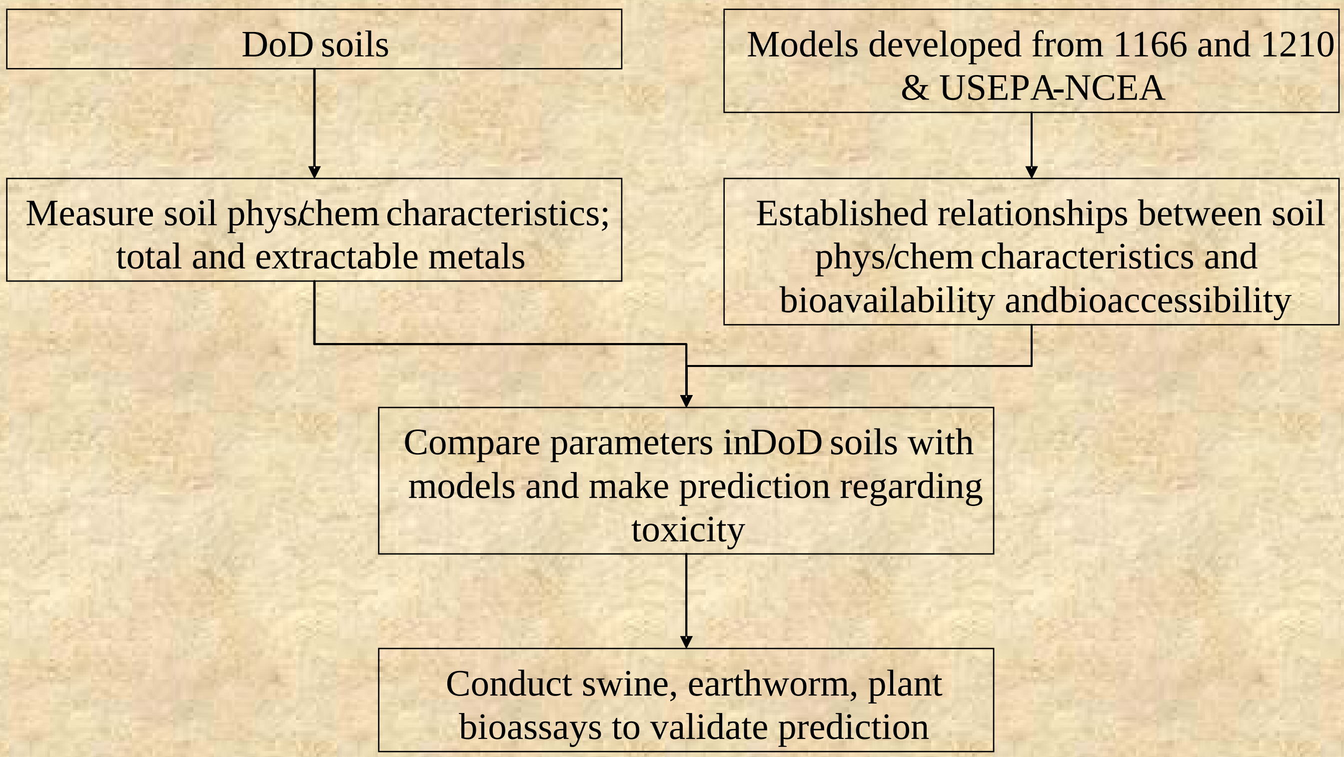
Objectives

- Demonstrate how soil properties can be incorporated into a screening tool to help predict bioavailability and toxicity of As, Cd, Cr, and Pb
- Demonstrate that *in vitro* methods can be used to prioritize sites, affect risk decisions, or justify *in vivo* studies
- Seek regulatory acceptance of *in vitro* methods and the Soil BioAccessibility Tool (SBAT) for initial human RA, and the suite of ecological metal bioavailability methods for ecological RA through validation studies with field-contaminated soils
- Demonstrate application of *in vitro* methods and SBAT screening to prioritize and justify site-specific studies that may significantly reduce cleanup costs

