Aquatic Life Water Quality Standards
Technical Support Document for
Copper Biotic Ligand Model

Triennial Water Quality Standard Amendments to Minn. R. chs. 7050 and 7052

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Authors

Bruce Monson, Ph.D., Phil Monson, M.S.

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Minnesota Pollution Control Agency

520 Lafayette Road North | Saint Paul, MN 55155-4194 | www.pca.state.mn.us | 651-296-6300
Toll free 800-657-3864 | TTY 651-282-5332

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TECHNICAL SUPPORT DOCUMENT FOR COPPER (Cu)

Contents

ABSTRACT

From the Minnesota *State Register*, Volume 33 (35), March 2, 2009:

Copper is an element and an environmental contaminant associated primarily with industrial activities. The EPA revised the surface water aquatic life criteria methods and values in 2007 (Aquatic Life AWQC – Copper 2007 (EPA822R07001)). The [Environmental Protection Agency] EPA copper criteria revision uses a new method called the Biotic Ligand Model to determine toxic effects to aquatic organisms. Changes to the current [Water Quality Standards] WQSs for copper would involve compiling, reviewing and developing a revised criterion value. Efforts to revise the existing Minnesota standard will require reviewing existing aquatic life toxicity data from the published literature and other sources.

The Minnesota Pollution Control Agency (MPCA) has reviewed the EPA's Biotic Ligand Model (BLM) and plans to adopt this method as an alternate approach to the current WQSs for calculating protective of aquatic life WQSs on a site-specific basis for copper. In the future EPA plans to have other metal WQSs developed through the BLM. MPCA will retain the current WQSs, which are algorithms based on site-specific hardness concentrations, for use in calculating the Final Acute Value (FAV), Maximum Standard (MS), and Chronic Standard (CS). However, when sufficient data is available as discussed in this document, preference will be for use of the BLM.

MPCA adopts WQSs into Minn. R. chs. 7050 and 7052. When information is available, Class 2 WQSs will include acute (FAV and MS) protection based on aquatic life toxicity and chronic (CS) protection for aquatic life, human health, and fish-eating wildlife (Minn. R. ch. 7052). The copper BLM would supplement the current aquatic life-based WQSs and is the foundation of this Technical Support Document (TSD). The previously determined CS for protection of human health is not being revised, and is currently less stringent than the chronic copper WQSs based on aquatic life toxicity.

INTRODUCTION

Copper in the Environment

Copper is a common natural element that is found in geologic deposits that include cadmium and zinc as well. According to EPA (2007), naturally occurring copper ranges from 0.20 to 30 µg/L (parts per billion)in freshwater. Copper is associated with discharges from mining, leather processing, metal fabrication, electrical equipment production. Copper is found in municipal wastewater because of the corrosion of copper pipes. Copper sulfate is a common algicide to treat nuisance algal blooms in lakes and ponds (Cooke and Welch 2005), but can also toxic to the zooplankton that graze on the algae.

Toxicity of Copper

Copper is an essential micronutrient for plants and animals, but is toxic at low concentrations to fish and other aquatic life. Cupric ion (Cu^{+2}) is the primary toxic form of copper to algae (McKnight 1981) and to other aquatic life. Unlike other forms of copper, the cupric ion reacts with biological membranes, allowing it to pass into cells. Therefore, the concentration of the free metal ion is what determines the toxicity of copper in water. Water chemistry determines the speciation (i.e., chemical forms) of copper.

HOW AND WHY WATER QUALITY STANDARDS ARE DEVELOPED

U.S. EPA National Clean Water Act 304(a) Aquatic Life Criteria

Copper is an essential micronutrient and occurs naturally in surface waters, but slightly above the background concentrations copper can be toxic to invertebrates in particular, as well as to fish. Minnesota has had copper water quality standards (WQSs) based on total hardness based on EPA's last revised National Ambient Water Quality Criteria (AWQC)[1] in 1985 and adopted by MPCA in 1990. In the 2007 revised criteria document, EPA has developed a more accurate approach, the Biotic Ligand Model (BLM) to better account for the competitive binding of copper to other molecules in the water, which has the effect of reducing the bioavailability of the copper (i.e., the toxicity) to aquatic organisms. Bioavailability is defined as "…the relative facility with which a chemical is transferred from the environment to a specified location in an organism of interest." (EPA 2007).

