Toxicity of Metal-Contaminated Sediments to Benthic Invertebrates

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Department of the Interior
U. S. Geological Survey

Mining activities produce metal-contaminated sediments

- Metals enter aquatic ecosystems from mining, ore processing, and smelting.
- At neutral pH, metals tend to move from water to sediment:
  - settling of particulates (e.g. mine wastes);
  - precipitation of insoluble metal species;
  - sorption of metals on sediment particles.

➢ High concentrations of metals in bed sediments can lead to toxic effects on benthic organisms.

Applications of sediment toxicity testing

- Ecological risk assessment (e.g., Superfund)
- Document ecological injury (e.g., NRDAR)
- Pre- and post-remediation assessment
- Effluent monitoring/Toxicity Identification Evaluation
- Characterize waste or dredged material
- Establish or validate sediment quality guidelines

CERC mining-related sediment studies

Upper Columbia River (WA)

Clark Fork River (MT)

Whiskeytown NRA (CA)

San Carlos Reservoir (AZ)

Upper Animas River (CO)

Tri-State (MO/KS/OK)

Old Lead Belt (MO)

Viburnum Trend (MO)

Palmerton smelter (PA)

Vermont Copper Belt

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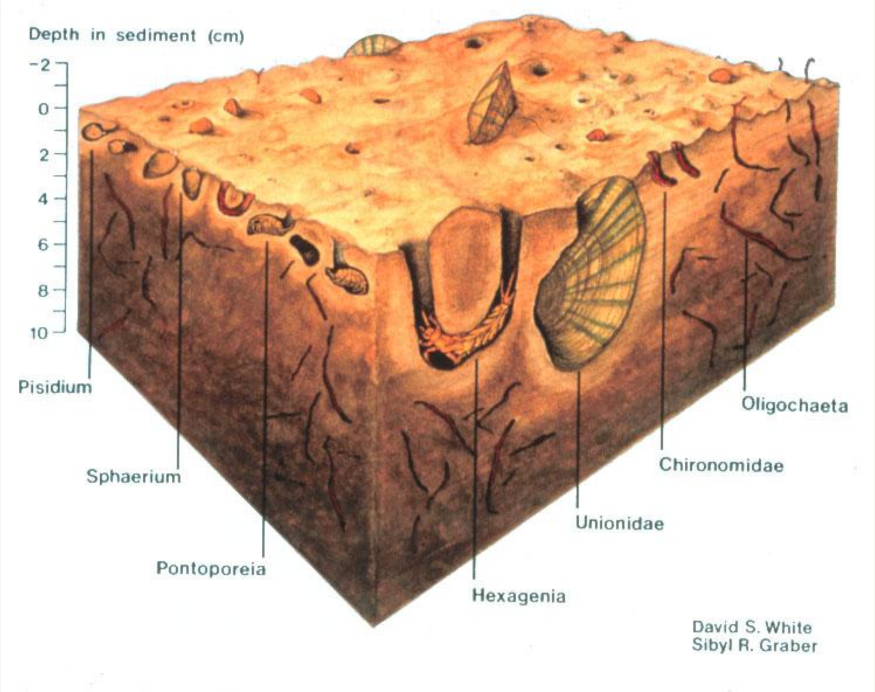
Types of sediment test methods

- **Whole-sediment toxicity testing**
  - Simulate natural water+sediment exposure
- **Pore-water toxicity testing**
  - Isolate water exposure route
- Elutriate testing (sediment-water suspension)
  - Effects of dredging or resuspension
- Sediment extracts or leachates
  - Source identification; prioritize cleanups

Whole-sediment testing



- Goal: simulate surficial sediments and overlying water
  - Allow development of limited depth gradient (3-4 cm)
  - Realistic role of overlying water (water quality, replacement rate)

Whole-sediment toxicity tests

- **Direct measure of effects on benthic organisms**
- **Support cause-effect findings**
- **Wide applicability**
- Limited special equipment is required
- Rapid and inexpensive
- Legal and scientific precedents
- Integrates interactions of contaminant mixtures
- Amenable to field validation

Pore-water testing

- Goal: isolate aqueous exposure route
  - **Use standard aquatic test organisms**
- Advantages:
  - Simplicity and sensitivity of test methods
  - **Compare aqueous vs. solid-phase exposure**
- Disadvantages
  - Difficulty of pore-water collection
  - Artifacts of testing with water-column organisms

Daphnid

Fathead Minnow

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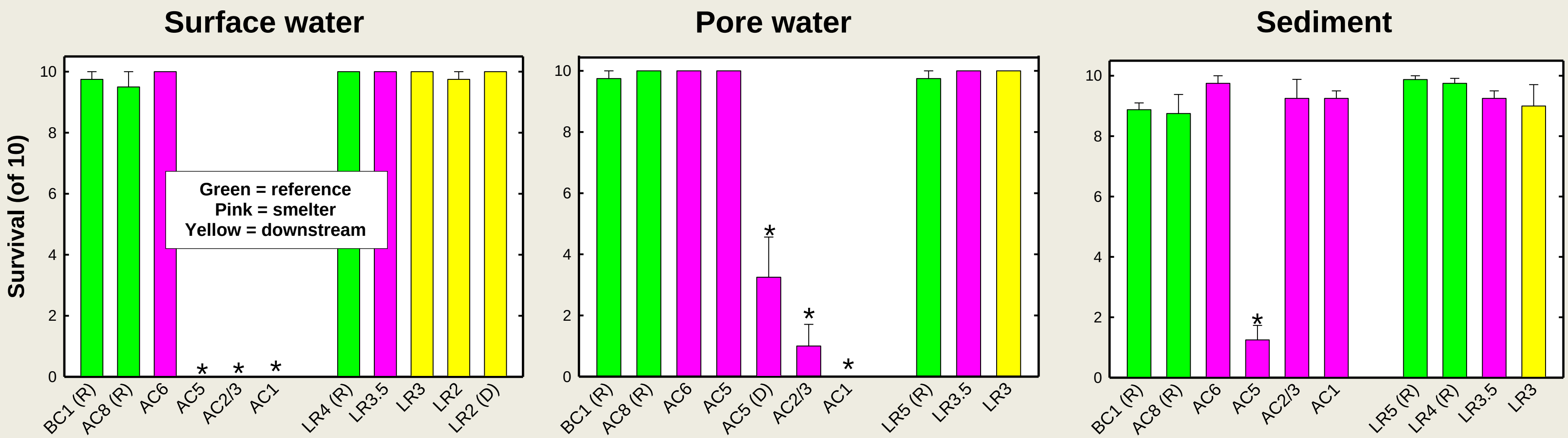
Comparison of exposure routes