Methodology

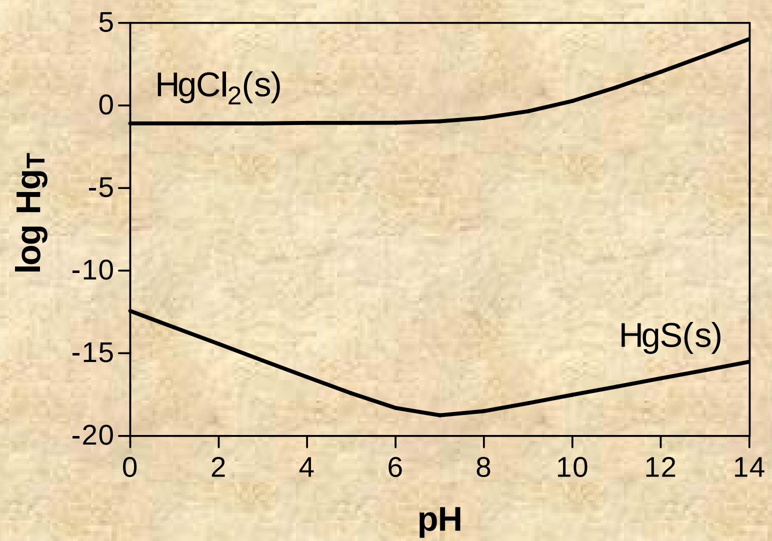


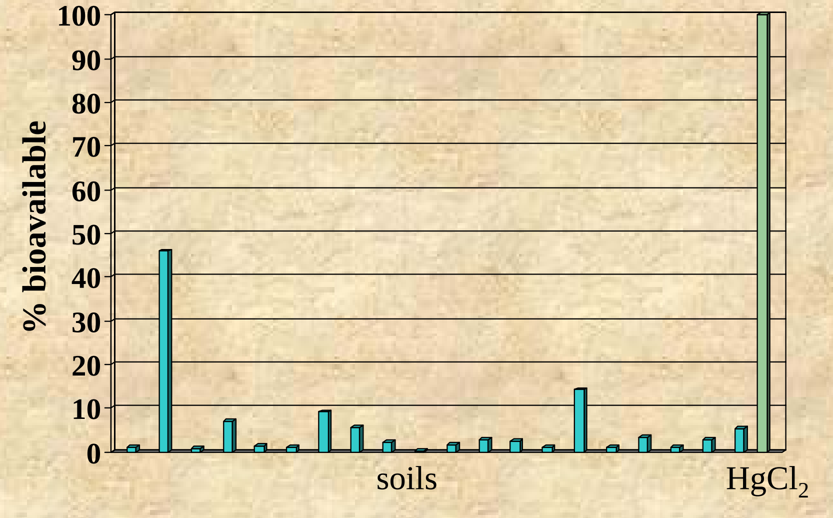
Methodology



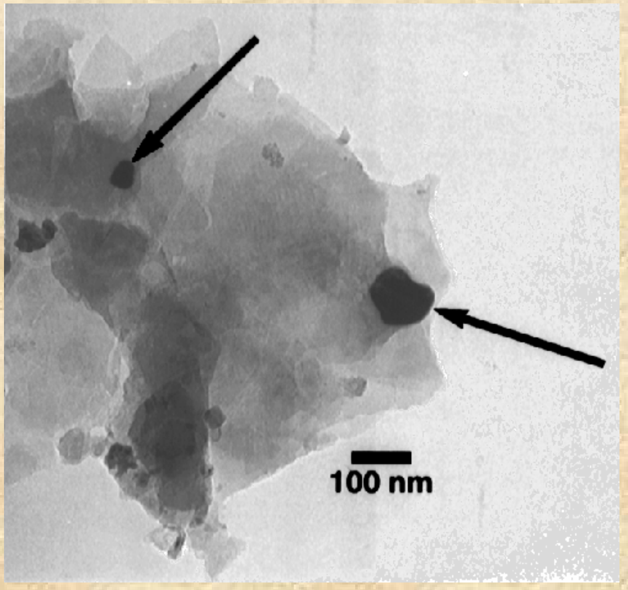
Technology Maturity – Case Study

Remediation of Lower East Fork Poplar Creek (LEFPC) in Oak Ridge, TN, a Hg-contaminated CERCLA site in early 1990s.



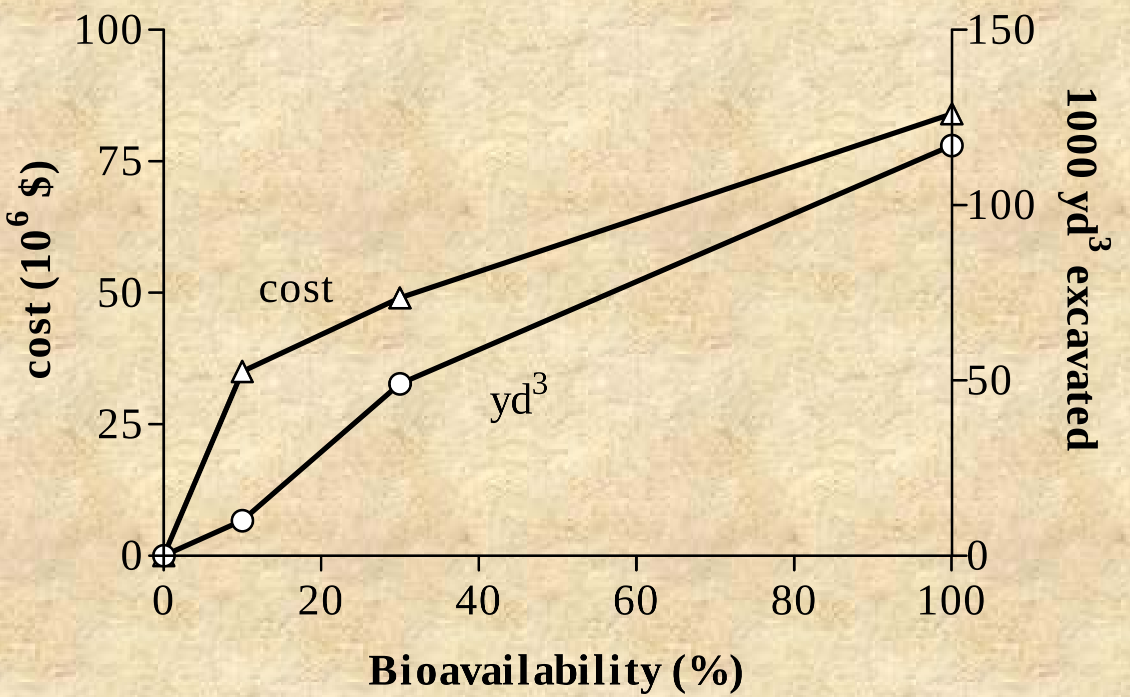


In vitro bioaccessibility and speciation studies led to the adoption of a site-specific relative Hg bioavailability.



Technology Maturity – Case Study

- Default bioavailability of 100% and RfD for $HgCl_2$.
  - Cleanup level of 50 mg/kg.
- Proposed relative bioavailability of 30% based on speciation and bioavailability studies.
  - Cleanup level of 180 mg/kg.
- After comments from the public, used bioavailability of 10%.
  - Cleanup level of 400 mg/kg.



