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# AN SAB REPORT: REVIEW OF THE BIOTIC LIGAND MODEL OF THE ACUTE TOXICITY OF METALS

## PREPARED BY THE ECOLOGICAL PROCESSES AND EFFECTS COMMITTEE OF THE SCIENCE ADVISORY BOARD

February 28, 2000

EPA-SAB-EPEC-00-006
Honorable Carol M. Browner
Administrator
U.S. Environmental Protection Agency
1200 Pennsylvania Ave., NW
Washington, DC 20460

Subject: Review of the Biotic Ligand Model of the Acute Toxicity of Metals

Dear Ms. Browner:

At the request of the EPA Office of Water, the Ecological Processes and Effects Committee (EPEC) of the Science Advisory Board (SAB) met on April 6-7, 1999 to review the Biotic Ligand Model (BLM) for predicting the acute toxicity of metals to aquatic organisms. The BLM has been developed to improve the estimation of the bioavailable fraction of dissolved metals, such as copper and silver, that may pose a risk to aquatic organisms in surface waters. The Agency proposes to incorporate the BLM in its approach to establishing water quality criteria that will be protective of aquatic organisms.

The relevant scientific questions surrounding use of the BLM include: the extent to which it realistically models metals chemistry, and thus bioavailability, of metals in the water column; the extent to which it accurately captures the major exposure routes and mechanisms of toxicity of metals to water column organisms; and the extent to which the BLM represents an improvement over existing methods for developing and adjusting water quality criteria. The Committee's evaluation of these points, summarized in the accompanying SAB report, form the basis for responding to the specific charge questions posed by the Office of Water.

In general, the Committee found that the BLM can significantly improve predictions of the acute toxicity of certain metals across a range of water chemistry parameters. The theory and empirical validations performed to date are an important step toward a geochemically and biologically robust approach for incorporating bioavailability concepts into water quality criteria. The Committee concluded that the model could be a practical aid in site-specific water quality regulation and assessment, complementing and in some cases providing a ready alternative to current empirical (e.g., Water-Effect Ratio) approaches. Over the longer term, the Committee sees potential broader applications, including: the development and application of sediment quality guidelines; site-specific risk assessments and remediations; natural resource damage assessments; chemical registrations; and product risk assessments.

At the same time, the Committee observed that there has not yet been sufficient time to validate the model in a number of areas, including: a broad range of aquatic organisms; longer term exposures; a wide variety of metals; or a comprehensive range of water chemistry parameters and naturally occurring field conditions. Particular areas in need of further validation were identified. We also provide recommendations regarding appropriate use of the BLM pending this additional validation.

We encourage the Agency to continue its efforts to incorporate the best science and models into its approach to deriving and adjusting water quality criteria. We hope our review of the BLM will be helpful in that regard, and we look forward to a response from the Assistant Administrator for Water.

Sincerely,

/signed/
Dr. Joan M. Daisey, Chair
Science Advisory Board

/signed/
Dr. Terry F. Young, Chair
Ecological Processes and
Effects Committee
Science Advisory Board

/signed/
Dr. Charles A. Pittinger, Acting Chair
for Review of the BLM
Ecological Processes and
Effects Committee
Science Advisory Board

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**U.S. ENVIRONMENTAL PROTECTION AGENCY**
**SCIENCE ADVISORY BOARD**
**ECOLOGICAL PROCESSES AND EFFECTS COMMITTEE**

**Review of the Biotic Ligand Model**

April 6-7, 1999


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# 1. EXECUTIVE SUMMARY

The BLM is a mechanistic bioavailability model which considers the influence of both biotic and abiotic (organic and inorganic) ligands in the calculation of the bioavailability of metals to aquatic organisms. The U.S. EPA's Office of Water requested that the Ecological Processes and Effects Committee (EPEC) of the Science Advisory Board review the current state of validation of the BLM relative to the current dissolved metal concentration criteria. Specifically, the Committee was asked to comment on the model's proposed application for deriving and adjusting aquatic life criteria for metals as part of the Agency's proposed integrated approach for the water column, sediments and interstitial water. This report summarizes conclusions reached by the Committee following review of the draft document, *Biotic Ligand Model of the Acute Toxicity of Metals*, and Agency presentations and discussions at the April 6-7, 1999 review meeting.

