Biotic Ligand Models
Application to data poor metals

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What are Biotic Ligand Models and where do they come from?

- Gill Surface Interaction Model – Pagenkopf 1983
  - Describes interaction of metals with fish gills and competition from other ions

- Humic Ion Binding Model V – Tipping 1992
  - Describes binding of metals with natural organic matter and competition from other ions

- Biotic Ligand Model – Di Toro 2001
  - Combines both of these models to describe toxicity as a function of water chemistry
Comparability Between Different BLMs

- Similarities between BLMs for different metals and different organisms
- Consistency of Biotic Ligand stability constants for competing ions
- Suggests similarity of interaction between many different fish and invertebrate species
- Similarity of interaction between many algal species to metal toxicity
## Comparability Between Different BLMs

<table>
<thead>
<tr>
<th>Metal</th>
<th>Organism</th>
<th>$\text{Log}<em>{10}K</em>{\text{BL}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Toxic</td>
</tr>
<tr>
<td>Mn</td>
<td>Fish</td>
<td>2.63</td>
</tr>
<tr>
<td>Mn</td>
<td>Invertebrate</td>
<td>2.23</td>
</tr>
<tr>
<td>Cu</td>
<td>Invertebrate$^a$</td>
<td>8.02</td>
</tr>
<tr>
<td>Zn</td>
<td>Fish$^b$</td>
<td>5.5</td>
</tr>
<tr>
<td>Zn</td>
<td>Invertebrate$^c$</td>
<td>5.3</td>
</tr>
<tr>
<td>Ni</td>
<td>Invertebrate$^d$</td>
<td>4.0</td>
</tr>
</tbody>
</table>

- $^a$ - De Schamphelaere & Janssen 2004 *Environ Toxicol Chem* **23**:1365
- $^b$ - De Schamphelaere & Janssen 2004 *Environ Sci Technol* **38**:6201
- $^c$ - De Schamphelaere et al. 2006 *Environ Toxicol Chem* **24**:1190
- $^d$ - Deleebeeck et al. 2008 *Environ Toxicol Chem* **27**:2097
- $^e$ - Binding constant for the toxic metal
“Biotic Ligand” Interactions

- Consistency in binding constants for major competing ions (e.g. Ca$^{2+}$, H$^+$)
- For different toxic metals
- For different test species
- Consistency of biological interaction?
- Predictability for other cases?
Metal Bioavailability

- Large effect due to DOC for many metals
  - For both acute and chronic toxicity
- Effect of DOC predictable using speciation models
  - WHAM6, VisualMINTEQ
- Relative importance of DOC and competing ions depends on the metal
  - Strength of binding to DOC is important
Metal bioavailability

Increasing importance of DOC

Metal
- Pb
- Cu
- Zn
- Ni
- Cd

Increasing importance of competing ions

Expectations based on strength of binding to DOC

based on information from Tipping 1998 Aquatic Geochemistry 4:3-48.
Metal bioavailability

- **Metal**: Pb, Cu, Zn, Ni, Cd

- **Simple bioavailability correction based on DOC only**
- **Effects from both DOC and competing ions**
- **Principal bioavailability effect due to DOC, some effects of competing ions**
- **Simple bioavailability correction based on hardness only**

Effects from both DOC and competing ions
Lead Bioavailability

- Clear effect of DOC on toxicity
- Lead speciation complicated by precipitation with phosphate
  - BLM development complicated by precipitates
- Proposed EU approach applies a DOC correction

Effect of DOC on Pb toxicity to *L. stagnalis* (snail) and *P. rapida* (rotifer)
Iron and Aluminium

- Chemistry dominated by precipitation behaviour
- Toxic effects under some conditions
- Testing to assess effect of water chemistry
- Toxicity reduced by DOC
- BLM development for aluminium
- Empirical model for iron
Manganese Bioavailability

- Evidence of a protective effect from hardness
- Chronic BLM development
  - Competition from Ca\(^{2+}\) for fish and invertebrates
  - Competition from H\(^{+}\) for algae
- Limited effect of DOC (limited binding of Mn)
Cadmium Toxicity

Effect of water hardness on cadmium toxicity, derivation of a PNEC as a function of water characteristics. ESR RAR Cd (2007)
Silver

- Relatively abundant acute ecotoxicity data
- Clear effects of some water quality parameters on toxicity
- Acute BLMs for fish and invertebrates
- Validation studies suggest relatively poor performance at low hardness and low sulphide levels
- Moderate predictive ability
Predicting Chronic Silver Toxicity

- No organised chronic testing for silver
- Chronic tests available for a range of species
- Chronic bioavailability effects less pronounced than acute bioavailability effects
- Limited effect of competing ions (Na$^+$, Cl$^-$)
- Bioavailability effects due to DOC and sulphide
- Alternative approach for chronic toxicity
Chronic Toxicity of Silver

- Silver is strongly bound by both DOC and sulphide in freshwaters
- Sulphide expressed as Chromium Reducible Sulphide (CRS)
- CRS is typically related to DOC
  - High CRS tends to be associated with high DOC
- CRS is typically present at higher concentrations than Ag
Silver and CRS Concentrations

Comparison of dissolved silver (red) and CRS, either measured (green) or estimated from DOC (blue). Monitoring undertaken in the UK between Jan 2010 and April 2011. CRS concentrations are higher than silver concentrations in all cases. Data from European Precious Metals Federation.
Chronic Silver Bioavailability?

- Accounting for bioavailability effects on chronic silver toxicity
- Silver will be toxic under conditions where the molar concentration of silver exceeds the molar concentration of CRS
- Comparable to SEV/AVS approach for sediments
- Validation using chronic testing required
Summary

- BLMs combine 2 important components to describe metal bioavailability
- One of these components may be more important than the other in many cases
- Focus on the most important bioavailability modifying effects
- Validation of the models likely to be required prior to adoption by regulatory agencies