Palmerton smelter, PA (Besser et al. 2009)



- Tested surface water, pore water, and sediment with *Hyalella*
- Toxicity in surface water and pore water from same three sites
- **Limited toxicity of whole sediment (one site)**
- Consistent with metal inputs from groundwater seepage
- Fine sediments scarce in contaminated stream reach

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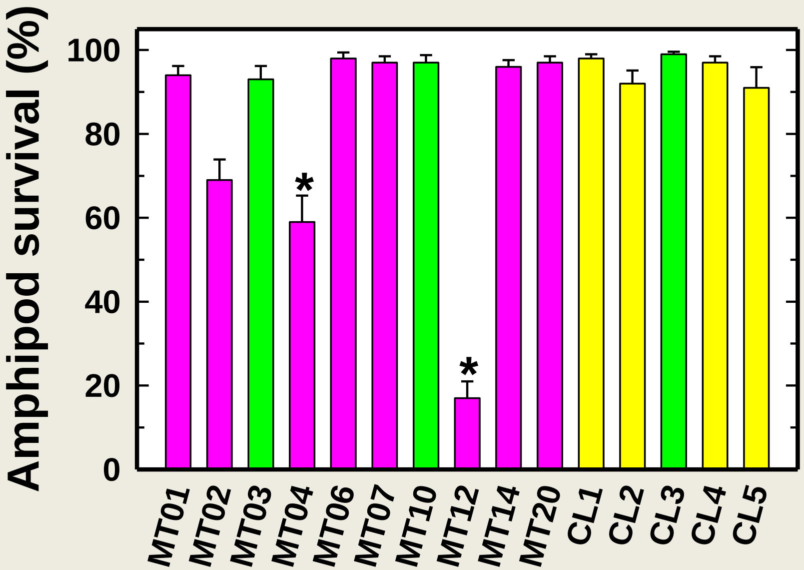
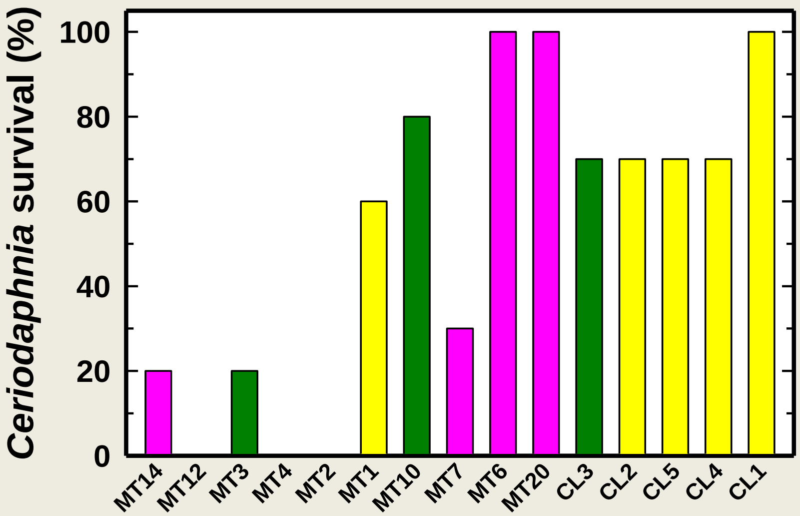
Hyalella

Sediment vs. Pore-water tests

Viburnum Trend MO (Besser et al 2008a)

Ceriodaphnia





- Whole-sediment tests with *Hyalella* (left) identified several toxic sites
- Pore-water tests with *Ceriodaphnia* (right) were more sensitive, but had variable survival in reference sites (green)
  - Limited tolerance for PW constituents (e.g. ammonia)

Characteristics of sediment test organisms

- **Sensitivity to toxicants (metals)**
- **Availability / Ease of culture**
- **Life cycle / Potential endpoints**
- Taxonomic group
- Distribution and abundance
- Ecological importance

