The Biotic Ligand Model: Unresolved Scientific Issues and Site- and Species-specific Effects on Predicted Cu Toxicity

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Background

- The Biotic Ligand Model (BLM) is used to evaluate the site-specific toxicity of copper to aquatic organisms
  - Can be used to develop site-specific water quality criteria (EPA, 2007)
  - Ongoing investigations into different aspects of the Cu-BLM: geochemical, biological
- Current research: quantifying Cu-organic carbon complexation in low hardness waters and subsequent implications for predicting fish toxicity using the BLM

Presentation Outline

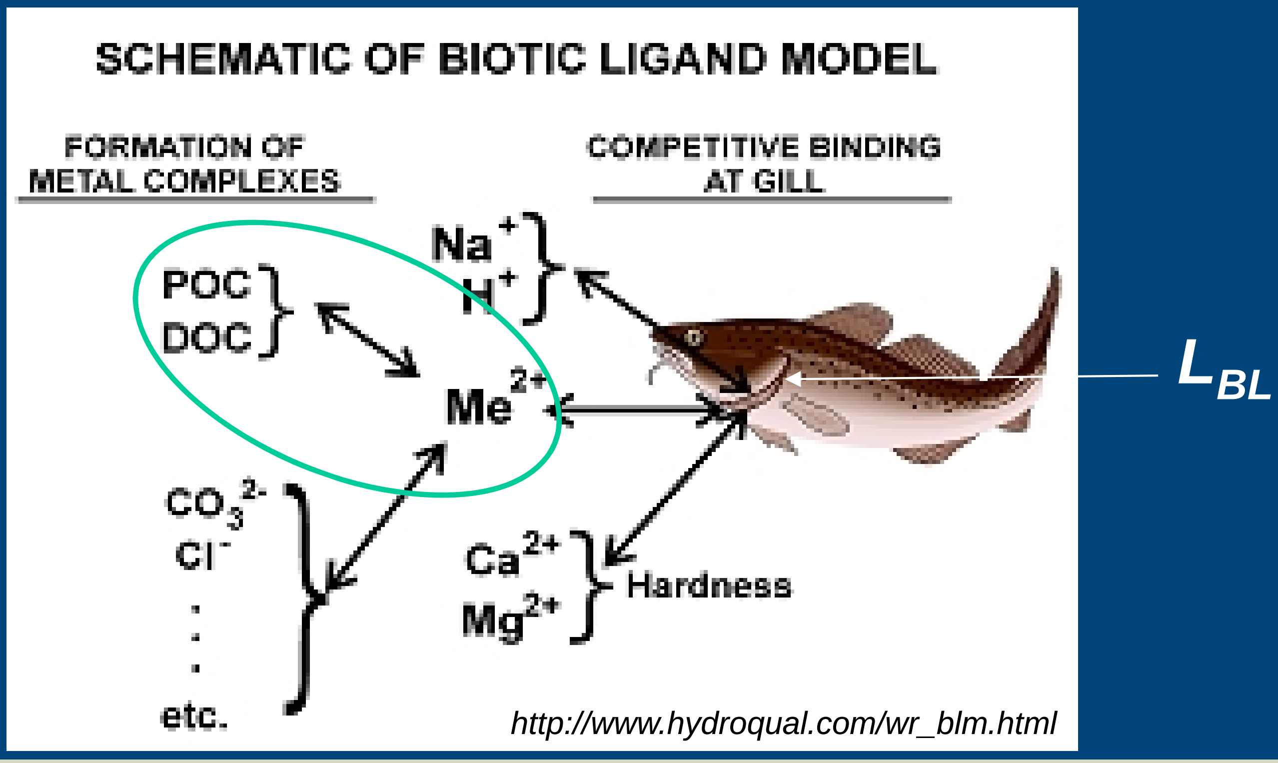
- Overview of BLM
- Site-specific Cu-binding studies and metal-DOM binding
- Cu toxicity in low-hardness waters
- Approaches to incorporating Cu binding constants of “biotic ligands” into BLM

BLM: Background

- Water quality criteria for Cu (and many other metals) expressed as a function of hardness.
  - Increased hardness => decreased toxicity => higher WQC
    - Observed in many controlled experiments
- Well understood that Cu toxicity to aquatic biota is affected by other constituents in water
  - Dissolved organic carbon has been found to reduce Cu toxicity
- BLM developed to numerically address the influence of multiple chemical factors on Cu toxicity

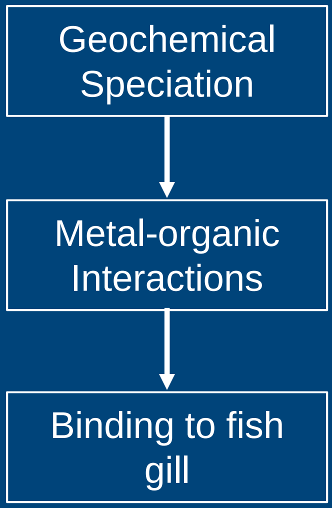
BLM: Conceptual Model

- Cu speciation/sorption to gill binding sites ("biotic ligand") affects bioavailability and toxicity



BLM: Conceptual Model (cont.)

- BLM: predict concentration of dissolved Cu that would cause toxicity to aquatic biota over a range of water quality conditions
  - BLM uses “lethal accumulation” on gill to estimate toxicity
- Three elements of model
  - Geochemical speciation code CHESS (Santore and Driscoll, 1995)
    - Calculates inorganic metal speciation
  - WHAM V model (Tipping, 1994)
    - Calculates degree of metal-organic interaction
  - Biotic ligand (e.g., fish gill) binding constant (Di Toro et al., 2001)



BLM Illustration: Acute WQC in the Presence of DOC

Site-water chemistry parameters are needed to evaluate a criterion. This is analogous to the situation that previously existed for the hardness-based WQC, where a hardness concentration was necessary in order to derive a criterion. Examples of CMC calculations at various water chemistry conditions are presented in Figure 5 and Appendix G.

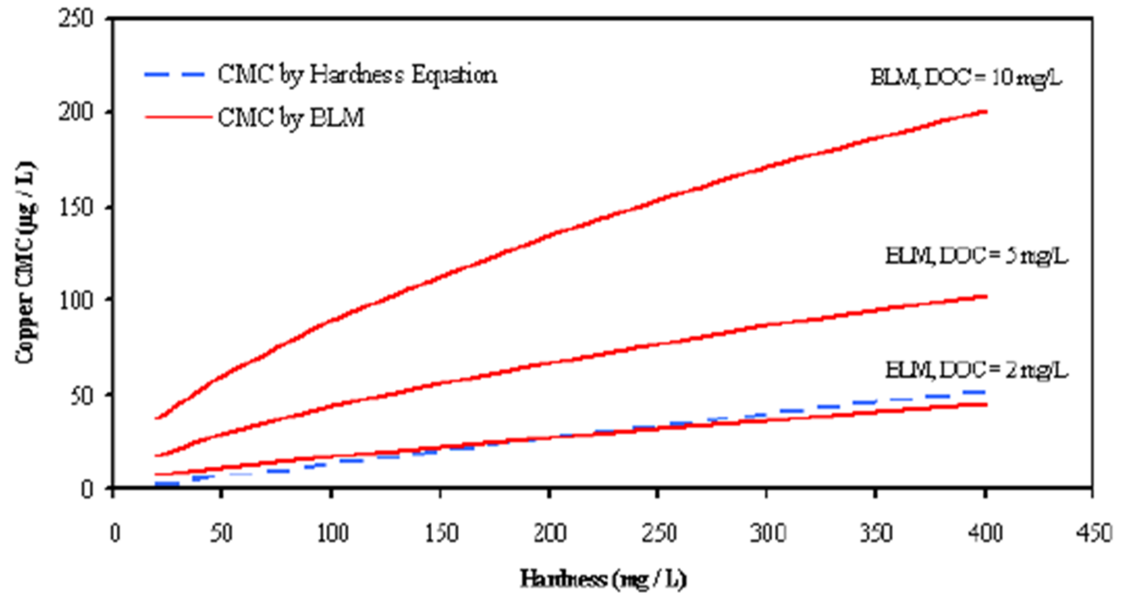


Figure 5. Comparison of CMC calculated by BLM or Hardness Equation Alkalinity (11 - 245 mg CaCO3/L) and pH (7.3 - 8.7) Covary with Hardness