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Technology Maturity – CU-1210

Soil Characterization

•21 soils from 5 soil orders

•Broad range in chemical properties associated with binding metal

•Spiked with Cd 300 mg/kg as Cd $(NO_3)_2$, 300 mg/kg Zn as $Zn(NO_3)_2$, or 2000 mg/kg Pb as $Pb(NO_3)_2$, 250 mg/kg As as Na_2HAsO_4

Lettuce Bioassay
(Lactuca sativa var, Paris Island Cos)

•20 seeds per pot

•Harvest at 40 days

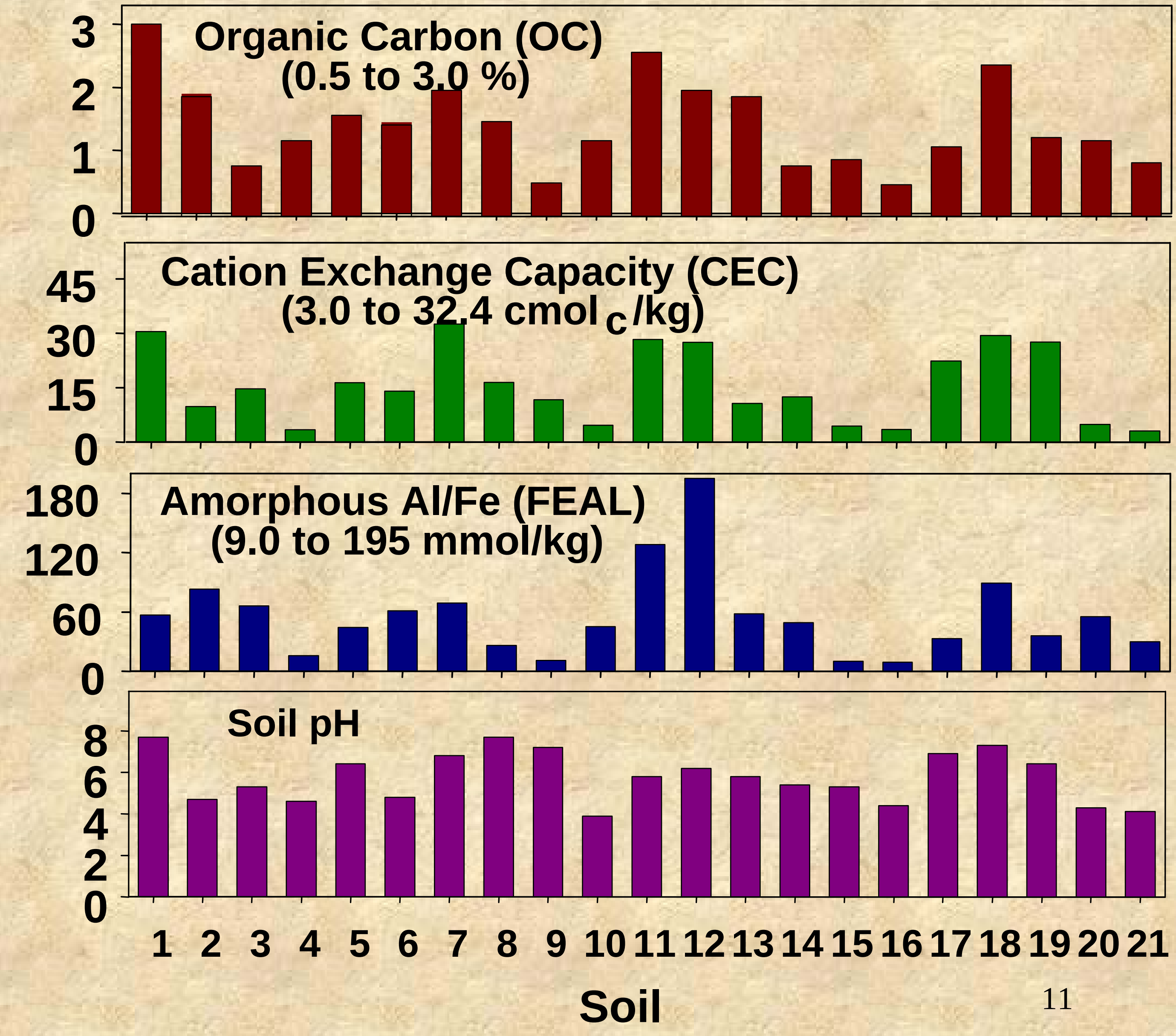
Endpoints Measured

•Tissue metal

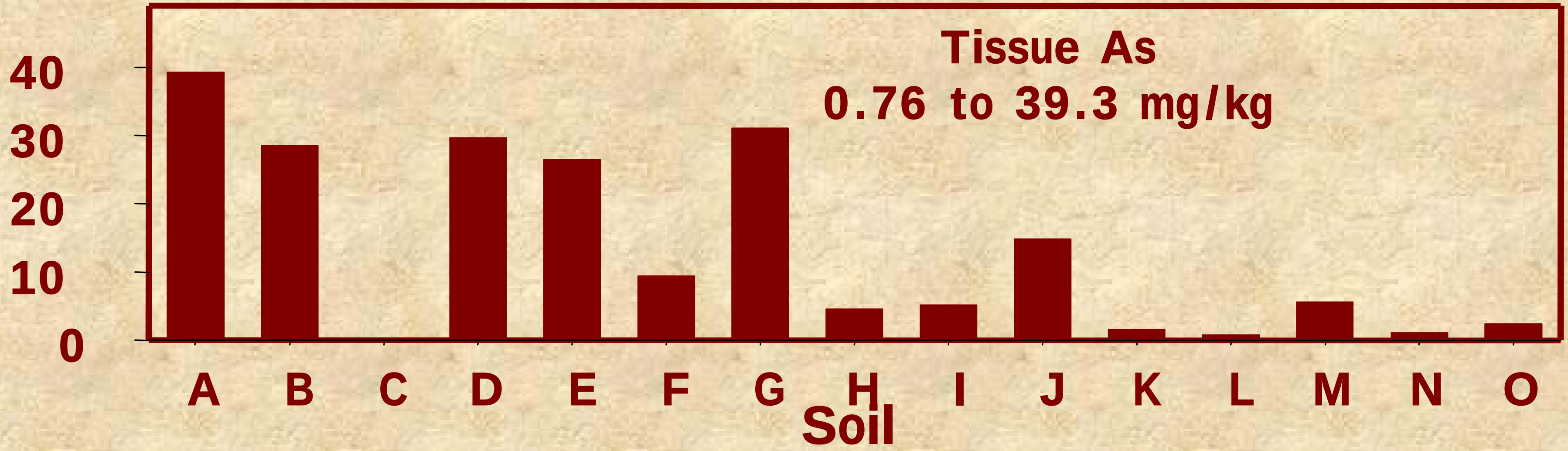
•Dry matter growth

Technology Maturity – CU-1210

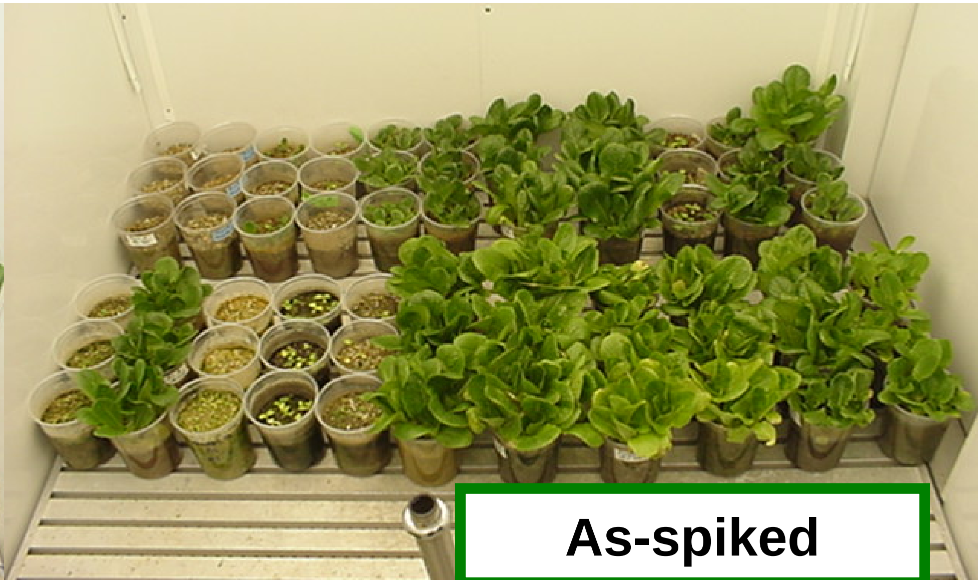
