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# Biotic ligand models, metal bioavailability and regulatory application

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Biotic ligand models are tools used to predict the trace metal concentration in the water column that will have an adverse effect upon an aquatic organism. This Environmental Brief outlines how biotic ligand models have been developed, and how they are now being applied to set and implement regulatory quality standards.

The ecotoxicity of many trace metals to aquatic organisms depends on water chemistry conditions. This has been taken into account during the setting of environmental quality standards for metals in the past, predominantly through the use of water hardness-based corrections. These water hardness corrections were based on the observation that metal toxicity was generally lower at high hardness than at low hardness in laboratory ecotoxicity tests. Regions with soft waters were identified as being particularly sensitive to trace metal toxicity and so where assigned relatively low environmental quality standards.

Fish gills were identified as the site of metal uptake causing toxicity, and experiments led to the development of the Gill Site Interaction Model (*1*) which relates the level of toxicity to the degree of accumulation of metal on the gill surface. If the binding constant for metal at the fish gill is known then the degree of metal accumulation at the gill can be related directly to the free ion activity in the water that the gill is exposed to. This model also resulted in the calculation of stability constants for metal binding to fish gills. The competitive effect of the hardness cations $Ca^{2+}$ and $Mg^{2+}$ on metal toxicity could then be interpreted in terms of their competition with divalent trace metals binding to ligand sites on the fish gills.

Another factor in defining the toxicity of a metal is the degree of binding to dissolved organic carbon (DOC) such as humic and fulvic acids, because the metal-organic complexes do not contribute directly to the organism toxicity. Advances in chemical speciation modelling were provided by models, such as the Windermere Humic Aqueous Model or WHAM (*2*), which are able to describe the interactions between trace metals and humic and fulvic acids in natural waters. These models enabled the free ion activities of metals in natural waters to be predicted, and where comparisons with direct measurements of free ion activities were possible there was typically good agreement (*3*).

A further key development in the understanding of trace metal toxicity was achieved through combining both the Gill Site Interaction Model with the aqueous speciation model WHAM to produce the Biotic Ligand Model (BLM) (*4*). This model treated the metal binding sites present on the fish gills as an additional ligand in the chemical speciation model, and enabled the equilibrium speciation of metal between gill ligands, DOC, solution complexes, and the free ion activity of the metal to be predicted. This

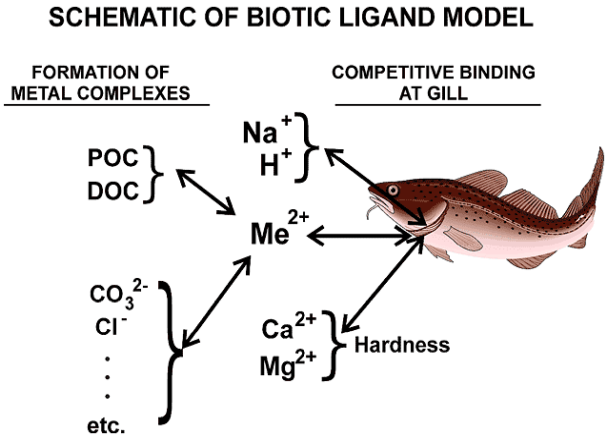


***Figure 1.****Schematic of the biotic ligand model, showing the chemistry speciation component on the left and biological interactions on the right. $Me^{2+}$ represents a divalent metal ion. POC is particulate organic carbon; DOC is dissolved organic carbon. Adapted from (4).*

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development provided the first direct link between the dissolved concentration of a metal, as is measureable in filtered samples by routine analytical methods, and the level of toxicity experienced by an organism in complex natural waters.

The BLM considers the inorganic speciation reactions of the metal and system components, and the binding of cationic species to both DOC (usually assumed to be present as fulvic acid only) and the "Biotic Ligand", which is an assumed metal binding site on the animals gills (or some other exposed membrane surface). This concept is shown schematically in **Figure 1**. The interactions between a trace metal and cations in the bulk solution, such as $H^+$, $Na^+$, $Ca^{2+}$ and $Mg^{2+}$, are much more complex than is predicted by the hardness-based metal standards historically used, because all the cations interact competitively at the binding sites on both the DOC in solution and the biotic ligand on the organism. Therefore, a solution based measurement of either the free ion activity or some other "available" fraction, is unable to completely replicate the sensitivity of the organisms to changes in the water chemistry.

## Does the biotic ligand model work?

Validation studies have shown that the bioavailability models which have been developed for specific species can be applied to understand the effects of bioavailability on other species from the same trophic level (*5*). The extrapolation of the BLMs between different species requires a bioavailability correction to be made for each individual species within a species sensitivity distribution (SSD) (or even each individual toxicity endpoint within the database) to the same specific set of water chemistry conditions (*6*). This correction allows the relative sensitivity of different organisms to be compared under conditions for which they have not necessarily been tested.

The calculation of a site-specific bioavailability normalised SSD requires a water quality standard, which may be derived from data for a particular set of water chemistry conditions, to be corrected for the local water chemistry conditions at each site. This site-specific standards result in calculated dissolved metal concentrations against which compliance can be assessed by routine regulatory monitoring, provided that the required supporting parameters which are required for the bioavailability normalisation are available.

Within Europe, the development of bioavailability based environmental quality standards for metals has followed this type of approach, using an SSD of chronic ecotoxicity data which is normalised to different water chemistry conditions using a suite of BLMs developed for different trophic levels. The BLM normalised SSD is then calculated for a diverse range of European water chemistries in order to identify the most sensitive water chemistry conditions which are likely to be encountered. The environmental quality standard is expressed as a "bioavailable metal" concentration, which ensures a high level (e.g. 95%) of protection in regions with sensitive waters (i.e. where bioavailability is maximised). Exposure monitoring data for dissolved metal can be converted into a "bioavailable metal" concentration using the BLM for comparison against the environmental quality standard. This approach allows the environmental quality standard to be expressed as a single value (for example across the whole of Europe), whilst also enabling it to be corrected to local conditions and ensuring a consistent level of acceptable potential risk.

In practice, the available regulatory monitoring data do not tend to include measurements of dissolved organic carbon, which are required for the BLM calculations, although pH is commonly measured. This omission occurs because water hardness has historically been required in most cases. It is possible to estimate the concentrations of other major ions in solution from the concentration of calcium or other parameters (*7*) with sufficient precision to allow robust BLM calculations. The routine regulatory use of BLMs marks a step change in the way water quality is assessed and delivers a clear evidence-driven link to environmental protection.

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