Evaluating Cu-Organic Complexation in a Low-hardness Stream

Site-specific Cu Binding Studies

- Purpose: Evaluate Cu binding properties of ambient DOM
- Performed laboratory studies of site-specific Cu binding in low-hardness waters
  - Finding: Stream DOM had less ability to complex Cu than calculated by the BLM

Methods

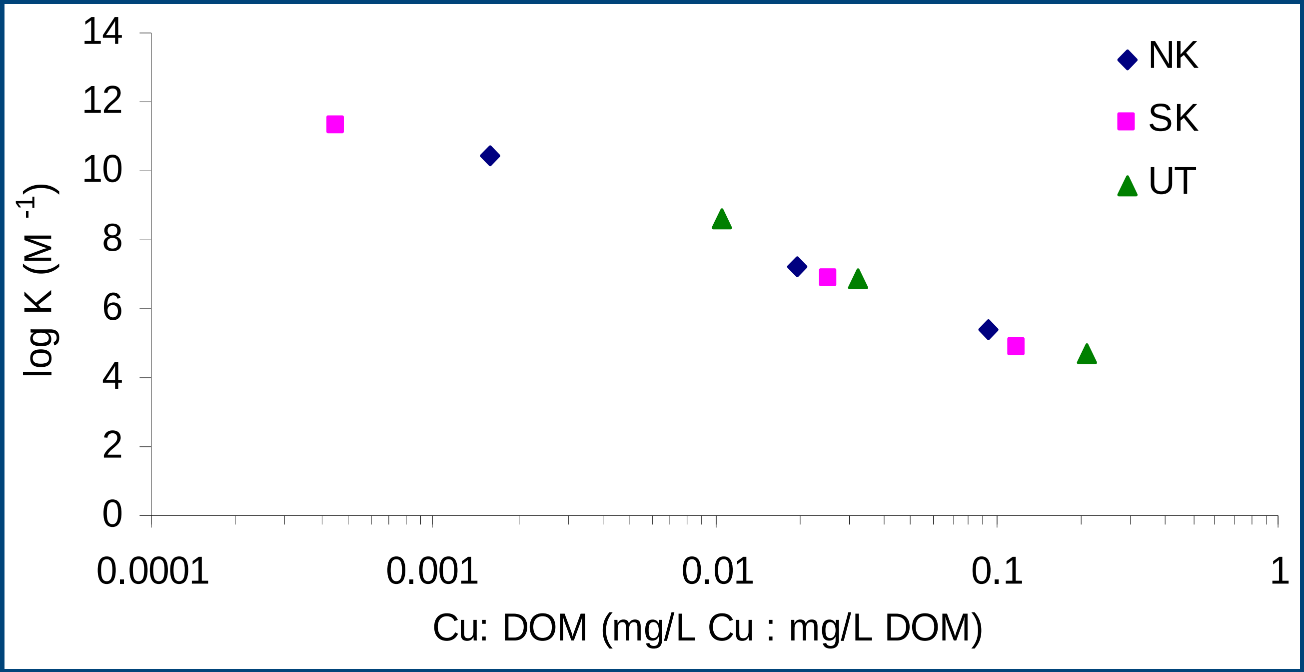
- Isolated DOM from three low hardness headwater streams in AK
- Cu-ISE titration
  - Fit to a 2-ligand model
- CLE-SPE (competitive ligand exchange-solid phase extraction)
  - Environmentally relevant [Cu]
- Used MINTEQ and empirically derived “effective log K” to estimate free Cu^{2+}
- Compared to BLM free Cu

Ambient Water Quality

- pH: 7.1–7.6
- Alkalinity: 13.5–33.9 mg/L as $CaCO_3$
- Hardness: 13.4–28.4 mg/L as $CaCO_3$
- Dissolved Cu: 0.2–1.3 µg/L
- DOC: 1.3–2.2 mg/L

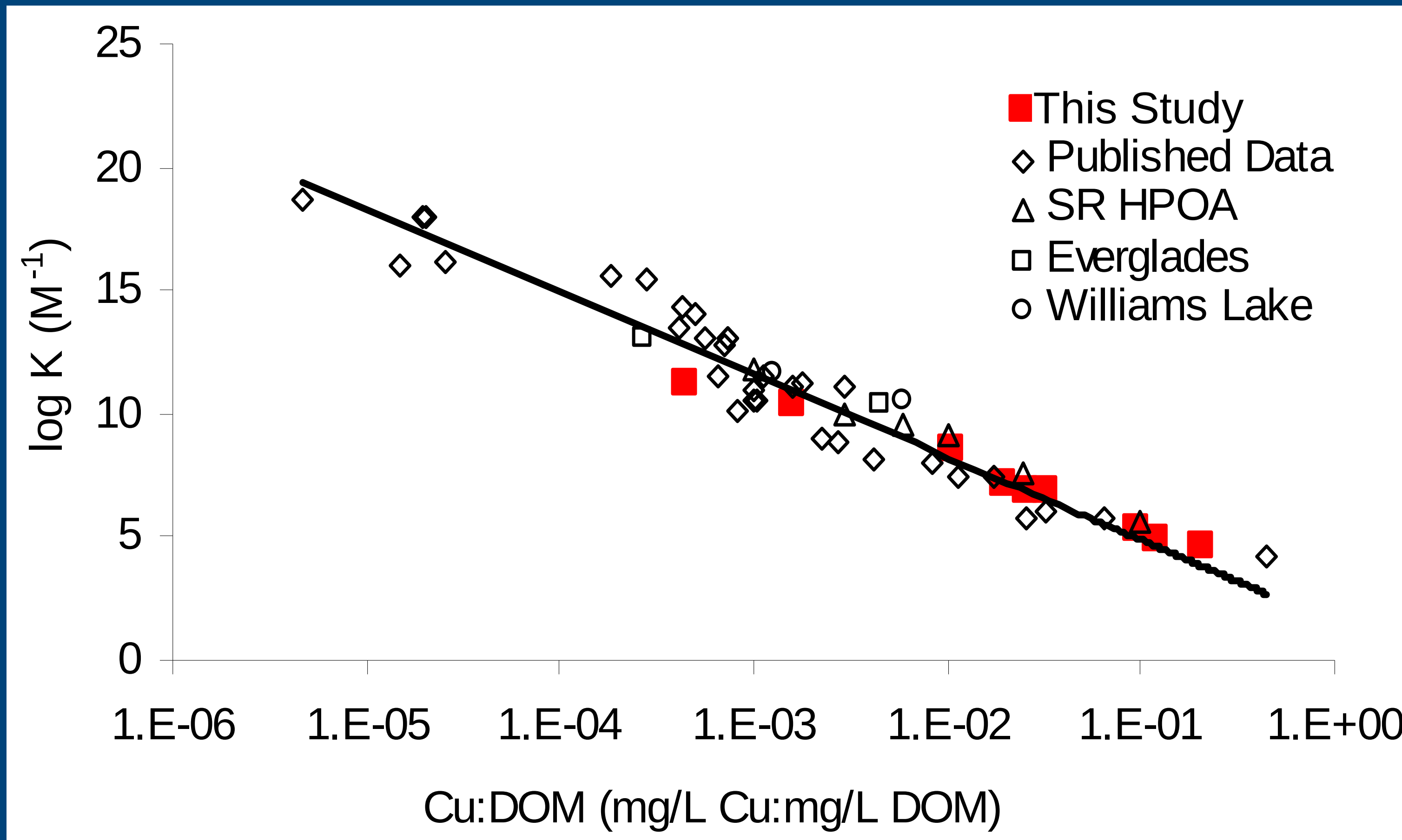
Results: Titration and CLE-SPE

"Effective log K" (net Cu complexation) of site waters a function of Cu:DOM ratio



