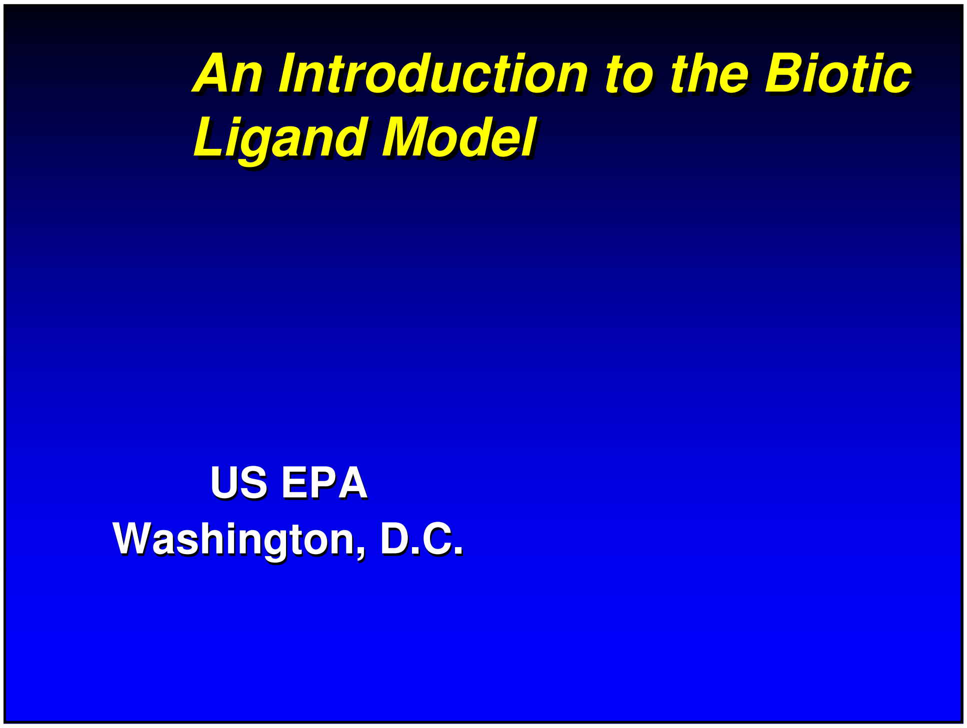
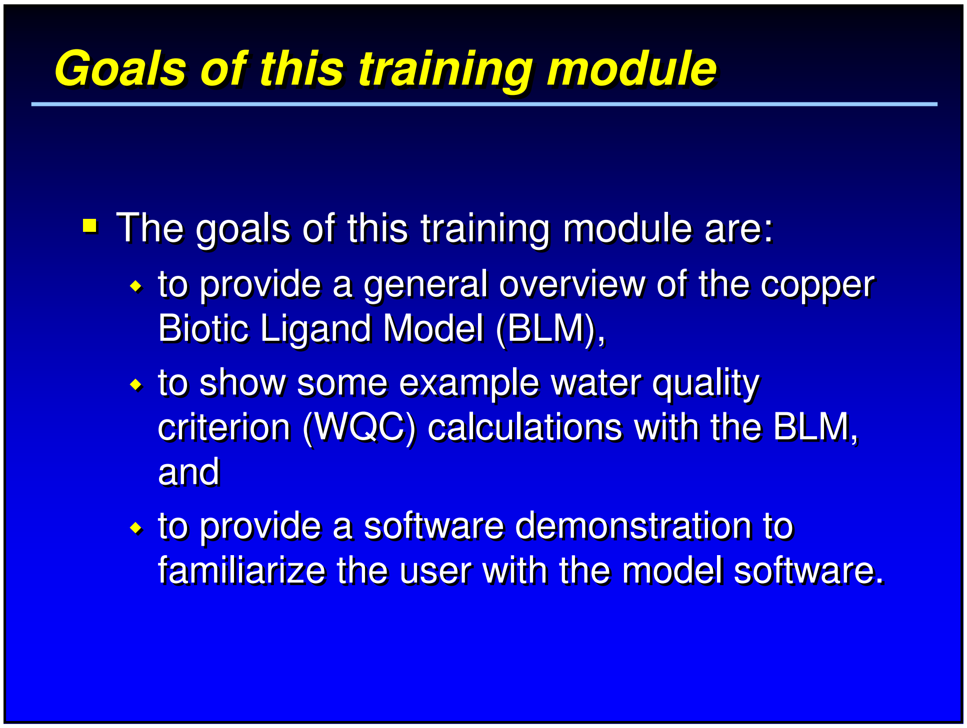


An Introduction to the Biotic Ligand Model

US EPA
Washington, D.C.



Goals of this training module

- The goals of this training module are:
  - to provide a general overview of the copper Biotic Ligand Model (BLM),
  - to show some example water quality criterion (WQC) calculations with the BLM, and
  - to provide a software demonstration to familiarize the user with the model software.

Outline of the training module

1. Basic Definitions
2. Criteria Background
3. Background and Technical Summary
4. Biotic Ligand Model Examples and Case Studies
5. BLM Demonstration
6. Contact Information and Bibliography of Cited and Supplemental References

Section 1: Basic Definitions

What is the Biotic Ligand Model?

- Before we begin, let's start with a basic definition of the Biotic Ligand Model, or "BLM" for short:
  - The BLM is a computer model that uses 10 water chemistry parameters (the "model inputs") to calculate a freshwater copper criterion ("the model output")
  - The BLM is the basis of EPA's 2007 national recommended 304(a) freshwater criterion for copper

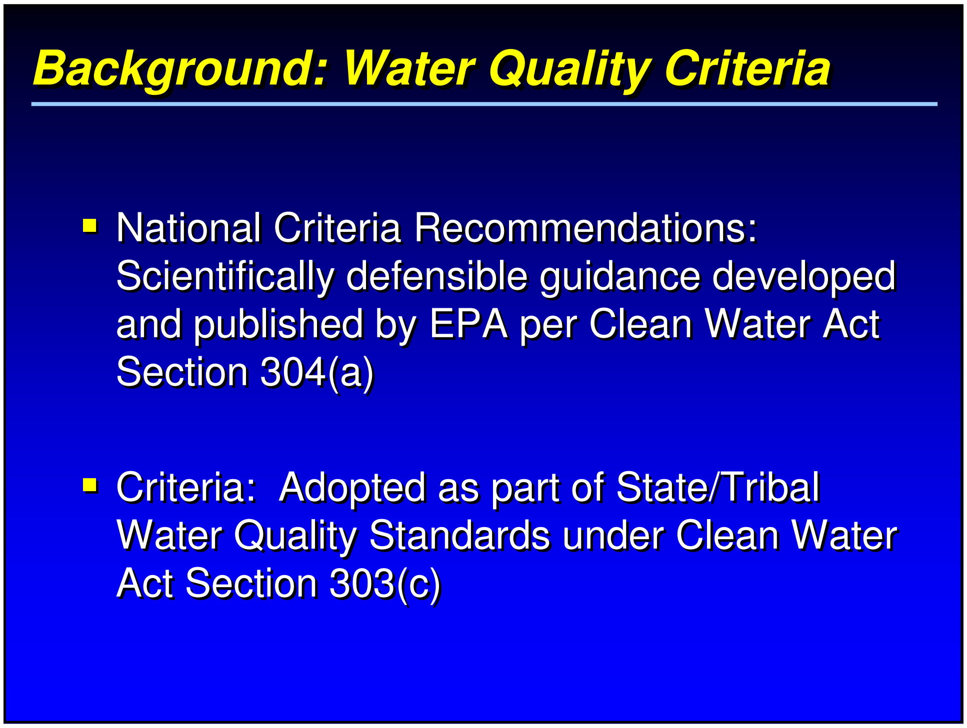
Key terms and acronyms

- ACR - Acute to chronic ratio
- AWQC – Ambient water quality criteria or criterion
- BLM – Biotic Ligand Model
- DOC – Dissolved organic carbon
- GMAV – Genus mean acute value
- LC50 – Lethal concentration associated with 50% mortality of a test population
- NOM – Natural organic matter
- WER – Water effect ratio
- WQC – Water quality criteria or criterion

Section 2: Criteria Background

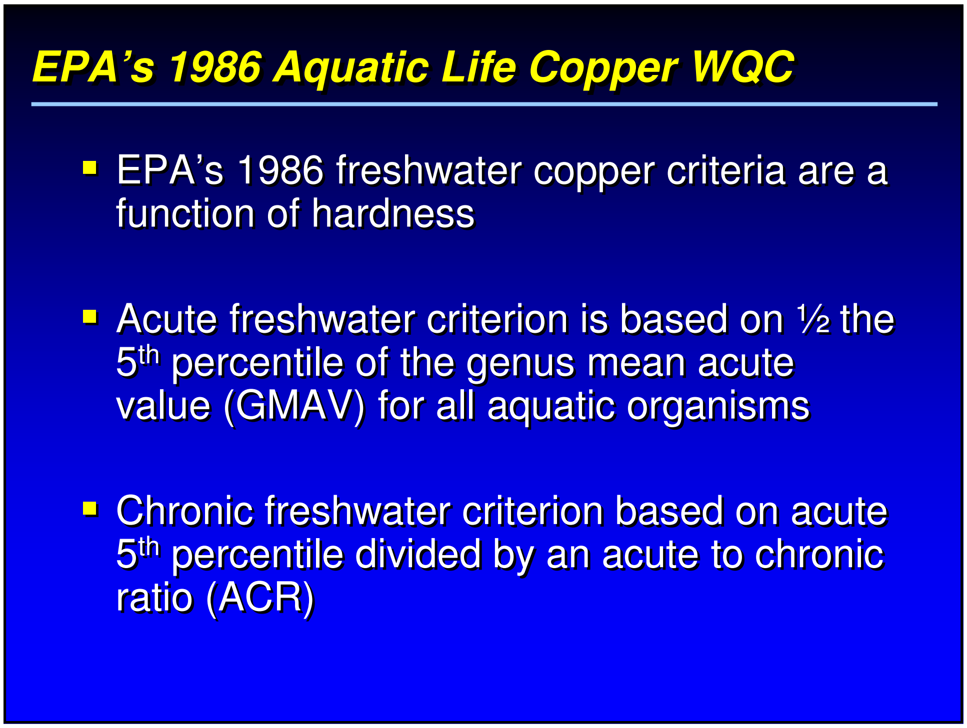
Key points to learn in this section

- Water quality can affect metal toxicity (in particular, Natural Organic Matter [NOM], and pH have a strong affect on copper, but hardness cations, alkalinity, and sodium also play a role)
- Failure to consider these effects may make a WQC overprotective or underprotective for a large number of sites where permits for metals discharges are needed
- The BLM can be used to consider these effects when developing copper criteria



