Monitoring Implications of Using the Copper Biotic Ligand Model (BLM) and EPA’s Update of Ambient Water Quality Criteria for Copper

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State Collaborators
- Colorado, Massachusetts, New Jersey, South Carolina, Virginia, West Virginia, Wisconsin, and more to come …
Presentation Overview

- Background: Water Quality Criteria
- Biotic Ligand Model (BLM)
- Comparison of 1986 and Updated Copper Criteria
- Copper BLM Implementation Project
- Monitoring Implications
- Summary, Conclusions, and Next Steps
Background: Water Quality Criteria

- National Criteria Recommendations: Scientifically defensible guidance developed and published by EPA per Clean Water Act Section 304(a)

- Criteria: Adopted part of State/Tribal Water Quality Standards under Clean Water Act Section 303(c)
Why Update the AL Copper Criteria?

- There are currently 629 rivers and streams listed as impaired for copper and 5 for contaminated sediments due to copper.
- The existing aquatic life criteria for copper are underprotective for some waters and overprotective for others.
- The current criteria relies on expensive Water Effects Ratio (WER) testing to develop site specific criteria. A study showed using the Biotic Ligand Model will cost on average 15% of the cost of WER testing.
- The updated criteria utilizes the best available science, including the scientifically established relationships between copper toxicity and water chemistry parameters.
Background: 1986 Aquatic Life (AL) Copper Criteria

- 1986 Copper Criteria are a function of hardness
  - Acute Copper Criteria: $e^{(0.8545\ln(\text{hardness})-1.465)}$
  - Chronic Copper Criteria: $e^{(0.9422\ln(\text{hardness})-1.464)}$

Effect of Hardness on Copper Toxicity to Fathead Minnows (Erickson et al., 1996)

![Graph showing the relationship between hardness and copper toxicity](image)
Limitations of 1986 AL Copper Criteria

- Potentially under-protective at low pH
- Over-protective at higher dissolved organic carbon (DOC)
- The same copper concentration exerts different degrees of toxicity from time to time and from place to place
- Criteria do not typically reflect the effects of other water chemistry factors that are also known to affect metal toxicity
- Requires site-specific water quality criteria adjustments using Water Effect Ratio (WER) procedure
Office of Science and Technology

**Update to National Copper Criteria**

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**Draft Update Released December 2003**

- Uses the Biotic Ligand Model (BLM) to calculate freshwater criteria on a site-specific basis

- BLM model used as a replacement for the hardness equation

- Predicts acute freshwater water quality criteria using an approach similar to that of predicting organism toxicity; chronic criteria derived from acute using acute to chronic ratio

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**Final Update Release Expected Nov/Dec 2006**
The Biotic Ligand Model (BLM) is a bioavailability model that uses receiving water body characteristics and monitoring data to develop site-specific water quality criteria.

**Biotic:** of or relating to living organisms

**Ligand:** any molecule that binds to another

**Model Background and Development**

- Free Ion Model (1980s): Chemical model
- Gill Model (1996): Toxicological model
- Refinement and incorporation into criterion (2000-2004)
BLM Model Inputs and Outputs

**BLM Input Data**
- Temperature
- pH
- Dissolved Organic Carbon (DOC)
- Major Cations (Ca, Mg, Na, & K)
- Major Anions (SO₄ & Cl)
- Alkalinity

**BLM Output Data**
- Site-Specific Copper Criteria
- Copper Speciation
### Example of BLM Input Parameter Measurements

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.8</td>
</tr>
<tr>
<td>DOC</td>
<td>5.0 mg/L</td>
</tr>
<tr>
<td>Ca</td>
<td>11.8 mg/L</td>
</tr>
<tr>
<td>Mg</td>
<td>5.0 mg/L</td>
</tr>
<tr>
<td>Na</td>
<td>1.5 mg/L</td>
</tr>
<tr>
<td>K</td>
<td>0.6 mg/L</td>
</tr>
<tr>
<td>SO₄</td>
<td>3.4 mg/L</td>
</tr>
<tr>
<td>Cl</td>
<td>1.2 mg/L</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>43 mg/L</td>
</tr>
<tr>
<td>Hardness</td>
<td>50 mg/L</td>
</tr>
</tbody>
</table>
Copper BLM Framework

Competing Cations

Organic Ligand Complexes

Cu - DOC → Free Metal ion Cu^{+2} → Free Metal ion Cu^{+2} → Gill Surface (biotic ligand) → Copper Binding Site

Inorganic Ligand Complexes

Cu OH^+ → Cu CO_3^{+} → Cu Cl^+
Copper BLM Output vs. Measured Toxicity

- Fathead minnows, Lab
- Fathead minnows, Field
- D. pulex (CT DEP, Dunbar, 1996)
Comparison of Criteria Approaches

Alkalinity and pH Covary with Hardness

Comparison of CMC calculated by BLM or Hardness Equation

- CMC by Hardness Equation
- CMC by BLM

BLM, DOC = 2 mg/L
BLM, DOC = 5 mg/L
BLM, DOC = 10 mg/L
1986 WER-adjusted vs. BLM-derived Criteria