Increasing Cu relative to ambient DOM results in lower log K

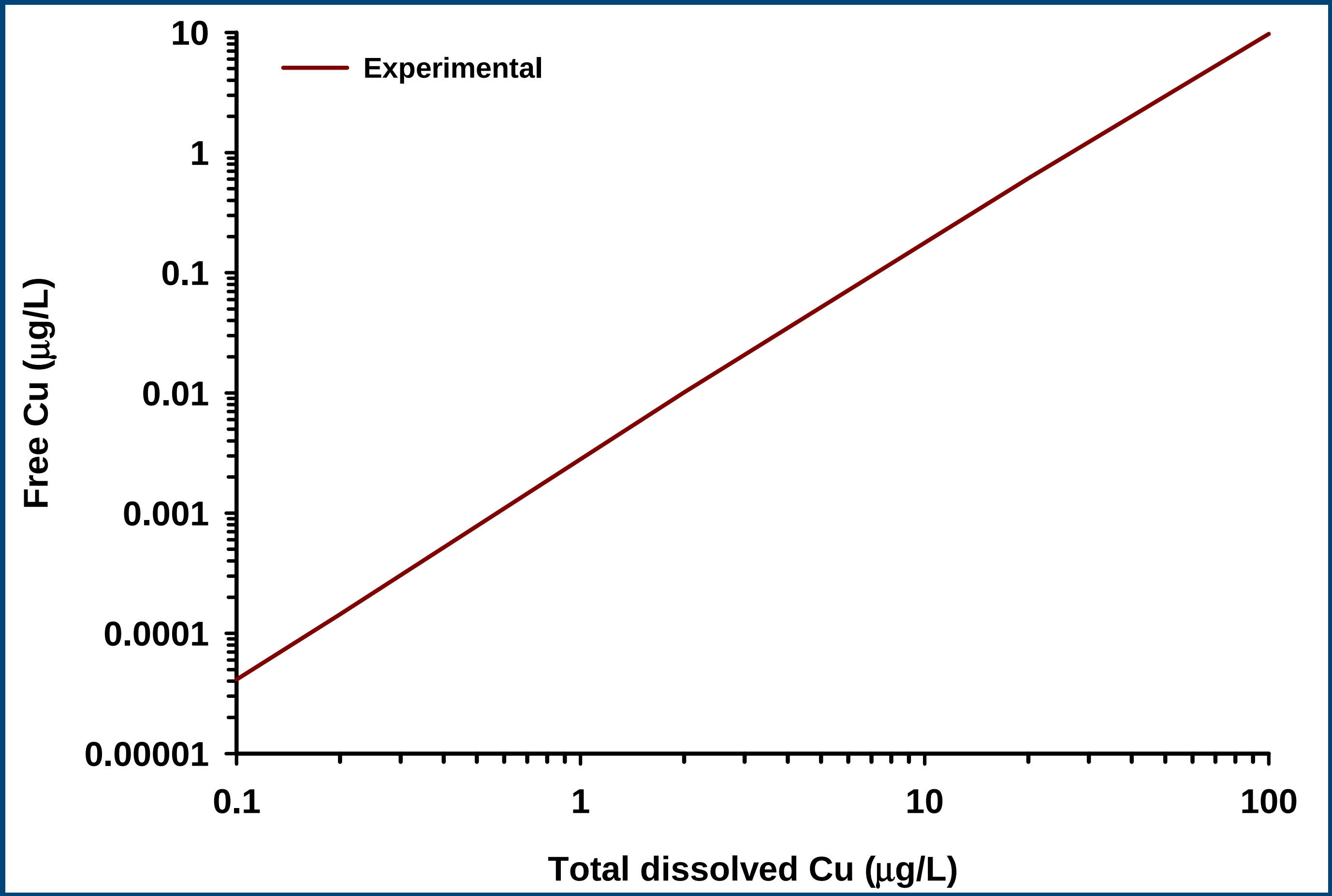
Comparison with Other Studies



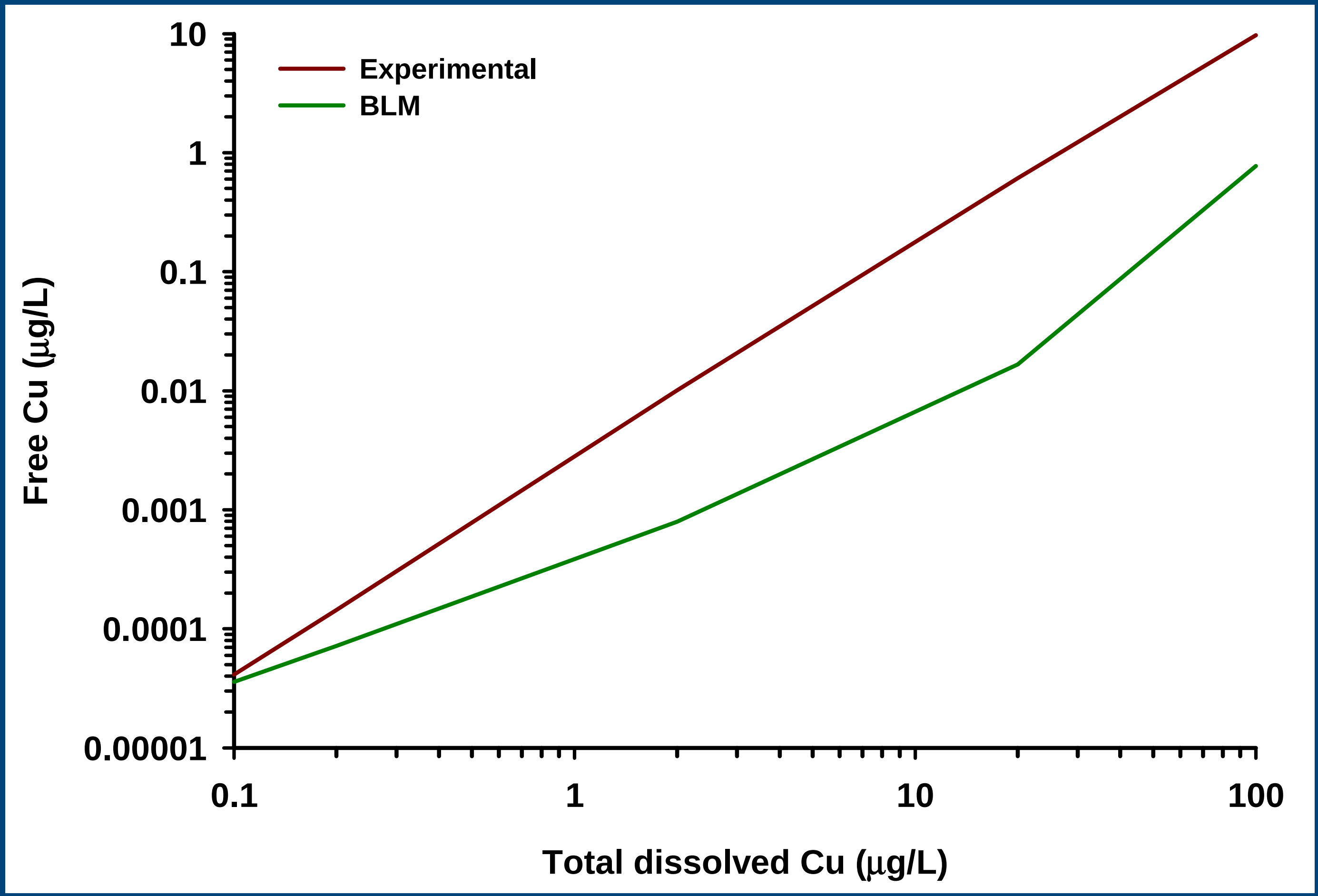
Site-Specific Cu Binding Summary

- Cu-organic binding a function of relative amounts of Cu and DOM present – net affinity changes as more Cu is added
  - Distribution of binding sites in DOM
    - High affinity (high log K) sites less abundant than lower affinity sites
    - As Cu concentrations increase, progressive shift to binding with lower affinity sites
- Cu:DOM ratio is important in predicting complexation

