# Implementation of the Biotic Ligand Model for Derivation of Freshwater Aquatic Life Criteria for Copper on a Site-Specific Basis in State Water Quality Standards

**Draft Guidance Document**

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# EXECUTIVE SUMMARY

In 2007 the U.S. Environmental Protection Agency (EPA) published nationally recommended ambient freshwater aquatic life criteria for copper (Cu) based on the application of the biotic ligand model (BLM). The BLM is a metal bioavailability model that uses water quality data to develop site-specific water quality criteria (WQC) for Cu. Input data for the BLM include: temperature, pH, dissolved organic carbon (DOC), major cations (Ca, Mg, Na, & K), major anions ($SO_4$ & Cl), alkalinity, and sulfide.[1] The collection of Cu data is required to utilize certain BLM tools (e.g., Fixed Monitoring Benchmark).

The Alaska Department of Environmental Conservation (DEC) reviewed EPA's 2007 Cu BLM and has developed this "performance-based approach (PBA)" to calculate WQCs protective of aquatic life for Cu on a site-specific basis.[2] In accordance with Endnote 20 in the *Alaska Water Quality Manual for Toxic and Other Deleterious Organic and Inorganic Substances* DEC authorizes this performance-based approach for derivation of wastewater discharge permit limits for Cu considered to be protective of aquatic life.[3] This document ensures the derivation of BLM-derived criteria is done in a protective, transparent, consistent, and reproducible manner, and documents how said Cu criteria will be implemented in the derivation of water quality-based effluent limits (WQBELs). This PBA is applicable to development of wastewater effluent discharge limits. It's envisioned that Publicly Owned Treatment Works (POTW) who have significant concentrations of DOC in their waste streams and control over the range of BLM inputs would be the primary users. Other permittees interested in application of the biotic ligand model may do so under 18 AAC 70.235 (Site-specific criteria).

Sections 1.0 - 3.0 of this document provide the context and background for the development of a discharger-specific project plan that utilizes this PBA. Sections 4.0 – 10.0 provide explicit directives pertaining to key data requirements, analysis, and how DEC will interpret the results to establish binding water quality criteria for Cu (aquatic life).

Application of the BLM for derivation of site-specific criteria for waterbodies where the purpose would be to assist with implementing other water pollution control programs (e.g., calculation of Total Maximum Daily Loads, 401 certifications) will be considered by DEC on a case-by-case basis. Applications authorized under the Clean Water Act (CWA) and must be reviewed and approved by EPA under the CWA section 303(c) in order to become effective.

The PBA addresses:

- The definition of a "Site" for the purposes of this PBA
- The collection of site-specific water chemistry data to derive BLM inputs.



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[1] https://www.epa.gov/wqs-tech/copper-biotic-ligand-model. Referenced January 10, 2024.

[2] EPA has stated in materials that accompanied the release of the 2007 Cu criteria document that incremental implementation of the BLM may be the most feasible and efficient means of implementing the updated criteria. See https://www.epa.gov/sites/production/files/2015-11/documents/Cu-implementation-training.pdf

[3] The performance-based approach stems from EPA's Alaska rule, so-named because of a settlement, and is described at 65 FR 24648 (April 27, 2000), https://www.govinfo.gov/content/pkg/FR-2000-04-27/pdf/00-8536.pdf. In EPA's words, "the key to a 'performance based' WQS program is adoption of implementation procedures of sufficient detail, and with suitable safeguards, so that additional oversight by EPA would be redundant." *Id.*

- Data requirements for using the BLM and means of accounting for environmental variability.
- How to determine appropriate default parameters when water quality data are not available; and,
- How DEC will interpret and apply BLM output data in state water pollution control programs (e.g., Alaska Pollutant Discharge Elimination System (APDES[4].)), when applicable.

Alaska's hardness-based WQCs, identified at 18 AAC 70.020(b)(11) or 18 AAC 70.236(b), apply to waters outside of the state-defined site boundaries. Discrete locations where BLM-derived criteria have been adopted via the PBA will be published by DEC in the respective draft permit fact sheet together with the inputs used to derive the criteria and subject to public comment. Final permit limits for Cu will reflect the draft fact sheet and associated information. It is strongly recommended that interested parties engage in a detailed discussion with DEC two to three years in advance of committing resources to a project utilizing the approach outlined in this document.