DEVELOPMENT OF DRAFT COPPER STANDARDS

Criteria Derivation Process

The criteria derivation process includes the following six steps:

1. Compile and review data

[1] AWQC are published by EPA under requirements of Section 304(a) of the Clean Water Act, so are also know as National or Federal 304(a) criteria.

2. Develop water quality – toxicity model (e.g. Biotic Ligand Model for Copper)
3. Determine genus mean acute values (GMAVs) and genus mean chronic values (GMCVs); rank them by sensitivity
4. Calculate final acute and chronic values (FAV and FCV)
5. Derive the maximum concentration (MC = FAV/2) and chronic concentration (CC)
6. For Minnesota rules, final acute and chronic WQSs are needed for salmonids in Class 2A waters and nonsalmonids for Class 2B waters.

All but the last step is reviewed and developed in the EPA criteria document (EPA 2007). In addition, the MPCA has reviewed the latest scientific publications for relevant critical reviews of the BLM. A literature review of toxicity values for copper was not included in this evaluation because (a) the final EPA criteria document for copper was published only two years earlier and (b) the model was calibrated to a set of acute toxicity values, thereby making it very difficult to recalculate the toxicity values based on new information.

Biotic Ligand Model (BLM)

EPA's 2007 revision of the copper standard is based on the Biotic Ligand Model (BLM) and replaces the hardness-based approach to calculating the water quality criterion. The BLM directly accounts for the bioavailability of copper depending on the water chemistry of the water body. The BLM is meant to account for chemical binding and interactions that influence copper binding to fish gills. The model only calculates the acute water quality criterion. The chronic criterion is then calculated from an acute to chronic ratio. BLM requires ten water quality inputs for copper: temperature, pH, alkalinity, dissolved organic carbon (DOC), major cations (Ca, Mg, Na, K), and major anions (Cl, SO_4). Copper is measured for use in comparing to the site-specific criteria, but it is not required input for the BLM. The result is primarily driven by the DOC concentration. The BLM-based water quality criterion is sometimes more stringent and other times less stringent than the hardness-based water quality criterion. All copper concentration output from BLM is given as total dissolved copper concentrations in micrograms per liter (µg/L).

As DOC increases, copper becomes increasingly bound to DOC, thereby reducing its bioavailability and allowing for a higher concentration for the protective criterion. However, if pH is low even at high DOC, the criterion could be much lower than the hardness-based criterion. This is important because many lakes and rivers in northern Minnesota have high DOC because of humic acids that lower the pH. Consequently, they can have high DOC but low pH, resulting in a mixed effect on the final acute value (FAV).

To get to the stage where the BLM can be used to calculate an FAV, measures of acute toxicity results (LC50 and EC50s)[2] with the necessary water chemistry parameters were compiled by EPA. Out of 600 acute freshwater toxicity tests with aquatic organisms and copper, 350 were used to derive normalized LC50 values. If the toxicity test results were in total copper, the value was multiplied by the conversion factor, 0.96, to get dissolved copper concentration. Species Mean Acute Values (SMAV) were calculated from the normalized LC50 and Genus Mean Acute Values (GMAVs) were averaged from the SMAVs. The

[2] Acute toxicity is measured by the concentration of the pollutant that leads to mortality or severe effect in 50% of the test organism, LC50 and EC50, respectively.

resulting 27 GMAVs were ranked by sensitivity and the 5th percentile method was used to derive a reference FAV. BLM was calibrated to give the reference FAV for the normalized water chemistry. A site-specific FAV can then be calculated from BLM by changing the model input to site-specific water chemistry.

The eight family minimum was not met to calculate the Final Chronic Value (FCV) for copper. Therefore, EPA (2007) developed a revised final acute-to-chronic ratio (FACR), 3.22. The reference FAV of 4.67 µg/L is divided by 2 to get the maximum (acute) criteria of 2.337 µg/L and it is divided by the FACR to get the FCV (chronic criteria) of 1.45 µg/L.

Invertebrates represented the ten lowest SMAVs and all four of the most sensitive GMAVs were invertebrates; therefore, the FAV did not need to be recalculated for nonsalmonids. This was true for the current copper standard as well. The most sensitive species to copper was *Daphnia pulicaria*, with an SMAV of 2.37 µg/L. Consequently, the acute reference criterion is equal to the lowest SMAV.

