Implementation Procedures for the Site-Specific Application of Copper Biotic Ligand Model (BLM)

Iowa Department of Natural Resources
Water Quality Bureau

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1.0 Introduction

Metal bioavailability and toxicity have long been recognized to be functions of water chemistry. For example, formation of inorganic and organic metal complexes and sorption on particle surfaces can reduce metal toxicity. As a result, metal toxicity can be highly variable and dependent on ambient water chemistry when expressed as total or dissolved metal concentrations.

The Biotic Ligand Model (BLM) was developed to incorporate metal speciation and the protective effects of competing cations into predictions of metal bioavailability and toxicity. The BLM is a metal bioavailability model that uses receiving water body characteristics to develop site-specific water quality criteria. The BLM requires ten input parameters to calculate a freshwater instantaneous copper criterion including: temperature, pH, dissolved organic carbon (DOC), calcium, magnesium, sodium, potassium, sulfate, chloride, and alkalinity. Copper concentrations are also needed to derive single-value criteria using a probability-based method that develops a fixed-site criterion from time-variable instantaneous water quality criteria (IWQC). This probability-based method is called Fixed Monitoring Benchmark (FMB). The BLM is used to derive the criteria rather than used as a post-derivation adjustment such as the hardness based criteria. This allows the BLM-based criteria to be customized to represent the particular water under consideration.

The purpose of the document is to provide implementation procedures for the site-specific application of the copper BLM standard on a case-by-case basis. To that end, the document provides instructions for site-specific water chemistry data collection and the procedure to derive copper BLM criteria using the site-specific data. The implementation procedure ensures that the site-specific application of the copper BLM approach will produce predictable, repeatable copper BLM values used in the NPDES permitting process.

The copper BLM criteria will apply to the entire Site, as defined in Section 2.0. Outside of the Site boundaries, the hardness-based criteria apply. The Sites where copper BLM based criteria have been developed will be published on the DNR website.

2.0 Site Definition

In the general context of site-specific criteria, a Site may be a state, region, watershed, waterbody, segment of a waterbody, category of water (e.g., ephemeral streams), etc., and the site-specific criterion is to be derived to provide adequate protection for the entire Site.

This guidance will refer to a Site that is generally defined as "a segment of a waterbody". The determination of a Site depends on several factors, such as the number of known discharges, tributaries, and the waterbody type (such as streams or lakes). The factors are then combined to best define the size of the geographic site where sampling occurs and where the criteria derived from the BLM is applied.

Important note: the hardness based copper criteria apply beyond the boundaries of "the Site" used to develop the copper BLM criteria.

Some major considerations when defining the area to be included in the Site include the following:
1) The Site has to be large enough since outside the Site boundary the hardness-based copper criteria presented in 567 IAC Chapter 61 apply. Thus, the Site boundary should be at a location where the hardness based copper criteria can be met downstream of the Site boundary.
2) The site boundary determination needs to consider both the acute and chronic criteria effects and applies to both criteria. Small sites may be appropriate for developing acute criteria, but usually are not appropriate for chronic criteria because metals are conservative pollutants. For chronic criteria, the smaller the defined Site, the more likely the permit limits will be controlled by a criterion for an area that is outside the Site, but which could have been included in the Site without increasing the cost of sample collection.
3) Too large an area might unnecessarily increase the cost of sample collection. As the size of the Site increases, the spatial and temporal variability is likely to increase, which may increase the number of water samples needed to derive the site-specific criteria.
4) Special considerations are likely to be necessary when defining a Site with multiple discharges. The number of sampling locations will depend on the stream's hydrologic features and point sources that are expected to

change water quality, and that the resulting site-specific criteria must be protective of the entire Site. Also, multiple discharges can collaborate on water chemistry data collection and obtain the copper BLM criteria at a reduced cost.

