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Case Study - Deriving Site-Specific Water Quality Criteria and Safe Thresholds for Metals Based on Bioavailability to Aquatic Organisms

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Problem Statement: The total concentration (or the acid-recoverable concentration) of a metal in surface waters has historically been the easiest form to measure reliably and repeatably in aquatic environments. However, since the 1990s, total metal concentrations in surface waters have proven to be very poor predictors of potential toxicity to aquatic organisms, and thus are not useful for either developing, or comparing to water quality criteria.

Scientific Issues: The potential toxicity of metal in surface waters to an organism is controlled by a number of processes: the concentration of free metal ions dissolved in the water; the complexation of some fraction of these free metal ions to natural binding agents in the water (e.g., natural organic matter); and, in the organism, the competition of other natural constituents (cations from Hardness (e.g., calcium) and acidity (hydrogen ion) for binding sites, on gills and other metal binding sites ("biotic ligand" sites on the organism). The fraction of the total metal in the water that actually can bind to these "biotic ligand" sites is the bioavailable fraction of metal. The bioavailable fraction of a metal to an organism (and the associated risk of toxicity) depends heavily on both the surface water's natural chemistry, and the different sensitivities of the organisms in the water. The metal's bioavailability and organism sensitivity are typically measured in controlled laboratory tests in standard water chemistries, also tested in a range of water chemistries representing the range of local water types in an area (a country, for instance), and most recently, predicted with well-validated chemical speciation and organism binding models, like “biotic ligand models” or BLMs, that can be used to establish locally-protective water quality criteria, or to conduct local risk assessments for aquatic communities.

Current risk assessment: Safe thresholds for metals have traditionally been set to protect the most sensitive organisms, using tests in standard laboratory waters that maximize the bioavailability of the metals. These safe thresholds are then used to set country-wide water quality criteria, and as No-Effect Concentrations used for comparison to ambient metal concentrations, for risk assessments. These single-value safe thresholds are conservatively protective, but are usually grossly overprotective for areas where local water chemistries reduce metal bioavailabilities. Further, metals are naturally found everywhere in natural waters, and some of these single-value safe thresholds may be at or below natural metal concentrations. Thus, this conservative approach of comparison of local measurements to a single threshold may erroneously indicate the need for risk management, when in fact thee local metal background, plus any other added metal, may be below a local safe threshold determined by considering bioavailability factors.

Approaches in the US (and US States), Australia/New Zealand, and the European Union (and its Member States) have been evolving since the 1990s to use stepwise tiered approaches, beginning with comparison of measured total metal concentrations in a water body and comparison to a single-value conservative National criteria, then if needed, comparison of the dissolved fraction of metal to the National criteria, then if needed, measurement or prediction of the bioavailable fraction of metal in the water and comparison to an estimate of the bioavailable safe metal threshold.

Discussion questions:

1. What are the challenges to shift from total metal concentration to addressing bioavailability of metals in aquatic criteria?

2. Are the tiered approaches presented a process to develop improved methods for metal criteria?

Example: comparison of the tiered approaches being adopted in the US, Australia, and the European Union:

Step	**US Approach (US EPA guidance)**	**Australia-New Zealand Approach**	**European Union Approach**
Step 1	Identify goals for protection	Identify goals for protection	Identify goals for protection
Step 2	Identify waters, and design sampling plan including total metals, dissolved metals, natural water chemistry (Hardness, pH, NOM/DOC, ...)	Identify waters, and design sampling plan including total metals, dissolved metals, natural water chemistry (Hardness, pH, NOM/DOC, ...)	Identify waters, and design sampling plan including total metals, dissolved metals, natural water chemistry (Hardness, pH, NOM/DOC, ...)
Step 3	Identify conservative (national) Water Quality Criteria (WQCs), for metals: criteria adjusted by water Hardness)	Identify conservative (national) Water Quality Guidelines (WQGs), for metals: criteria adjusted by water Hardness	Identify/develop generic Environmental Quality Standard (EQS), based on bioavailability in sensitive waters
Step 4	Compare measurement(s) of Total Metal to WQC (abandoned by EPA in 1993; replaced by Step 5)	Compare measurement(s) of Total Metal to Hardness-adjusted WQG	
Step	If exceeded, compare	If exceeded, compare	Compare dissolved

5	dissolved metal to WQC	dissolved metal to WQG	metal to Generic EQS (bioavailable)
Step 6	• If exceeded, determine local safe threshold based on site-specific toxicity estimate(s): • Use sensitivity of local (not national) species (EPA "Recalculation Procedure") • Test local sensitive species in local waters (EPA "Water Effect Ratio") to experimentally determine metal bioavailability • Enter local water chemistry data into Biotic Ligand Model (BLM) to predict bioavailable metal concentration.	• If exceeded, determine local safe threshold based on site-specific metal speciation: • Local metal speciation measurements • Toxicity testing (e.g., in local waters) • Speciation and other modeling	If exceeded, use user-friendly BLM-based look-up tool ("Bio-Met") to predict local bioavailability
Step 7	If exceeded, develop options for reducing point-source discharges and runoff, until local safe threshold is achieved (EPA "Total Maximum Daily Load" identification)	If exceeded, develop options for reducing point-source discharges and runoff, until local safe threshold is achieved	If exceeded, perform other refinements based on local conditions