Based on 414 cases of dissolved copper in Minnesota waters, the range of concentrations is 0.04 to 9.21 µg/L, with a median of 0.956 µg/L and geometric mean of 0.962 µg/L. The interquartile range (25th – 75th percentile) is 0.71 – 1.39 µg/L. Of course, whether or not these background concentrations meet or exceed the BLM-based WQS depends on the site-specific water quality.

Sensitivity Analysis

Running BLM for the "normalization chemistry" as noted in Table 1, footnote f, of the Ambient Criteria for Copper (Table 1), and then varying DOC, pH, SO_4, and temperature, gives the results summarized in Table 2.

As noted in EPA documents, the FAV output from BLM is most sensitive to DOC and pH (http://www.epa.gov/waterscience/criteria/copper/faq/data-requirements.pdf). In the normalization chemistry, DOC is very low (0.5 mg/L) and sulfate (SO_4) is moderately high. Therefore, individual parameters were changed in the input to see what effect it had on the FAV, MC, and FCV. DOC concentrations of 5 and 10 are common and 12 mg/L is the median concentration in Minnesota streams and many lakes. The pH was increased to 8 and 8.5, which are typical levels in Minnesota waters.

Table 1 Input to BLM for "normalization chemistry" used by EPA (2007)

Temp	pH	DOC	HA	Ca	Mg	Na	K	SO_4	Cl	Alkalinity	S
°C		mg/L	%	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L as $CaCO_3$	mg/L
20	7.5	0.5	10	14	12.1	26.3	2.1	81.4	1.9	65	0.0003

Table 2 Output from BLM (as total dissolved Cu concentration): variations on normalization chemistry

BLM Sensitivity to Change in Value	Sample Label	FAV, µg/L	MC (FAV/2), µg/L	FCV (FAV/ACR), µg/L	Relative to Normalized
	Reference: Mn R. Ch. 7050 at Hardness = 100 mg/L as $CaCO_3$	33.6	17.3	9.4	
	Normalized	4.68	2.34	1.45	
Low – temperature, total hardness, sulfate	Temperature 15°C	4.53	2.26	1.41	1.0
	Temperature 25°C	4.87	2.43	1.51	1.0
	TH 50 mg/L	4.45	2.23	1.38	1.0
	TH 100 mg/L	4.79	2.39	1.49	1.0
	TH 200 mg/L	5.48	2.74	1.70	1.2
	TH 400 mg/L	6.56	3.28	2.04	1.4
	SO_4 8 mg/L	4.91	2.45	1.52	1.0
	SO_4 20 mg/L	4.87	2.43	1.51	1.0
	SO4 40 mg/L	4.80	2.40	1.49	1.0
Moderate – pH	pH 6.5	1.23	0.62	0.38	0.3
	pH 7	2.47	1.23	0.77	0.5
	pH 8	8.31	4.15	2.58	1.8
	pH 8.5	13.44	6.72	4.17	2.9
High – DOC	DOC 2 mg/L	17.9	9.0	5.6	3.8
	DOC 5 mg/L	43.9	22.0	13.6	9.4
	DOC 10 mg/L	89.1	44.6	27.7	19.1
	DOC 12 TH 85 (normalization TH)	107.6	53.8	33.4	23.0
	DOC 12 TH 50	105.8	52.9	32.9	22.6
	DOC 12 TH 100	109.0	54.5	33.8	23.3
	DOC 12 pH 6.5	23.3	11.6	7.2	5.0
	DOC 12 pH 8.5	308.5	154.2	95.8	66.0

The BLM was run for a range of DOC concentrations (0.5 – 12 mg/L) at total hardness of 100 mg/L and 50 mg/L. The results showed a linear response of the FAV to DOC, increasing at a rate of 9x (Figure 1). Increasing pH by a half unit (8.0) and a whole unit increased the FAV by a factor of nearly 2 and 3, respectively. Changes in SO_4 and temperature had little effect and did not change the FAV appreciably. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) make up total hardness. At the normalization chemistry, with Ca concentration at 14.0 mg/L and Mg concentration at 12.1 mg/L, total hardness is 85 mg/L as $CaCO_3$. Changes in hardness to 50 and 100 had very little effect on FAV. Increasing hardness to 200 and 400 only increased FAV 20% and 40%, respectively. DOC was set at 12 mg/L as a median concentration is a representative value for all lakes and rivers in Minnesota. With only DOC increased, FAV increased by a factor of 23. Changing TH at this level of DOC has no effect, but increasing the pH to 8.5 along with the DOC of 12 mg/L increased the FAV by a factor of 66. EPA (2007) presented a figure showing the copper