Modeling Free Cu: Empirical Data



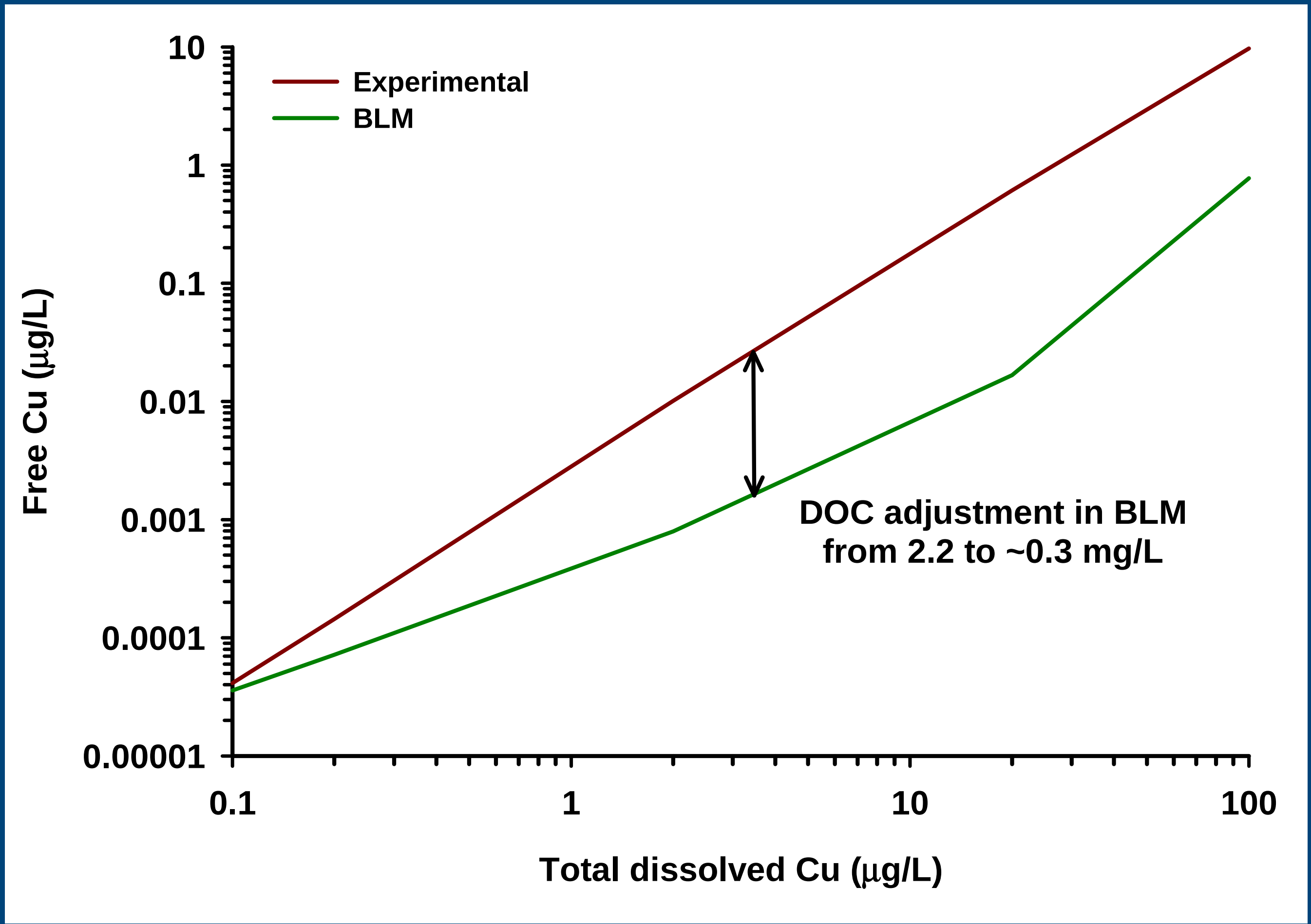
Modeling Free Cu: Comparison to BLM



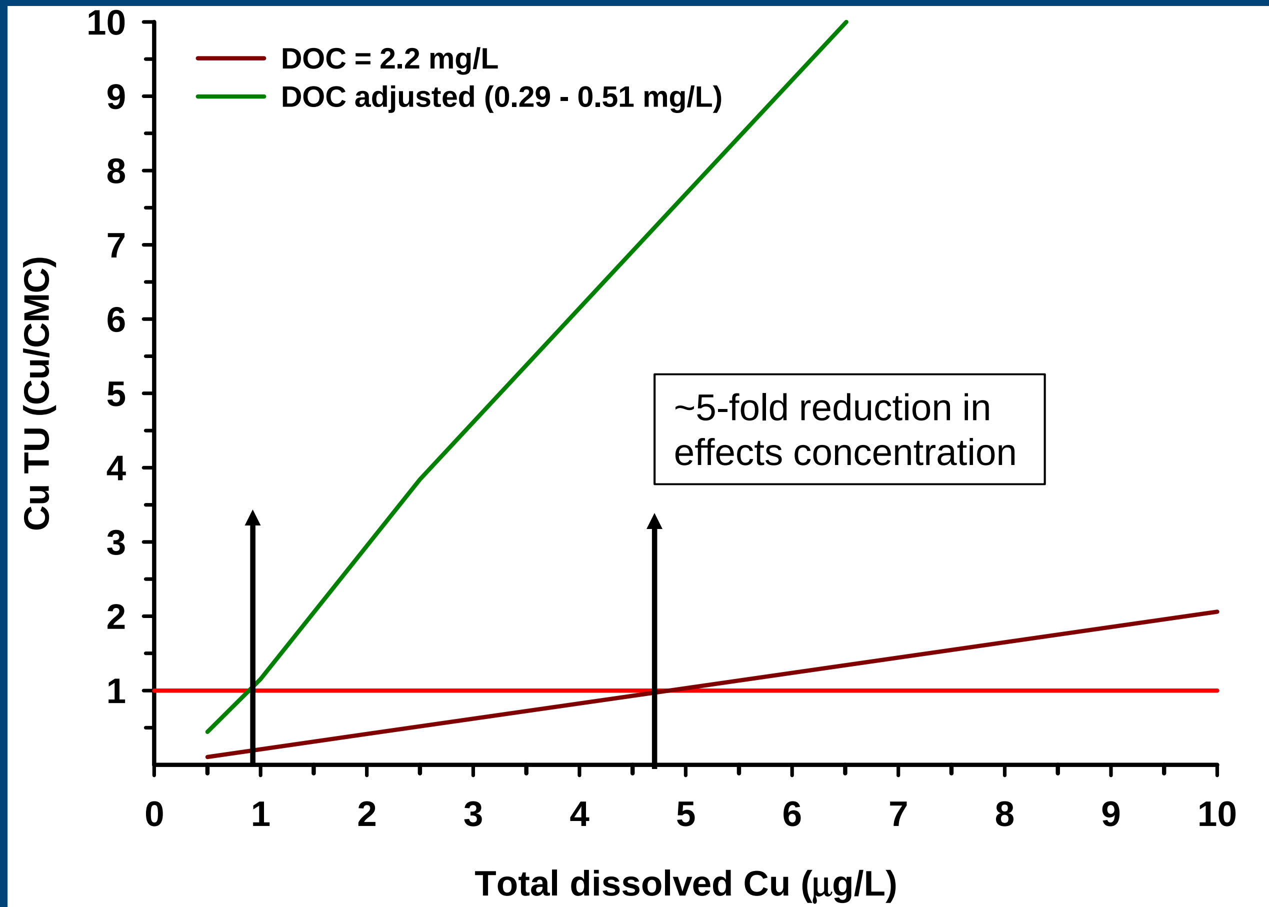
Adjusting DOC Concentrations in BLM to "Match" Empirical Data

- Previous authors (De Schamphelaere et al., 2004; Welsh et al., 2008) proposed adjusting DOC concentration (input to BLM) to match Cu-DOC complexation toxicity results
  - Adjustment factor of 2 used
- This study: adjust [DOC] from 2.2 mg/L to approx. 0.3 mg/L to match experimental data
  - Adjustment factor of approximately 8