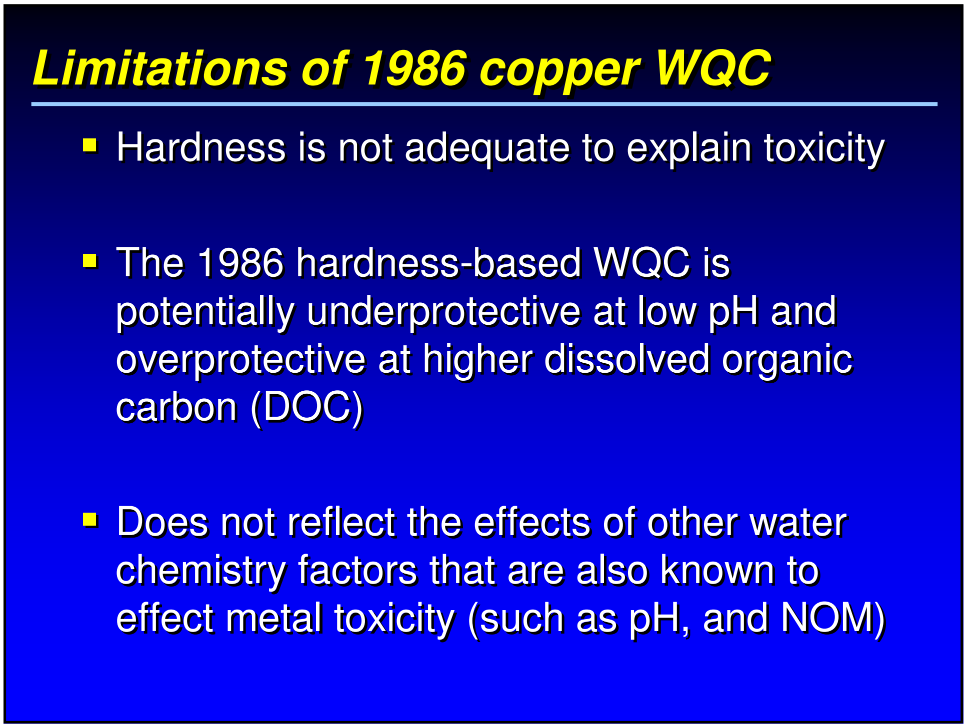
Background: Water Quality Criteria

- National Criteria Recommendations: Scientifically defensible guidance developed and published by EPA per Clean Water Act Section 304(a)
- Criteria: Adopted as part of State/Tribal Water Quality Standards under Clean Water Act Section 303(c)



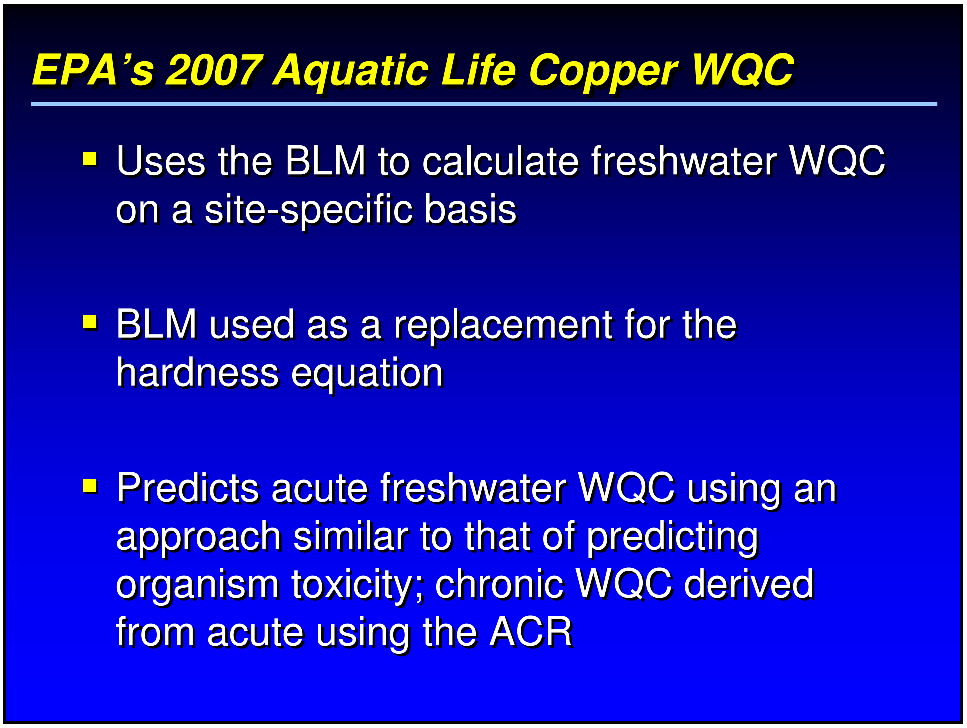
EPA's 1986 Aquatic Life Copper WQC

- EPA's 1986 freshwater copper criteria are a function of hardness
- Acute freshwater criterion is based on ½ the 5th percentile of the genus mean acute value (GMAV) for all aquatic organisms
- Chronic freshwater criterion based on acute 5th percentile divided by an acute to chronic ratio (ACR)



Limitations of 1986 copper WQC

- Hardness is not adequate to explain toxicity
- The 1986 hardness-based WQC is potentially underprotective at low pH and overprotective at higher dissolved organic carbon (DOC)
- Does not reflect the effects of other water chemistry factors that are also known to effect metal toxicity (such as pH, and NOM)



EPA's 2007 Aquatic Life Copper WQC

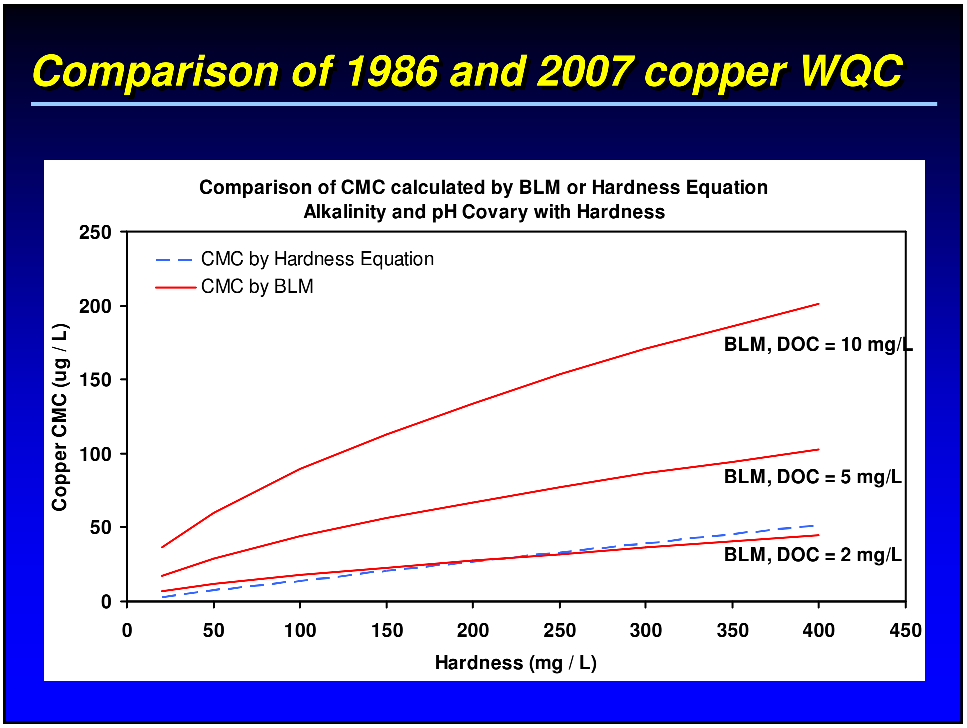
- Uses the BLM to calculate freshwater WQC on a site-specific basis
- BLM used as a replacement for the hardness equation
- Predicts acute freshwater WQC using an approach similar to that of predicting organism toxicity; chronic WQC derived from acute using the ACR

Why is the BLM an improvement to the hardness-based WQC?

- Using the BLM allows regulators and dischargers to account for the effect of water chemistry parameters (e.g., DOC, pH, major ions, and alkalinity) on metal toxicity to aquatic organisms
- Using the BLM provides more accurate WQC without the expense or time required for deriving a water effect ratio (WER)

How do the hardness and BLM-based WQC compare?

- As you will see in the next graph, there is remarkably good agreement between the hardness and BLM equation at low DOC concentrations
- At higher DOC concentrations, the BLM calculates very different WQC values as compared to the hardness equation
- This is really the whole point of the model: to provide an easy way to estimate how WQC values should respond to changes in water chemistry variables such as DOC, pH, alkalinity, Ca, Na, etc.



