Validation of Biotic Ligand Model Performance in Extremely Hard Surface Waters

SETAC NA - Baltimore
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Background

- Copper regulations inaccurate for Arid West surface waters
  - Elevated hardness (e.g., up to 1200 mg/L)
  - No co-variance between hardness and alkalinity
- Dischargers create effluent-dependent ecosystems
Project Objectives

• Conduct series of acute Water Effect Ratio studies with a range of natural waters
  • 3 species (*C. dubia*, *D. pulex*, *P. promelas*)
  • 7 sites to encompass range of WQ conditions
  • High- vs. low-flow conditions
• Statistical comparison of BLM and empirical results
  • Focus on role of alkalinity vs. hardness in very hard waters (> 400 mg/L)
  • Under what conditions are BLM predictions more or less valid?
Biotic Ligand Model (BLM)

- Uses water chemistry and metal-organism interactions to predict metal toxicity.
- Toxicity occurs when metal accumulation reaches a critical concentration within the most sensitive tissue (e.g., the gills of freshwater fish).
- Relates Cu toxicity to pH, DOC, Ca, Mg, alkalinity.
- Key component of freshwater CMC in draft AWQC (USEPA 2003)
BLM Basis

Active Metal Sites

DOC → Cu^{2+} → Cu, CuOH

H^{+}

Ca^{2+}, Na^{+}, Mg^{2+}?

Inorganic Complexes: \{SO_4^{2-}, Cl^-, HO^-, CO_3^{2-}\}

Gill Surface

[DiToro, 2000]
BLM Input Data

- Water chemistry from WER studies
  - Site and lab waters
  - All flow conditions
- Water chemistry from calcium/magnesium studies
  - Influence of elevated Ca (30 – 400 mg/L) and Mg (30 – 250 mg/L) on copper toxicity to fish and daphnids
## Water Quality – Base Flow

<table>
<thead>
<tr>
<th>Site</th>
<th>Hardness (mg/L as CaCO₃)</th>
<th>Alkalinity (mg/L)</th>
<th>DOC (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandia Canyon, NM</td>
<td>56</td>
<td>124</td>
<td>4.4</td>
</tr>
<tr>
<td>Santa Ana R., CA</td>
<td>188</td>
<td>164</td>
<td>2.5</td>
</tr>
<tr>
<td>S. Platte R., CO</td>
<td>280</td>
<td>204</td>
<td>9.8</td>
</tr>
<tr>
<td>Calapooia R., OR</td>
<td>284</td>
<td>228</td>
<td>1.2</td>
</tr>
<tr>
<td>Salt R., AZ</td>
<td>388</td>
<td>180</td>
<td>6.9</td>
</tr>
<tr>
<td>Las Vegas Wash, NV</td>
<td>780</td>
<td>128</td>
<td>5.4</td>
</tr>
<tr>
<td>Pinal Cr., AZ</td>
<td>1100</td>
<td>16</td>
<td>0.7</td>
</tr>
</tbody>
</table>
## Ca:Mg Study Design

<table>
<thead>
<tr>
<th>Ca:Mg</th>
<th>Ca (mg/L)</th>
<th>Mg (mg/L)</th>
<th>Hardness (mg/L as CaCO₃)</th>
<th>Alkalinity (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09</td>
<td>43.0</td>
<td>239.0</td>
<td>1070</td>
<td>152</td>
</tr>
<tr>
<td>0.11</td>
<td>36.6</td>
<td>189.0</td>
<td>820</td>
<td>144</td>
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<td>0.16</td>
<td>42.1</td>
<td>166.0</td>
<td>640</td>
<td>152</td>
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<td>0.26</td>
<td>43.5</td>
<td>101.0</td>
<td>420</td>
<td>148</td>
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<td>0.67</td>
<td>32.9</td>
<td>31.5</td>
<td>196</td>
<td>144</td>
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<td>2.24</td>
<td>105.0</td>
<td>29.0</td>
<td>395</td>
<td>140</td>
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<td>3.86</td>
<td>172.0</td>
<td>33.1</td>
<td>580</td>
<td>140</td>
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<td>5.48</td>
<td>271.0</td>
<td>29.3</td>
<td>810</td>
<td>140</td>
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<td>7.10</td>
<td>383.0</td>
<td>38.6</td>
<td>1030</td>
<td>140</td>
</tr>
</tbody>
</table>
BLM Results

Observed Cu LC50 (µg/L) vs. Predicted Cu LC50 (µg/L)

Fathead minnow
C. dubia
D. pulex

61% within bounds

Model Adjustment: None
Potential Solutions

• Determine impact of individual water quality parameters on model output (i.e., residual analysis)

• Characterize the importance of calcium and magnesium on copper toxicity at very high hardness
Saturation Issues in Hard Water

Alkalinity (mg/L as CaCO$_3$)

- Over-saturation
- Corrected inputs

$r^2 = 0.6473$

$r^2 = 0.9759$
Model Adjustment: Carbonate precipitation by Ca and Mg
Potential Solutions

• Determine impact of individual water quality parameters on model output (i.e., residual analysis)

• Characterize the importance of calcium and magnesium on copper toxicity at very high hardness
Ca:Mg Results

- Ceriodaphnia dubia -

![Graph showing Ca:Mg results with Mg and Ca treatments.]

Log $K_{Mg-Gill} = 3.6$

Log $K_{Ca-Gill} = 3.6$
Ca:Mg Results
- Fathead minnows -

Mg has no impact up to 50 mg/L (Erickson et al. 1996)
Mg Influence on FHM Predictions

$r^2 = 0.407$

$P < 0.0001$

-Lab water
-Site water

Residual (Predicted:Observed) vs Mg (mM)
Mg Influence on Gill-Copper Accumulation

When Mg > 2 mM: Gill-Cu = -0.991 * (Mg) + 9.909
Constant Gill-Cu = 7.927
BLM Results

Model Adjustment: Carbonate and Mg Influence

86% within bounds
Water Effect Ratio Results
- Measured -

WER = Site LC50 / Lab LC50
Conclusions

• BLM predictions accurate for the most sensitive aquatic organisms
• BLM input corrections should be considered in high hardness surface water
• Model performance improved by incorporating Mg-biotic ligand interactions
Acknowledgements

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