Standard sediment test organisms

Amphipod *(Hyalella)*

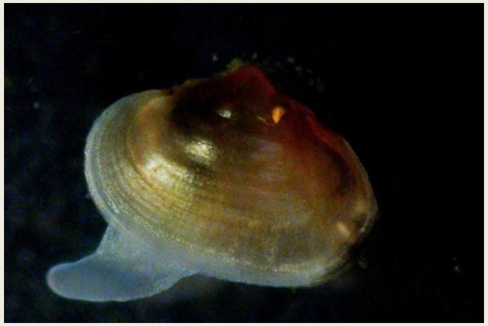
Midge *(Chironomus)*

***Oligochaete (Lumbriculus*)**

Alternative test organisms

Mayfly *(Hexagenia)*

Mussel *(Lampsilis)*



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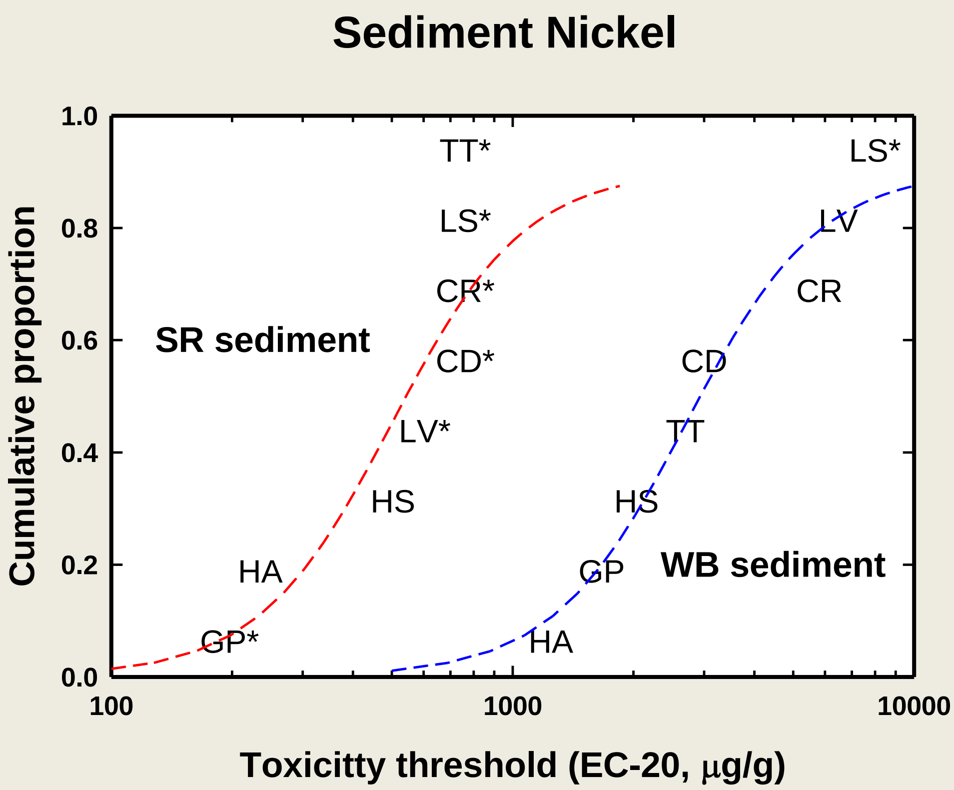
Sensitivity of benthic taxa to metals

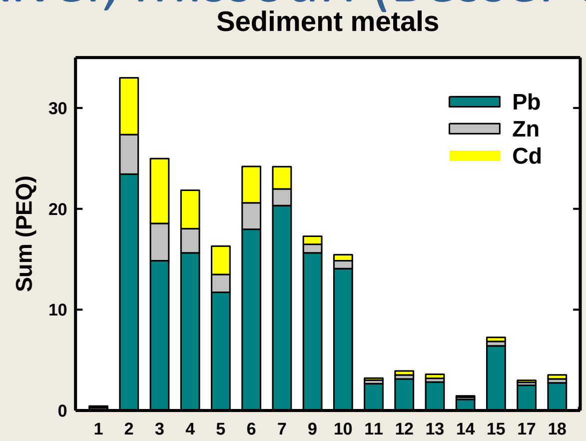
Ni-spiked sediment (Besser, unpublished data)



- Differences among species:
  - HA=*Hyalella (amphipod)*
  - GP=*Gammarus (amphipod)*
  - HS=*Hexagenia (mayfly)*
  - CD, CR=*Chironomus (midge)*
  - TT=*Tubifex (oligochaete)*
  - LV=*Lumbriculus (oligochaete)*
  - LS=*Lampsilis (mussel)*
- Sediment differences
  - ➢ Metal bioavailability

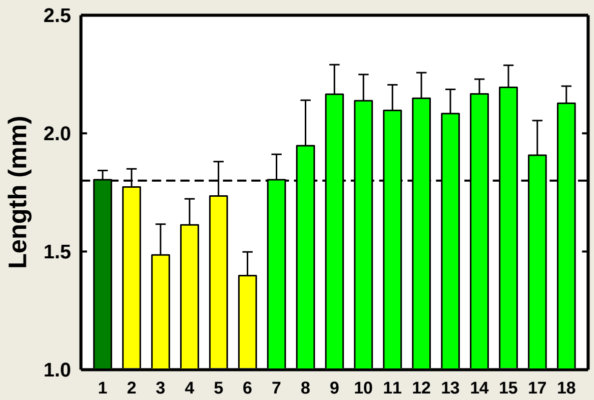
Differences in sensitivity

Big River, Missouri (Besser et al. 2010)

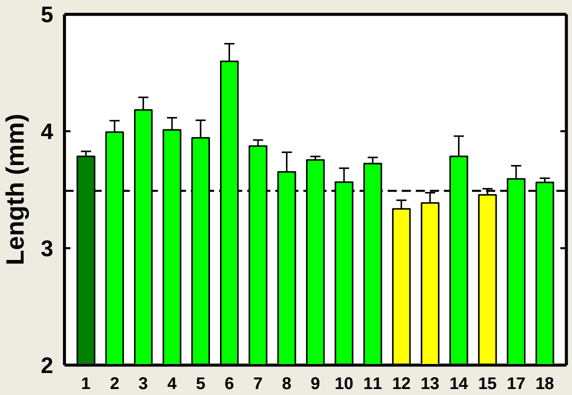


Mussel length

Lampsilis



Amphipod growth



Hyalella

- Toxicity to mussels was more closely associated with sediment metals.