Comparison of 1986 and 2007 copper WQC

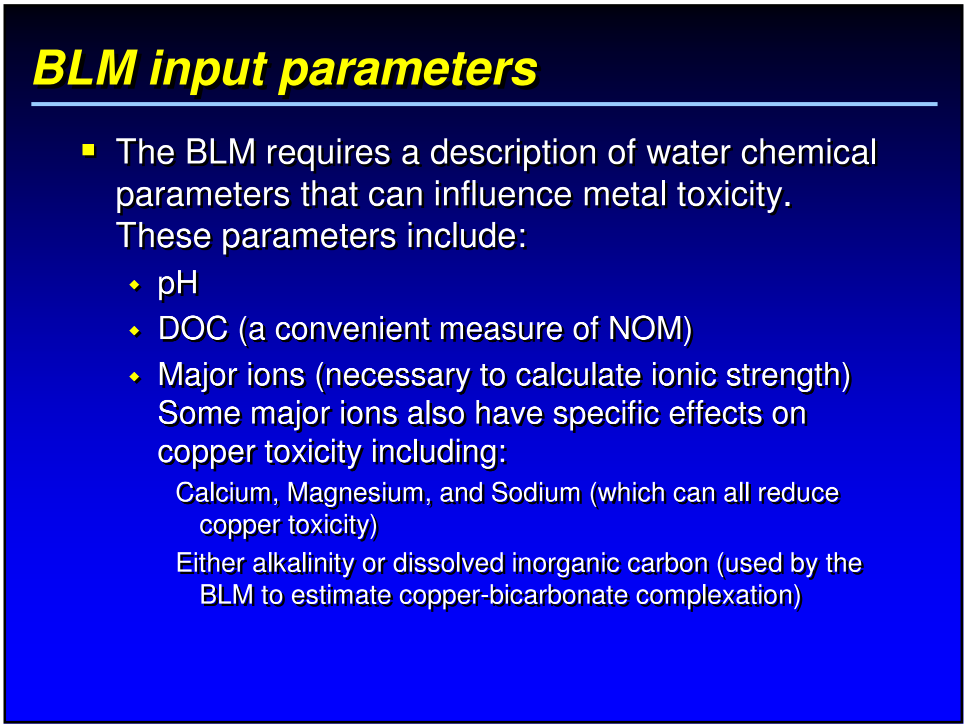
Section 2 summary:

- The BLM can be incorporated in the WQC derivation process and is fully consistent with the 1985 Guidelines for Derivation of Ambient Water Quality Criteria (Stephan et al., 1985)
- Using the BLM allows regulators and dischargers to account for the effect of water chemistry (e.g., DOC, pH, major ions, and alkalinity) on metal toxicity to aquatic organisms
- Using the BLM provides more accurate WQC without the expense or time required for deriving a WER

Section 3: Background and Technical Summary of the BLM

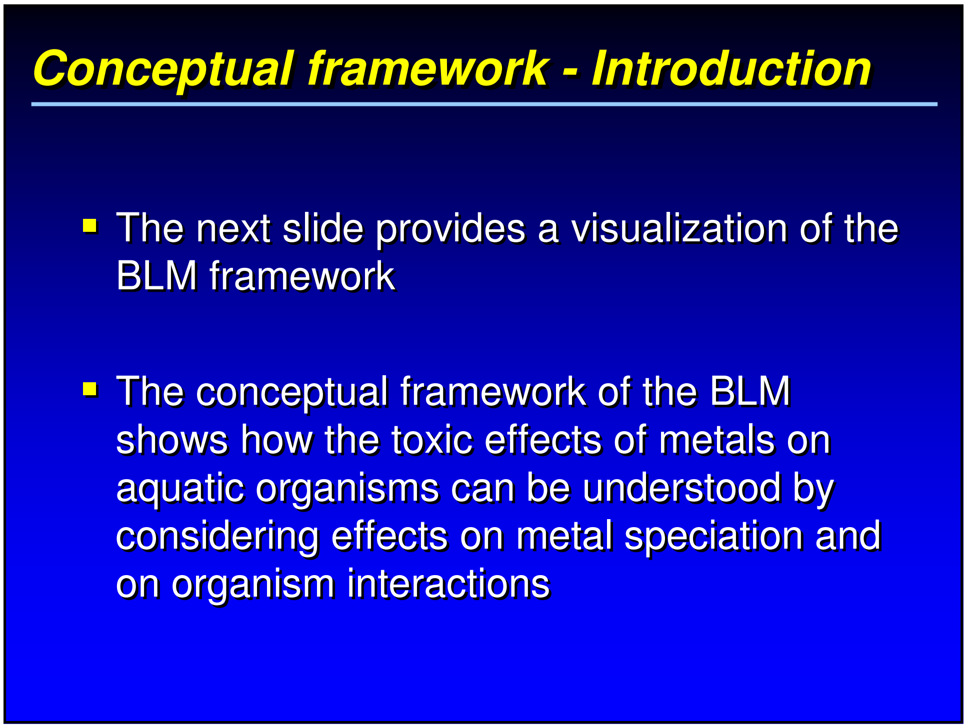
History of the BLM

- The ideas behind the BLM are not new. Similar ideas were proposed nearly 30 years ago (such as Pagenkopf's Gill Surface Interaction Model, and the Free ion activity model)
- The BLM is a recent adaptation of these ideas that makes use of several recent advancements:
  1. Recent information on the physiology of metal toxicity
  2. The availability of good, general purpose descriptions of NOM interactions with metals
  3. The widespread use of computers to allow distribution of easy-to-use computer programs such as the BLM



BLM input parameters

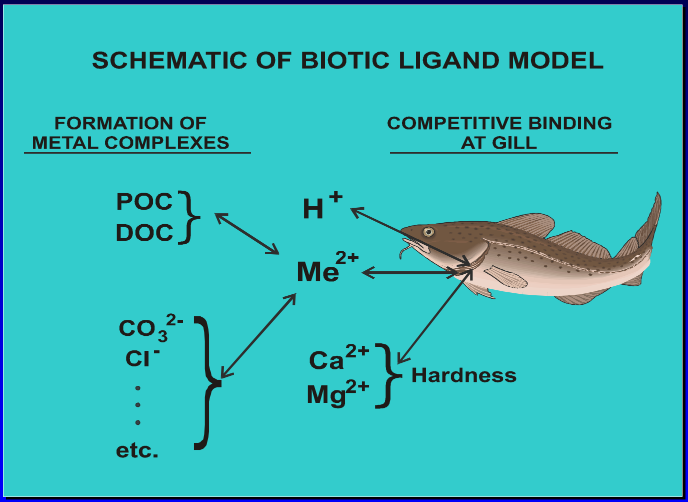
- The BLM requires a description of water chemical parameters that can influence metal toxicity. These parameters include:
  - pH
  - DOC (a convenient measure of NOM)
  - Major ions (necessary to calculate ionic strength) Some major ions also have specific effects on copper toxicity including:
    - Calcium, Magnesium, and Sodium (which can all reduce copper toxicity)
    - Either alkalinity or dissolved inorganic carbon (used by the BLM to estimate copper-bicarbonate complexation)



Conceptual framework - Introduction

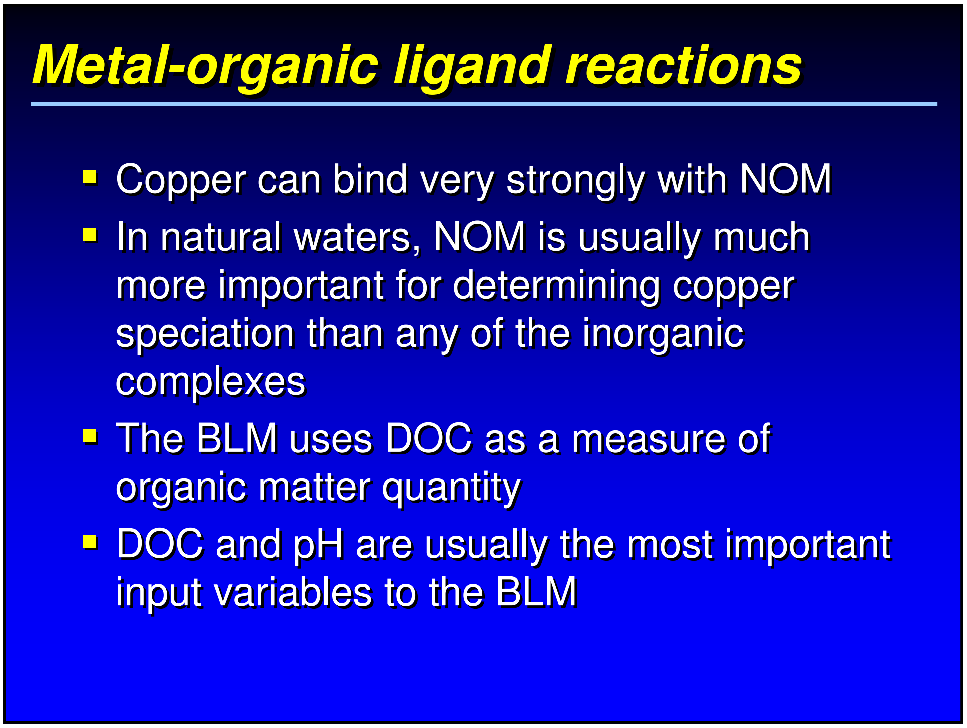
- The next slide provides a visualization of the BLM framework
- The conceptual framework of the BLM shows how the toxic effects of metals on aquatic organisms can be understood by considering effects on metal speciation and on organism interactions