3.0 Work Plan

The work plan describes the scope of the data collection study for developing the copper BLM criteria. The work plan includes, at a minimum, the following elements:

a. Purpose of the study;
b. Description of the facility and its effluent characteristics including effluent copper levels and potential sources;
c. The route of discharge flow and design low flows for the receiving stream;
d. The description of the Site Selection according to Section 2.0. The Site boundaries must be clearly defined;
e. Sampling location(s);
f. Temporal sampling collection protocols and seasonality;
g. Description of other details of the study, such as flow measurement, numbers of sampling events proposed, the sampling parameters (refer to Table 1 for the list of sampling parameters. Copper sampling is required when Fixed Monitoring Benchmark (FMB) methodology for criteria derivation is used), sampling schedules, and QA/QC methodology; and
h. Summary of consultation with Iowa Department of Natural Resources (DNR) in order to assure the study will respond to all concerns with respect to the uniqueness of the specific site.

4.0 Data Collection

Water chemistry data are required to use the copper BLM. The BLM calculates a copper criterion value for each set of input parameters (e.g., each sampling event). For example, if 24 sampling events for a particular Site are collected, the BLM will calculate 24 unique instantaneous water quality criteria (IWQC). Two different methods can be used to derive single-value copper criteria (both acute and chronic) for a Site based on IWQCs: (1) Using a percentile or geometric mean of the IWQC, and; (2) Calculating BLM Fixed Monitoring Benchmarks (FMB). The FMB method is discussed in detail in Section 7.2. Each method of criteria derivation requires a different approach to data collection: (1) data collection without copper, and (2) data collection with copper. Both data collection approaches require sampling of the 10 copper BLM input parameters shown in Table 1. The data collection approach selected will dictate the criteria derivation method. If copper data are collected, the FMB method is used to derive the copper criteria; if copper data are not collected, a percentile or geometric mean of the IWQCs is used to derive the final copper criteria. See section 7.0 for more information on copper BLM criteria derivation. The two data collection approaches are described in detail in the following subsections.

4.1 Data Collection without Copper

Samples should be collected at or beyond the point the discharge is completely mixed with the stream flow. The default maximum mixing length is 2000 feet (IAC 61.2(4)"b"). Thus, the sampling location should be located at least 2000 feet downstream of the discharge point of interest when site-specific mixing zone data are not available.

Plant performance during sampling events
- Normal operating conditions (not influenced by sudden loading change),
- Carbonaceous biochemical oxygen demand (CBOD) and suspended solids concentrations are within permit limits.

Stream conditions during sampling events
- Stable flow condition (not impacted by storm or runoff conditions),
- Water quality conditions compatible with those occurring during time periods when nonpoint source inputs of organic matter and suspended solids are relatively low (not impacted by storm or runoff conditions).

The following sampling conditions must be met
- For each sampling event, obtain a representative stream sample that is relatively unaffected by recent runoff events that might elevate the total suspended solids (TSS) and organic matter concentrations. Sampling must

not occur during rainfall/runoff conditions.

- At least 72 hours is recommended between a rainfall/runoff period and the collection of samples.
- For each sampling event, grab samples must be collected.
- pH and temperature must be measured on site.
- Collect, transport, handle, and store samples based on Quality Assurance/Quality Control (QA/QC) protocols. Obtain a sufficient volume so that some can be stored for additional testing or analyses if unusual results are obtained. Store samples at 0 to 4°C in the dark with no air space in the sample container.
- During the sampling event, measure effluent parameters that are normally required to be reported in the National Pollutant Discharge Elimination System (NPDES) Discharge Monitoring Report for the discharge under study. These measurements provide information on the representativeness of the effluent samples.
- For the sampling event, obtain stream flow data at the nearest relevant gaging station, rainfall data, and any other relevant meteorological information for the preceding two weeks.
- Use chain-of-custody procedures for all samples.
- Begin the chemical analysis as soon as is practicable, but no later than the holding time specified in 40 CFR 136 after sample collection.