# 1.0 Introduction

State water quality standards (WQS) are implemented via Alaska's water pollution control programs and are authorized under the CWA and Alaska Statute 46.03.080. This includes issuing effluent permits for APDES/state discharge permit and conducting water quality assessments and reporting per §303(d) and §305(b) of the CWA. Alaska may also adopt site-specific WQCs under 18 AAC 70.235 which reflect designated/protected uses and their respective WQCs determined to be protective of those uses.

## 1.1 Cu in the Environment

Cu is a metal commonly found in Alaska's natural environment. According to the EPA, naturally occurring Cu can range in freshwater aquatic ecosystems from 0.20 to 30 µg/L (parts per billion) (EPA, 2007). Natural sources that release Cu into aquatic systems include volcanic activity, geologic deposits and the weathering and erosion of rocks and soils. Cu has also been traced to a variety of anthropogenic sources including current and legacy mining activities,[5] marine antifouling paint,[6] publicly owned treatment works (POTWs), and urban storm water runoff.

## 1.2 Toxicity of Cu

Cu is an essential micronutrient for both plants and animals (EPA, 2007). However, at higher concentrations Cu can result in acute lethality or chronic lethal/sub-lethal effects to certain aquatic life species or life stages. Chronic effects of Cu include inhibition of photosynthesis, metabolism, and growth in aquatic plants and algae; reduced feeding, growth, and reproduction, as well as gill damage in aquatic invertebrates; and significant effects on behavior, growth, changes in metabolism and organ or cellular damage, and changes in olfactory-mediated behaviors in freshwater fish species

[4] 18 AAC 83.990(2): "Alaska Pollutant Discharge Elimination System" or "APDES" means the state's program, approved by EPA under 33 U.S.C. 1342(b), for issuing, modifying, revoking and reissuing, terminating, monitoring and enforcing permits, and imposing and enforcing pretreatment requirements under 33 U.S.C. 1317, 1328, 1342, and 1345

[5] The first documented Cu mining claim in Alaska was in 1867.

[6] Srinivasan, M and Swain, G. 2007. Managing the use of Cu-based antifouling paints. Enviro. Management, Vol. 39(3), pp 423-441.

(Meyer and Adams, 2010; Baldwin *et al.,* 2003; NMFS, 2014; Sommers *et al.,* 2016, Meyer and Deforest, 2018).

# 2.0 Alaska Aquatic Life Criteria for Metals

Alaska adopted a hardness-dependent methodology[7] to calculate WQCs for select metals in WQS at 18 AAC 70.020(b). Hardness-dependent metal WQCs vary by in-stream hardness values and do not account for the effects of other principal physicochemical properties that can affect metal bioavailability. Metal bioavailability is the fraction of total metals biologically available for the incorporation into biota (John and Leventhal, 1995). Alaska's existing hardness-dependent WQCs do not explicitly account for DOC, pH, or other parameters that affect the bioavailability (and potential toxicity) of metals. More information about hardness-dependent metals criteria can be found in section 3.2.

## 2.1 Freshwater Criteria for the Protection of Aquatic Life

DEC requires all WQCs include applicable magnitude, duration, and frequency values for implementation of WQC in state water pollution control programs. The following describes how BLM-derived instantaneous water quality criteria (IWQCs) values will be reconciled and applied:

| **Alaska Water Quality Criteria** | |
|---|---|
| **Magnitude** | The BLM-derived WQC must protect the water body over the full range of ambient water chemistry conditions, including during conditions when copper is most bioavailable and toxic.[8] |
| **Duration** | The acute criteria duration is a 1-hour average.[9]<br>The chronic criteria duration is a 4-day average. |
| **Frequency** | The BLM-derived WQC may not be exceeded more than one time in a three-year period. |

Additional information on criteria derivation is located in sections 9 and 11.

# 3.0 Biotic Ligand Model

The BLM is a mechanistic metal bioavailability model that considers the influence of both the abiotic and biotic (inorganic and organic) factors in determining the bioavailability of metals to aquatic organisms (Di Toro *et al.*, 2001). The BLM incorporates multiple water chemistry parameters and calculates instantaneous water quality criterion (IWQC) for acute and chronic toxicity endpoints to aquatic organisms. The BLM represents a more comprehensive approach to determining how other components of water chemistry can affect the bioavailability of Cu and potential toxicity.