Generalized BLM framework



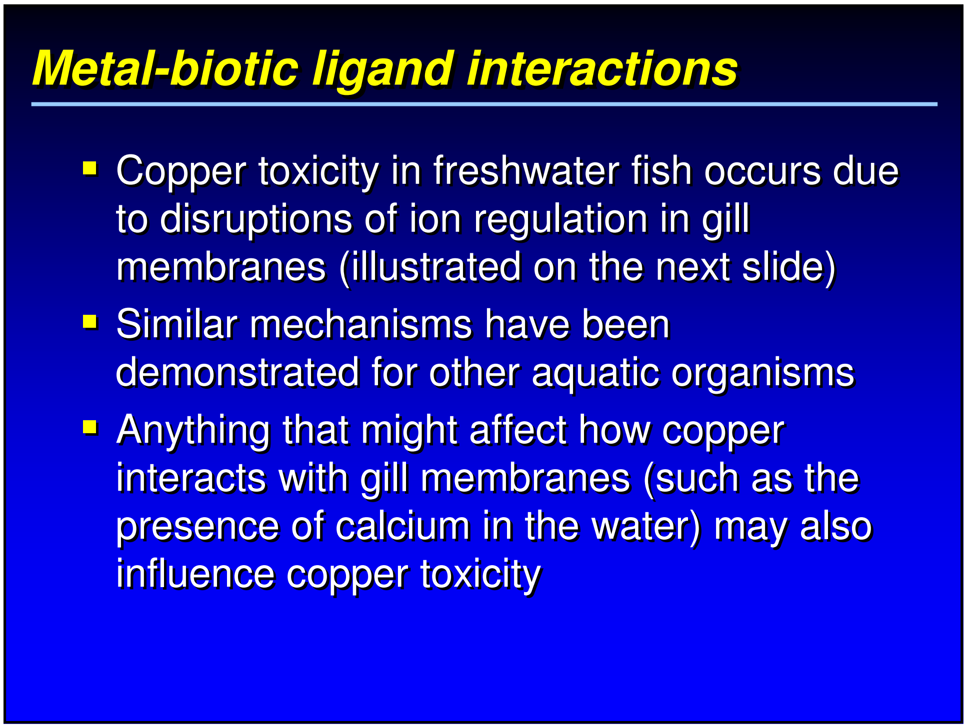
Metal-inorganic ligand reactions

- Copper can bind with several inorganic ligands, notably bicarbonate, carbonate, and hydroxide
- In natural waters, copper bicarbonate complexes are among the dominant inorganic copper species
- The importance of bicarbonate complexes is one of the reasons why pH and alkalinity have an affect on copper toxicity



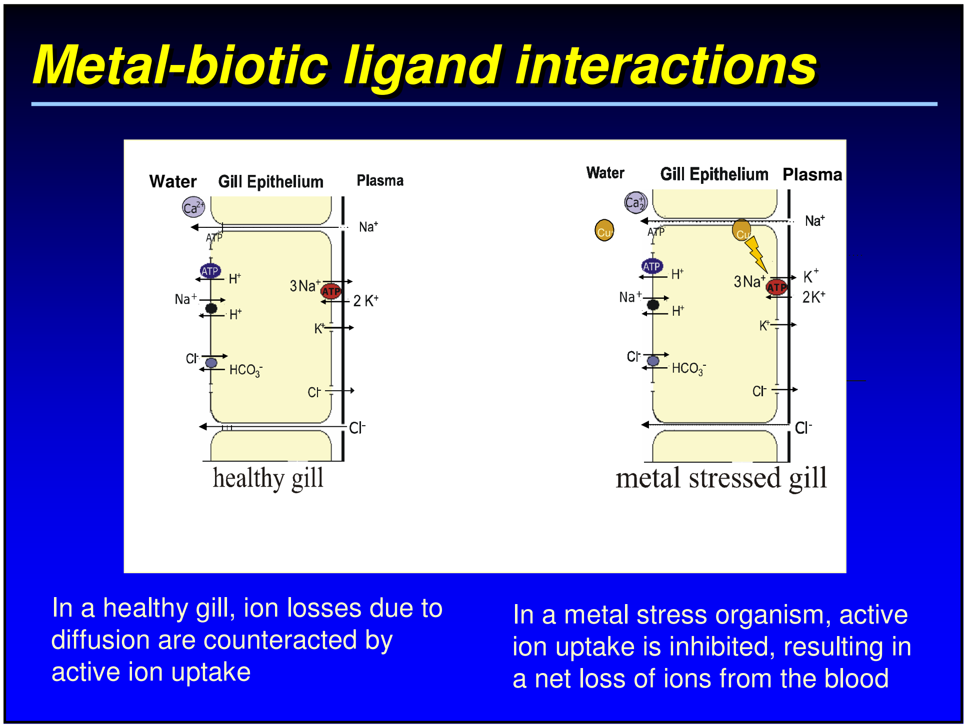
Metal-organic ligand reactions

- Copper can bind very strongly with NOM
- In natural waters, NOM is usually much more important for determining copper speciation than any of the inorganic complexes
- The BLM uses DOC as a measure of organic matter quantity
- DOC and pH are usually the most important input variables to the BLM



Metal-biotic ligand interactions

- Copper toxicity in freshwater fish occurs due to disruptions of ion regulation in gill membranes (illustrated on the next slide)
- Similar mechanisms have been demonstrated for other aquatic organisms
- Anything that might affect how copper interacts with gill membranes (such as the presence of calcium in the water) may also influence copper toxicity



Metal-biotic ligand interactions

In a healthy gill, ion losses due to diffusion are counteracted by active ion uptake

In a metal stress organism, active ion uptake is inhibited, resulting in a net loss of ions from the blood

Summary & conclusions

- Water chemistry affects metal toxicity
- Metal concentration is important, but not the sole determinant of toxicity
  - Organic & inorganic complexation matters
  - Competition at the organism also matters
- Toxicity can be predicted by knowing the metal: biotic ligand concentration

Section 4: Biotic Ligand Model Examples and Case Studies

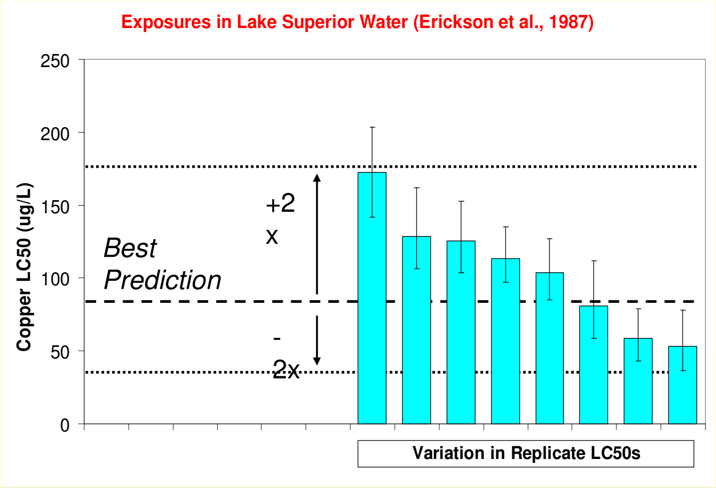
Topics of discussion

- The BLM can predict copper toxicity that agrees well with many published studies designed to show how water chemistry affects toxicity
- The BLM can also be used to derive WQC while considering the effects of the local water chemistry

Outline for this section

- In this section we will first review the existing methods for derivation of site-specific WQC
- Four case studies with BLM and traditional methods will be presented
  1. Pennsylvania Discharger study
  2. Pennsylvania Copper Group
  3. Colorado Mining Effluent
  4. Kansas River
- Finally, a comparison of the BLM and hardness equation will be made for a large number of sites

Variability in measured Cu LC50s



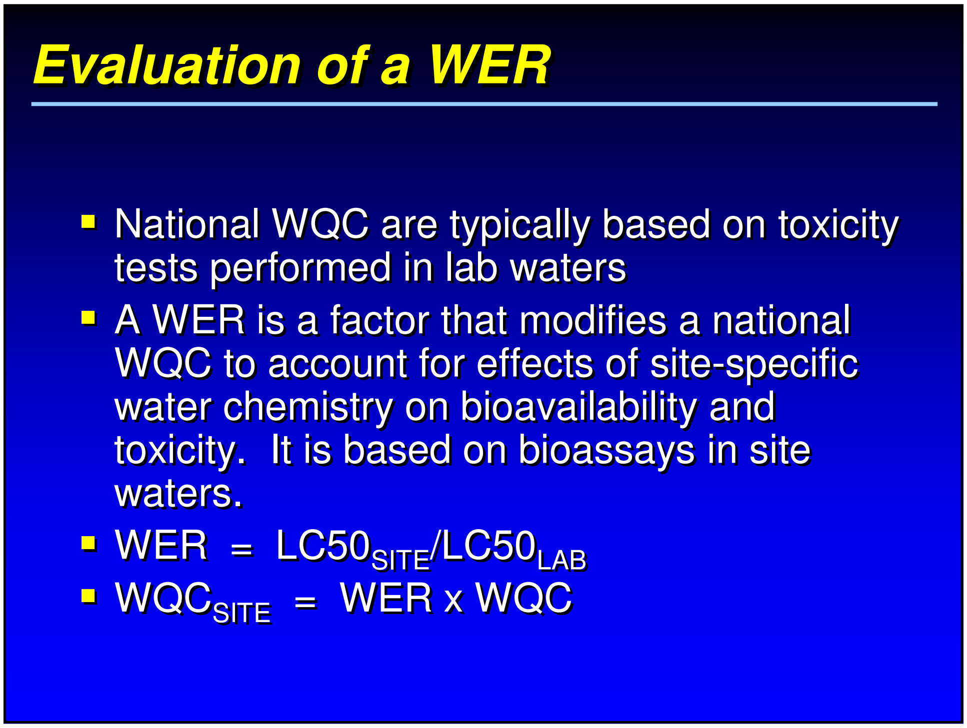
Measured LC50s can be variable. A reasonable comparison between measured and predicted toxicity is that predictions should be within a factor of 2 of most measurements, since replicate LC50 values often show similar variability.