In general, the Committee found that the BLM can significantly improve predictions of the acute toxicity of certain metals across an expanded range of water chemistry parameters compared to the WER. The theory and empirical validations performed to date were viewed as an important step toward a geochemically and biologically robust approach for incorporating bioavailability concepts into water quality criteria. The Committee concluded that the model could be a practical aid in site-specific water quality regulation and assessment, complementing and in some cases providing a ready alternative to current empirical (e.g., Water-Effect Ratio) approaches. Over the longer term, the Committee sees potential broader applications, including: the development and application of sediment quality guidelines; site-specific risk assessments and remediations; natural resource damage assessments; chemical registrations; and product risk assessments.

At the same time, the Committee observed that there has not been sufficient time to validate the model with what would be considered a broad range of aquatic organisms, a wide variety of metals partitioned across key environmental compartments, or a comprehensive range of water chemistry parameters and naturally occurring field conditions. Particular areas in need of further validation were identified. It was recommended that the model's use in regulatory contexts be guided by the Agency to ensure that any forthcoming applications are supported by and conform with the then-current state of validation.

The Committee responded to four specific charge questions posed by the Agency:

1. **Does the BLM improve the Agency's ability to predict toxicity to water column organisms due to metals (copper and silver) in comparison to the currently applied dissolved metal concentration criterion?**

In comparison to the currently applied dissolved metal concentration criterion, the BLM has to date been shown to predict with reasonable accuracy (generally within a factor of two of measured values) the acute toxicities of copper and silver to fish. Currently, the model has been shown to predict acute toxicity, to a limited number of water column organisms, for selected metals, under equilibrium conditions.

**2. Is the scientific and theoretical foundation of the model sound?**

The scientific underpinnings of the BLM appear to be sound. The strength of the model lies in the fact that it is built upon a mechanistic paradigm with a strong physiological basis, i.e., predicting binding at the site of action (gill in fish) and the mechanism of acute toxicity (blockage of sodium and calcium channels) for metals (copper and silver).

**3. In comparison to the current WER adjustment for aquatic life criteria, will the application of the BLM as a site-specific adjustment reduce uncertainty associated with metals bioavailability and toxicity?**

Application of the BLM would not necessarily reduce uncertainty relative to empirical data. However, its predictiveness over a wide range of environmental conditions makes the BLM a more versatile and effective tool for deriving site-specific WQC compared to the WER.

**4. Are the data presented for validation of the BLM sufficient to support the incorporation of the BLM directly into copper and silver criteria documents?**

It appears premature to use the BLM to revise the protocol for deriving national ambient water quality criteria at this time, primarily because the model has not yet been validated for a sufficiently diverse set of aquatic organisms and endpoints, coupled with the full range of water quality conditions. However, the Committee concluded that the BLM could have current, practical applications for calculating site-specific modifications to ambient copper criteria, and to a lesser extent silver, as an alternative or complementary method to the current water-effects ratio (WER) approach.

Finally, the Committee provided recommendations for further research to provide additional validation in the following areas:

a) Prediction of chronic and sub-acute toxicities, not currently supported by the BLM.

b) Broadening the supporting database to include greater taxonomic and functional diversity and additional comparisons with the water effect ratio method.

c) Gaining better mechanistic and kinetic understanding, i.e., distinguishing relative differences in binding affinity and toxicity mitigation among hardness cations (e.g., Ca, Mg, Mn) and with other “biotic ligands” besides the fish gill, and evaluating predictability of the model under non-equilibrium water quality conditions.

d) Distinguishing the events and kinetics of DOC complexing with divalent cations and biological uptake to improve interpretations of model predictions.

e) Applicability to multiple metals, and sensitivity analyses for varying water chemistry conditions.