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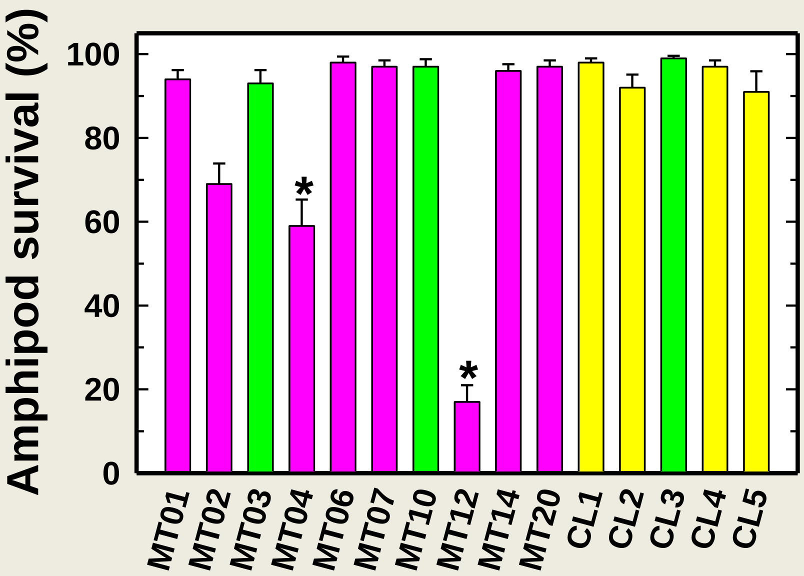
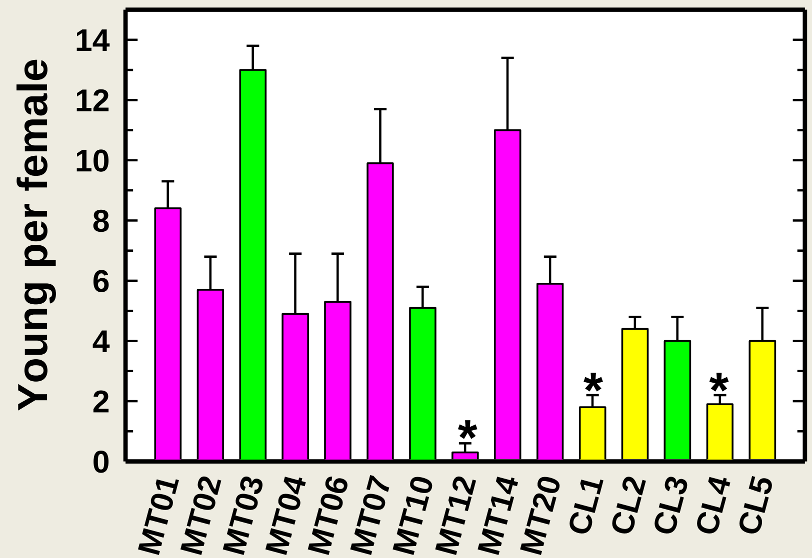
Test endpoints

- Survival
  - Severe effect; acute or chronic test
- Growth (length or weight)
  - Often more sensitive than survival
- Biomass production
  - Sensitive; integrates effects on survival and growth
- Reproduction
  - Sensitive but variable; long/complex test methods;
- Bioaccumulation
  - Document bioavailability; characterize dietary exposure of fishes

Hyalella survival and reproduction

Viburnum Trend, MO (Besser et al. 2008a)





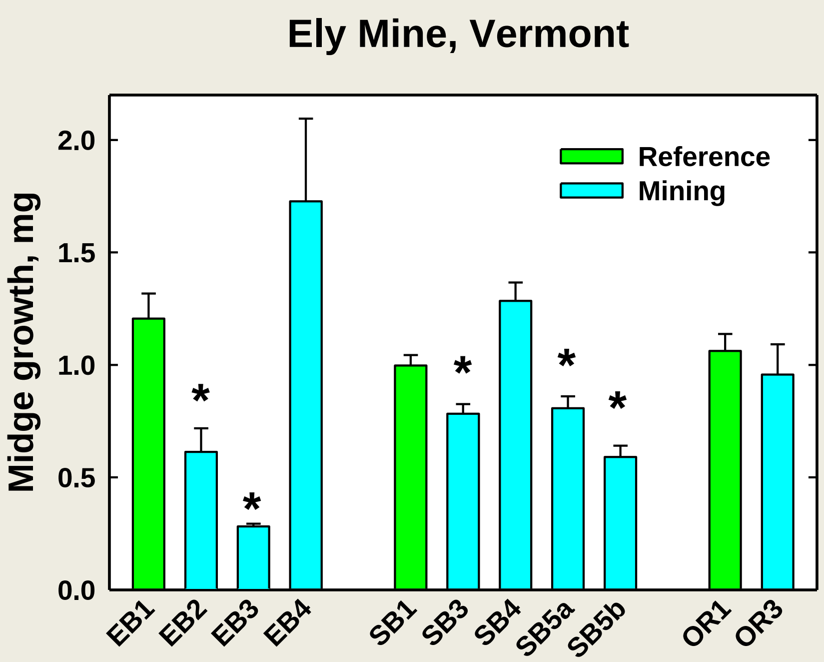
- Survival was high in reference sediments (green); few toxic sites
- Reproduction was sensitive, but varied among reference sites
  - Influence of nutrients, organic matter, etc.

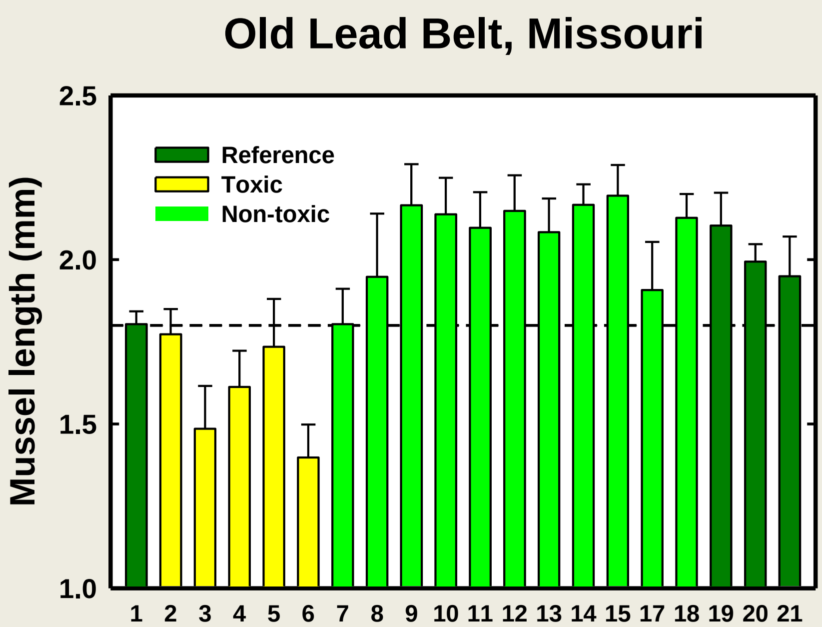
Interpretation of toxicity data

- **Control sediments** – define test performance
  - Quality assurance for studies with field-collected sediment
  - Treatment comparisons in experimental studies
- **Reference sediments** – define ‘baseline’ conditions
  - Single site for simple study area (e.g. upstream/downstream)
  - Multiple sites (‘reference envelope’) to represent broader area
- **Concentration-response** relationship
  - Experimental studies (e.g., spiking) or field data with gradient of metal concentrations
  - Estimate toxicity value (e.g., LC50, EC20)