USEPA site-specific WQC methods

- Three methods are available for use:
    - Recalculation procedure
    - Water Effect Ratio (WER) procedure
    - Resident species procedure
- Data from WER studies can be used to test the BLM. However, the BLM can calculate a WQC directly, without the need for a WER approach
- WER studies are a convenient source of data, but we do not recommend that the BLM be used to replicate a WER study for copper. It is preferable to use the BLM to calculate a WQC directly
- For these examples, we will use the BLM to calculate a WER only as a means for comparison

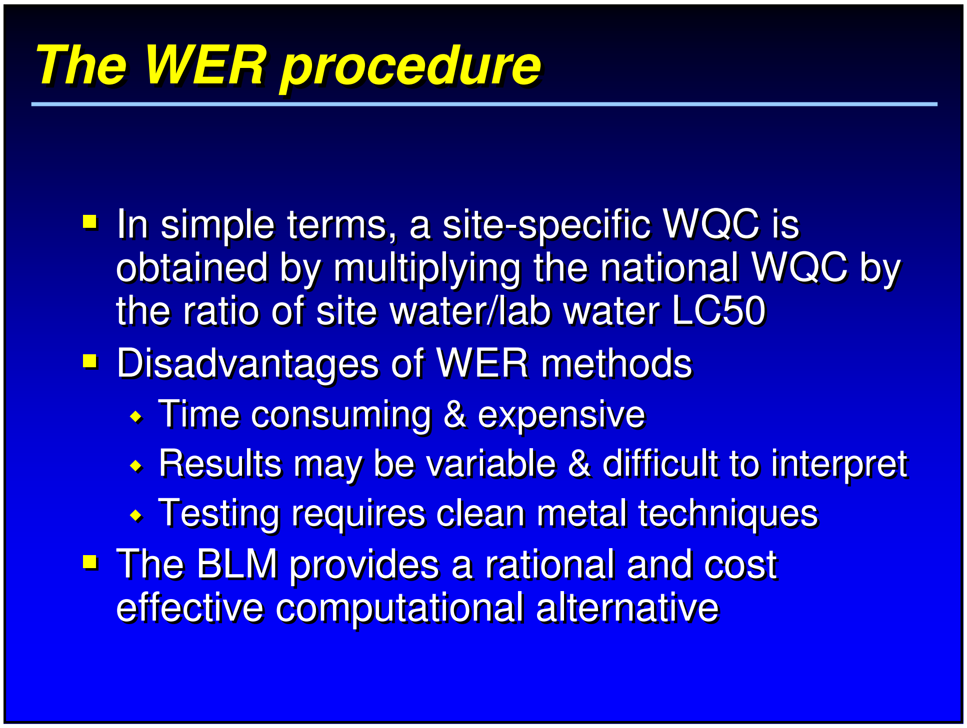
BLM is an improved method for deriving WQC

- The BLM can be integrated in the 1985 Guidelines for Derivation of Ambient Water Quality Criteria (AWQC or WQC; Stephan et al., 1985)
- The BLM allows consideration of the most important water quality variables that control copper toxicity (e.g., pH, DOC, alkalinity, major ions)
- The BLM is more comprehensive than the hardness equation, and is an expedient and cost-effective alternative to the WER
- The BLM derived WQC are sometimes lower and sometimes higher than the WQC derived by the hardness equation



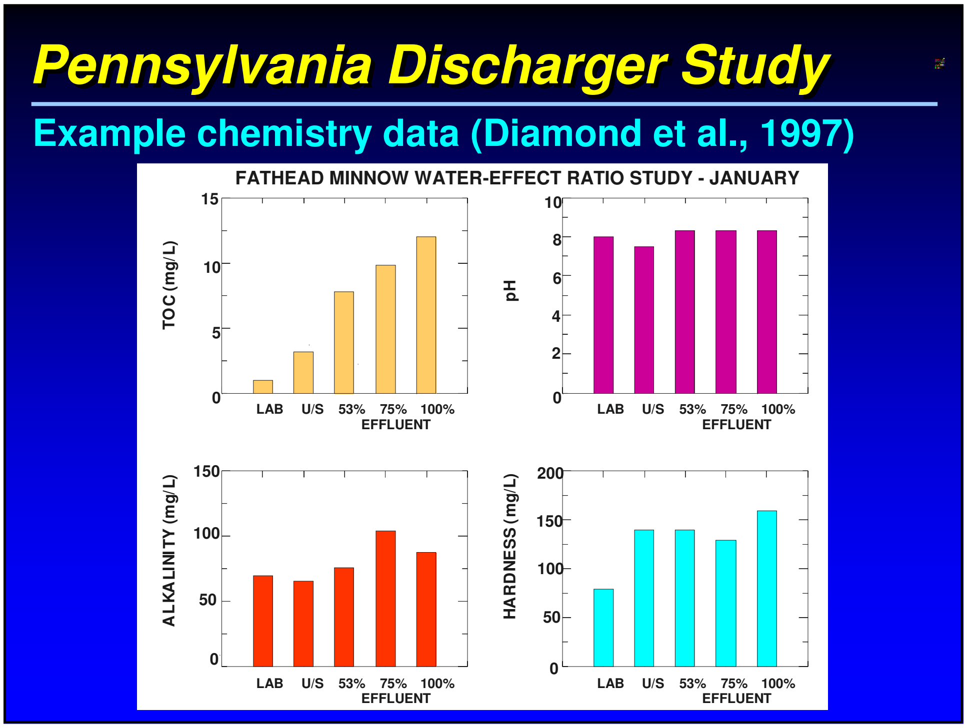
Evaluation of a WER

- National WQC are typically based on toxicity tests performed in lab waters
- A WER is a factor that modifies a national WQC to account for effects of site-specific water chemistry on bioavailability and toxicity. It is based on bioassays in site waters.
- WER = $LC50_{SITE}/LC50_{LAB}$
- WQC_{SITE} = WER x WQC



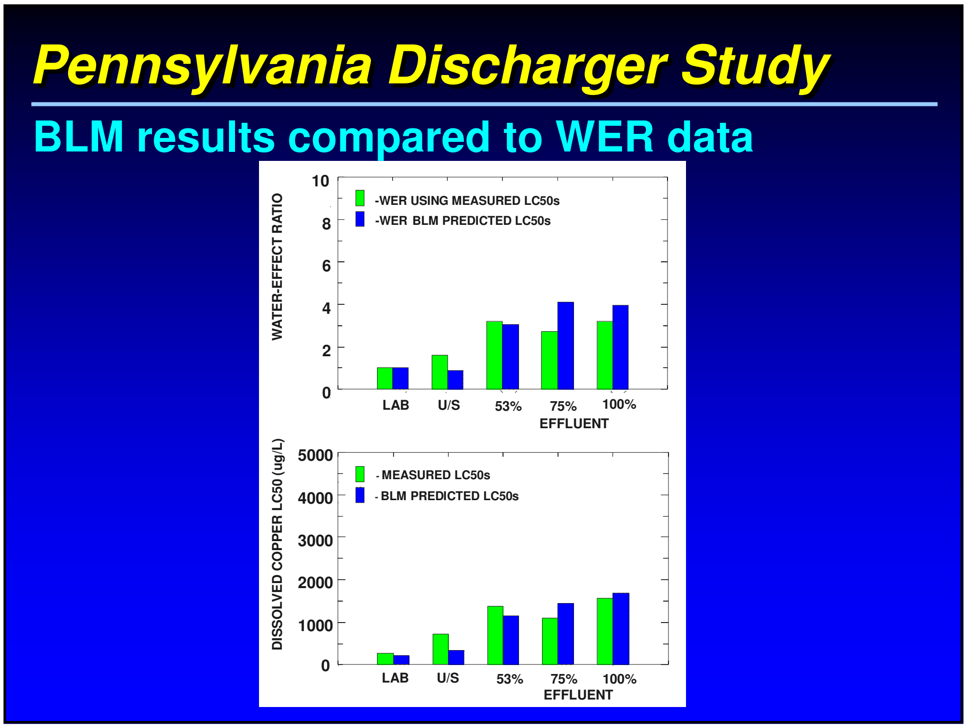
The WER procedure

- In simple terms, a site-specific WQC is obtained by multiplying the national WQC by the ratio of site water/lab water LC50
- Disadvantages of WER methods
    - Time consuming & expensive
    - Results may be variable & difficult to interpret
    - Testing requires clean metal techniques
- The BLM provides a rational and cost effective computational alternative



Pennsylvania Discharger Study

Example chemistry data (Diamond et al., 1997)



