Society of Environmental Toxicology and Chemistry

Technical Issue Paper

Environmental Toxicity of Metals in Freshwater

Metals in the Environment

Metals are abundant in the environment, and while they occur naturally, their release into the environment can be increased through human activity. High metal concentrations, of even metals that are essential for life, can adversely impact ecosystems. Metals can also interact with natural chemical constituents in ways that modify their toxicities to organisms. Because metals are distributed unevenly in the environment, their impact to ecosystem health varies from site to site. In freshwater bodies, such as rivers and lakes, differences in water chemistry on metal toxicity are profound – metal toxicity to the same organism can vary by a factor of 50 depending on water chemistry in the area where the water has been collected. Identifying maximum metal concentrations that still allow for protection of ecosystems from metal toxicity is therefore challenging.

Metals in water bodies are often managed by regulatory agencies through establishing numeric levels that the agency considers acceptable, which can be referred to generically as protective values for aquatic life (PVALs). Examples of PVALs include recommended Water Quality Criteria in the US and Environmental Quality Standards in the EU. PVALs that account for the influence of water chemistry on the toxicity of metals, broadly termed bioavailability-based approaches, are becoming more common.

Metal Ecotoxicity

As early as the 1930s, researchers observed that the toxicity of metals to aquatic organisms varies with water chemistry. While the initial emphasis was placed on the influence of water hardness, subsequent findings contributed to a broader understanding of modifying factors that need to be considered in order to predict metal toxicity at a given location. For example, elements that compose water hardness (calcium and magnesium) can compete at biological binding sites with metals, decreasing metal availability to aquatic organisms, while dissolved organic carbon can bind (complex) with metals in the water, also decreasing their availability to organisms. Such modifying factors influence metals speciation, which refers to the chemical form of the metal, such as a free metal ion or metal bound to another chemical. Metal speciation, in turn, is directly related to the availability and toxicity of a metal to aquatic organisms. Collectively, the influence of water chemistry and metal speciation on the toxicity of metals to aquatic organisms is described as bioavailability. In other words, metal toxicity can be predicted by metal concentration, as well as the degree of complexation and competition.

Toxicity of metals in freshwater is influenced by concentration, complexation, and competition.

Bioavailability-based models have been developed to determine the influence of water chemistry on metal speciation and to relate metal speciation to metal toxicity in mechanistically based approaches. The most robust of these mechanistic models are called Biotic Ligand Models (BLMs).

BLMs have been used to derive bioavailability-based PVALs in the US (for example for copper) and in the EU (for example for nickel). However, broader development of BLM-based PVALs has been hampered by the complexity of BLMs, such that many PVALs for metals around the world are still based on simple hardness relationships that were developed in the 1980s. BLMs require an extensive number of geochemical parameters, some of which may not be routinely measured, and also demand experience with metals speciation concepts that routine practitioners may not have. In attempts to make bioavailability concepts more accessible and easier to utilize, simpler empirical-based models, using multiple linear regressions (MLRs), have been developed more recently. However, in general, application of both mechanistic and empirical bioavailability-based models has lagged behind their scientific development.

Due to the availability of competing approaches for modeling metals bioavailability in freshwater, a clear need for robust, objective, and comprehensive approaches for model development, evaluation, and selection emerged. Therefore, a group of experts in environmental toxicology, chemistry, modeling, and regulatory application from around the globe representing various sectors (academia, business, government, and nonprofit associations) convened at a SETAC Workshop to address this issue. The objective of the workshop was to take stock of the current state of the science of metals bioavailability-based aquatic toxicity models, examine the performance of the models, and identify recommended approaches in the use of these models in the determination and application of bioavailability-based concentrations for metals that are intended to protect aquatic life (such as criteria and standards).

The workshop focused on models relevant to metals for which:

1. Aquatic toxicity varies substantially (such as among a given aquatic species) across waters with differing characteristics.
2. Toxicity to aquatic organisms in the environment is driven primarily by waterborne exposure.

Notable examples of such metals include aluminum, cadmium, cobalt, copper, lead, nickel, silver, and zinc. The outcomes from the workshop were summarized in a series of papers in *Environmental Toxicology and Chemistry* and are briefly described in this paper.

Challenges

Challenges to the use of bioavailability-based metals aquatic toxicity models include:

- The divergence of model development approaches and the associated methods of validation. The number of models and validation approaches causes regulatory authorities to grapple with evaluating the appropriateness of different models, primarily on technical merit but also in terms of their accessibility to the user.
- The practicality of implementing models in regulatory programs. Professionals charged with developing discharge permits or other applications of regulatory protective values may not have the resources necessary to fully evaluate the details of the models they could be asked to use, and the complexity of some models limits straightforward communication of their inner workings.
- The requirement of a variety of water chemistry parameters as input variables for some models. These requirements necessitate either collection of additional data on water quality characteristics or some means to estimate values appropriate to individual surface waters.

Application

The scientific community agrees that the science behind metals bioavailability-based aquatic toxicity models is sufficiently robust to use for environmental management.

Metals bioavailability-based aquatic toxicity models can be applied in two distinct areas in a regulatory context:

1. To manage metals in the environments for the derivation of recommended PVALs.
2. To identify risk-based goals, which can be used to set discharge levels or cleanup goals.

Many jurisdictions already use some forms of bioavailability-based aquatic toxicity models for some metals. However, some jurisdictions have not kept pace with the rapid pace of progressions in model development.

Bioavailability-based aquatic toxicity models for metals are at a state of maturity that supports their use to derive metal concentrations in water that are protective of aquatic life.

As metals bioavailability-based aquatic toxicity models are used to estimate PVALs, there are important issues to consider at model selection and application.

The following should be considered during model selection:

- The water chemistry parameters and aquatic organisms used in model development should be relevant for the region where the model is to be applied.
- The water chemistry parameters that are required to operate the model should be easily obtainable.
- The accuracy of the model, as demonstrated by model calibration and validation results, should be optimal in the ranges of water chemistry parameters for the region where the model is to be applied.
- The model should be easy to use. This includes the level of training required to use the model, compatibility of the model with commonly available computer software, similarity between the output of the model to what is required by the regulatory framework in question, and the ability of users to collect the water chemistry data to use the model.

The following should be considered during model application:

- The models should be informed by mechanistic understanding of metal toxicity and of metal speciation.
- The use of simplified tools should be acceptable as long as the tools accurately reflect predictions of the full model toxicity.
- The models should undergo qualitative and quantitative validation to test the ability of a species-specific model to accurately predict an ecotoxicity endpoint.
- The choice of the most appropriate model should be transparently communicated even though it is understood that different models can be used for different situations.
- The models should be applied within appropriate ranges of water chemistry for a given jurisdiction.

Path Forward

Bioavailability-based aquatic toxicity models for metals in freshwater are at a state of maturity that supports their use to derive metal concentrations in water that are protective of aquatic life. Further, the state of the science can support expanded incorporation of metals bioavailability-based toxicity models into regulatory frameworks for the protection of freshwater around the world.

Resources

Schlekat C, Stubblefield W, Gallagher K (eds). 2020. State of the Science on Metal Bioavailability Modeling (special series). Environ Tox Chem. 39(1): 42-130.

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