Adjusting DOC Concentrations



Implications: Estimating Cu Toxicity with Adjusted DOC



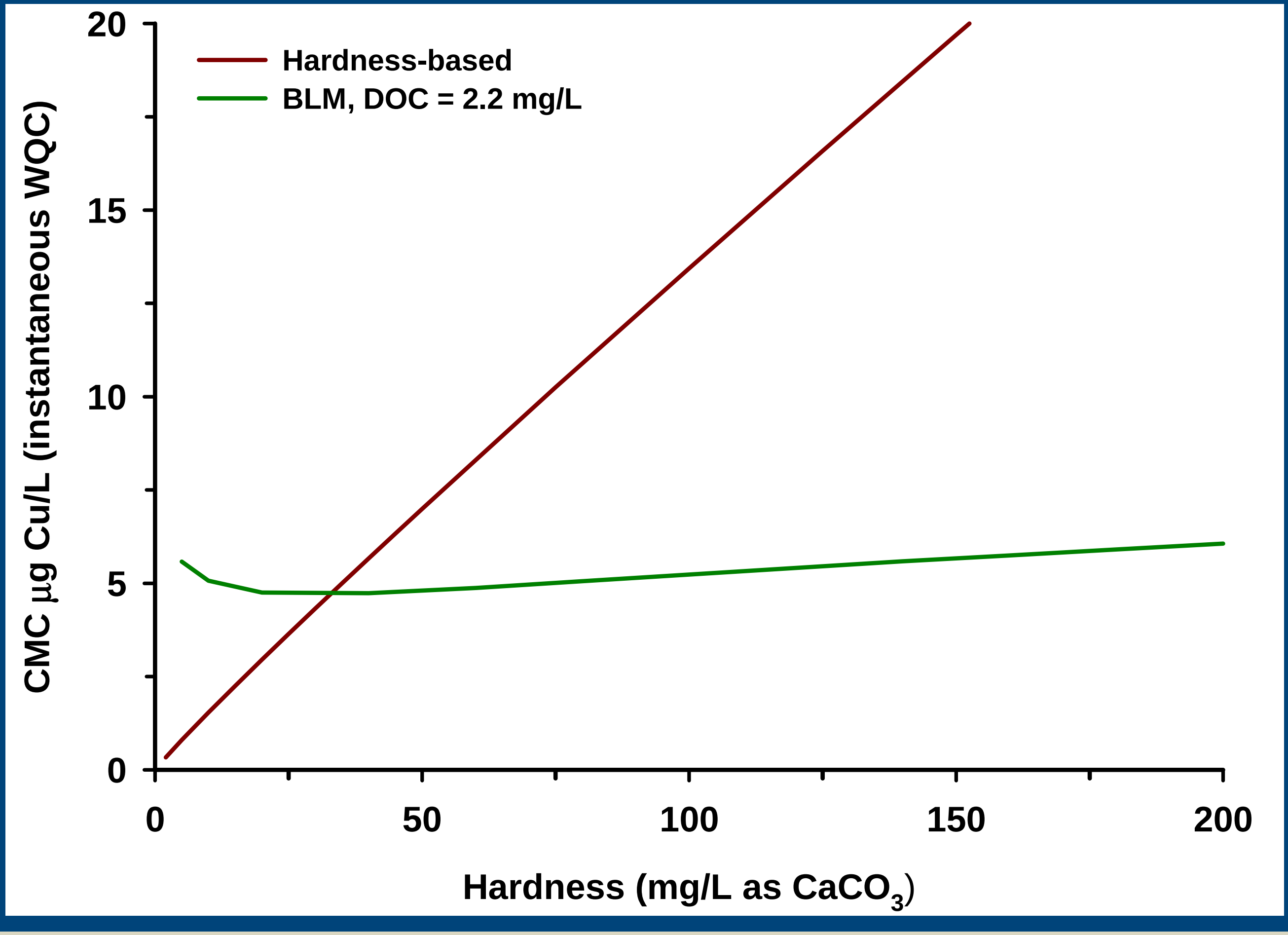
Summary of Cu Binding Results

- BLM under-predicted free Cu compared to site-specific estimates
- Needed to lower DOC in BLM to attain same free Cu results – similar findings to other researchers (e.g., De Schamphelaere et al., 2004; Welsh et al., 2008), but somewhat greater magnitude of adjustment
- Results in a ~ 5-fold decrease in instantaneous WQC compared to BLM

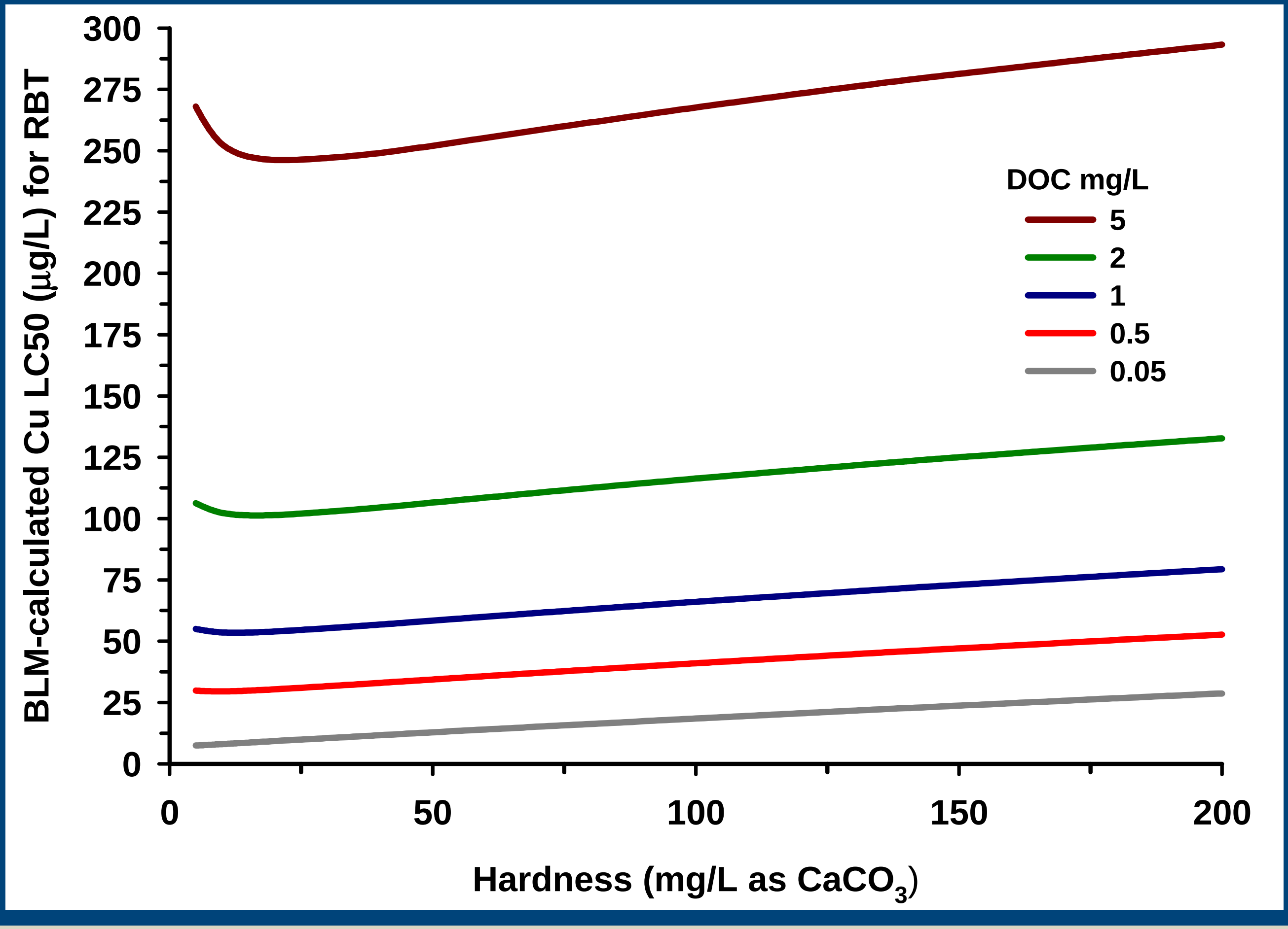
Other Issues: Modeling Cu in Low Hardness Waters?

