Toxicity of Metal-Contaminated Sediments to Benthic Invertebrates

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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
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
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
Sediment vs. Pore-water tests
Viburnum Trend MO (Besser et al 2008a)

- 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*)
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)

- Toxicty to mussels was more closely associated with sediment metals.
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
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)

- 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
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: \((\text{SEM}-\text{AVS})/\text{TOC}\)
  - 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
Application of sediment ESB
(Tri-State Mining District; MacDonald et al 2009)

- *Hyalella* survival corresponds to \[\frac{\text{SEM-AVS}}{\text{TOC}}\]:
  - Narrower range of uncertainty (low AVS, low TOC)
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.