Biotic Ligand Model-Based Water Quality Assessment of Copper

Ron MacGillivray and Namsoo Suk
Delaware River Basin Commission
HDC-SETAC 2017 Spring Meeting
Outline

* Sources and Toxicity of Copper
* Surface Water Quality Criteria for Copper – Guidance and Regulations
  * EPA Aquatic Life Ambient Freshwater Quality Criteria – Copper 2007 Revision
  * Draft Estuarine/Marine Biotic Ligand Model, EPA Estuarine/Marine Copper Water Quality Criteria July 2016
  * DRBC regulations
* Implementing bioavailability-based water quality criteria
  * Monitoring and assessment
* Summary
  * Tiered approach
Copper in Surface Water

- **Natural sources** include weathering and erosion of rocks and soils
- **Anthropogenic sources** include mining, agriculture, pesticide use, metal and electrical manufacturing, industrial and municipal WWTP, sludge from POTWs, and more.
  - In marine environment **antifouling paints**
- **Copper Toxicity** – metals binding to ion channels interfere with essential element uptake
- 2016 DRBC Water Quality Assessment report
  - Multiple exceedances in Zone 5 of the CCC FW criterion for copper at DRBC regulatory hardness of 74 mg/L CaCO₃ (not confirmed with sample specific hardness)
  - Multiple exceedances of DRBC CMC and CCC marine criteria were observed for copper in Zones 5 and 6.
  - Water quality attributes influence the partitioning and toxicity of copper
Biotic Ligand Model

Figure 5. Comparison of CMC calculated by BLM or Hardness Equation. Alkalinity (11 – 245 mg CaCO₃/L) and pH (7.3 – 8.7) Covary with Hardness.
State of Delaware’s copper FW criteria is calculated using the EPA Biotic Ligand Model.

New York allows use of BLM for a site-specific criteria value for copper.

New Jersey and Pennsylvania “cite the BLM, not as a copper criterion, but as an alternative site-specific criterion method”.

Current DRBC FW WQC for copper are hardness based.

Section 3.10.5.E. of DRBC’s Water Quality Regulations provides that Commission will consider requests to modify stream quality objectives for toxic pollutants based upon site-specific factors.
Why is WQC accuracy including factors that affect bioavailability important?

If this does not happen, time and resources could be spent characterizing sites that were perceived to be impaired due to inaccurate criteria, while other sites that should be listed as impaired are not.

EPA FW BLM based WQC for copper uses multiple parameters (≤1 ppt) Zones 2, 3, 4

* Quality and quantity of data needed for BLM
## DRBC Monitoring for BLM Input Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>MDL</th>
<th>LOQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>APHA 4500-CL-(E)</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Alkalinity (Titrimetric, pH 4.5)</td>
<td>APHA 2320</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>pH</td>
<td>YSI 6-series</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Salinity</td>
<td>YSI 6-series</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Temperature</td>
<td>YSI 6-series</td>
<td>-5</td>
<td>-5</td>
</tr>
<tr>
<td>Calcium</td>
<td>200.7_ELS</td>
<td>0.0992</td>
<td>1</td>
</tr>
<tr>
<td>Copper, Dissolved</td>
<td>200.7_ELS (ICP-AS)</td>
<td>1.8</td>
<td>5</td>
</tr>
<tr>
<td>Copper, Dissolved</td>
<td>200.8_ELS (ICP-MS) Scan</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>Magnesium</td>
<td>200.7_ELS</td>
<td>0.0155</td>
<td>1</td>
</tr>
<tr>
<td>Dissolved Organ Carbon (DOC)</td>
<td>APHA 5310-B</td>
<td>0.4</td>
<td>3</td>
</tr>
<tr>
<td>Potassium</td>
<td>200.7_ELS</td>
<td>0.0036</td>
<td>1</td>
</tr>
<tr>
<td>Sodium</td>
<td>200.7_ELS</td>
<td>0.303</td>
<td>1</td>
</tr>
<tr>
<td>Sulfate</td>
<td>EPA 300.0</td>
<td>0.0008</td>
<td>0.8</td>
</tr>
</tbody>
</table>
How to Implement FW BLM Criteria in Delaware River Zones 2, 3 & 4?
Estimates for Missing Water Quality Parameter Data

C1: Model Sensitivity Analysis: Zone 2 Site 2008 to 2012

Based on sensitivity analysis, caution needed when using estimated values for DOC.
Factors that affect copper speciation

DOC

$\text{CO}_3^{2-}$

$\text{Cl}^-$

$\text{etc.}$

Competitive binding at biotic ligand

$\text{H}^+$

$\text{Cu}^{2+}$

$\text{Ca}^{2+}$

$\text{Mg}^{2+}$

(Adapted from Santore et al. 2001).
How would estuarine/marine BLM criteria be implemented in Zones 5 and 6?
Issues:

* How will waters outside the applicable parameter range (pH 7.5 to 8.5) for the SW-BLM be assessed? A range of pH between 6.5 to 8.5 is typically observed in the Delaware Estuary.
* Salinity between 1 to 3 ppt not included in FW or SW model
* Capacity of estuarine/ marine BLM to recalculate with site specific species in local water?
Copper in tidal Delaware River and Bay
(illustrative and not for regulatory compliance)
EU Tiered Approach

Merrington et al. ET&C, 2016

Tier 1: Comparison with generic EQS_{bioavailable}
- Exceedance
  - Pass

Tier 2: Use of user-friendly tool to predict bioavailability
- Exceedance
  - Pass

Tier 3: Local refinement
- Exceedance
  - Pass

Tier 4: Failing to achieve good chemical status

Good chemical status
Improving monitoring data for BLM
- high quality low detection limit metals data
- site-specific dissolved organic carbon (DOC) in Delaware River
  - sensitivity analysis, ecoregion database defaults

A tiered approach to implement bioavailability-based water quality criteria may best utilize limited resources

Coordination among DRBC, basin states, EPA, and stakeholders should continue on criteria development, monitoring and assessment of copper