- Ran series of BLM simulations to further evaluate implications of Cu-DOC complexation in low hardness waters
- Used site-water data as base water quality
  - Temperature = 19°C
  - pH = 7.13
  - DOC = 2.17 mg/L (HA = 10%)
  - Ca, Mg = 4.09, 1.1 mg/L (hardness = 14.7 mg/L $CaCO_3$)
  - K = 0.1 mg/L
  - SO_4 = 1.7 mg/L
  - Cl = 0.5 mg/L
  - Alkalinity = 22.3 mg/L $CaCO_3$
  - S = 0.001 mg/L (default, non-functional)

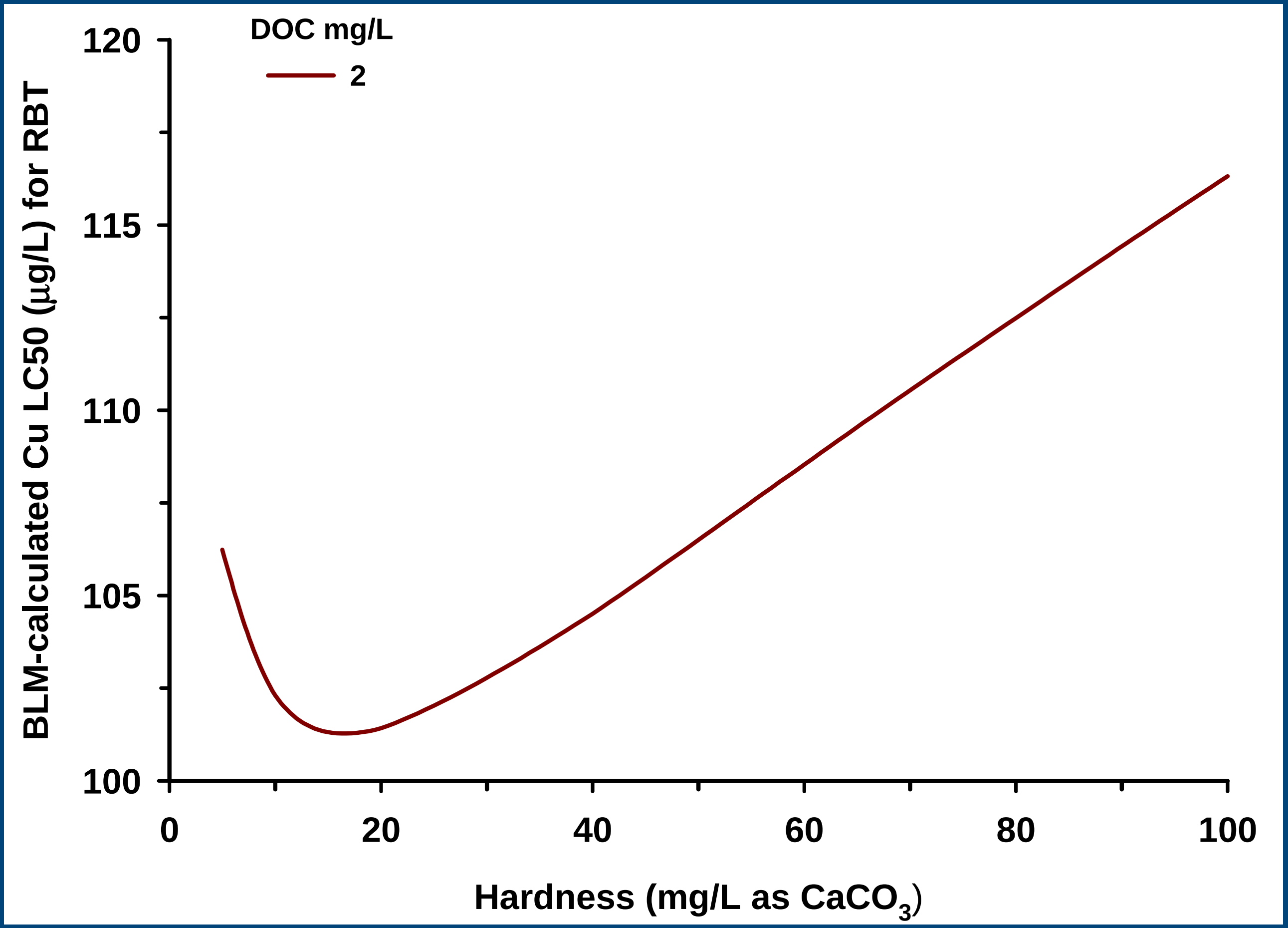
Simulation Results: Varying Hardness; Unadjusted DOC



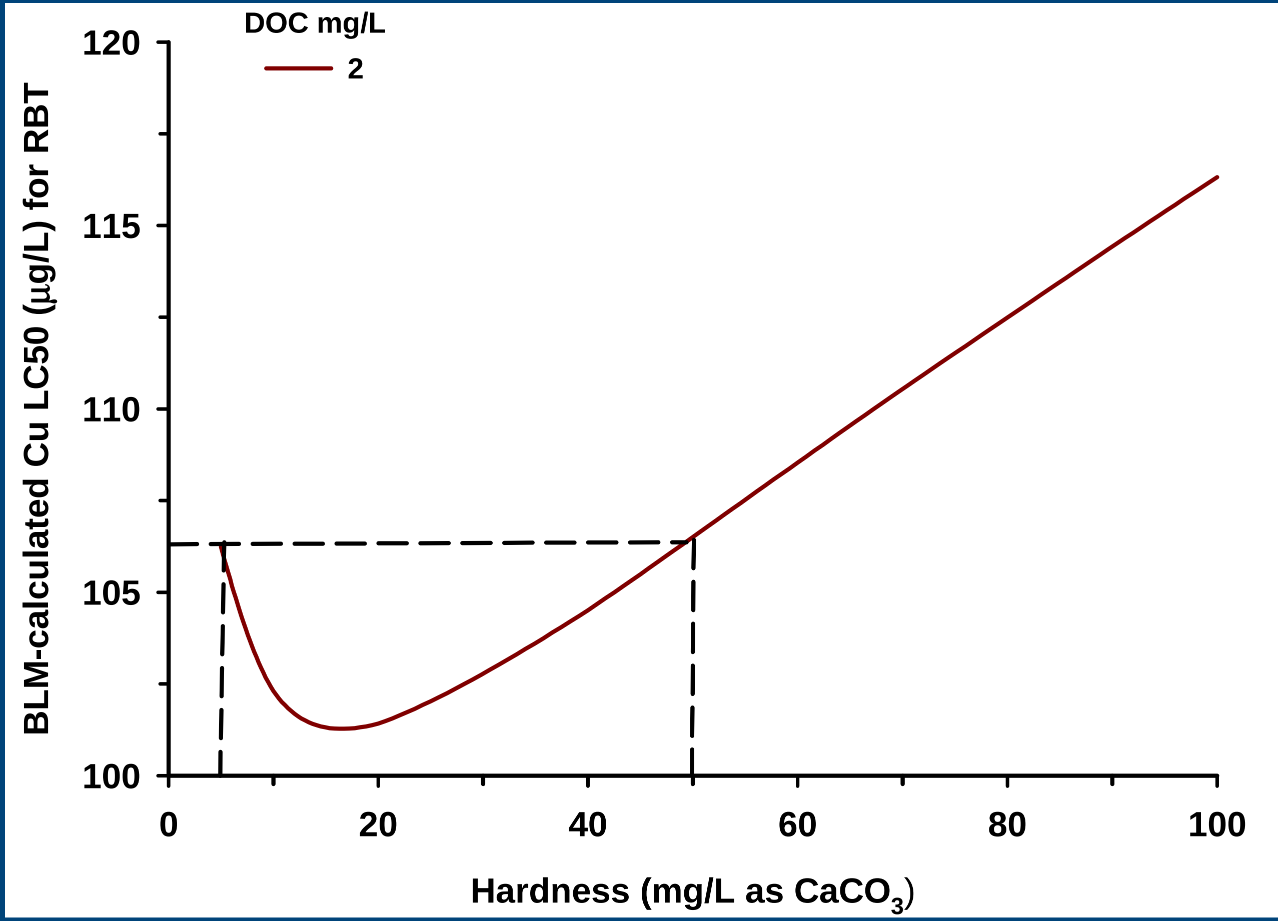
Simulation Results: Rainbow Trout LC50 Varying Hardness and DOC



Hardness Simulation: Artifact of DOC Complexation?