Range in soil Properties



Technology Maturity – CU-1210

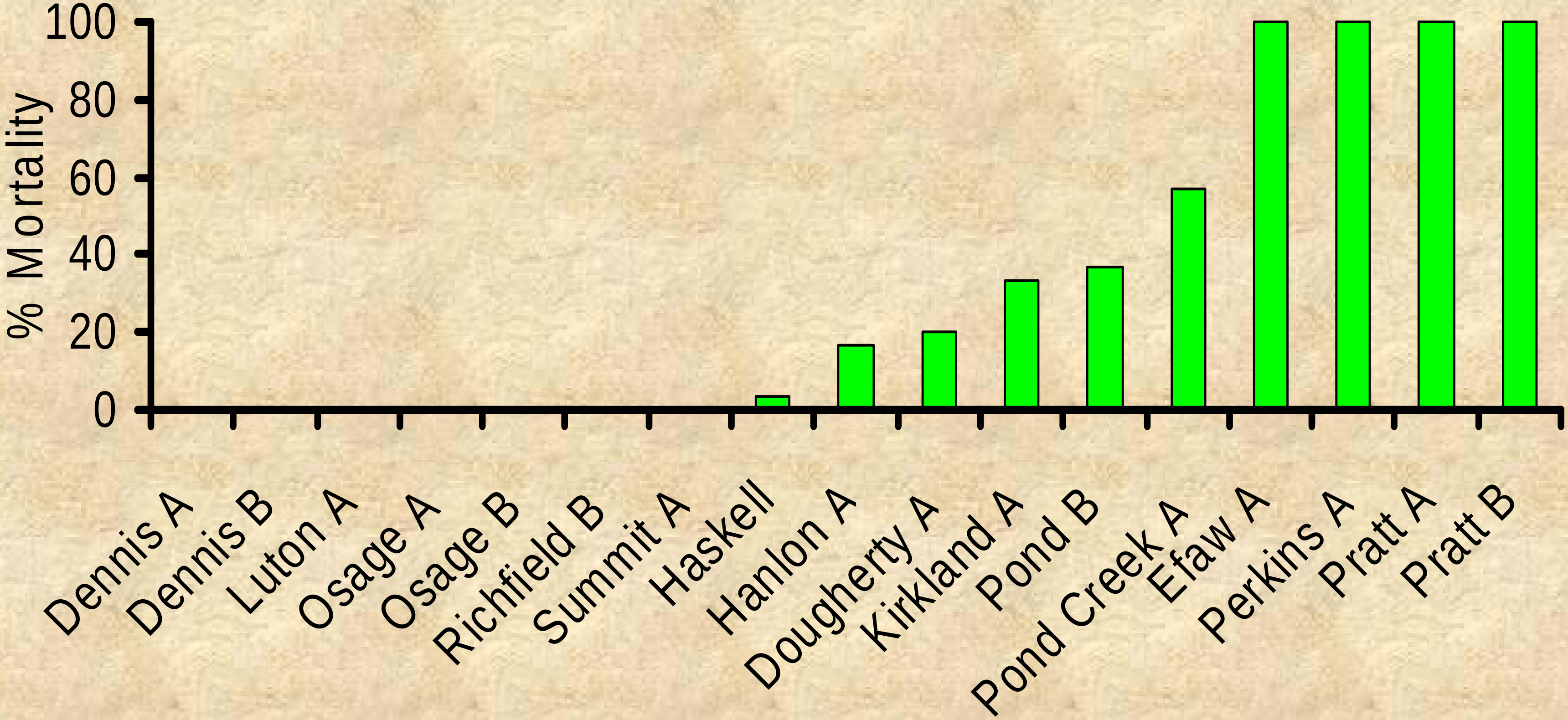


Results 250 mg As/kg



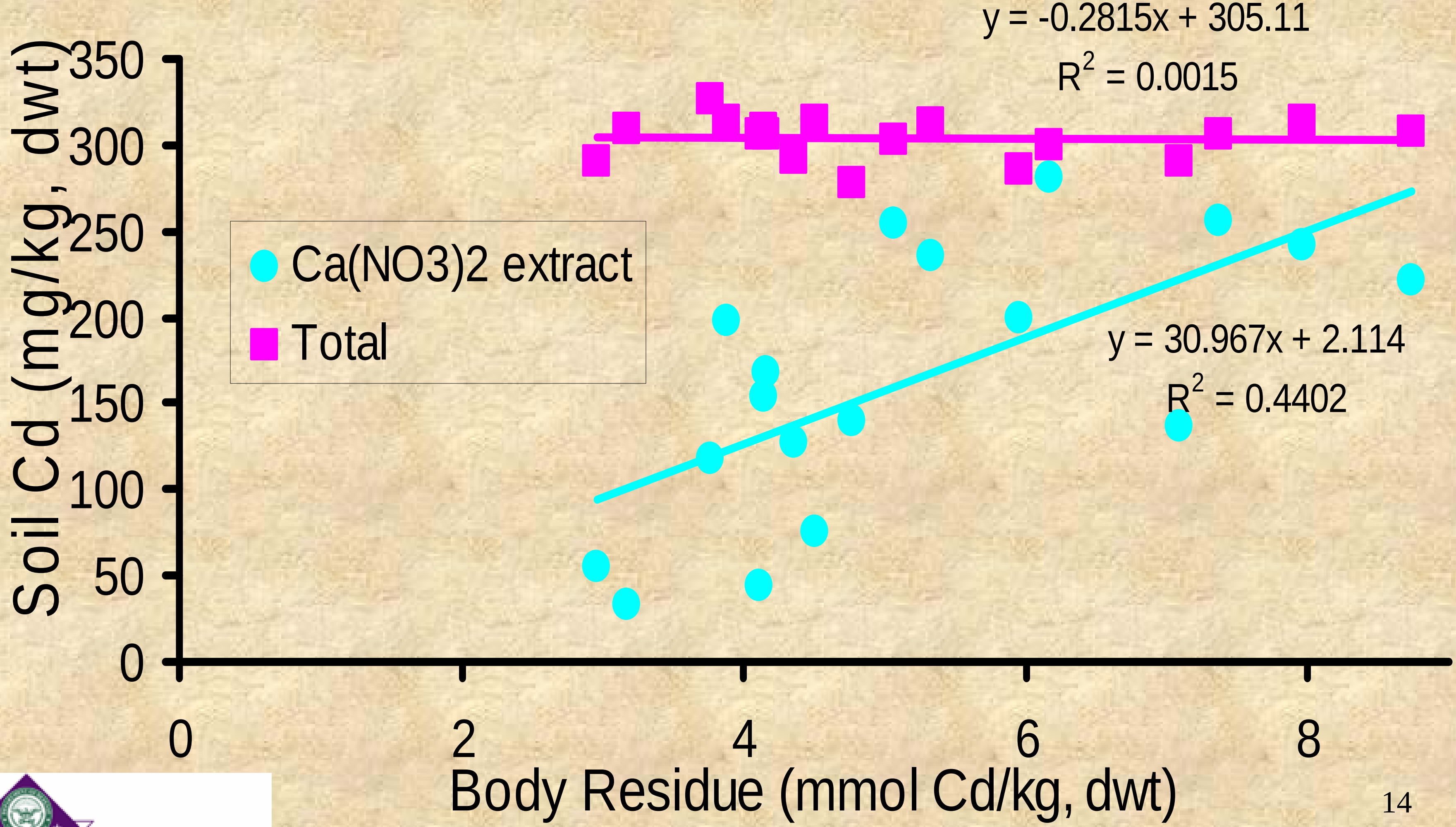
Technology Maturity – CU-1210

Earthworm mortality in soils differing in physical/chemical characteristics, BUT all spiked with Pb (2000 mg/kg)