<u>The following requirements regarding the number of samples must be met</u>

- Water quality data describe seasonal attributes of a stream.
- At least monthly sampling for two years is required to be collected (minimum of 24 sampling events).
- One year of sampling data collected once per month during a representative year (a total of 12 sampling events) will also be acceptable if the instantaneous copper criteria have low variability. Specifically, if the BLM-derived instantaneous copper criteria from one-year of sampling have a coefficient of variation (CV) less than or equal to 0.53, the BLM-derived instantaneous copper criteria are deemed to have low variability. One year of sampling data collected in a representative year will be acceptable and the second year of sampling will not be required. The CV value of 0.53 is derived using regression tree analysis based on the IWQCs derived from ambient monitoring data of the 10 BLM input parameters and the DOC concentrations. At or below the breakpoint CV value of 0.53, the relative change for both the instantaneous criteria and the DOC concentrations reach the lowest variability; thus a CV value of 0.53 is selected as the threshold value to use the geometric mean approach.
- If the stream area has been or is currently under either drought or flood conditions, contact the DNR to discuss additional sampling requirements. An extended period of sampling may be required to ensure a full range of stream conditions have been assessed. Drought and/or flooding events can impact the results of many of the inputs used in the model.
- If weather conditions (such as ice cover) prevent sample collection during certain months of the year, supplemental samples should be collected in other months. Supplemental samples should be uniformly distributed among the remaining months.

<u>Special considerations</u>

Because BLM input parameters may vary spatially within a Site, multiple sampling locations may be required. The unique characteristics of each Site are considered, including variability of BLM input parameters. For example, relatively homogenous systems may require fewer sampling locations as compared with more heterogeneous water bodies.

For Sites with more than one NPDES permit, water quality samples are taken below each NPDES permit discharge just above the next discharge and below all discharges at a location where complete mixing occurs.

4.2   Data Collection with Copper

In addition to the 10 parameters shown in Table 1, instream copper must be monitored. The BLM model requires no more than 80% of the available input data are below detection limits; however the confidence in the FMB is increased as the percentage of non-detects decreases. The detection limits for the copper concentration testing method must be able to provide enough detected copper concentration values to be used in the BLM model to derive FMB values.

All other sampling requirements such as sampling conditions, number of samples, sampling site location selection and

special conditions are the same as the Data Collection without Copper approach as described in Section 4.1.

5.0 QA/QC

Quality assurance and quality control will be documented throughout the sampling and reporting process through the following measures:

1. All laboratory analyses will be completed by DNR certified labs and all analytes included in the copper BLM (see Table 1) will pass annual proficiency tests (PTs; where applicable). Annual proficiency tests are required as a part of the DNR certification process. Certification will be administered per Chapter 83 of the Iowa Code.
2. Labs will complete and use an DNR-approved quality assurance manual (required as a part of the laboratory certification process) for analyses completed as a part of this project.
3. Documents required as a part of the certification process include (as listed in the laboratory certification application):
   a. Quality Assurance Program Plan
   b. Sampling instructions
   c. Example chromatograms (for the UST program)
   d. Example of an analysis report, and
   e. Proficiency test results (for analytes being certified)
   f. Standard operating procedures for each analyte being certified
   g. Application forms and fees
   h. Travel instructions to the laboratory (for the onsite appraisal required as a part of the certification process)
   i. Questions about the laboratory certification process should be directed to the DNR Laboratory Certification Officer
4. All analyses will be completed using DNR-approved methods. The appropriate method for analyses must be determined by the laboratory, technical contract in the water quality bureau, and DNR certification program.
5. 10% of field sampling collection events (rounded up to the next whole number) will be replicated and analyzed, on an annual basis, to document that samples are representative of conditions in the stream. Replicate events should be randomly selected prior to initial sample collection.
6. 10% of laboratory samples analyzed (including field replicates and rounded up to the next whole number) will be replicated for each analyte in the copper BLM, on an annual basis, to document precision within the laboratory. Replicate samples for each analyte should be randomly selected prior to initial sample collection.
7. All replicate samples will meet a <20% Relative Percent Deviation (RPD) or will be re- collected (field) or re-run (laboratory).
   a. Calculate the Relative Percent Deviation (RPD) as follows:
   RPD = (s / x) *100
   Where s is the standard deviation of the duplicate values, and x is the mean of the duplicate values.
   b. If RPD<20%, then the final reported value is the mean of the duplicate values
   c. If RPD>20%, then sample is re-run.
8. %RPD values will be reported in the final report and approved by DNR.
9. A minimum of 24 samples must be collected for two years, one from each month for use with the model, unless the permittee can demonstrate low variability between samples. DNR will determine if fewer than 24 samples can be collected to be used in the model.
10. Labs must report all sample analyses using the units listed in the table below for each analyte.
11. Detection limits for each parameter must be sufficiently low to be used with the model.
12. All sample analyses must be submitted to DNR. DNR will run the model to determine the site specific copper criteria.