Equivalent LC50, 10-fold Difference in Hardness



BLM Simulations: Summary

- Outputs at low hardness in BLM suggests Cu preferentially bound to DOC rather than the biotic ligand (gill)
- BLM may under-predict toxicity of Cu because of DOC complexation (log K data)
- Degree of under-predicted toxicity of Cu may be exacerbated in soft water

Predicting Cu Toxicity: Implications of Biotic Ligand Component

- Cu toxicity a function of relative complexation: log K of DOC v. log K of biotic ligand
- Biotic ligand not as refined as other two BLM components
- Current BLM uses a constant log K value for the biotic ligand
  - – Shifts in relative log K of DOC in water v. constant log K in biotic ligand alter predicted toxicity

Biotic Ligand (gill) Log K in the BLM

Cu_Rainbow_Trout_06-10-07 - Notepad

File Edit Format View Help

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Column model parameter file, Ver 3.00
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Number of Components, Species, Phases, Linked Lists
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Component Charge  Type  Activity  Site Den
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Cu,         2,       2,       2,       1
DOC,       -1,       2,       1,       .0006
Ca,         2,       2,       2,       1
Mg,         2,       2,       2,       1
Na,         1,       2,       2,       1
K,          1,       2,       2,       1
SO4,       -2,       2,       2,       1
Cl,        -1,       2,       2,       1
CO3,       -2,       2,       2,       1
S,         -2,       2,       2,       1
BL,        -1,      11,       1,       3E-05
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BL-Mg,    11,  1,   0,    0,     0,  0,  0,  0,   1,  0,  0,  0,  0,  0,  0,  1,  3.600     0.000     0.000
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BL-Na,    11,  1,   0,    0,     0,  0,  0,  0,   0,  1,  0,  0,  0,  0,  0,  1,  3.000     0.000     0.000
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Linked Lists
--------------------------------------------------------------------------------
Phase    iTemp iMonte  H   Cu DOC Ca   Mg   Na  K SO4  Cl CO3   S BL  Log Ks  Var Log K   Delta H    Temp
--------------------------------------------------------------------------------
File I/O and System Description
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 2                              |  Type of file (1 = ASCII, 2 = LOTUS)
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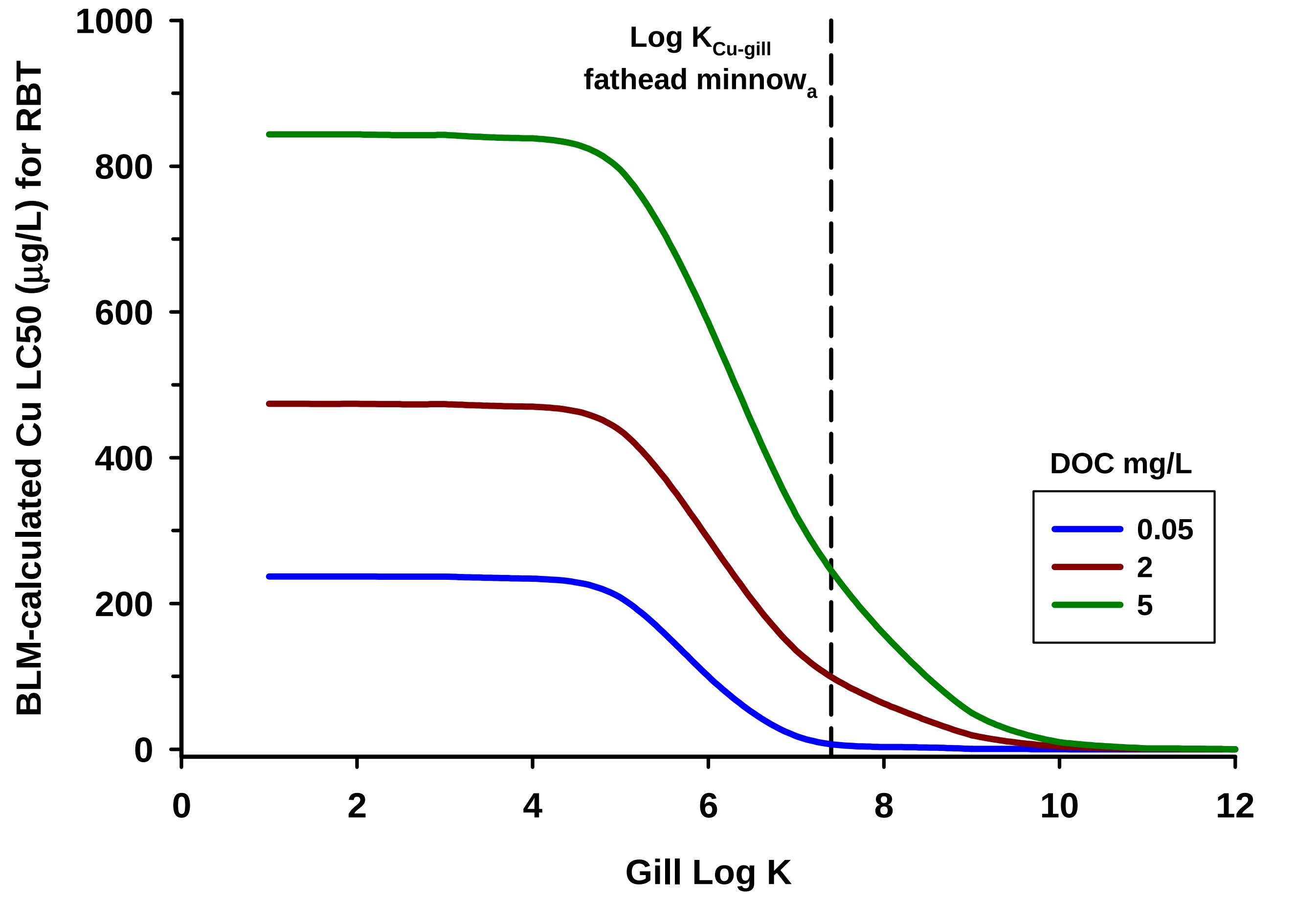
Log K in the BLM



$_a$Playle et al. 1993. Ca = 5.7 mg/L; used in BLM

Shifts in Apparent Gill Log K with Hardness?

