Classes of Pollutant (Metals)

Aquatic Ecotoxicology

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Assessing the Effects of Metals

- Public Awareness
  - Manufacture and use lead to releases
    - They’re mined, not grown
  - Potential for adverse effects has lead to regulatory controls
  - Regulating releases is complex

Assessing the Effects of Metals

Risk Assessment

- How much discharged
- Dilution effect
- Concentration of toxic effects
- Concentration of safe levels
- Probability effects will occur

Assessing the Effects of Metals

Non-point and Natural Sources

- Erosion and runoff of metal bearing minerals and soils
- Building and construction materials
- Automotive parts
- Domestic products
- Burning of fossil fuels
- Body wastes (2 mg Cu/person/day)

Assessing the Effects of Metals

Analytical Complexity

- Analytical targets
  - Parts per million (mg/L)
  - Parts per billion (ug/L)
  - Parts per trillion (ng/L)
- Requires specialized techniques
- Must measure in presence of many natural and synthetic chemicals
- Expensive
- Full site characterization may be > $100,000
- A better method is needed

Assessing the Effects of Metals

Scientific Advances (20 years of building)

- Better descriptions of metal behavior in water
- Behavior is more predictable even under changing water conditions
- Understanding metal behavior in soils and sediments

Key Terminology

- Bioavailability
  - The degree to which the toxic species of a metal is available to interact with the biotic ligand to exert its toxic effect

Key Terminology

Mode of Action

- Copper and possibly other metals bind to specific active sites (w/in chloride cells) on the gill membrane
- Copper interacts w/ specific enzymes that regulate sodium and chloride levels in the organism
- Sodium uptake is inhibited and thus the organism suffers ionic imbalance and dies

Key Terminology

Ligands

- Chemical structures that bind with another chemical or metal
- Ligands in water
  - Organic
    - Dissolved organic carbon
      - Humic and fulvic acids
  - Inorganic
    - Carbonates
    - Hydroxides
  - Biological ligands
    - Gill membranes

Key Terminology

Metal speciation

- Metals are found in different forms in the environment
- These are referred to as metal “species”
- Changing in the environment is called “speciation” or “transformation”
- Important point: Not all metal species are toxic

Assessing the Effects of Metals

Metal complexation

- Metals can form complexes with dissolved organic carbon in the environment
- Metals can also adsorb to the surface of suspended organic carbon
- Metals can also adsorb to the surface of minerals
- Each process may detoxify metals

Assessing the Effects of Metals

Metal toxicity testing

- Determining the toxicity of a metal
- Standard methods exist to determine toxicity
- The bench-mark acute test is called an LC50
  - Concentration that kills 50% of the exposed population
  - Fish, invertebrates
  - Small number of organisms
  - Exposed to increasing concentrations of chemical
  - Chemical added to clean lab water

Assessing the Effects of Metals

Metal toxicity testing

- Lab control water differ from natural waters
- Test methods essentially measure metal ion toxicity (the most toxic form)
- If compared to “total metal” concentrations in natural systems, toxicity is often overestimated
  - Total metal = dissolved + sorbed metal
  - Dissolved metal = ionic + other species & complexes
- Often in natural waters only small ionic fraction
- Essential to know concentration, complexation and competition in the system in question

Assessing the Effects of Metals

History of Metal Water Qualtiy Criteria

- Development of US EPA Water Quality Criteria (WQC) had evolved with our understanding of how aquatic chemistry effects metal toxicity
- Initially the total extractable metal concentrations were compared with criteria
- The criteria were developed primarily using data for metal ions
- Many aquatic sites exceeded the criteria

Assessing the Effects of Metals

History of metal water quality criteria

- Site specific investigation often showed no effects on resident populations
- Something prevented toxicity
- Research showed metal toxicity was decreased by increasing water hardness and increasing water pH
- Criterion was adjusted to consider site specific water hardness

Assessing the Effects of Metals

History of metal water quality criteria

- Toxicity was still over predicted at some sites
- Research showed metal toxicity was decreased by increasing particulate matter
- Criteria adjusted to apply to the “dissolved” rather than “total” metal fraction
- Evidence that toxicity is still over estimated
- Thus, confounding factors still exist

Assessing the Effects of Metals

The Biotic Ligand Model

- Other confounding factors identified
- This model developed to better estimate metal toxicity
- Calculates site specific bioavailability of metals
- Focused mostly on copper and silver
- Cd, Pb, Ni, and Zn underway

Assessing the Effects of Metals

Effect of Ligands and Hardness

- Organic ligands in water
  - Complex metals thus unable to enter chloride cells
  - Binding strength of metal
    - Dissolved organic carbon > gill
- Inorganic ligands
  - Inhibited from entering chloride cells
- Water hardness
  - Calcium competes from same sites in chloride cells

The biotic ligand model calculations

- Model assumes a fixed amount of metal bound to the physiologically active gill sites causes toxicity
- Amount of metal in the water must exceed the combined capability of:
  - Dissolved organic carbon to bind the metal
  - Calcium to out-compete metal binding active sites
  - Water chemistry to transform metal to non-toxic form
  - Mineral particles to incorporate metal in matrix

The biotic ligand model calculations

- Each process affects metal bioavailability
- The Biotic Ligand Model calculates the bioavailable fraction of the metal at the gill
- Can be used over a broad range of water conditions

Applicable organisms

- Toxic mechanisms appear to be the same for a variety of organisms
- Similar mechanisms control bioavailability
- Freshwater
  - Fish
  - Invertebrates (Daphnids)
- Estuarine
  - Bivalves (*Mytilus*)

Biotic Ligand Model

- Gill is not necessarily where toxicity exerted
- Site of action may occur elsewhere
  - Biotic Ligand Model rather than
  - *Gill Model*

USEPA Site-specific WQC Methods

- Three methods are available for use
  - Recalculation procedure
  - Water Effects Ratio (WER) procedure
  - Resident species procedure