Comparisons to reference site(s)

(Seal et al. 2010; Besser et al. 2010)





- Ely Mine, VT: upstream reference sites to match each stream segment
- Big River, MO: multiple reference sites (both upstream and regional)
  - Wide range of sediment type from headwaters to mouth

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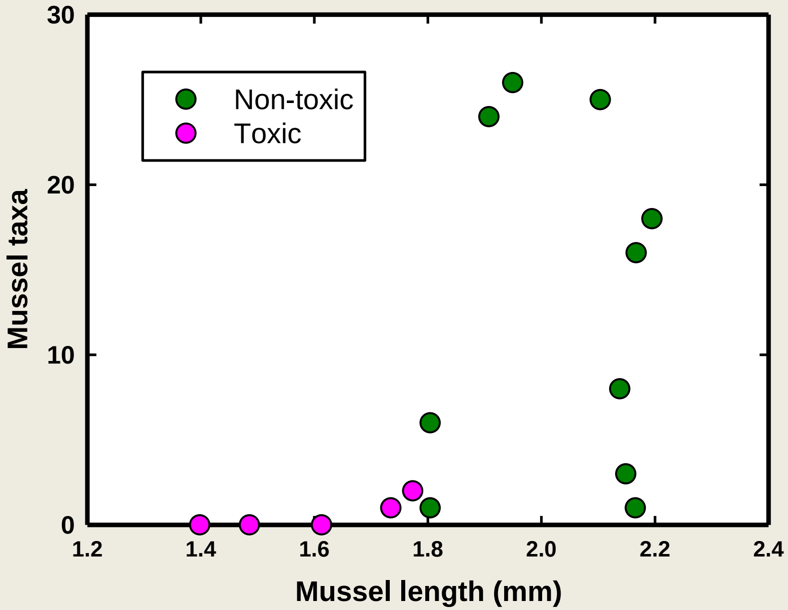
Laboratory-Field Comparisons

- Establish **cause-effect** relationships
  - Community data can be influenced by historic impacts (e.g. species loss) and habitat alteration
  - Lab tests use taxa of interest, minimize influence of habitat
- Estimate site-specific **toxicity thresholds**
  - Use of local species or surrogate
  - Simulate ambient water quality

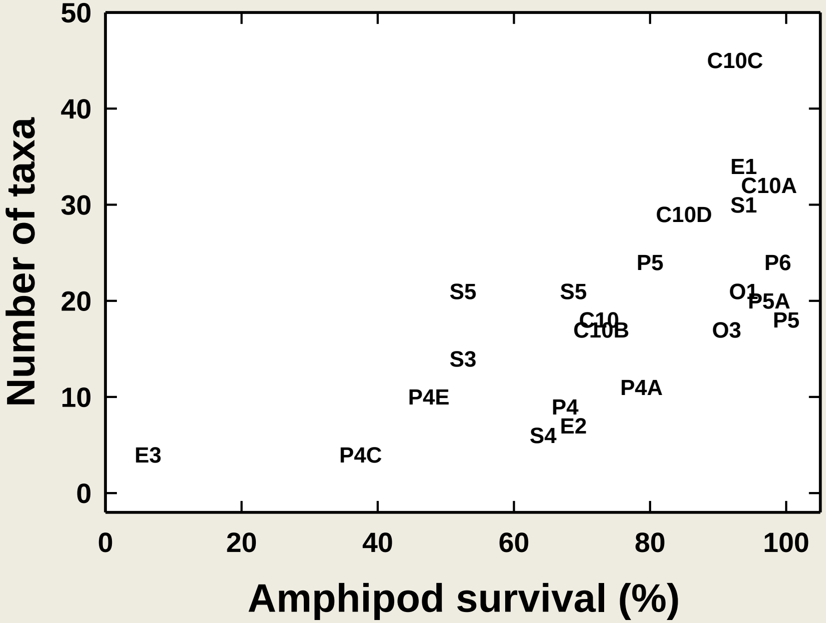
Laboratory vs. field responses

(Besser et al. 2010; Seal et al 2010, in press)

Old Lead Belt, Missouri



Vermont Copper Belt



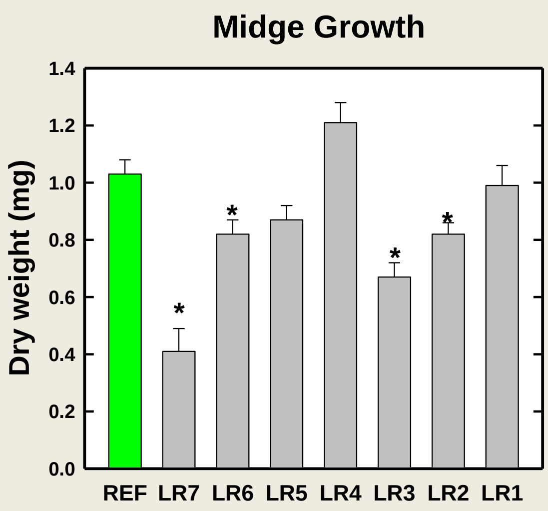
- Missouri: reduced mussel growth predicts community impacts
- Vermont streams: gradient of amphipod survival vs. benthos taxa richness
  - Acid sites (red): low taxa richness, but sediment not toxic