Table 1. Parameters required as a part of the copper biotic ligand model. Note: approved laboratory methods may only apply to one program and are subject to change. Consult the DNR laboratory certification officer prior to certification.

Analyte	Units	Annual (Proficiency Test) PT required	Minimum significant figures required
Temperature	°C	No (field sampled)	1 digit after decimal
pH	s.u.	No (field sampled)	1 digit after decimal
Dissolved Organic Carbon	mg C/L	Yes	2 digits after decimal
Calcium	mg/L	Yes	2 digits after decimal
Magnesium	mg/L	Yes	2 digits after decimal
Sodium	mg/L	Yes	2 digits after decimal
Potassium	mg/L	Yes	2 digits after decimal
Sulfate	mg/L	Yes	3 digits after decimal
Chloride	mg/L	Yes	2 digits after decimal
Alkalinity	mg CaCO3/ L	Yes	2 digits after decimal
Copper (for FMB method only)	µg/L	Yes	1 digit after decimal

13. All chemical constituents should be measured as <u>dissolved concentration</u> and the samples should be filtered in the field.
14. All parameters must be analyzed using approved methods specified in 40 CFR Part 136. Information on these analytical methods is available on the EPA website. Although DOC is not regulated as a contaminant, there are several scientifically-defensible methods available to measure DOC, such as EPA Method 415.3 (Dissolved and Total Organic Carbon and UV Absorbance at 254 nm in Source Water and Drinking Water), as well as methods developed by ASTM International and Standard Methods for the Examination of Water and Wastewater.

6.0 Final Report Requirements

The final report submitted to DNR must include the general and sample information listed below.

<u>General Information</u>
   a. Identity of the samplers and the laboratory;
   b. Description of the facility;
   c. A detailed description of the Site using a map with sampling locations clearly indicated;
   d. Name, location, and description of the discharger; description of the effluent and the receiving water;
   e. Identification of each sampling station;
   f. Procedures used to obtain, transport, and store the samples;
   g. Any pretreatment, such as filtration, of the effluent and site water;
   h. Results of all chemical and physical measurements on actual water samples including the ten parameters for the BLM model inputs, and/or concentrations of total recoverable or dissolved copper, TSS, etc.

<u>Sample Information</u>
   a. Date and time of each sampling of the Site water;
   b. Effluent flow during each sampling event;
   c. Upstream flow during each sampling event, either measured directly or estimated from relevant neighboring gages;
   d. Prior meteorological conditions affecting flow and sampled water quality;
   e. Measurements of all chemical concentrations, and testing methods;
   f. Summary of all sampling data in an Excel spreadsheet or other format that is compatible with the copper BLM model;
   g. The final report must be submitted to DNR's Wasteload Allocation Staff for approval;
   h. DNR will review the sampling data, run the copper BLM and calculate the final copper BLM criteria based on the criteria development procedure in Section 7.0.

7.0 Criteria Development

Two different criteria derivation methods can be used depending on whether enough quantifiable instream copper data are collected. Section 7.1 describes the criteria derivation procedure when copper data are not collected. Section 7.2 describes the criteria derivation procedure when copper data are available. The decision process for which method is used to derive the criteria is shown in Appendix A.

7.1 Criteria Derivation without Copper Data

The BLM calculates dissolved copper criteria values for each set of input parameters (e.g., each 'sampling event'). Thus, with 24 sampling events, the BLM calculates 24 unique instantaneous water quality criteria (IWQC). There are several options for developing a single numeric site- specific criterion from the BLM output. The site-specific criterion should protect the water body (i.e., its designated use for aquatic life) under a variety of circumstances (e.g., seasonal conditions, high and low flows) and should not be exceeded more than once every three years on average. Site-specific conditions will influence the selection of an appropriate statistical metric for calculating a numeric criterion for copper.