# 2. INTRODUCTION

## 2.1 Background

The Biotic Ligand Model (BLM) is a model that incorporates metal speciation and the protective effects of competing cations to predict metal binding at the fish gill or other site of action of acute metal toxicity in aquatic organisms (i.e., the "biotic ligand") (Figure 1). The Agency has proposed that the BLM be included in an integrated approach to metals management, including establishment of metals water quality criteria. National ambient water quality criteria (WQC) consist of 3 components: the concentration of the pollutant that will protect 95% of aquatic species; a time period over which exposure is to be averaged; and the allowable frequency for exceeding the criteria. The allowable concentrations of the pollutant generally are based on laboratory toxicity tests using a specified array of test species, and are expressed in terms of a criterion maximum concentration (CMC) to protect against acute (short-term) effects and a criterion continuous concentration (CCC) to protect against chronic (long-term) effects.

***Dissolved Metals***—In 1993, the Agency issued technical guidance specifying that national aquatic life criteria for metals be derived using the relationship between toxicity and dissolved metal, rather than total recoverable metal (EPA, 1993), in order to more accurately reflect the bioavailable fraction of metal in test solutions. (The change to dissolved criteria requires the application of a conversion factor to convert criteria previously expressed in terms of total recoverable metal.) In an effort to further refine the assessment of metals bioavailability in the water column, the Agency has subsequently supported development of the Biotic Ligand Model (BLM), which considers biotic ligands, as well as abiotic organic and inorganic ligands, in the calculation of bioavailability of metals. In the current review, the SAB is asked whether the BLM will improve toxicity predictions in comparison to the dissolved metal concentration criterion.

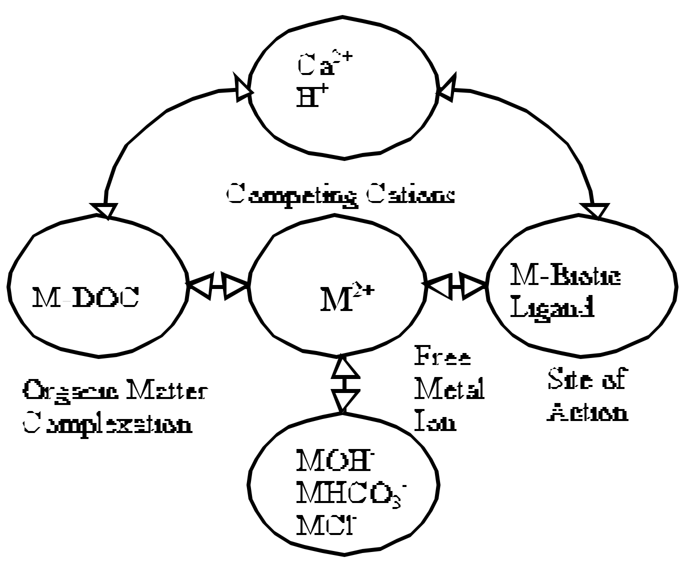


**Figure 1**. Biotic Ligand Model

***Site-Specific Considerations—***In the case of cationic metals, toxicity is hardness-dependent because hardness ions compete with metal ions for binding sites on respiratory membranes. Thus, a site-specific correction for hardness is incorporated into the national WQC for these metals by expressing the CMC and CCC in the form of equations that yield the criteria values (in micrograms per liter) as a function of total hardness. As an example, the equations for copper are as follows:

$$CCC = e^{0.8545(\ln \text{hardness}) - 1.702}$$

$$CMC = e^{0.9422(\ln \text{hardness}) - 1.700}$$

In addition, the Agency has created three procedures by which national WQC may be modified to reflect site-specific conditions relating to: differences in sensitivities of species at the site relative to species used to derive the national criterion; differences in site water chemistry relative to laboratory test water; and simultaneous consideration of both types of differences.

The Agency's current guidance on making the second type of correction, effects of site water chemistry on toxicity, is called the Water-Effects Ratio (WER). Guidance on applying the WER approach for metals was most recently issued in 1994 (EPA, 1994). In the current review, the SAB is asked whether a model-based approach (the BLM) would be an improvement over the empirically based WER for making site-specific adjustments of WQC for metals.

