

THE BIOTIC LIGAND MODEL ADDRESSES EFFECTS OF WATER CHEMISTRY ON METAL TOXICITY

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A metal's toxicity to a single species can vary widely in different bioassay tests (to determine its concentration by its effect on an organism's health and survival). This results in difficulty in establishing environmentally acceptable criteria that can be applied with certainty. Water Quality Criteria are used in regulatory programs to ensure that the quality of natural waters will achieve their desired uses. For example, in the United States, some criteria are designed to protect 95% of the species. This is accomplished by plotting

the species sensitivity distribution and setting the criteria at the 5% level, as shown in Figure 1.

Related approaches are used in other jurisdictions. The toxicity of cationic metal (with positively charged ions) can vary greatly with the chemistry of water. For example, it has been known for some time that water hardness affects the toxicity of a number of metals. Therefore, the available toxicity data often are extrapolated to a constant hardness value, for example, 50 mg/L as CaCO₃, to remove this effect on the observed distribution. The hardness factor is then included in the criteria as an adjustment. Meyer (2002) has collated most of the published data on toxicity of metals to aquatic organisms to investigate effects of water quality parameters on observed toxicity. Figure 2 shows the reported data for the toxicity of copper to *Daphnia* as a function of water hardness. While it is evident that hardness affects toxicity, the greater than 10-fold variation remaining in toxicity suggests that factors other than hardness are involved.

How can the greater than 10-fold variation in the toxicity that has been observed at a constant hardness be explained? Both biological and chemical factors may be at play. Test organisms often are cultured in water of a standard chemical composition that may be considerably different from that of the test water. Acclimation of organisms to the test water has been shown to have an effect on the observed toxicity. However, this effect is not sufficiently large to explain the variation in the toxicity that is shown in Figure 2.