Technical Maturity – CU-1210

Cd bioaccumulation in earthworms: Total soil Cd or $Ca(NO_3)_2$ extract



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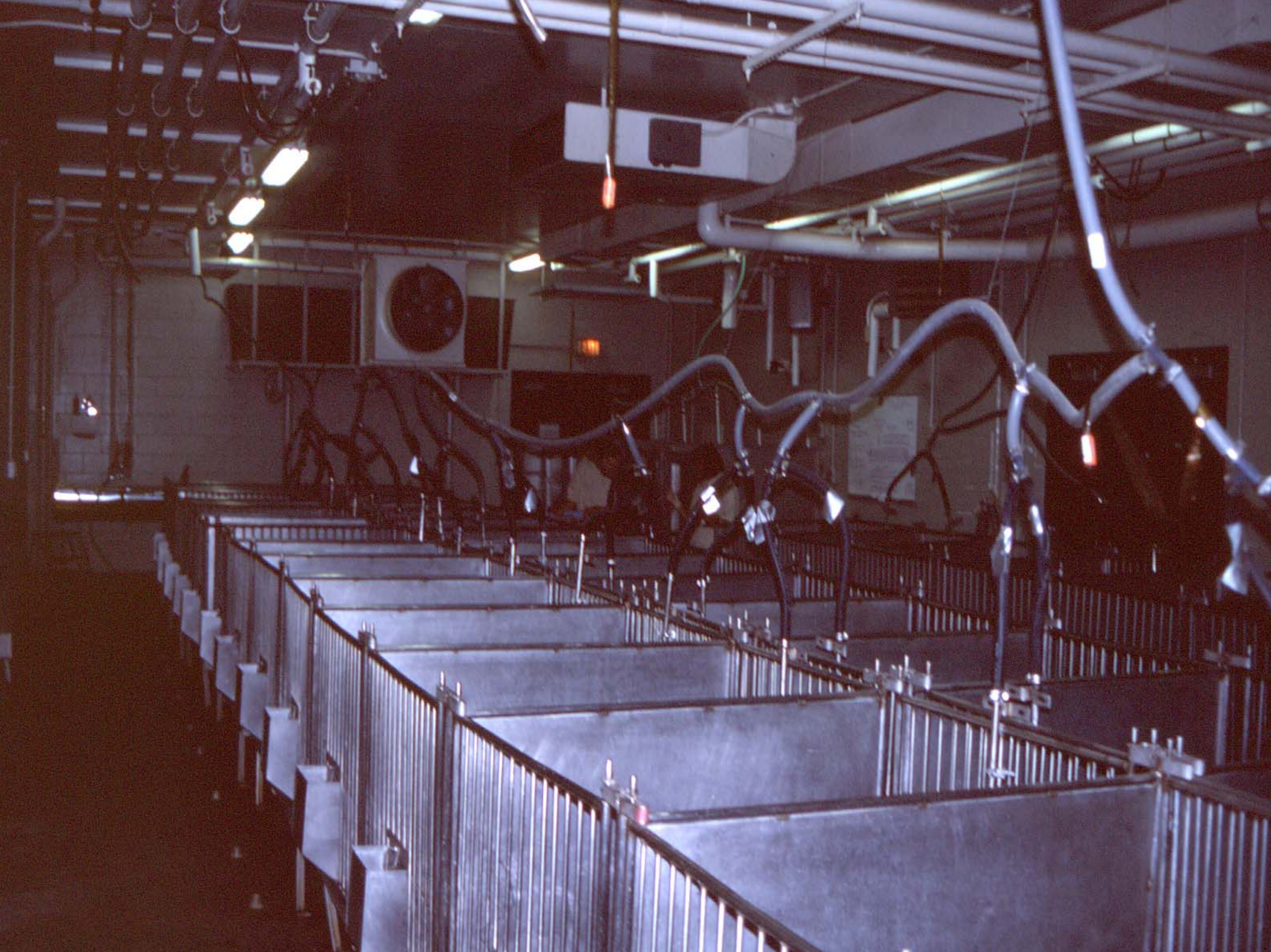
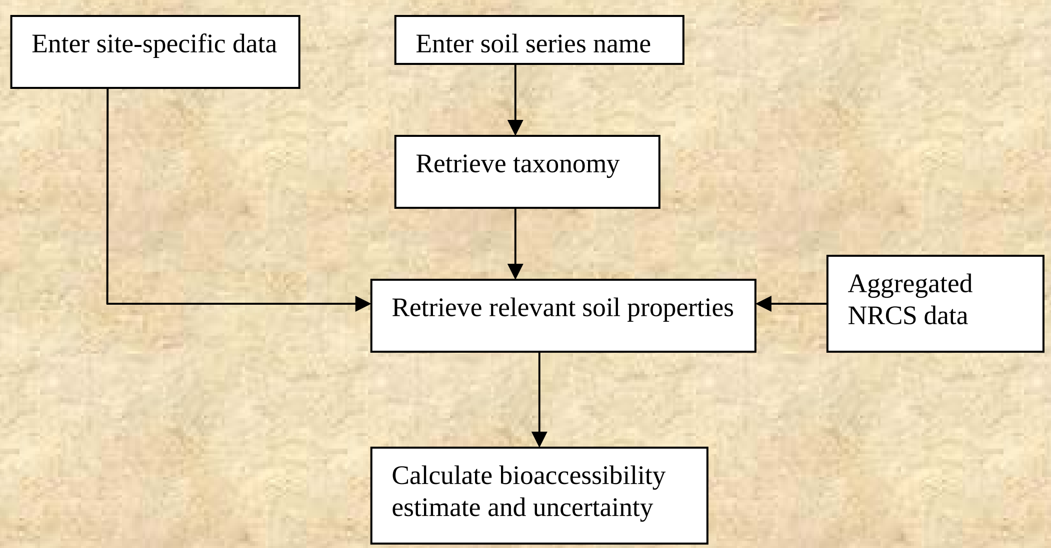
Technology Maturity – Swine Model

- Versatility--assess bioavailability of metals, inorganic, and organic compounds
- Surrogate for children, adults, and pregnant
  - Compare differences between ages & conditions
- Applicable to pharmaco-/toxicokinetic studies
- Identification of sites of accumulation
- Multiple responses to assess RBA
- Detection of untoward effects



Technology Maturity – SBAT

- Predictive model (SBAT) was developed under SERDP CU-1166 based on the correlation of soil physical and chemical properties with decreased metal bioaccessibility



	A	B	C	D	E	F
1	Bioaccessibility Tool:	Spreadsheet Application for Bioaccessibility Prediction				
2						
3	Series:	Allen		Great Group:	Paleudults	
4						
5	Estimated Parameters					
6						
7	Horizon:	A		B		
8		Value	Coverage	Value	Coverage	
9	Organic carbon					
10	(TOC) % weight	1.29	59.8	0.21	53.4	
11						
12	Carbonate content					
13	(TIC) % weight	0.192	12.2	0.004	9.7	
14						
15	Clay content					
16	% weight	11.7	62.9	34.6	56.6	
17						
18	Iron content					
19	% weight	0.863	52.6	2.245	46.7	
20						
21	pH					
22	SU	5.2	62.9	5.1	56.6	
23						
24	Site-Specific Parameters					
25						
26	Horizon:	A		B		
27	Organic carbon					
28	(TOC) % weight					
29						
30	Carbonate content					
31	(TIC) % weight					
32						
33	Clay content					
34	% weight					
35						
36	Iron content					
37	% weight					
38						
39	pH (SU)					
40						
41	Bioaccessibility Estimates					
42						
43		Bioaccessibility (%) for Horizon				
44	Metal	A		B		Parameters Used
45	Cr (III)	15.5		28.9		TOC Clay
46						
47	Cr (VI)	22.9		41.4		TOC pH
48						
49	As (V)	30.4		14.6		Iron pH
50						
51	As (III)	26.8		13.8		Iron pH
52						