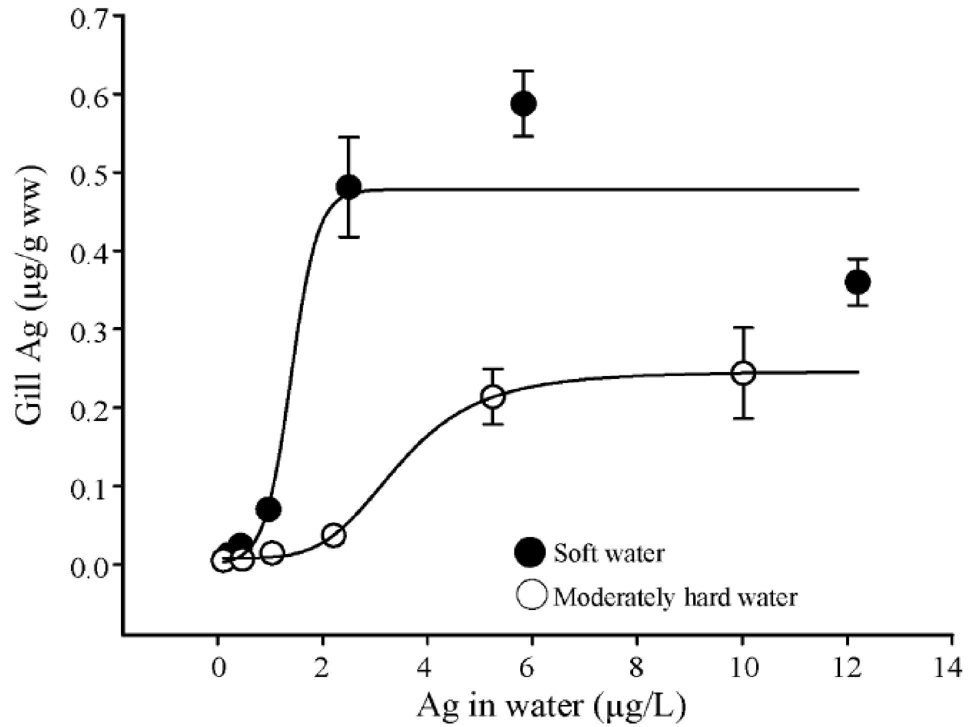
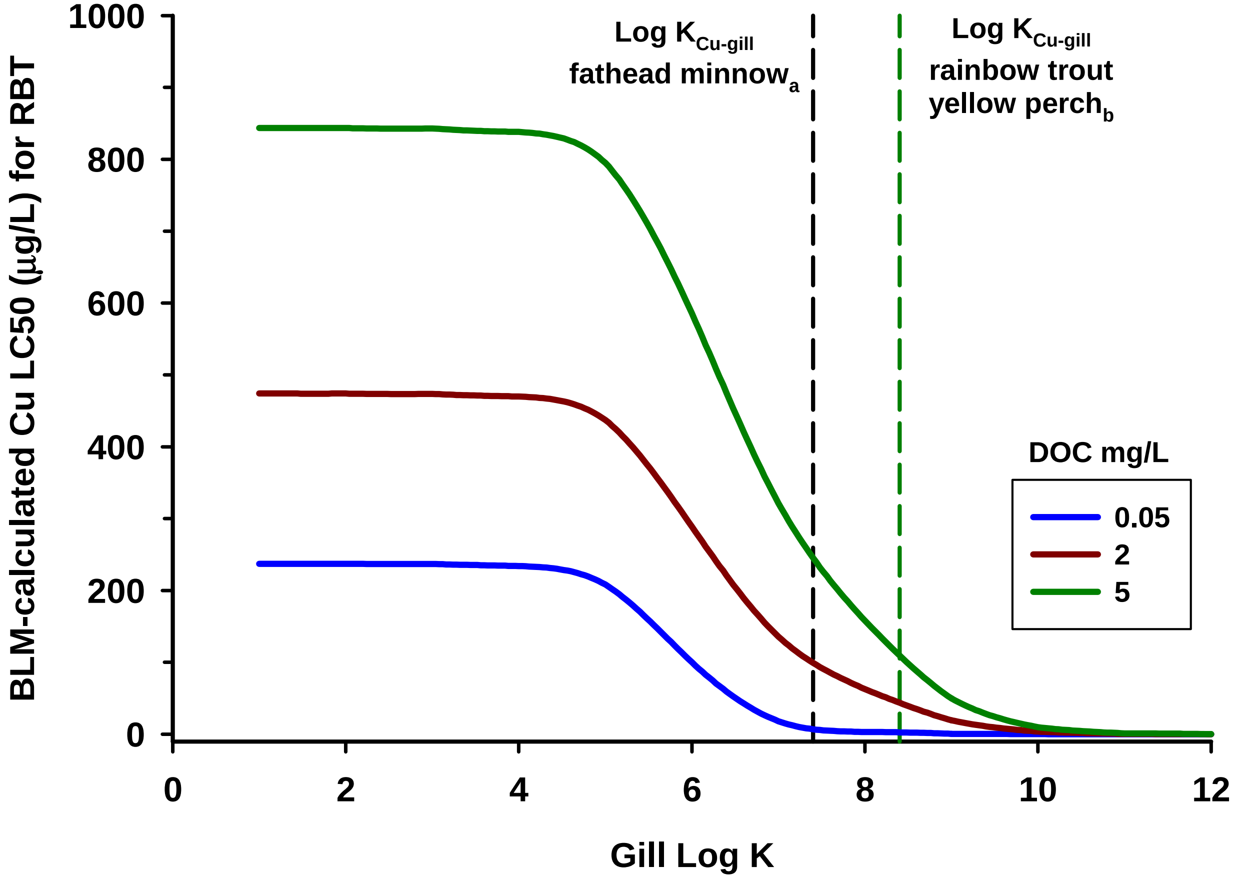


Fig. 4. Silver (Ag) accumulation on the gill (wet weight; ww) of *Pimephales promelas* (previously acclimated to soft water or moderately hard water) during 1-h Ag exposure in soft water. Error bars represent standard error.

Bielmyer et al., 2008.

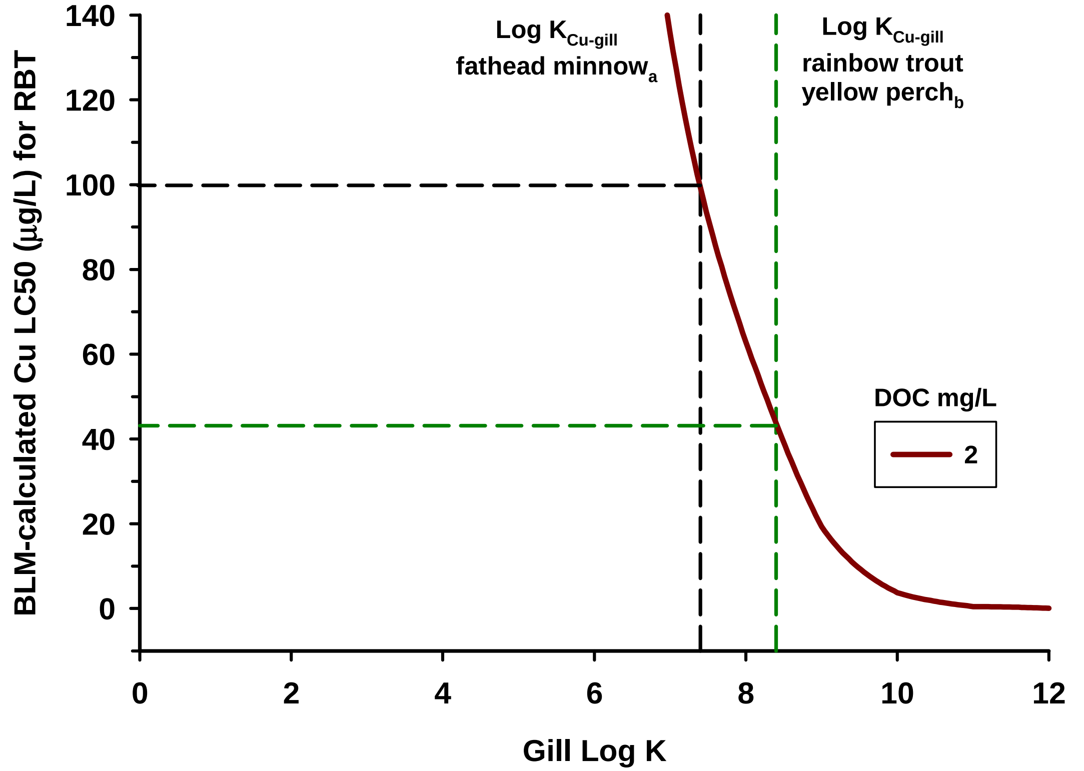
Measured Gill Log Ks in Different Species



[a]Playle et al. 1993. Ca = 5.7 mg/L; used in BLM

[b]Taylor et al. 2003. Ca = 5.2 mg/L

Effects of Varying Log K on Predicted Toxicity



[a] Playle et al. 1993. Ca = 5.7 mg/L; used in BLM
[b] Taylor et al. 2003. Ca = 5.2 mg/L

Biotic Ligand Log K Summary

- Gill Log K known to change with water chemistry – dynamic
- Using Log Ks developed for different species may result in ~ 2-fold change in LC50 at DOC = 2 mg/L
- Variable log K in gill + variable log K in site water = variable predicted toxicity

Conclusions

- BLM under-predicted free Cu compared to site-specific estimates
- Needed to lower DOC in BLM to attain same free Cu results – similar findings to other researchers (e.g., De Schamphelaere et al., 2004; Welsh et al., 2008), but somewhat greater magnitude of adjustment
  - ~ 5-fold decrease in instantaneous WQC

Conclusions (cont.)

- Simulation modeling with BLM suggests Cu preferentially bound to DOC rather than the biotic ligand (gill) at low hardness
- Degree of under-predicted Cu toxicity
- Variable log K in gill + variable log K in site water = variable predicted toxicity
- Uncertainty in Cu toxicity can be reduced with supplemental site-specific data
  - Cu-DOC complexation
  - Species-specific toxicity testing