Pennsylvania Discharger Study

BLM results compared to WER data

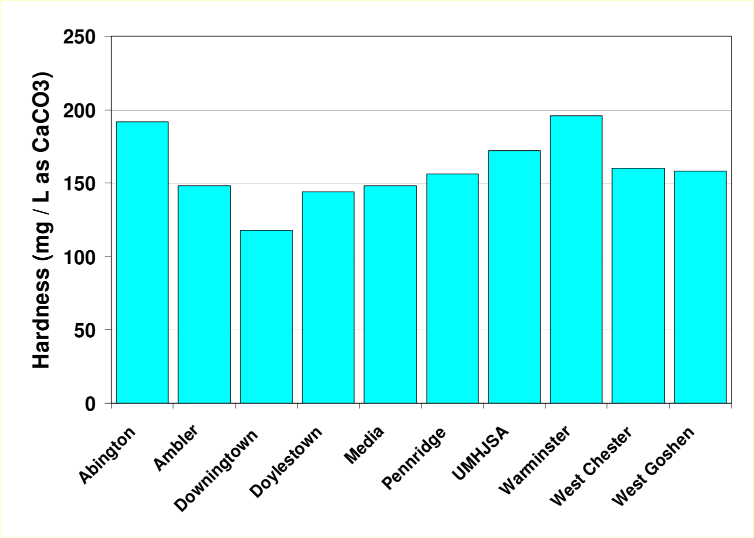
Pennsylvania Copper Group

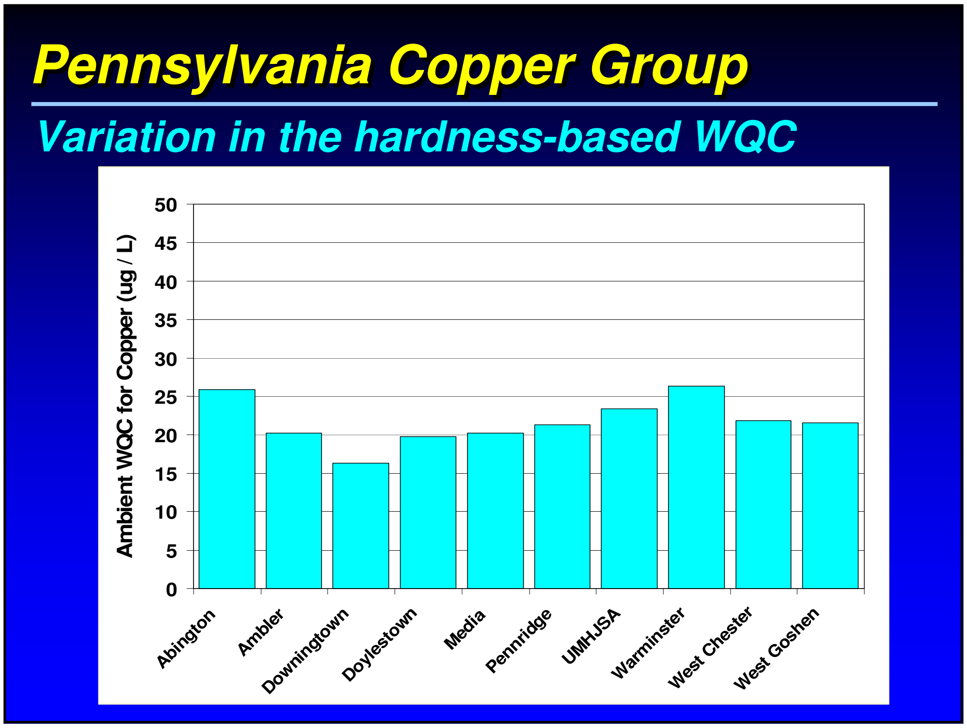
Hall and Associates, 1998

- This example involved a WER study for 10 streams in Pennsylvania impacted by WWTP effluent
- Copper toxicity to *Ceriodaphnia dubia* was measured in these waters to support development of site-specific WQC