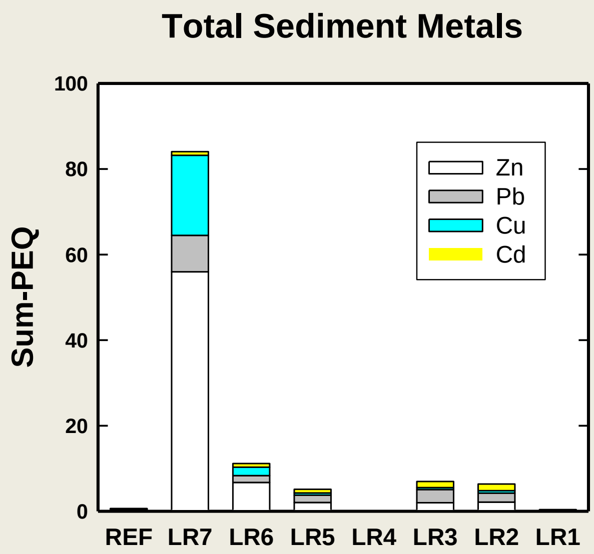
Metal bioavailability in sediment

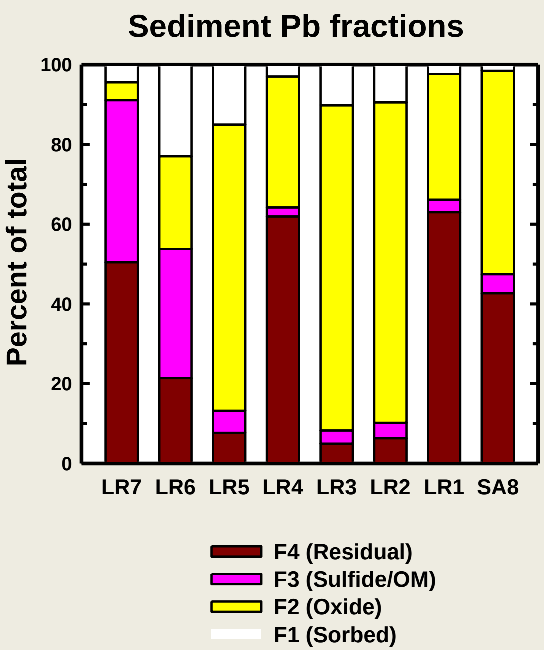
- Estimate **available metal fractions**
  - Selective extractions (e.g., Luoma 1989, Tessier et al. 1984)
- Characterize major **metal-binding phases**
  - Acid-volatile sulfide and total organic carbon (Ankley et al 1996; USEPA 2005)
  - AVS strongly limits metal solubility: Ag, Cu, Pb, Cd, Zn, Ni
  - TOC has weaker binding but high capacity; more stable
  - ➢ Allows **estimation of pore-water metals** (highly bioavailable)

Metal fractions and bioavailability

Lake Roosevelt, WA (Besser et al. 2008b; Paulson and Cox 2007)







- Upstream site (LR7) was most toxic and had greatest total metals
- Downstream toxic sites (LR3, LR2) had much lower total metals
  - Metals are in easily-extractable fractions (F1 and F2)

Metal bioavailability in pore water

- Measure **dissolved metal** concentrations
  - Field: Push-point (large volume) or airstone (small volume)
  - Lab: Centrifuge or pressure (large volume)
  - Lab or Field: Peeper (small volume)
- **Free or labile metal** fraction
  - Specialized samplers (e.g., DGT)
  - Geochemical modeling
  - Biotic ligand models (BLM): model metal binding to site of uptake

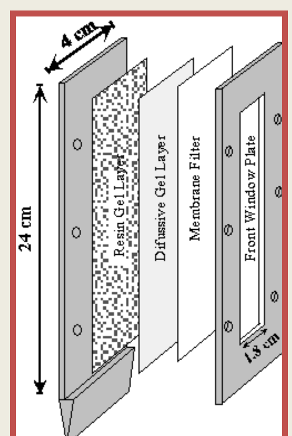
Pore-water sampling methods

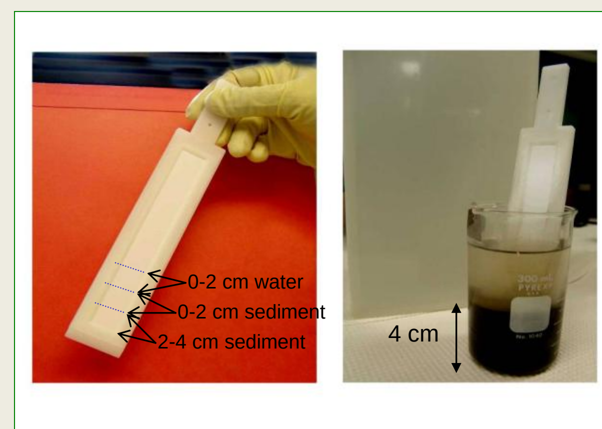
Push-point

Centrifuge

Peeper

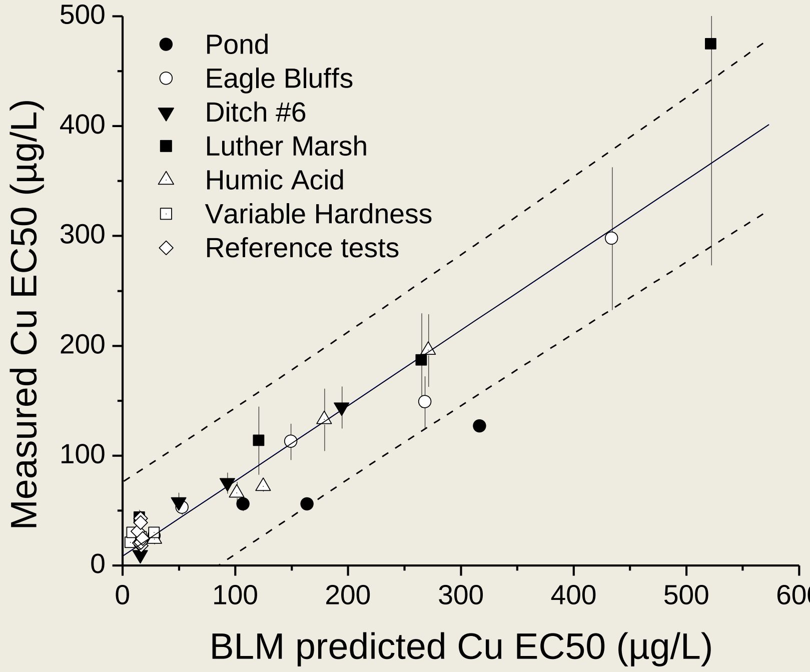
DGT (Zhang et al. 1995)





BLM models for pore water?