### 2.2 Charge to the Committee

The Committee met in Washington, DC on April 6-7, 1999 to review the draft document, *Biotic Ligand Model of the Acute Toxicity of Metals* (EPA, 1999); the BLM is proposed for incorporation into the Agency's approach for deriving aquatic life criteria for metals in the water column. The Charge to the Committee included the following questions:

a) Does the BLM improve the Agency's ability to predict toxicity to water column organisms due to metals (copper and silver) in comparison to the currently applied dissolved metal concentration criterion?

b) Is the scientific and theoretical foundation of the model sound?

c) In comparison to the current WER adjustment for aquatic life criteria, will the application of the BLM as a site-specific adjustment reduce uncertainty associated with metals bioavailability and toxicity?

d) Are the data presented for validation of the BLM sufficient to support the incorporation of the BLM directly into copper and silver documents?

The Committee's response to each of these questions is contained in the sections that follow. The Committee's comments on the suitability of the BLM for applications involving sediments and interstitial (pore) water are contained in a companion SAB report on the Metals Mixtures Equilibrium Sediment Guideline (ESG) (EPA-SAB-EPEC-00-007) and summarized briefly in Section 3.

# 3. GENERAL COMMENTS

The BLM is a mechanistic bioavailability model that has to date been shown to significantly improve our ability to predict the acute toxicity of certain metals across an expanded range of water chemistry parameters. The theory and empirical validations performed to date are an excellent beginning in the development of a geochemically and biologically robust approach for incorporating bioavailability concepts into water quality criteria. The model, which will be an important component of the Agency's integrated metals methodology (discussed further in EPA-SAB-EPEC-00-005, SAB, 2000), opens the way for what may be the next generation of water quality criteria for metals in the form of tissue-residue based guidelines. In the near-term, the model can be a practical aid in site-specific water quality regulation and assessment, complementing and in some cases (e.g., in predicting acute toxicity of copper to water-column organisms) providing a ready alternative to current empirical (e.g., WER) approaches.

The distinguishing feature of the model, in contrast to approaches based only upon estimation of free metal ions as the toxic species, is its capability to predict the competition of the free metal ion with other cations (e.g., Ca, H) and other ligands (DOC) for binding with the "biotic ligand" (the site of membrane transport and route of direct uptake of freely dissolved metals). The presence of these cations and ligands in solution can mitigate toxicity in a predictable fashion based on their relative concentrations and strengths of binding. The model allows changes in toxicity under equilibrium conditions to be estimated across ranges of key water quality parameters (pH, alkalinity, hardness, and DOC). Furthermore, through the model's ability to integrate the binding site density of the biotic ligand, conditional stability constants for the metal-ligand complex and competing cations, and measured or postulated water quality conditions, the acute toxicological effects of a metal in a broad range of waters can be normalized to a common metric (e.g., gill-metal LC50). This unifying feature offers a powerful and consistent approach to comparing potential effects of metals among differing surface waters and changing conditions within a single water body.

The Committee emphasizes, however, that a fundamental assumption of the BLM is that toxicity is driven by exposure to dissolved metal alone, rather than combined toxic effects from dissolved and dietary exposures. While this may be largely true for acute effects, understanding of dietary exposure (via uptake of metal-DOC complexes or bioaccumulated metals in aquatic prey species) may be necessary to predict chronic effects for particular metals. Suspended particulates include algae and detritus which are consumed by aquatic organisms (such as grazers and filter feeders) and may be a major dietary route of exposure for some aquatic organisms.

Applications of the BLM that appear to be adequately supported for regulatory use (e.g., certain WQC, NPDES and TMDL calculations) are specifically described in responses to the charge questions below. These are distinguished from applications which the Committee believes will require further validation (e.g., for interstitial water; for silver) or, in other cases, critical evaluation as to whether the BLM is appropriate and sufficiently robust (e.g., for predicting chronic toxicity; for a broad range of metals). Because the issues of adequate validation and the directions of further research are pervasive across the charge questions, the following discussion summarizes the Committee's recommendations in this area.

### *Additional Validation Needs*

As the authors have acknowledged in the review materials, additional validation and verification of the BLM is necessary before the full potential of the model can be realized. Given the relative newness of the BLM, there has not been sufficient time to validate the model with what would be considered a broad range of aquatic organisms, a wide variety of metals partitioned across key environmental compartments, or a comprehensive range of water chemistry parameters and naturally-occurring field conditions. Certain underlying physical, chemical, and ecological questions (e.g., the composition and comparability of different sources of DOC, the significance of non-respiratory uptake mechanisms) are distinct from the BLM model *per se*, yet will be fundamental to establishing appropriate guidelines for the model's application and interpretation. There is a suite of factors that should be investigated over time that may improve the model's predictability and improve our understanding of its strengths or limitations.