Figure 1

Copper WQC Fresh Water Species

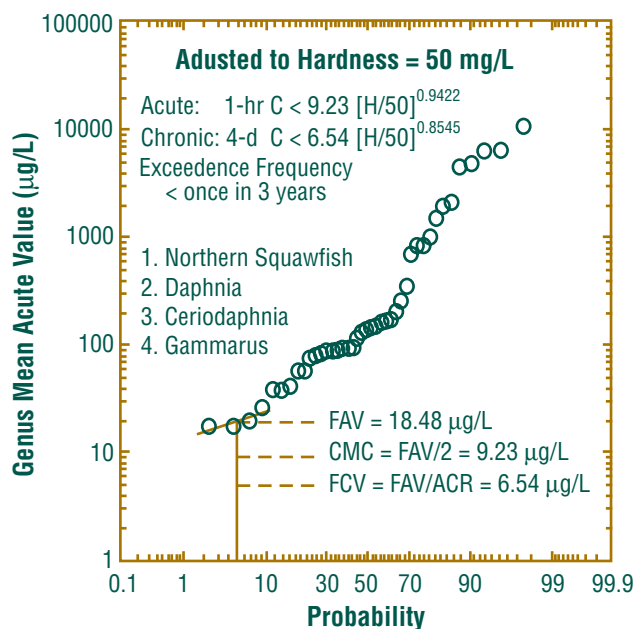
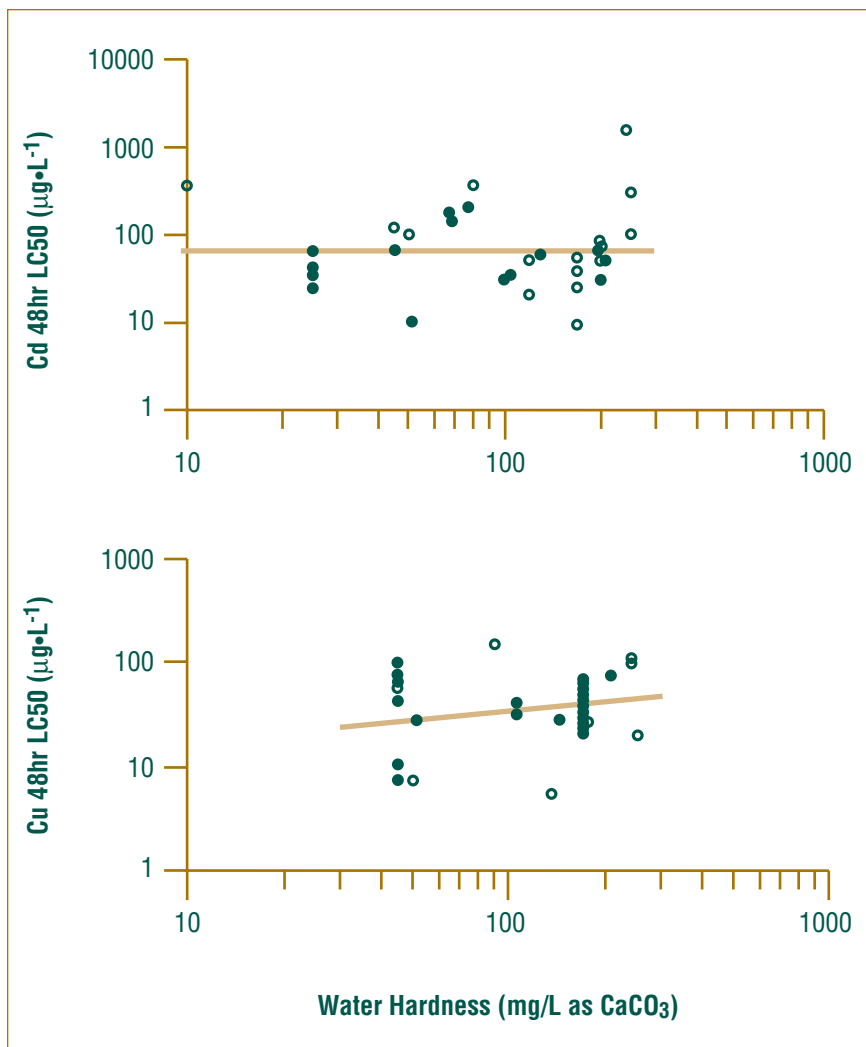


Figure 2

Intra-species Toxicity Test Variability
Daphnia



Effects of Water Chemistry on Metal Toxicity

Water chemistry is known to affect acute toxicity of dissolved metals by two very different processes. Calcium ions, a component of the hardness discussed above, are physiologically essential to organisms. Increased calcium ion or hardness concentration interferes with organisms’ ability to take up potentially toxic trace metals. In the absence of uptake or interaction of the potentially toxic metal with an organism, there can be no toxicity exerted. Many of the metals are toxic to aquatic organisms due to their interference with the organisms’ ability to take up calcium, and thus regulate their level of this required element. Other metals, as shown in Table 1, interfere with the organisms’ ability to regulate sodium ion.

Thus, the toxicity of dissolved metals results from their interference with ionic regulation, which in fish occurs in the gills. Other ions, such as hydrogen ions, can moderate this toxicity by interacting with the metals as they try to bind to the gill receptor sites.

The second way in which water’s chemical composition is able to affect the toxicity of a potentially toxic trace metal in the dissolved phase is through a change in the chemical form, or species, of the trace metal. Trace metals such as cadmium, copper, zinc and others can form complexes with a number of inorganic and organic ligands (small molecules that bind to larger ones) or complexing agents that are present in natural waters. The milieu of chemical forms that are present are referred to by environmental chemists as the metal’s “**chemical speciation.**” The chemical species present include simple inorganic complexes with hydroxide and carbonate ions that are always present. In brackish water, chloride complexes of cadmium and other metals can become important species. Natural organic matter, often dominated by humic substances (decomposing organic matter), is present in natural waters and can dominate the speciation of many metals. The uncomplexed, or free metal ion species,

of a trace metal is considered bioavailable (metabolically available) and thus is responsible for toxicity.

