# Metals Toxicity & the Biotic Ligand Model

The bioavailability of metals to aquatic organisms is highly dependent on water chemistry conditions that vary from site to site. For example, complexation with dissolved organic carbon (DOC) and competition with cations such as calcium reduce metals bioavailability. Other site-specific factors, such as pH, also influence metal speciation, with different metal species having different degrees of bioavailability. Ultimately, this means that the concentration of a given metal, on a total recoverable or dissolved basis, that may present toxicity to aquatic life is highly variable among sites.

Regulatory criteria that do not account for the key factors affecting metal bioavailability could be greatly over- or under-protective of the aquatic life uses that they are intended to protect. Over-protectiveness can result in extensive effort and cost to manage a problem that does not exist, while under-protectiveness can result in unacceptable risk of detrimental effects on the aquatic community.

Properly accounting for metal bioavailability is critical to reduce uncertainty in any metals risk assessment or site-specific water quality evaluation, including the development of National Pollutant Discharge Elimination System (NPDES) permits and total maximum daily loads (TMDLs) in the United States. Members of Windward were early collaborators in the development of a tool called the Biotic Ligand Model (BLM), which allows for mechanistic predictions of bioavailability and toxicity for several metals. We are actively involved in the ongoing development of BLMs for additional metals, as well as for metal mixtures. We have extensive experience in the application of metal BLMs in support of proposed ambient water quality criteria (AWQC) updates for both the US Environmental Protection Agency (EPA) and individual states, site-specific assessments, and evaluations of whether criteria are protective against toxicity endpoints of concern for threatened and endangered species.

## Criteria Development

One application of the BLM is in deriving AWQC that vary as a function of water chemistry conditions. In the United States, some metals criteria are adjusted only as a function of the hardness concentration, while others are not adjusted for any site-specific water chemistry condition. Windward personnel have collaborated with EPA to develop nationally recommended BLM-based copper criteria for both freshwater and salt water. We developed BLM-based criteria following EPA guidelines for aluminum, lead, silver, and zinc, and an approach to address time-variable water quality guidelines that result when bioavailability factors are considered. This approach, the Fixed Monitoring Benchmark (FMB), uses a probabilistic analysis to recommend a single number for use in developing a NPDES permit.

Windward has also collaborated in extensive evaluations of whether BLM-based freshwater copper criteria are protective of threatened and endangered species. For example, over the last several years, concerns have been raised that low copper concentrations can cause olfactory impairment in juvenile Pacific salmon, which can impact their ability to avoid predators. These evaluations have demonstrated that the BLM-based copper criteria protect juvenile salmon from olfactory impairment, while the hardness-based copper criteria still used in most states sometimes do not.

## Model Development

Windward staff have been instrumental in developing BLMs for numerous metals, including aluminum, cadmium, cobalt, copper, lead, nickel, and silver, as well as zinc in freshwater and copper in salt water. Saltwater models for other metals are also under development. In addition, a metal mixture BLM was recently developed by members of the Windward team as part of an international metal mixture modeling evaluation project. These various BLMs were developed to predict toxicity to one or more model organisms as a function of several water chemistry parameters, including DOC, pH, alkalinity, calcium, and several other cations and anions. Some of the BLMs are publically available through downloadable software packages, and more will be accessible soon.

## Site-Specific Evaluations

The EPA water quality criterion for copper in marine waters is based on protection of the blue mussel Mytilus, the marine organism most sensitive to copper toxicity. A study that was published in the Marine Pollution Bulletin (authored by Windward's Robert Santore, among others) reported that samples taken from Shelter Island Yacht Basin off of San Diego Bay have copper concentrations frequently exceeding the EPA marine water quality criterion of 3.1 µg/L. Toxicity tests using the most sensitive life stage of Mytilus galloprovincialis, however, found that these samples were not toxic, indicating that the marine water quality criterion of 3.1 µg/L might be overprotective. Copper bioavailability and toxicity in marine waters can be modified by chemical factors such as changes in salinity, pH, or the presence of natural organic matter (NOM). These factors are not considered by the current EPA marine copper criterion, but they have been incorporated into the marine copper BLM, making it better able to predict a protective copper criterion in chronic exposures for M. galloprovincialis. Marine copper BLM predictions for Shelter Island Yacht Basin indicate that a site-specific criterion for copper that would be protective of all marine organisms—including M. galloprovincialis—would be greater than the current criterion of 3.1 µg/L. This is important because while copper concentrations exceed the EPA marine water quality criterion by two- to three-fold in some areas, they are nearly all less than the BLM-predicted safe chronic level because the BLM accounts for site-specific copper bioavailability.

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