This does not mean that the model should not be used at all in its present state, but rather that it is not ready for indiscriminate use by the federal, regional, tribal or state authorities. The model's use in regulatory contexts should be guided by the Agency to ensure that any forthcoming applications are supported by and conform with the current state of validation. Development of specific guidance by the Agency on the model's use, with flexibility to allow expanded applications in the future, would be helpful in this regard.

Outstanding needs principally relate to:

#### a) Chronic and Sub-Acute Toxicity

The model does not account for chronic or sub-acute toxicity, although this may be incorporated through future research. For metals that have a small acute-to-chronic ratio (ACR), such as copper with an ACR of 2x, the model may predict chronic toxicity with simple adjustments in model parameters. For other metals with moderate to large ACRs, and where the mode of toxicity appears to be different for acute and chronic effects, there is some doubt as to the applicability of the model. Furthermore, there is a need to evaluate acute toxicity contributed by non-dissolved metal species, and acute mechanisms of action not directly related to impairment of physiological function at the gill surface. Other methods may be required to adequately address other mechanisms of metal toxicity. These could include mechanisms of toxicity unrelated to the gill; or toxicity linked to chronic uptake at the gill at concentrations lower than those that affect the gill itself (e.g., damage to dermal surfaces such as fin erosion, internal effects to the liver, gut epithelia, reproductive processes, or energetics that have implications for populations).

### b) Broad Taxonomic Applicability

We recommend that additional testing be performed with a wider range of organisms (freshwater and marine, vertebrate and invertebrate, pelagic and benthic, representing multiple functional groups) and that additional studies be undertaken to compare water-effect ratios with predicted toxicity values generated by the BLM (i.e., model verification with independent data sets). Further, we recommend that a sensitivity analysis be performed with the model to identify those variables to which the model is most sensitive.

### c) Mechanistic and Kinetic Understanding

The model relies upon equilibrium assumptions, yet the importance of kinetic exchanges of metal between ligands in the micro-environment near the gill membrane is unknown. Better understanding of the relationship between biotic ligand metal concentration and expressed toxicity will help to improve the model's predictiveness. Distinguishing relative differences in binding affinity and toxicity mitigation among hardness cations (e.g., Na, Ca, Mg) will provide further improvements to the model. Further elucidation of these differences could provide insight into the validity and applicability of current, simplifying assumptions and models for metal toxicity that use hardness as a variable in site-specific water quality criteria calculations. There are also outstanding questions regarding the applicability of the model to other "biotic ligands" besides the fish gill (i.e., for non-piscine taxa of water column-dwelling organisms), particularly invertebrates and marine species, which may require collection of binding site density and conditional stability constant information specific to other taxa.

In addition to assumptions of molecular equilibrium at the biotic ligand, some data (e.g., pertaining to diluter cycling and toxicant delivery time; Ma et al., 1999) also raise questions of the predictability of the model under non-equilibrium water quality conditions, such as would be expected under dynamic field conditions (e.g., mixing zones, stream confluences).

### d) DOC Complexing

Distinguishing the events and kinetics of dissolved organic carbon (DOC) complexing with divalent cations and biological uptake will contribute greatly to interpretations of model predictions. DOC is not a uniform constituent; DOC generation in surface waters is the result of a complex set of degradation reactions which produce a myriad of dissolved organic ligands with different functionalities. The BLM, however, only allows DOC to be specified as percent humic acid, with the remainder of DOC modeled as fulvic acid. In testing the model's ability to predict copper toxicity, the authors assumed DOC to be 10 percent humic acid. However, the percent of DOC present as humic acid will vary with system type.

In addition, Dahm (1981) demonstrated that there is a distinct, two-phase depletion of organic material introduced into surface water systems: phase 1 involves physical complexing with cations on the order of hours, and phase 2 involves biological (microbial) uptake and metabolism on the order of several days. Yet, the model does not take microbial uptake and decomposition into account.