Pennsylvania Copper Group

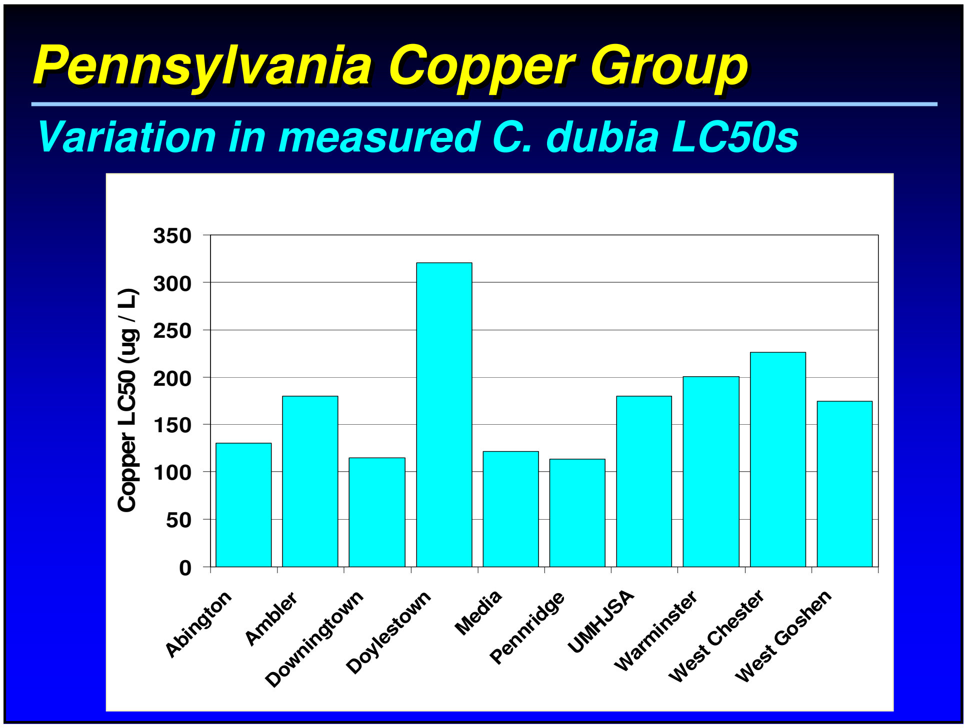
Variation in measured hardness





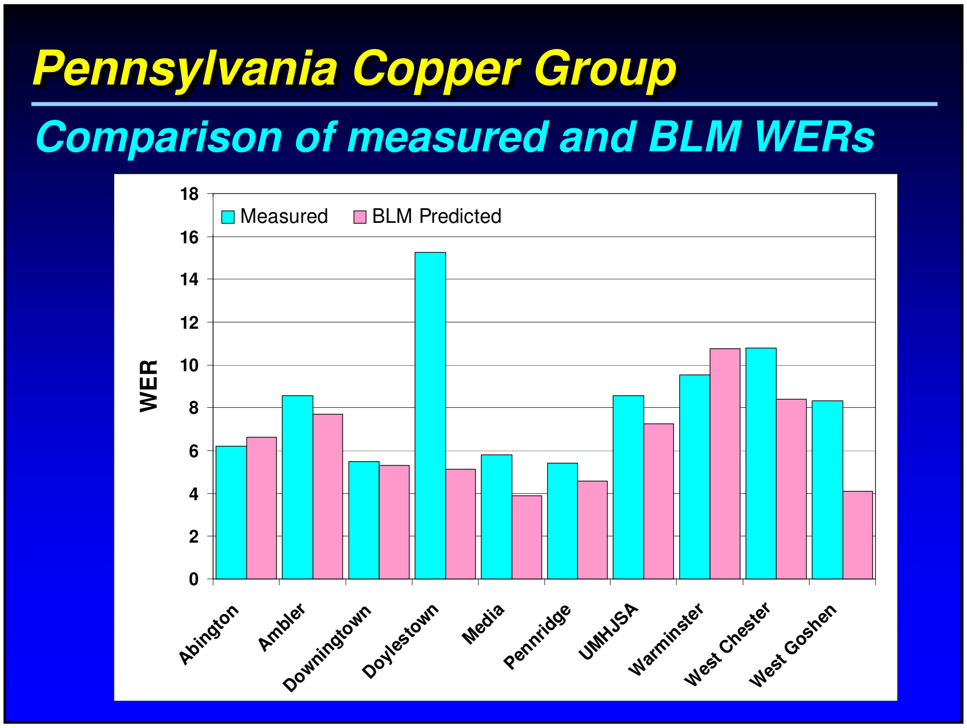
Pennsylvania Copper Group

Variation in the hardness-based WQC



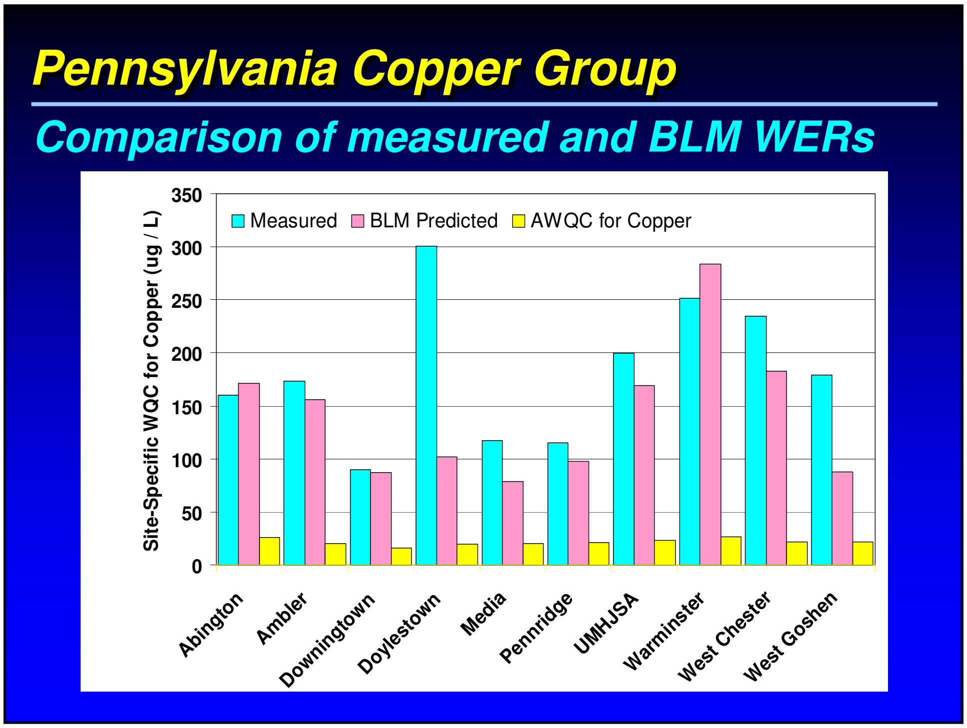
Pennsylvania Copper Group

Variation in measured C. dubia LC50s



Pennsylvania Copper Group

Comparison of measured and BLM WERs



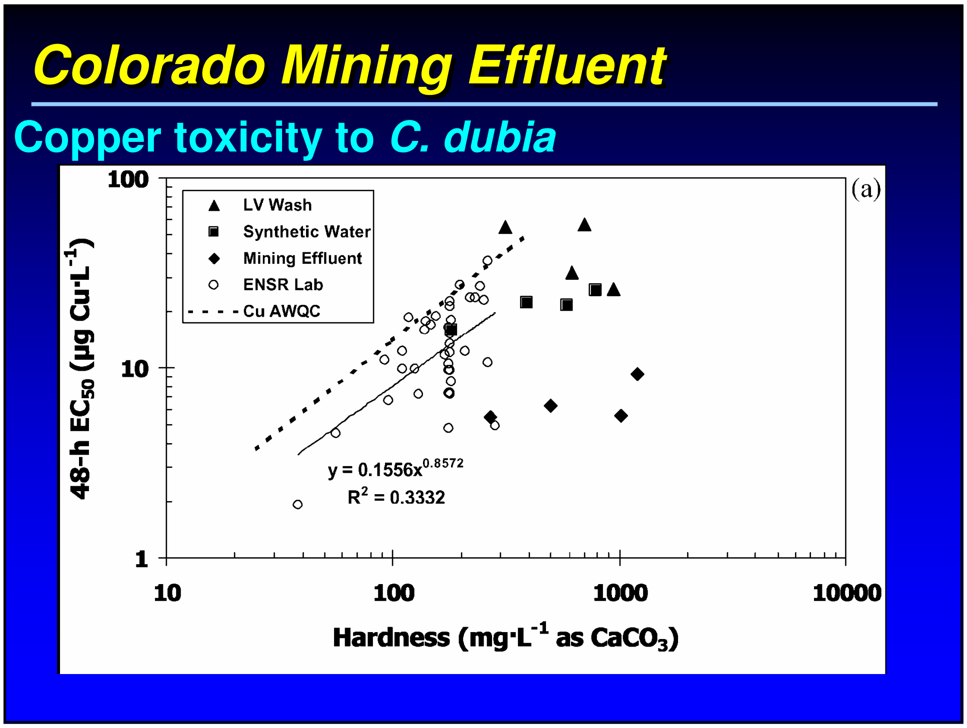
Pennsylvania Copper Group

Comparison of measured and BLM WERs

Colorado Mining Effluent

Gensemer, R.W., R.B. Naddy, W.A. Stubblefield, J.R. Hockett, R.C. Santore, and P.R. Paquin. 2002. Evaluating the role of ion composition on the toxicity of copper to *Ceriodaphnia dubia* in very hard waters. Comparative Biochemistry and Physiology, Part C 133:87-97.

- In this study, copper toxicity to *Ceriodaphnia dubia* was measured in very hard waters typical of arid regions in the western United States



Colorado Mining Effluent

Copper toxicity to *C. dubia*

Colorado Mining Effluent

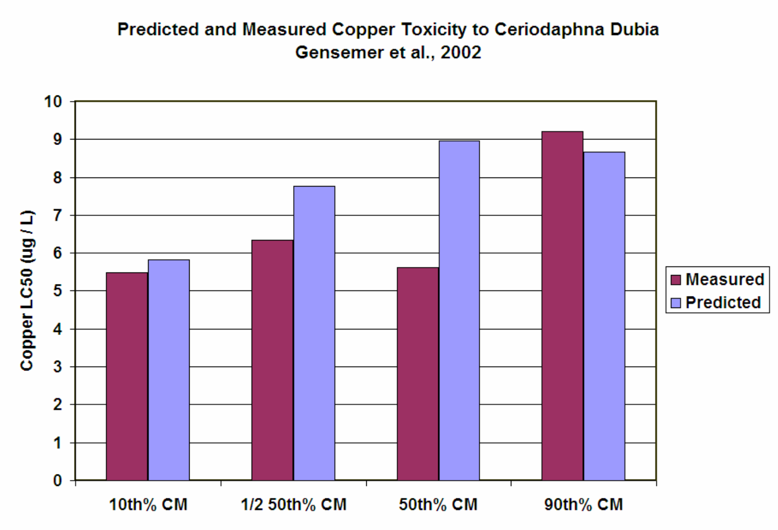
Mining effluent composition

Synthetic Waters Designed to mimic selected hardness levels within the range observed in the mining effluent

Sample	Hardness	pH	DOC	dissolved Cu 48 h EC50	95% CI
	mg/L as CaCO3		mg/L	ug/L	
10th percentile	270	7.2	0.5	5.49	(4.90–6.16)
1/2 50th percentile	496	7.3	0.5	6.35	(5.26–7.67)
50th percentile	1020	7.3	0.5	5.62	(4.66–6.79)
90th percentile	1200	7.2	0.5	9.22	(8.30–10.3)