(Copper toxicity and DOC; Wang et al 2009)



- BLM predicts acute copper toxicity across wide range of water quality

➢ Few BLM studies with pore-water

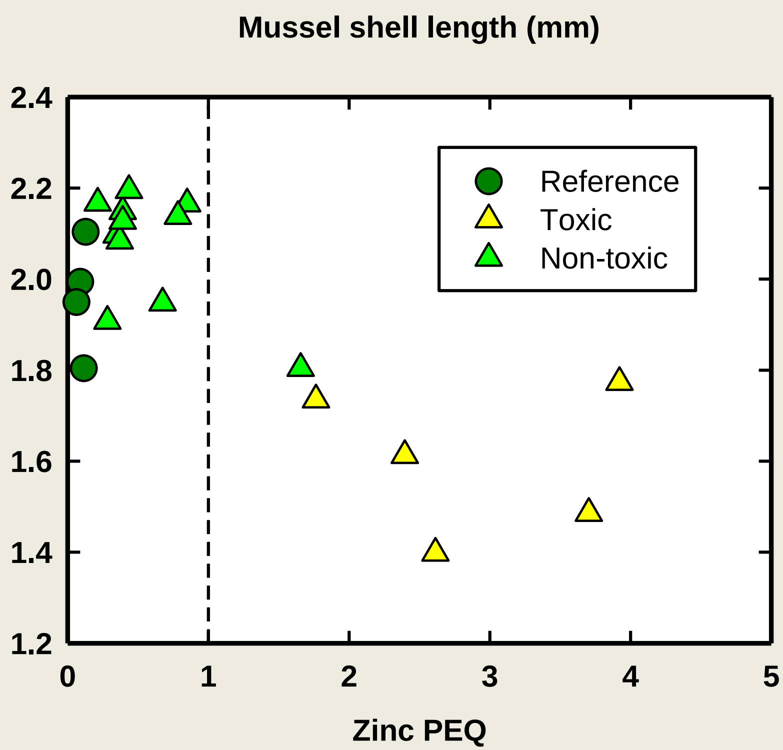
Sediment quality guidelines
(to protect benthic organisms)

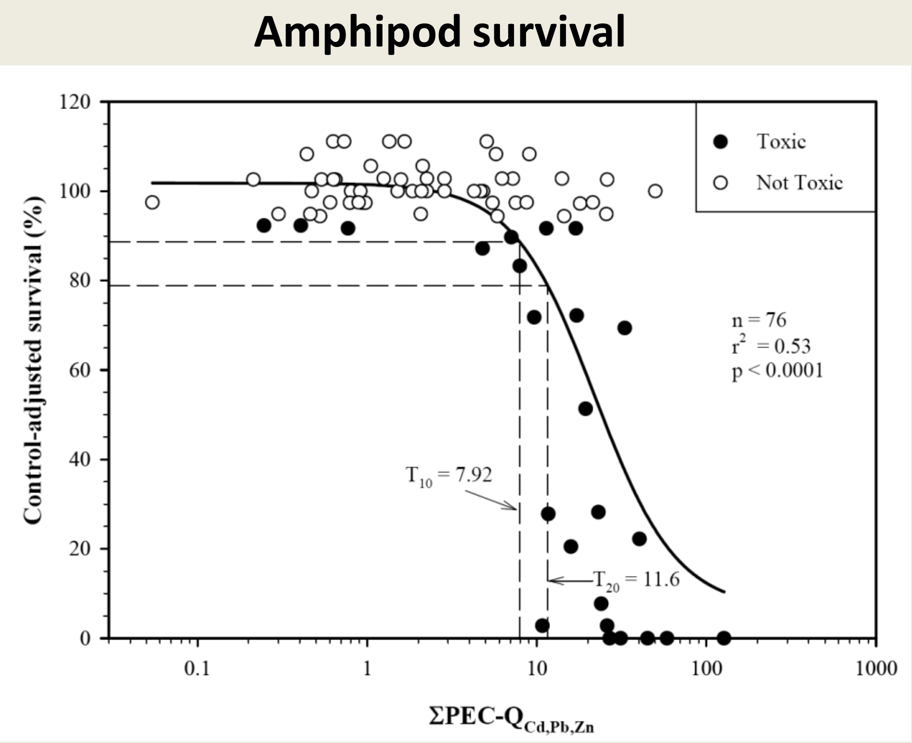
1. **Empirical SQGs** (MacDonald et al. 2000)
   - ➢ Based on frequency of toxicity in large datasets (sediments with multiple toxicants)

   – Probable Effect Concentration (PEC) is concentration associated with increased frequency of toxicity

   – PEC-Quotient = sediment metal concentration / PEC
     - Can sum PEC-Quotients to characterize metal mixtures

Application of PEC Quotients
(Besser et al. 2010; MacDonald et al 2009)





- Big River, MO (left): mussel toxicity at Zn-PEQ >1.0
- Tri-States (right): amphipod toxicity at Sum-PEQ near 10

Sedimentquality guidelines (continued)