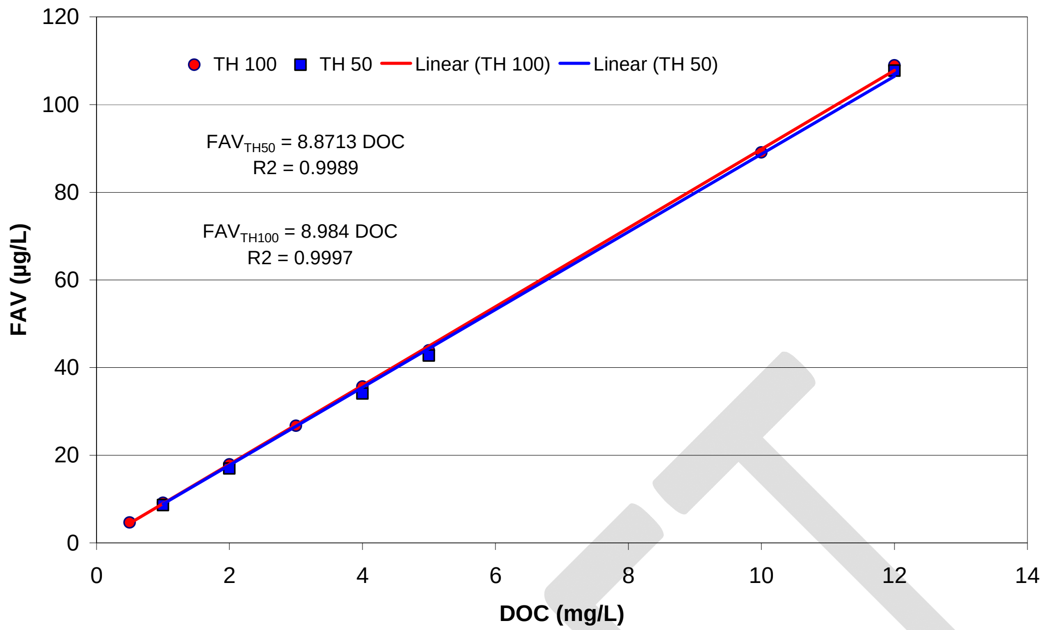

Figure 1 Sensitivity of BLM Output: FAV relationship to DOC at total hardness of 50 mg/L and 100 mg/L

maximum (acute) concentrations as a function of total hardness for several DOC concentrations (Figure 2). The predicted relationship based on the existing criteria hardness equation match closely to the DOC concentration set at 2 mg/L.

The limitation of this comparison is that water chemistry parameters are likely to change as a suite and not a change in a single value. Nevertheless, this provides a reasonable view of the sensitivity of the BLM-based FAV.