Table 1

Physiological mechanisms of toxicity in freshwater fish at acute criteria levels

Metal	Toxic Effect
Al	Blockade of Na ⁺ uptake
Ag	Blockade of Na ⁺ uptake
Cd	Blockade of Ca ²⁺ uptake
Cu	Blockade of Na ⁺ uptake
Zn	Blockade of Ca ²⁺ uptake

For some trace metals, for example silver and copper, only a very small fraction—perhaps less than one percent—of the soluble metal is present as the free metal ion. Water chemistry is strongly influenced by watershed characteristics; water chemistry can vary considerably between sites. This variability can greatly affect the fraction of the metal that is present as the free metal ion and therefore also affect the measured toxicity.

Chemical Speciation Models

A chemical model must be able to predict the free metal ion concentration that will occur in natural waters. Many chemical speciation models are available that provide excellent characterization of speciation in a solution containing inorganic and well-characterized organic ligands. Because natural organic matter is so important in the speciation of trace metals in natural waters, such a model must include an accurate description of natural organic matter reactions with trace metals. This has become available through the work of Edward Tipping in the UK. His Windermere Humic-Aqueous Model (WHAM) predicts the interaction between metals and organic matter, but requires only simple characteristics of the sample for its description. The model has been calibrated with a large number of samples of natural organic matter from a wide variety of locations.

Research of Playle and co-workers showed that uptake of a number of metals, including cadmium, copper and silver, onto fish gills leads to organism mortality, and that the uptake of the metals could be described by conventional chemical equilibrium models in which the gill was treated as a ligand described by a stability constant and reaction site concentration. In their work, they excised fish gills and analysed the concentration of metal on the gill surface. In the initial studies, the model was termed the “gill model.” The toxicity of dissolved metals was shown to be proportional to the accumulation of the metal on the gill. Playle’s work was extended, by analogy, to other organisms that were too small to enable organs to be excised and analysed for accumulation of trace metals. For these organisms, toxicity, rather than gill accumulation, was determined.

The toxicity to organisms is predicted by determining a “lethal accumulation” on the receptor site. The LA50 (lethal accumulation that results in mortality to 50% of the organisms) is a predictor of the toxicity irrespective of the test water chemistry. On the other hand, the LC50 (lethal concentration that results in mortality to 50% of the organisms) varies with changes in the water chemistry. The importance of this can be understood by considering the interplay of chemical and biological factors. It has been proposed for a long time that the free ion concentration of trace metals can be related to their toxicity. This relationship is true only if factors that do not affect the free ion concentration of the trace metal but that affect toxicity (e.g. hardness) are kept constant. However, this restriction does not apply if the lethal accumulation is considered.

The Biotic Ligand Model

Over the past decade, these advances made by biologists, chemists and engineers have culminated in the development of the Biotic Ligand Model (BLM), which has proven to be an effective tool to estimate toxicity of dissolved metals. The BLM mathematically integrates the interaction of trace metal with solution phase ligands to predict its speciation and its subsequent interaction with receptor sites on the organism. From a chemical and mathematical perspective, the organism’s receptor site is treated as a ligand, the “**biotic ligand.**” The BLM includes two features—one chemical and one biological—that enable it to predict toxicity of dissolved metals based on the accumulation of the metal on the receptor site. The

Figure 3

Aquatic Biotic Ligand Model—Conceptual Diagram
(after Pagenkopf, 1983)

