Incorporation of bio-availability for the freshwater compartment
Cu-example

OECD Meeting, 7-8 September 2011

K Delbeke
Aim

• Importance of bioavailability for copper effects to freshwater organisms

• BLM developments

• Acute (US) and chronic (EU) BLM developments and validations

• Use of BLMs for freshwater PNECs and quality criteria
Importance of bioavailability

Factor 30 difference EC$_{50}$ $D. magna$

same species, same strain, different waters

Evidence on site-specific toxicity related to
- DOC, pH, Hardness

Can we quantify the bio-availability effect?
Quantify/Predict Metal Toxicity
The BIOTIC LIGAND MODEL for fish & invertebrates

DOC
Organic complexes

Inorganic complexes (E.g. carbonates, hydroxides)

\( \text{Cu}^{2+} \)

\( \text{Ca}^{2+} \)
\( \text{Mg}^{2+} \)
\( \text{Na}^{+} \)
\( \text{H}^{+} \)

Toxicity

Competition

Toxic action or transport sites = biotic ligand (BL)

organism-water interface

Gill Site Interaction Model (Pagenkopf, 1983)

WHAM (Tipping, 1994)

Di Toro et al., 2001
Laboratory toxicity tests and chemistry

Derivation of stability constants

Development of mathematical structure of BLM

<table>
<thead>
<tr>
<th>‘BL’- constants</th>
<th>Cu-BLM $P. Promelas$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log $K_{Ca}$</td>
<td>3.6</td>
</tr>
<tr>
<td>Log $K_{Mg}$</td>
<td>3.6</td>
</tr>
<tr>
<td>Log $K_{Na}$</td>
<td>3.0</td>
</tr>
<tr>
<td>Log $K_{H}$</td>
<td>5.4</td>
</tr>
<tr>
<td>Log $K_{Cu}$</td>
<td>7.4</td>
</tr>
</tbody>
</table>

$Santore et al, 2001$
Acute BLM development

Variations in fish LC50: factor 100
Predicted within factor 2

Applicable to other species? = calibration of "Lethal accumulated concentration"

Santore, 2002
Acute BLM applications to other species

Acute Fish BLM applicable to range of invertebrates

Santore, 2002
Importance of bioavailability for chronic toxicity

Copper Risk assessment
• Copper effects data-base:

139 High quality NOEC
27 species SSD
HC5-50 : 6-8 µg Cu/L

BUT huge intra-species variability !!!
- P. promelas NOECs : between 5 and 338 µg Cu /L
- R. Subcapitata NOECs : 21-306 µg Cu /L
- D. magna NOECs : 16-164 µg Cu /L

→ BLM development/validation for chronic ecotoxicity
EU framework chronic BLM developments

Information available?

Limited

Speciation, chemical behaviour

3 BLMs

Level of (bio)availability correction

Level 1. Non normalized, NO correction possible

Level 2. Correction for chemical availability

Level 3. Species BLM based bioavailability correction

Level 3.b. Fully normalised SSD approach

Uncertainty related to (bio)availability

Includes abiotic and biotic uncertainty

Accounts for abiotic factors only

Basic correction for bioavailability

Full consideration of bioavailability

Relative uncertainty compared to fully normalised approach

3 BLMs + quantitative confirmation of cross reading for dissimilar taxonomic groups
Chronic Cu-BLMs developed and field validated

<table>
<thead>
<tr>
<th></th>
<th>Chronic fish BLM</th>
<th>Chronic D. magna BLM</th>
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<tbody>
<tr>
<td></td>
<td>De Schamphelaere et al., 2005</td>
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</table>

Relative toxicity of Cu-complexes

\[ R_{\text{CuOH}} = \frac{K_{\text{CuOHBL}}}{K_{\text{CuBL}}} \]

\[ R_{\text{CuCO}_3} = \frac{K_{\text{CuCO}_3BL}}{K_{\text{CuBL}}} \]

Copper constants

\[ \log K_{\text{CuBL}} = 8.02 \]

\[ \log K_{\text{CuOHBL}} = 7.32 \]

\[ \log K_{\text{CuCO}_3BL} = 7.01 \]

Competition constants

\[ \log K_{\text{HBL}} = 5.4 \]

\[ \log K_{\text{CaBL}} = 3.47 \]

\[ \log K_{\text{MgBL}} = 3.58 \]

\[ \log K_{\text{NaBL}} = 3.19 \]

Algae Bioavailability model

\[ (E_b C_{10}^{\text{Cu}^{2+}}) \ (nM) = -114 \ \text{pH} - 0.812 \ (R^2 = 0.91) \]

(De Schamphelaere et al., 2003).
Chronic Cu-BLMs domains

<table>
<thead>
<tr>
<th>Endpoint</th>
<th>Species</th>
<th>Range Phys-chem</th>
<th>Other boundaries</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEVELOPED/VALIDATED</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Algae growth</td>
<td><em>P. subcapitata</em></td>
<td>5.5-8.7</td>
<td>pH 10-500 H 0-20 DOC 0-20 Al&lt; 332 mg/L and Fe &lt; 307 mg/L</td>
</tr>
<tr>
<td>Invertebrate reproduction</td>
<td><em>D. Magna</em></td>
<td>5.5-8.5</td>
<td>pH 10-500 H 0-20 DOC 0-20 Al&lt; 332 mg/L and Fe &lt; 307 mg/L</td>
</tr>
<tr>
<td>Fish growth</td>
<td><em>O. mykiss / P. promelas</em></td>
<td>6-8.6</td>
<td>pH 12-360 H 0-18 DOC 0-18</td>
</tr>
</tbody>
</table>

### Algae
- O. subcapitata (NOEbc)
- C. reinhardtii (ErC50)
- C. reinhardtii (ErC10)

### Invertebrates
- D. Magna

### Fish
- O. mykiss / P. promelas

Measured versus predicted copper NOEC for *Brachionus calyciflorus* 4hr NOEC using the chronic *D. magna* model for the NOEC predictions

Measured versus predicted copper NOEC for *Brachionus calyciflorus* 4hr NOEC using the chronic *D. magna* model for the NOEC predictions

Chronic fish Cu-BLM prediction for 7 days larval growth of *P. promelas* (data from Erickson et al, 1996)
BLM applications to chronic ecotoxicity data-base

Copper Ecotoxicity database

- Algae
- Invertebrates
- Fish

Intra-species variations from 232 to <3

Normalized NOECs

Scenario river Otter United Kingdom
Scenario river Teme United Kingdom
Scenario ditch The Netherlands
Scenario river Rhine The Netherlands
Scenario river Ebro Spain
Scenario lake Monate Italy
Scenario acidic lake Sweden
BLM applications to chronic ecotoxicity data-base

Site-specific PNECs
BLM tools

• Acute BLMs: [http://www.hydroqual.com/wr_blm.html](http://www.hydroqual.com/wr_blm.html)

• Chronic BLMs:
  • User-friendly tool: [http://bio-met.net](http://bio-met.net)
Conclusions

• Copper toxicity varies clearly with water chemistry

• Acute BLMs were developed : US-EPA
  Chronic BLMs were developed for three trophic levels (algae, invertebrates and fish) - Europe.

• The applicability of the BLMs was demonstrated for a range of species and for a variety of natural surface water.

• The bio-availability normalization demonstrated significant reduction in the intra-species variability of ecotoxicity values.

• The incorporation of bio-availability has been crucial because it increased the reliability and ecological relevancy of the PNEC values.