**e) Applicability to Multiple Metals and Water Chemistry Conditions**

There is a need to validate the applicability of the model to other metals besides copper, and further work is needed to understand and resolve the larger uncertainties associated with silver toxicity relative to copper. It may be important to incorporate additional environmental ligands, such as suspended particulates, that are known to sorb divalent cations. The model should be tested under a broader range of water chemistry (e.g., pH, Ca, Mg, DOC) conditions, including a range of sources of DOC (e.g., from different waters, from interstitial versus overlying water, from allochthonous versus autochthonous sources, etc.), and conditions where several water chemistry parameters are varied simultaneously. A sensitivity analysis of the effects of varying these different water chemistry parameters would be useful when adequate data are generated.

Seasonal and diurnal shifts in water chemistry parameters such as pH and temperature will influence metals bioavailability, thus complicating efforts to obtain representative samples of site water for toxicity tests and to determine which water chemistry data should be used to parameterize the BLM. For example, Brick and Moore (1996) found that total acid-soluble metals concentrations, including copper and zinc, in river water samples increased 2-3 fold at night relative to the day. The Committee recommends, therefore, that further consideration be given to how water chemistry conditions are characterized for use in the BLM.

**f) Use of BLM-based WQC in Sediment Guidelines**

In addition to the charge questions about the BLM addressed in this report, the Agency also requested advice on the potential use of the BLM-derived or adjusted WQC in the interstitial water component of the Metals Mixtures Equilibrium Sediment Guidelines (ESG). The Committee's comments on use of BLM-based WQC in sediment guidelines are contained in a companion document (EPA-SAB-EPEC-00-005, SAB, 2000). In short, the Committee concluded that because the chemistry of interstitial water is not the same as the chemistry in the water column, it would be inappropriate to substitute the BLM-adjusted water column criterion for the water quality criterion in the ESG equation without additional validation experiments. The BLM, if validated for application to interstitial water, would allow consideration of additional site-specific chemistry conditions that affect metals bioavailability; the currently proposed IW component of the ESG is based on the water quality criteria Final Chronic Value for each metal, corrected only for site-specific hardness.

## 4. RESPONSE TO SPECIFIC CHARGE QUESTIONS

**Charge Question 1. Does the BLM improve our ability to predict toxicity to water column organisms due to metals (copper and silver) in comparison to the currently applied dissolved metal concentration criterion?**

In theory, the BLM should provide a more accurate measure of bioavailable metal than does the use of operationally defined "dissolved" metal. The evidence collected to date for copper and silver supports this theory for acute toxicity. In comparison to the currently applied dissolved metal concentration criterion, the BLM has been shown to predict with reasonable accuracy (generally within a factor of two of measured values) the acute toxicities of copper and silver to fish. However, this question bears some qualification to accurately reflect the model's current state of validation and verification. Currently, as the authors have attested, the model has been shown to predict acute toxicity, to a limited number of water column organisms, for selected metals, under equilibrium conditions. Preliminary results with *Daphnia pulex* and with metals other than copper and silver are promising, indicating that the model may well have broad applicability to a range of divalent metals and taxa. The mechanistic framework that the model provides for predicting bioavailability could lead to significant improvements over current criteria based upon dissolved metal concentrations.

**Charge Question 2. Is the scientific and theoretical foundation of the model sound?**

The scientific underpinnings of the BLM appear to be sound. The strength of the model lies in the fact that it is built upon a mechanistic paradigm with a strong physiological basis, i.e., predicting binding at the site of action (gill in fish) and the mechanism of acute toxicity (blockage of sodium and calcium channels) for metals (copper and silver). Additionally, the model incorporates water quality parameters such as DOC and pH for the first time, and it allows for prediction of toxicity under a broader range of environmental variables. It is the strength of the science behind the model that makes it attractive. While the model is built upon a strong fundamental and theoretical basis, it requires additional validation and verification as discussed above.