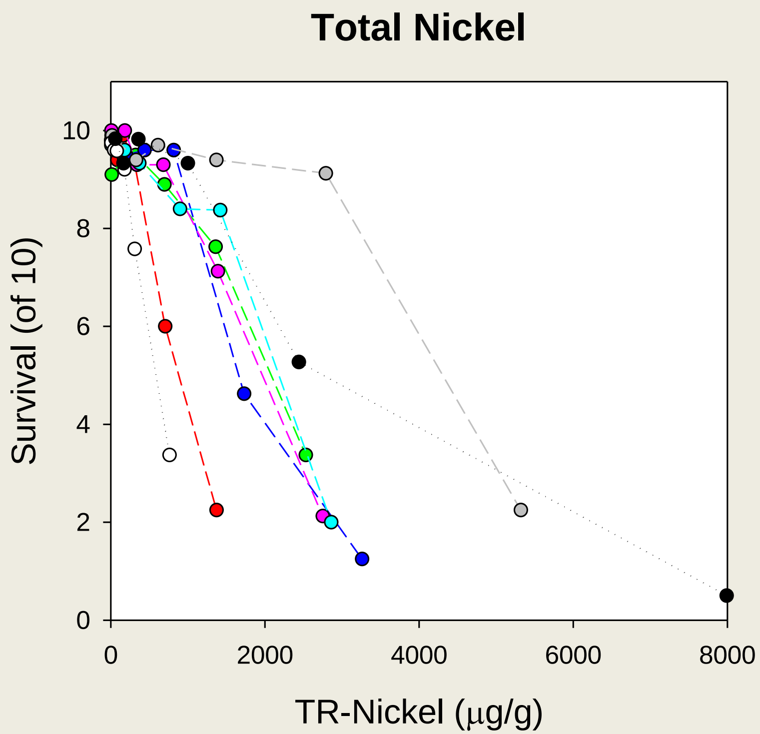
2. **Equilibrium Sediment Benchmarks** (ESBs; USEPA 2005)
   - Assumes pore water is primary exposure route

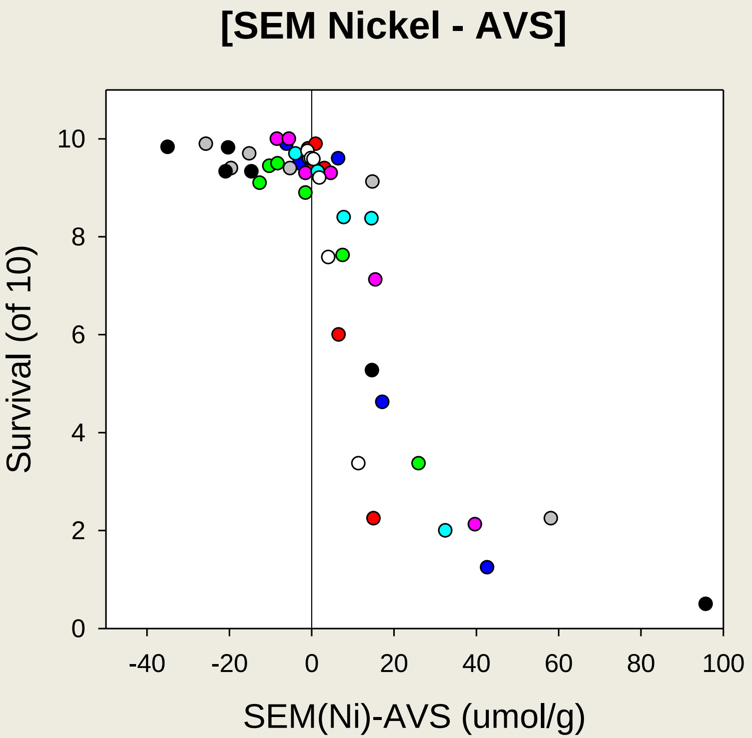
   – Normalize metals to acid-volatile sulfide (AVS):
     - No toxicity if simultaneously-extracted metals (SEM) > AVS
     - (SEM = sum of Ag, Cu, Pb, Cd, Zn, and Ni)

   – Then normalize to TOC: (SEM-AVS)/TOC
     - Range of uncertain toxicity = 130 to 3000 umol/g (USEPA 2005)

AVS normalization of nickel toxicity

Ni-spiked sediments (Besser, unpublished data)





- Wide range of toxicity (expressed as total Ni) among eight sediments
- Normalizing to [SEM-AVS] reduces variation among sediments

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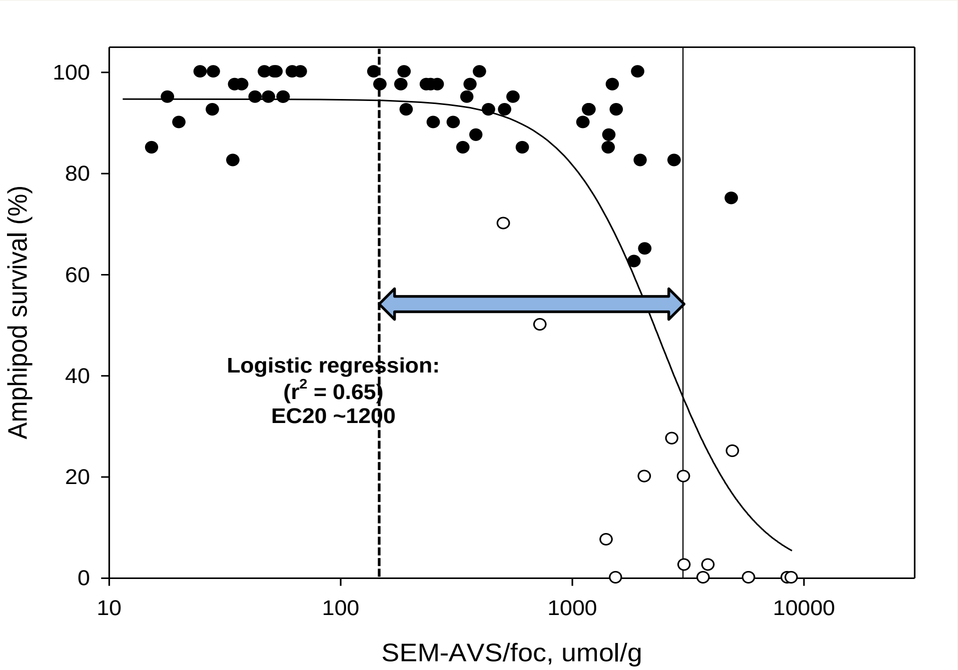
Application of sediment ESB

(Tri-State Mining District; MacDonald et al 2009)



- *Hyalella* survival corresponds to [(SEM-AVS)/TOC]:
  - Narrower range of uncertainty (low AVS, low TOC)

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Take-home points

- Sediment toxicity testing has many applications.
- Whole-sediment tests are realistic and broadly applicable.
- Test with multiple species and endpoints.
- Select of appropriate reference site(s).
- Validate toxicity vs. evidence of community impacts.
- Characterize controls on metal bioavailability.