- If the BLM-derived instantaneous copper criteria are relatively constant over a range of seasonal and flow conditions, (the CV is less than or equal to 0.53), then using the geometric mean of all instantaneous criteria is appropriate and will be used. A geometric mean is a measure of central tendency and is less likely to be affected by outliers than an arithmetic mean.
- If a water body exhibits significant seasonal variations in the BLM input parameters and BLM-derived instantaneous copper criteria, then seasonal criteria are developed using seasonal geometric means. In such water bodies, averaging on an annual basis could result in a criterion value that is potentially under protective during parts of the year (e.g., fall and winter).
- If the BLM-derived instantaneous copper criteria vary significantly (the CV is greater than 0.53) for reasons that cannot be easily explained (e.g. are not seasonal), either the 10th percentile copper BLM criteria or FMB method will be required to derive the final copper criteria. If the FMB method is selected, the second year of data collection must include instream copper sampling.
- If there are significant spatial differences in instantaneous BLM-derived criteria for a Site, data collected from different sampling locations need to be evaluated independently. The criteria selected must be protective of the entire Site.

7.2 Criteria Derivation with Copper Data

The site-specific BLM based copper criteria are derived by calculating Fixed Monitoring Benchmarks (FMBs) when instream copper data are collected along with the 10 input parameters for the copper BLM. The BLM model requires no more than 80% of the available input data are below detection limits; otherwise the criteria derivation method described in Section 7.1 has to be used.

The basic idea of the FMB is to identify the single value, for a given Site, which will produce the same exceedance frequency as the time variable distribution of instantaneous criteria calculated using the copper BLM, when compared to a given set of ambient copper measurements. One of the major differences between FMB and water quality criteria is that FMB are calculated, in part, using the IWQC from the copper BLM and a distribution of ambient copper concentrations, whereas water quality criteria are calculated using only the water quality characteristics of the receiving water, independent of copper concentrations.

An instantaneous criterion does not take into account variations in the BLM input parameters, some of which may vary substantially on a temporal and/or spatial scale. EPA developed a probability-based method that incorporates time variability in BLM-predicted instantaneous water quality criteria and in-stream copper concentrations. The methodology is used to derive a probability-based approach for developing a fixed-site criterion from time-variable results.

The copper BLM program will automatically calculate the FMB values based on the sampling data. The final FMB values ensure that the derived criteria will not be exceeded more than once in three years as required in the EPA 1985 Guidance Document for aquatic life criteria derivation *("Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses.")*

If there are significant spatial differences in instantaneous BLM-derived criteria for a Site, data collected from different sampling locations need to be evaluated independently. The criteria selected must be protective of the entire Site.

8.0 The Use of Copper BLM Criteria for Wasteload Allocations

If adequate site-specific water chemistry data that meet the requirements specified in this document are collected, the copper BLM criteria will be developed and used in wasteload allocations to derive water quality based limits. The copper effluent limits will be expressed as dissolved copper concentrations since the copper BLM criteria are based on dissolved copper form. EPA regulation 40 CFR 122.45(c) allows effluent limits to be expressed as dissolved metal concentration if the water quality standards are expressed as dissolved metal form. In addition, the following conditions will be considered:

- Where BLM-derived copper criteria are significantly affected by the effluent water chemistry of point source discharges such as for effluent dominated streams, this correlation will be considered when establishing the appropriate wasteload allocations under design conditions.
- If seasonal criteria are developed, seasonal wasteload allocations will be developed with consideration for the corresponding seasonal stream critical low flows and the influence of effluent water chemistry on BLM-derived copper criteria under design conditions.
- The implementation of the copper BLM criteria will also be consistent with the Wasteload Allocation Procedure document.

Appendix A: Criteria Derivation Decision Process

Note: Facilities have the option to collect additional data including copper concentrations so that the FMB method can be used to derive the final copper criteria.

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                          ┌─────────────────┐
                          │  Collect data for│
                          │   Copper BLM     │
                          └────────┬────────┘
                                   │
                                   ▼
 ◇ Does instantaneous      ◇ Is there copper          ◇ Derive criteria using
   criteria have    ◄─No──   monitoring? (with less  ─Yes─►  FMB
   CV >0.53?                  than 80% ND)
        │
        │No              Yes─┐
        ▼                    │
 ┌───────────────┐    ┌──────▼────────┐
 │Derive criteria│    │Derive criteria│
 │using geometric│    │using 10th     │
 │     mean      │    │  Percentile   │
 └───────────────┘    └───────────────┘
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