Technology Maturity – PBET

- The *in vitro* bioaccessibility method Physiologically Based Extraction Test (PBET) has been shown to correlate with the *in vivo* method for As and Pb

Milestone I - Workshop

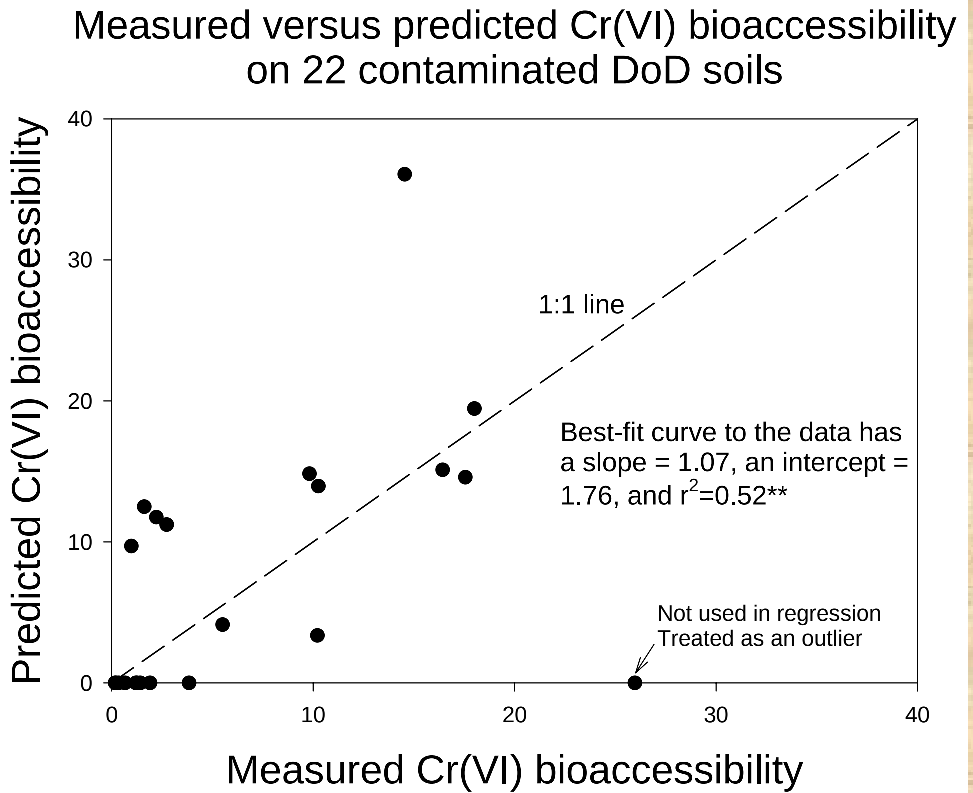
- 1 day workshop at project initiation
- State regulators, DoD end-users, EPA, federal agencies, scientists, and ITRC members
- Focus on past, current, and future research investigating soil metal bioavailability methodologies
- Focus on appropriate use of *in vitro* bioaccessibility to aid risk assessment
- Discuss end-user and regulatory needs for decision-making

Milestone II – Site Selection

- Ten soil sites will be used for ecological bioassay studies, one contaminated sample and one control sample will be taken from each site
- Four sites will be included in the *in vivo* swine dosing studies
- Site selection will be drawn from DoD sites including 40 soil sites previously studied under SERDP
- Focus on obtaining a variety of soil types
  - Sandy, high pH with limited capacity to sequester As, excellent capacity to sequester Pb and Cd
  - Silty, neutral pH soils with good to excellent capacity to sequester metals
  - Acidic, Fe-oxide rich soils with excellent capacity to sequester As, and potentially poor capacity to sequester Cd, Pb, and Cr

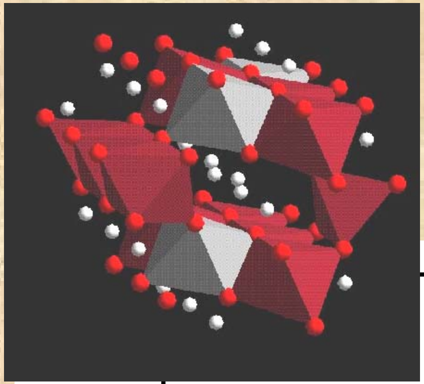
Milestone III – In Vitro Assessment and Soil Properties Modeling Comparison