**Charge Question 3. In comparison to the current WER adjustment for aquatic life criteria, will the application of the BLM as a site-specific adjustment reduce uncertainty associated with metals bioavailability and toxicity?**

Because the BLM is deterministic, its results may be infinitely precise, although possibly inaccurate. To evaluate the extent to which the BLM will reduce uncertainty relative to the WER approach, it is necessary to examine the variability (uncertainty) of model calculations, given realistic variations in its input parameters. The resulting distribution of model results could then be compared with the variability of the empirical data to begin answering this question.

Although application of the BLM may not reduce uncertainty relative to empirical data, its predictiveness over a wide range of environmental conditions makes the BLM a more versatile and effective tool for deriving site-specific WQC than the WER. The reasons are twofold. First, empirical data often are more convincing than modeled results, but may not be feasible to collect for all relevant environmental conditions. The BLM can consider the full range of environmental variables (pH, DOC, hardness, and alkalinity) that may exist at a given site over the course of a year (or longer). Second, the model can be executed repeatedly in practical applications. WERs are limited (and imprecise) in that they represent the water chemistry present at the time the water samples were collected and as such cannot define the range of bioavailability conditions (e.g., that associated with seasonal or episodic changes in water chemistry).

While there are remaining validation needs, as described in this report, the Committee supports use of the BLM as an alternative to the WER method for developing site-specific WQC in some cases (see Charge Question 4). We recommend that the model be utilized in parallel with the WER at sites in order to generate paired data sets using both approaches. These additional comparisons between the two approaches will be valuable for empirical verification, and the potential exists that at a given site, organisms and/or field conditions will need to be tested for which the BLM has not been validated.

Current applications for the BLM and WER, in addition to adjusting WQC for site-specific water chemistry, include effluent permitting under the National Pollutant Discharge Elimination System and the Total Maximum Daily Load procedure. Over the longer term, when more fully validated, the BLM may be useful in the development and application of sediment quality guidelines; in site-specific risk assessments and remediation; in natural resource damages assessment; in chemical registrations; and product risk assessments.

**Charge Question 4. Are the data presented for the validation of the BLM sufficient to support the incorporation of the BLM directly into copper and silver criteria documents?**

To address this question, it is important to clarify what is meant by "incorporation into the water quality criteria documents." There are several possible interpretations, including: (1) using the model to directly establish over-arching national water quality criteria (e.g., CMC and CCC calculations); and (2) modifying those criteria for site- or regional-specific risk assessments or permitting. We recommend somewhat different approaches for each.

**a) National Ambient Water Quality Criteria**

The current water quality criteria documents provide equations for tailoring metal criterion values to different waters based only upon varying water hardness. Clearly, there are convincing data and an emerging consensus that other water chemistry factors are or can be important in modifying metal toxicity. The Office of Water's *Water Quality Criteria and Standards Plan* (EPA, 1998) states that "EPA will update the aquatic life criteria derivation methodology to reflect new science and modeling capabilities." Given the importance of the decisions based upon these criteria, it is generally understood that major revisions should be performed only when the Agency is convinced that the revisions, including underlying models, are scientifically robust.

Current national ambient water quality criteria are based upon a statistical approach which, at least theoretically if not empirically, incorporates the toxicological responses of a broad range of taxa to contaminants. The criteria, however, do not excel at predicting responses across a wide range of field conditions. Research on the BLM has underscored these limitations. On the other hand, it would be impractical to generate databases representing the same taxonomic diversity, coupled with the full range of water quality conditions for a BLM-based criterion for every metal. Thus, it appears both premature and somewhat impractical to use the BLM model to revise the protocol for developing national ambient water quality criteria at this time. It is possible, however, that significant enhancements in the model's accuracy and applicability will be made in the near future so that the BLM can be incorporated into the CMC and CCC protocols.

**b) Site-Specific Modifications to Ambient Water Quality Criteria**

While it may be premature to incorporate the BLM into the documents to derive over-arching national water quality criteria, practical applications of the model for calculating site-specific modifications would be feasible in some cases and have precedent. The Water-Effects Ratio method of adjusting water quality criteria to specific waters, for example, was described in the 1994 *Interim Guidance on the Determination and Use of Water-Effect Ratios (WER) for Metals* (EPA, 1994). Similar guidance could be provided for prudent applications of the BLM to copper, and to a lesser extent to silver, as described below.