- 1986 Criteria with Water Effects Ratio (WER) Adjustment is comprehensive in scope, but sampling error is high and precision is low

- BLM is limited in model formulation, but sampling error is low

- Comparison WER-adjusted and BLM-derived site-specific copper criteria in Colorado and Massachusetts showed the two methodologies resulted in similar values
Advantages and Disadvantage of using the BLM to derive Copper Criteria

**Advantages**

- BLM-derived criteria utilizes the best available science and will likely result in more appropriate site-specific criteria.
- Improves our understanding of how water chemistry affects metal availability and toxicity.
- Water chemistry data are cheaper to obtain than site-specific toxicology data.
- BLM can be combined with streamlined WER testing.

**Disadvantages**

- The BLM requires more monitoring data and 1-2 days of training and practice before using.
Copper BLM Implementation Project

This workgroup-based project that involves EPA Regions and States to meet these goals:

- **Implementation Information**
  - “Frequently Asked Questions” (FAQs) Document to be released with final update in Nov/Dec 2006
  - Topics: Background on the BLM, Model Applicability, Minimum data requirements for model input, options for state to implement, permitting issues, monitoring and assessment issues

- **BLM Training Resources**
  - On-site hands-on training, web-based training

- **Communications and Stakeholder Outreach**
  - State Outreach, Conference Presentations, Fact Sheets, etc.
Implementation Information: FAQs

Copper Biotic Ligand Model (BLM) Criteria Implementation
Frequently Asked Questions (FAQs) Outline

0.0 Introduction

1.0 Background
1.1 What are the new national copper criteria and how are they different than the previous copper criteria?
1.2 What is the BLM? Where can I obtain a copy?
1.3 What water quality parameters (model inputs) are used in the BLM?
1.4 Of these, which are the most critical?

2.0 Model Applicability
2.1 Under what conditions can the BLM be used?
2.2 Are there any conditions for which the BLM should not be used?
2.3 Will new versions of the BLM be released in the future? How will this affect the copper criteria?
2.4 Do I have to use the BLM, or can I continue to use the hardness-based criteria?
2.5 How does the BLM compare to the WER, particularly in terms of cost?

3.0 Data Requirements
3.1 What are the preferred analytical methods to measure the water quality input parameters? How much does it typically cost to measure the 12 water chemistry parameters used in the BLM?
3.2 How many observations are adequate to use the BLM?
3.3 Should seasonal variability in the parameters be taken into account? If so, how?
3.4 How much uncertainty results from various sized data sets for developing a site-specific value for the copper criteria?
   3.4.1 Related issues: inter and intra-waterbody variability, of individual parameters (distributions of values) and co-variances between different parameters
3.5 If there are no data for some parameters, are there default values or estimations that can be used?
   3.5.1 Do these defaults need to be defined by eco region, water body type, and/or other some other factor(s)?
3.5.2 Develop one or more case studies to illustrate

4.0 Implementation Options:
4.1 How can the output from the BLM be used to select copper criteria (e.g., Monte Carlo simulation, analytical procedure)?
4.2 What are the options for states to adopt and implement the national criteria statement?

For more information, please contact:

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Monitoring Questions

- How will the BLM affect state water quality monitoring programs?
- How could states refine future monitoring efforts to use the BLM?
- How much does it cost to measure the BLM parameters?
  - approximately $150-$200 for all 10 parameters
- When and how will the updated copper criteria be implemented?
  - Some states have already started using a phased approach (CO)
- Will there be regional defaults or regression equations to fill in data gaps?
- How many data sets are enough to develop site-specific criteria?
- What will be the impact on ambient assessments?
- Can the criteria be developed on a site-specific, seasonal basis?
Environmental Benefits of using the BLM

- Increased precision of the BLM (compared to the hardness-based criteria) will lead to increased efficiency

- BLM-based criteria can be as much as 10 times less stringent than hardness-based criteria in waters with high DOC and neutral pH (which are typical of many water bodies)

- The cost savings of using the BLM instead of WER testing will be considerable for wastewater treatment plants

- Increased monitoring costs will pay greater dividends for environmental protection programs
Summary and Conclusions

- The BLM uses the best available science to develop site-specific criteria that are neither overprotective nor underprotective.

- The BLM simulates the interactions between chemical parameters (e.g., pH, DOC) and copper toxicity.

- The BLM can be used to calculate site specific copper criteria that agrees remarkably well with bioassay-based WER studies.

- BLM may eliminate the need for WER testing.
Next Steps

**Biotic Ligand Model**
- Saltwater BLM is under development
- EPA plans to update the zinc and silver aquatic life criteria using the BLM

**Stakeholder Outreach**
- EPA is open to hearing the ideas, concerns, and questions of States and other stakeholders.
- States are invited to participate in the next Copper BLM Implementation Working Group Call:
  Thursday May 18th, 1-2 PM ET

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