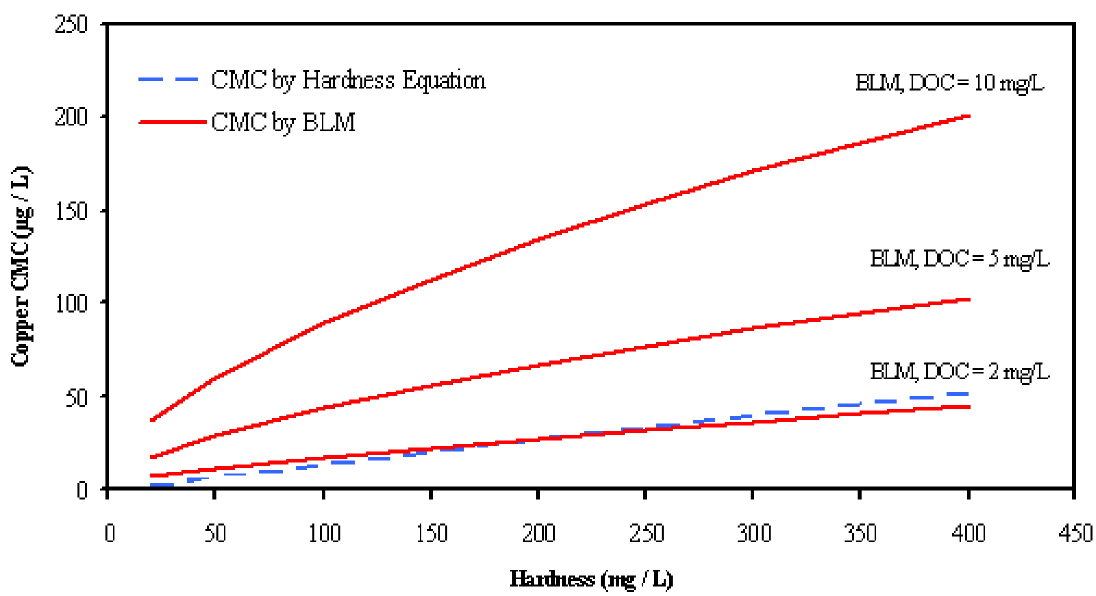

Figure 2 Comparison of BLM-based CMC and hardness equation for a range of DOC concentrations (EPA, 2007, Figure 5)

Minnesota's current chronic standard (CS) for copper in 2A and 2B waters is 9.8 µg/L. Results of the BLM (Table 2) show that at normalized chemistry with total hardness set to 100 mg/L the chronic criteria is 1.49 µg/L—well below the current standard. However, if DOC is increased from 0.5 mg/L to 12 mg/L (a mid-range DOC concentration in Minnesota), the site-specific chronic criteria becomes 33.8 µg/L. These results from the BLM indicate the hardness-based copper criteria are over protective in some instances and under protective in others, depending only on the differences in DOC. The BLM is less sensitive to pH, but still has much more of an effect on the output than the other water chemistry input parameters.

Implementation

The BLM has been shown to accurately predict LC50s within a factor of two when compared to observed LC50s in *Pimephales promelas* (fathead minnow) (Erickson et al. 1987 cited in EPA 2007) and in *Daphnia magna* (water flea) (Ryan et al. 2009).

Colorado has used the BLM as an alternative method for site-specific water quality criteria for several effluent-dominated stream segments (HydroQual 2008). A sensitivity analysis of BLM to water quality parameters showed the model output of insensitive to all parameters except pH and DOC. However, they warned that these results cannot necessarily be extrapolated to other states and should not be used as a rationale for not measuring other water chemistry parameters. The study for Colorado (HydroQual 2008) recommends one year of water quality data with a minimum of 24 sampling events. EPA recommends a minimum of four seasonal samples and estimates the total cost for one set of 10 input parameters is $325 - $1300.

CONCLUSION: INCREMENTAL IMPLEMENTATION

The BLM has been shown to generate appropriate water quality criteria for copper (EPA 2007, Van Genderern et al., 2007). Critical review of the BLM has found the model useful for predicting the effects of metals to aquatic biota; however, important research questions remain about the relationship between bioaccumulation and toxicity, circumstances where such an equilibrium model is not appropriate, and the relative importance of other pathways of uptake other than gill membrane transport assumed in BLM (Slaveykova and Wilkinson 2005).

Because using BLM to derive the site-specific water quality criterion for copper requires 10 water quality parameters in addition to the copper concentration, there are a paucity of sites that have sufficient water chemistry data to properly execute the BLM. Consequently, EPA regards "incremental implementation as the most feasible and efficient means of implementing the updated criteria (http://www.epa.gov/waterscience/criteria/copper/faq/implementation-issues.pdf). EPA recommends adopting the BLM methodology into State water quality standards to develop site-specific copper criteria on a targeted basis, while retaining the hardness-based standards for all other waters. This only requires the addition of a paragraph in Minn. rule Ch. 7050 noting that site-specific criteria for copper may be developed on a case-by-case basis using the approach described in EPA (2007). EPA recommends the state maintain a list of where the BLM is used to establish the copper criteria. As shown in Figure Cu-1, a DOC of 2 mg/L closely matches the maximum (chronic) standard based on total hardness.

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