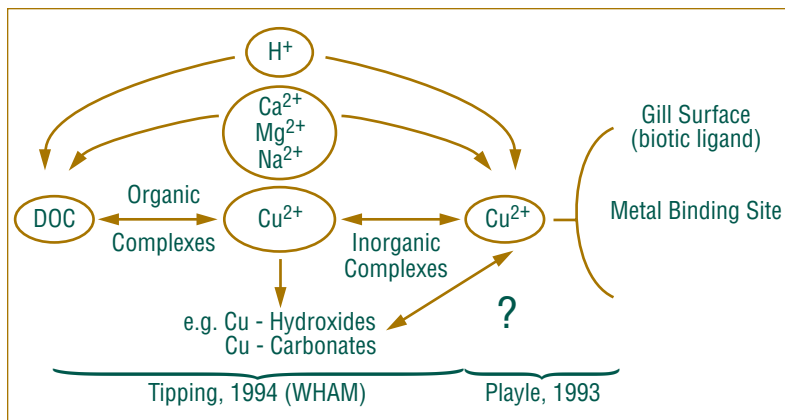
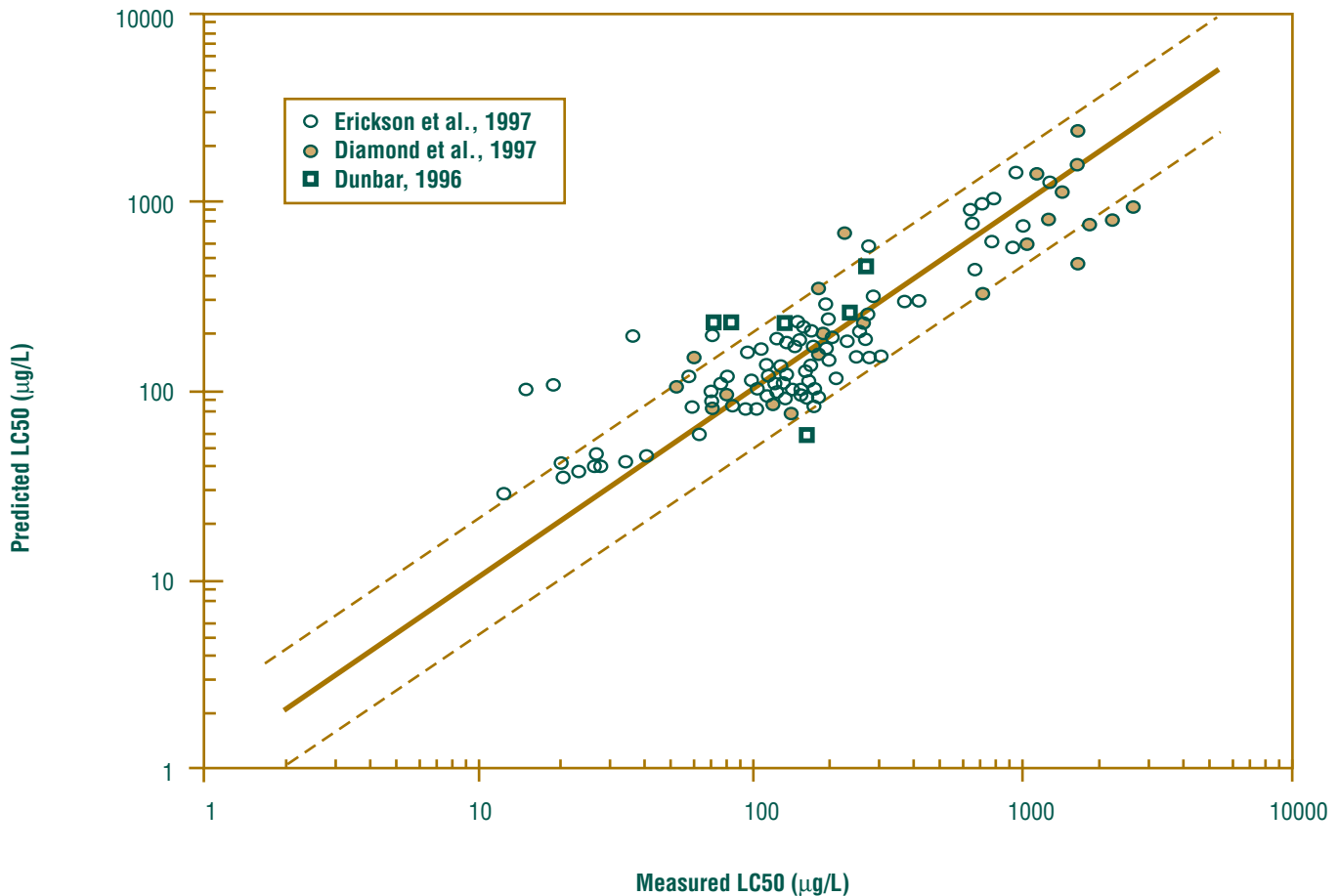