***Copper***

With several important caveats, the data presented for the validation of the BLM are sufficient to support its use for site-specific modification of the copper criterion. These caveats, listed below, generally reflect the need to avoid applying the model to water quality conditions or regulatory scenarios that are beyond the scope of the current validation effort. The Committee recognizes that additional studies are underway, and the level of validation is expanding to allow additional applications. Current limitations include the following:

(1) The model should presently be reserved for calculation of site-specific modifications to acute toxicity criteria, i.e., in estimating the criterion maximum concentration. The data are not sufficient to support the current use of the BLM in estimating chronic water quality criteria (i.e., the criterion continuous concentration). However, we recognize that for copper the CMC and CCC are not widely different and the ACR is typically less than 2.0.

(2) The model should presently be reserved for calculation of acute copper criteria for the protection of freshwater organisms excluding algae and macrophytes. It should not

be used in estuarine or marine applications until representative datasets have been used to validate the model's applicability for these waters.

(3) Caution should be used in estimating acute copper criteria when the calculations would be based solely upon predictions or measurements related to non-piscine biotic ligands (e.g., invertebrate respiratory structures). This is because there are less data currently available for the metal-ligand complex (e.g., binding site densities and conditional stability constants) in tissues of invertebrate species than for fish species. Additional data with sensitive species other than daphnids would help to eliminate this concern.

***Silver***

The Committee is less confident in the accuracy of silver acute toxicity predictions than for copper and we do not recommend that this approach be incorporated into the silver criteria document and used to derive the CMC at this time. The principal reason for reservation at this time is that the mechanisms by which silver binds to the biotic ligand under different conditions is not as well understood as for copper (see comments below). The relationship between silver bioaccumulated at the gill and silver toxicity is also unclear. The approach does appear to have merit as a complementary method to the existing WER approach for site specific modifications of WQC, but should be used with caution. The Committee recognizes that the WER approach also has limitations, namely that it utilizes a limited number of species and does not properly account for temporal variations in water quality. Thus, EPEC supports the continued development of the BLM. Parallel use of the model and WER approaches initially would be useful to provide additional validation of the BLM relative to empirical WERs.

There is no question that water chemistry parameters other than hardness, the sole parameter currently recognized in the criteria document, do significantly impact silver toxicity. However, quantitative predictions of acute silver toxicity using the model are more challenging than those with copper for a number of reasons. First, it appears that the level of silver accumulation on the gill varies over time, such that static equilibrium conditions are not necessarily achieved (Wood et al., 1999). Second, only a relatively small fraction of the measured total accumulation of silver at the gill may be associated with binding to physiologically active sites. The potential for accumulation of silver at other physiologically important binding sites not represented by the model is possible. Third, as the Paquin et al. paper in the review materials (EPA, 1999) indicates, variations exist in the strength of DOC binding sites with silver concentration. For these reasons, it has been difficult to demonstrate a consistent correlation of effects with total gill silver under a range of water quality conditions. Fourth, complexes of the ligand with silver chloride appear to contribute slight toxicity in addition to silver-ligand complexing. While this contribution has been incorporated into the present model, the toxicity of silver chloride appears to vary among fish species, particularly at high chloride concentrations (Figure 7, p. 3-97).

The Committee agrees with Paquin et al. (in EPA, 1999) that independent verification of the model in predicting acute silver toxicity with additional datasets is recommended to identify other potential inorganic ligands (e.g., sulfide) that form complexes with silver, and to assess the accuracy of the model under a broader spectrum of water quality conditions and aquatic organisms. We encourage the regulatory and scientific communities as they further apply the BLM model to collect paired datasets of water-effect ratio measurements and BLM measurements for copper, silver, and other metals to allow for model improvement and validation.

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# APPENDIX A:  ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| ACR | Acute-Chronic Ratio |
| BLM | Biotic Ligand Model |
| CCC | Criterion Continuous Concentration |
| CMC | Criterion Maximum Concentration |
| DOC | Dissolved Organic Carbon |
| ESG | Equilibrium Sediment Guidelines |
| NPDES | National Pollutant Discharge Elimination System |
| TMDL | Total Maximum Daily Load |
| WQC | Water Quality Criteria |
| WER | Water-Effect Ratio |