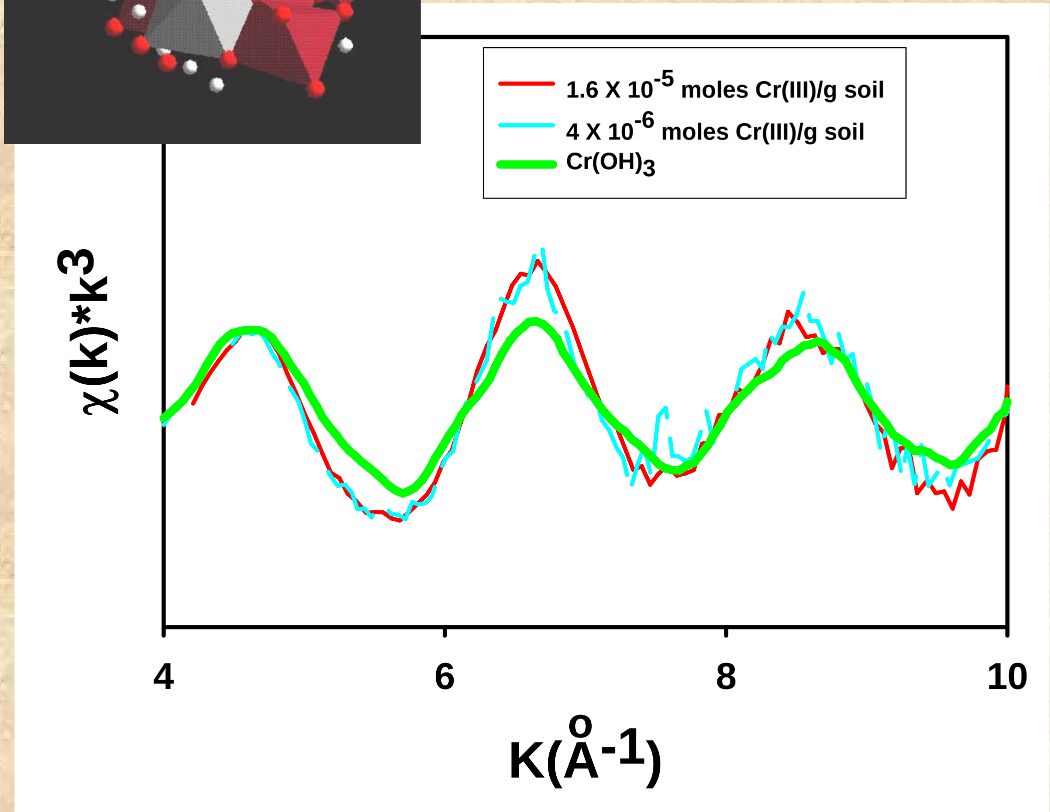
- Metal availability for plants and invertebrates modeled based on total metal levels and soil physical/chemical characteristics and measured using several wet chemical methods
  - Statistical relationships developed from a set of 26 soils (US EPA-NCEA, SERDP CU-1210) will be used for this estimate



Milestone III – In Vitro Assessment and Soil Properties Modeling Comparison

- Mechanisms of enhanced metal sequestration and solid-phase metal speciation will be quantified using a variety of high-resolution surface spectroscopy techniques





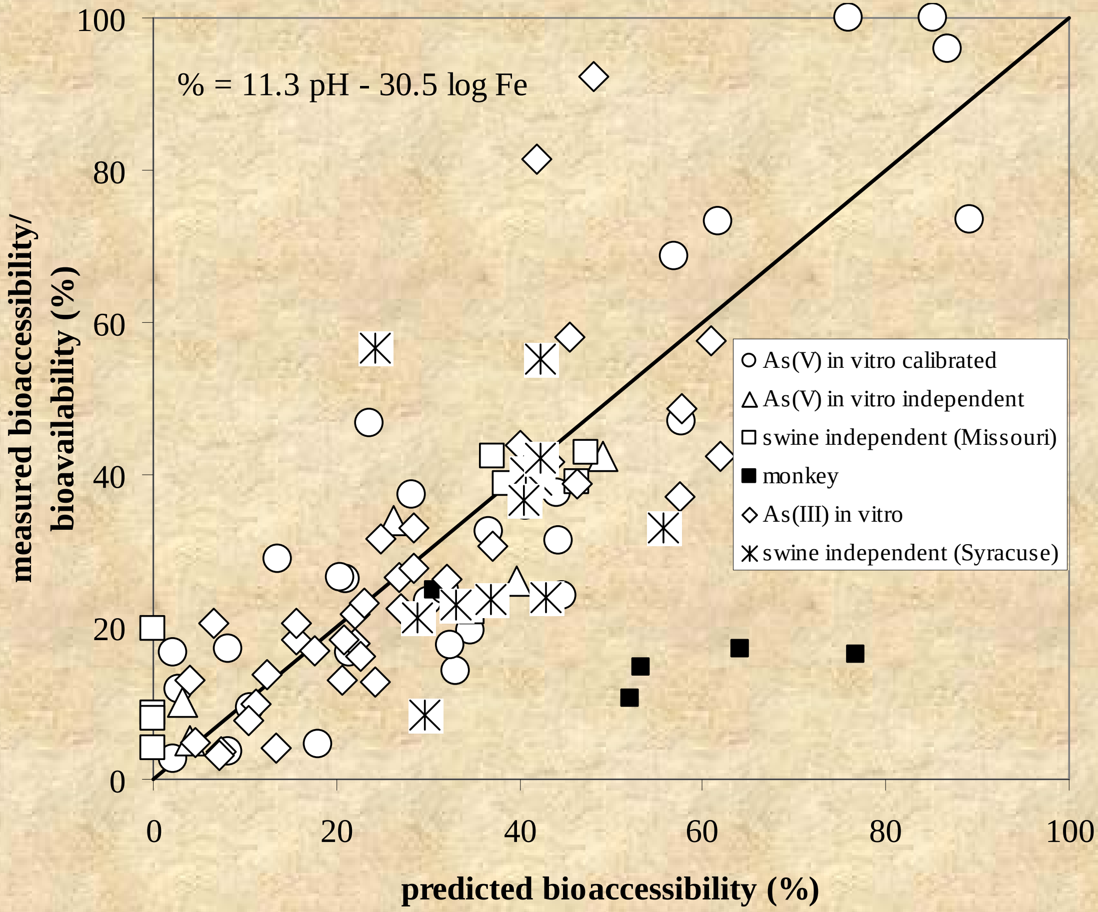
Milestone IV – In Vitro Assessment and In Vivo Assessment Comparison

- Ecological
  - Bioassays of earthworms and plants to determine metal toxicity
- Human Health
  - SOPs using the immature swine model will be followed to assess in vivo metal bioavailability
  - SOP has been used successfully to assess in vivo bioavailability of Pb and As

Milestone IV – In Vitro Assessment and In Vivo Assessment Comparison

- Hypothesis: Comparing *in vivo* and *in vitro* results and soil property-based models will show that uncertainty related to the use of models is acceptable

- Models can be used for initial estimates of toxic metal bioavailability



Summary

- Decreased bioavailability due to soil properties must be accounted for in human health and ecological risk assessment
- *In vitro* and modeling methods developed through SERDP require demonstration of their ability to justify *in vivo* studies moving away from 100% bioavailability
- Up front regulatory and end-user involvement will promote rapid and complete technology transfer