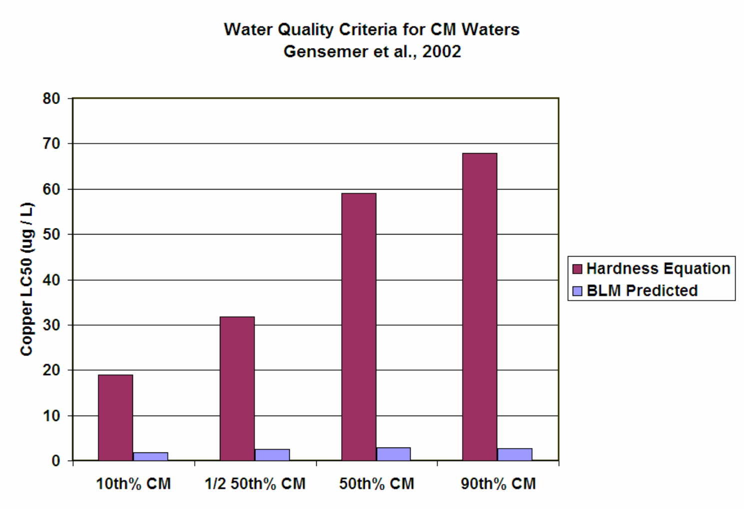
Colorado Mining Effluent

Observed and predicted toxicity

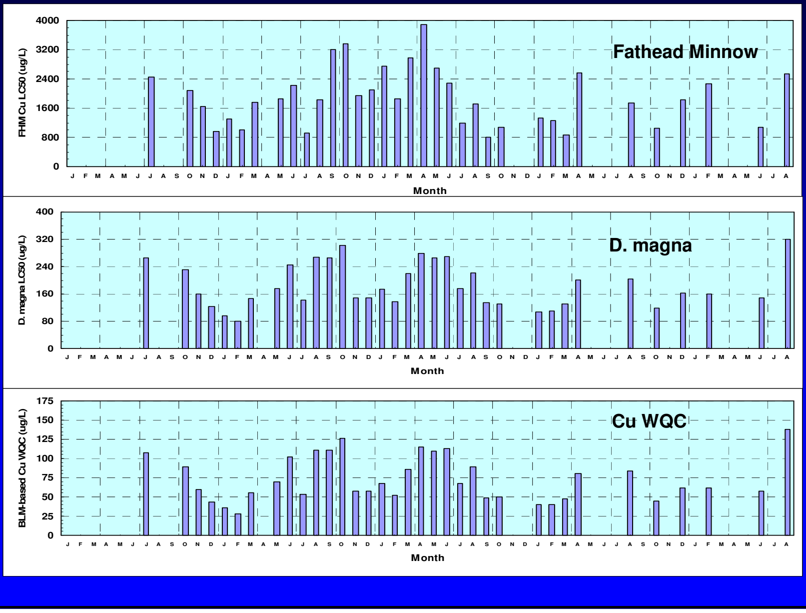


Colorado Mining Effluent

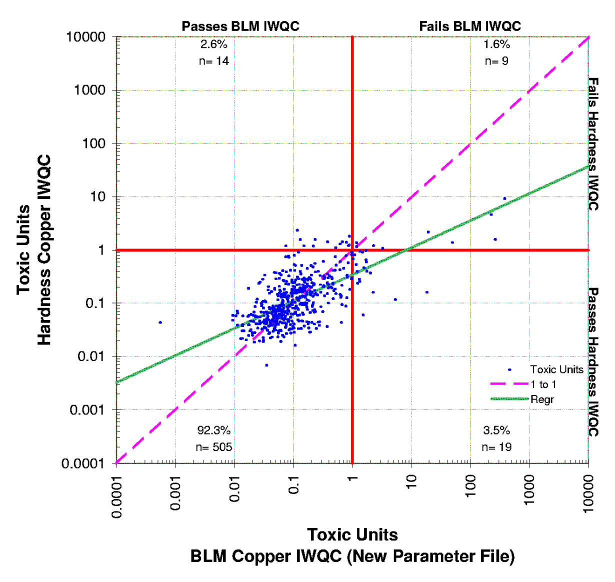
Acute WQC



Kansas River Cu WQC Analysis

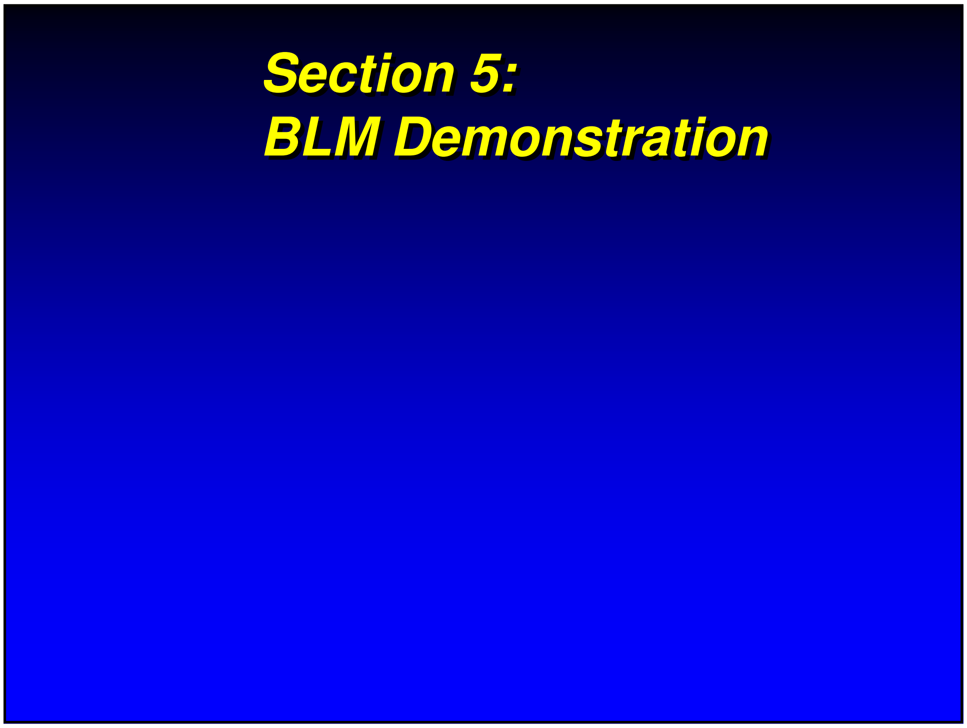


Comparison of waters classified as impaired by BLM or hardness equation

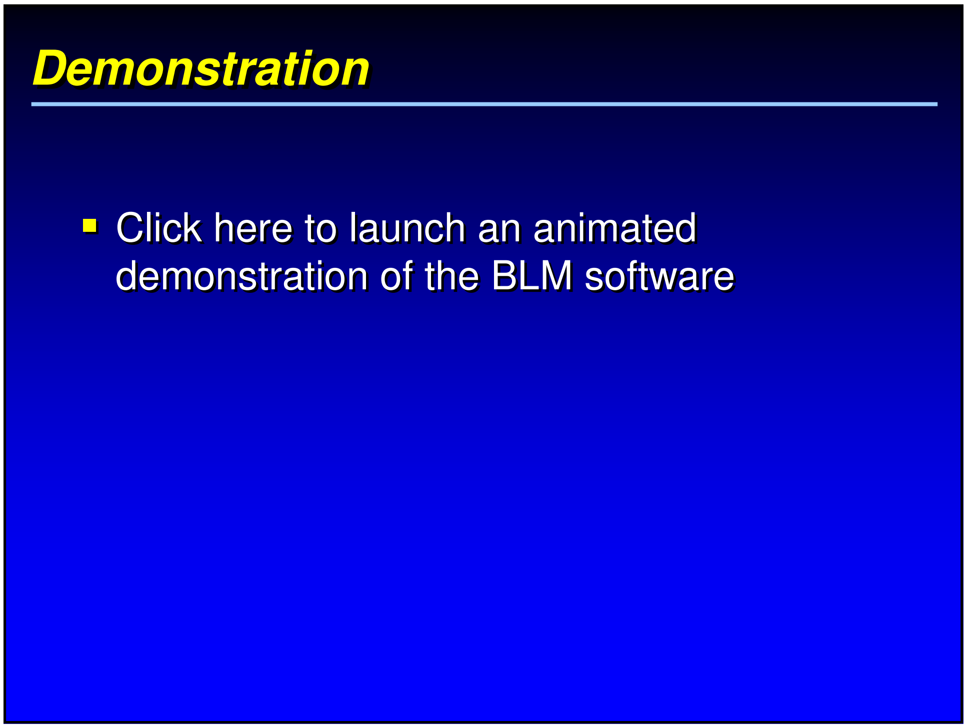


Summary and Conclusions

- The BLM can be used to calculate site specific copper WQC that agrees remarkably well with bioassay-based WER studies
- A site-specific WQC can be developed with the BLM in less time and with lower costs
- Compared with the hardness equation, the BLM generates WQC values that are sometimes higher, and sometimes lower, indicating the hardness equation may be over or underprotective

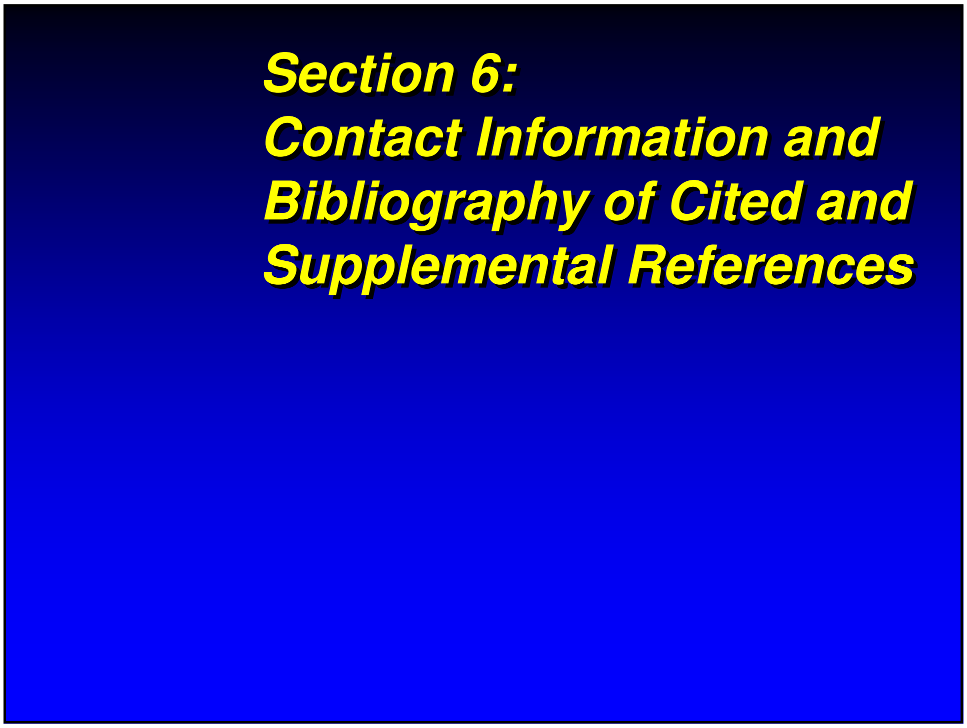


Section 5:
BLM Demonstration

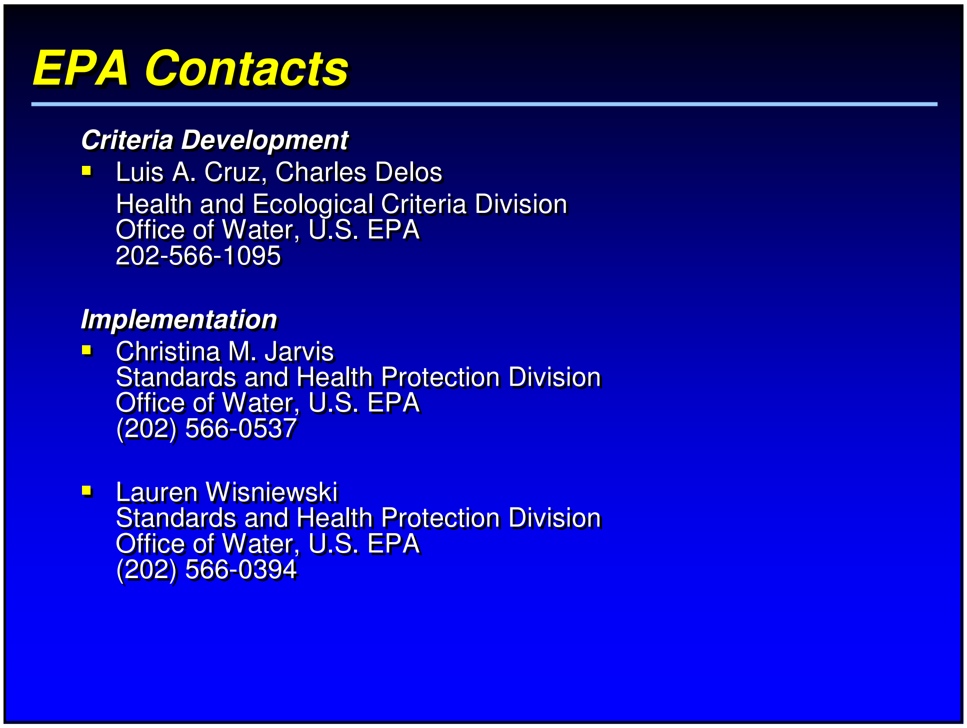


Demonstration

- Click here to launch an animated demonstration of the BLM software



Section 6: Contact Information and Bibliography of Cited and Supplemental References



EPA Contacts

Criteria Development

- Luis A. Cruz, Charles Delos
  Health and Ecological Criteria Division
  Office of Water, U.S. EPA
  202-566-1095

Implementation

- Christina M. Jarvis
  Standards and Health Protection Division
  Office of Water, U.S. EPA
  (202) 566-0537

- Lauren Wisniewski
  Standards and Health Protection Division
  Office of Water, U.S. EPA
  (202) 566-0394

Technical Contacts

HydroQual, Inc.

- Bob Santore
  315-484-6220
  rsantore@hydroqual.com

- Paul Paquin
  201-317-0804
  ppaquin@hydroqual.com

- Adam Ryan
  315-484-6220
  aryan@hydroqual.com

Bibliography

Cited and Supplemental References on the BLM and Related Topics

Click here to open a bibliography in Adobe PDF format