Figure 4

LC50 Model Performance

Fathead Minnow

BLM's features, based on concepts first described by Pagenkopf (1983), are shown schematically in Figure 3.

The accuracy of the Biotic Ligand Model toxicity predictions for copper is shown in Figure 4, which shows toxicity results for a number of waters of varying water chemistry. The measured toxicity varied by more than two orders of magnitude. The solid line shows the BLM-predicted toxicity and the dashed lines represent factors of two above and below that value. Virtually all results can be predicted to within a factor of two of the measured value.

The BLM approach permits the rational explanation of the effect of variation in water chemistry on the toxicity of metals to aquatic organisms. Metals are known to be less toxic in organic-rich waters. Effects of pH, dissolved organic carbon and other factors not commonly considered can be incorporated into water quality criteria. The model can be used for site-specific criteria by adjusting the generic values to

account for local differences in these factors. Presently, bioassay testing often is applied to ascertain if there is a difference in toxicity at a site from that anticipated from the criteria. However, extensive testing would be required in order to describe the different toxicity that may result from different site-specific water chemistry parameters. It is much more cost-effective and introduces less uncertainty if the BLM is used to predict toxicity under a widely varying set of conditions. Therefore, the BLM promises to be an important tool for use in development of discharge permits, watershed planning, risk assessments or in any scenario that requires an understanding of bioavailability in relation to water chemistry. In addition, the US Environmental Protection Agency is developing water quality criteria for a number of metals using the BLM to account for differences in toxicity resulting from the chemistry of the waters used for bioassay testing.

Additional Reading

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About the Author

Herbert E. Allen, Ph.D. is a Professor of Environmental Engineering at the University of Delaware, USA. Before joining that faculty, he was the Director of the Environmental Studies Institute and Professor of Chemistry at Drexel University in Philadelphia from 1983 until 1989. Before that, he spent nine years as a member of the faculty of the Department of Environmental Engineering at the Illinois Institute of Technology in Chicago. Dr. Allen received his Ph.D. in Environmental Chemistry from the University of Michigan. Dr. Allen's research has been concerned with fate and effects of trace metals in aquatic and soil environments. He is well-known for his studies on the bioavailability of metals. His principal areas of research are methods to predict metal availability to both aquatic and terrestrial organisms for the development of site-specific criteria. He has authored more than 180 technical publications, has edited 7 books and has prepared numerous reports and proceedings papers. From 1994 until 2000, he headed a multi-university consortium of universities, supported by the US Environmental Protection Agency (EPA), which conducted research on fate and effects of metals and organic in natural water systems. Dr. Allen also heads the newly formed EPA Center for the Study of Metals in the Environment.

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Fact Sheet on Environmental Risk Assessment

This is the seventh in an occasional series of *Fact Sheets* to be produced by ICMM on metal-specific issues in environmental risk assessment. Authorship selection and editorial review are coordinated by Dr. Anne Fairbrother of Parametrix, Inc. Each *Fact Sheet* is reviewed for technical merit by Dr. Erik Smolders of Katholieke Universiteit (Catholic University) Leuven, Belgium, and by a panel of experts in metal-related regulatory issues. While the *Fact Sheets* reflect the views of the authors, they are intended to provide an objective review of each topic. ICMM hopes these publications provide insights into complex issues in regulatory science, and welcomes questions and comments.

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