For chemical toxicity to occur to an aquatic organism, it requires the transfer of the chemical from the external environment to biochemical receptors on or in the organism at sites where the toxic



[7] This methodology is based on EPA's nationally recommended criteria contained in the *1995 Updates: Water Quality Criteria Documents for the Protection of Aquatic Life in Ambient Water*, (EPA-820-B-96-001, September 1996) and adopted by reference at Note 20 in the *Alaska Water Quality Criteria Manual for Toxic and Other Deleterious Organic and Inorganic Substances.*

[8] See Section 11.0 of this document.

[9] The version of the Cu biotic ligand model recommended by EPA (version 2.2.3) calculates acute criteria that are protective of a 1-hour duration, as the model was developed in accordance with the 1985 Guidelines.

effects can happen, refer to Figure 1. This receptor is generalized as the biotic ligand and is the location where interactions with metals occur, e.g., ion transfer mechanisms on a fish gill surface.

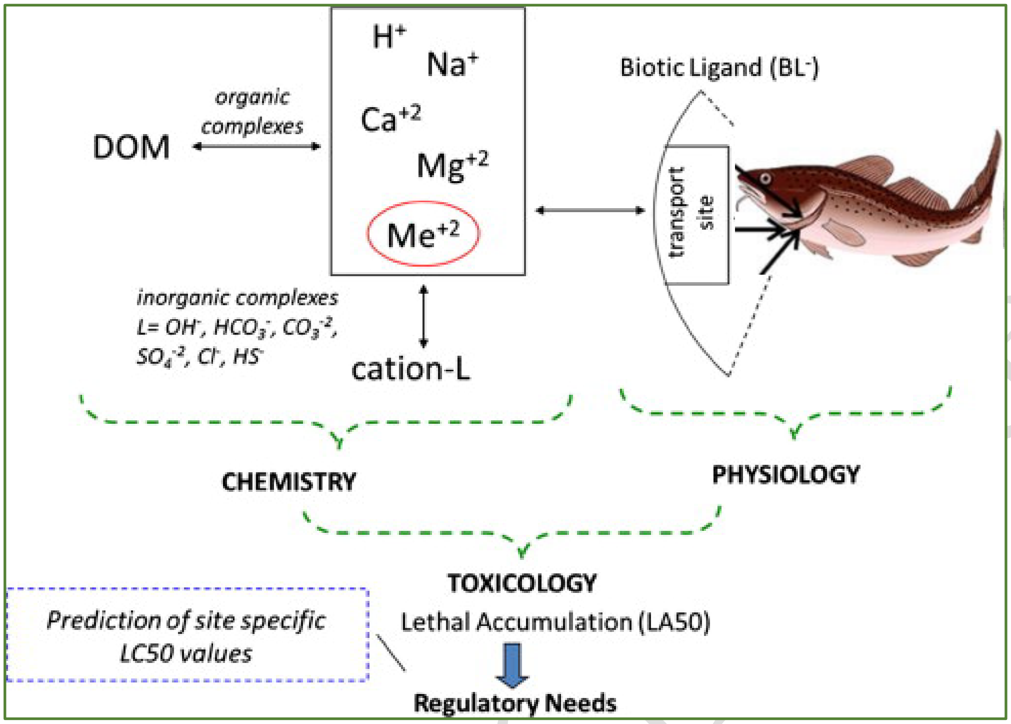
The degree to which metals are bioavailable and cause toxicity to aquatic organisms is determined by site-specific geochemical conditions controlling the speciation, precipitation and/or complexation of metals. Cu has four oxidation states (elemental Cu, Cu(I), Cu(II), and Cu(III)) but the environmentally relevant form of Cu in aquatic environments is Cu(II). The cupric ion ($Cu^{2+}$) and to a lesser degree Cu monohydroxide ($CuOH^{+}$) are considered the bioavailable forms of Cu in aquatic environments (EPA, 2007). Unlike other forms of Cu, bioavailable forms of Cu react with receptors on biological membranes and interfere with ion transfer at the cell surface of an organism. Therefore, the concentration of bioavailable Cu and the degree to which it interacts with biological membranes is what determines the toxicity of Cu in water.

In 2007, EPA published national 304(a) freshwater Cu criteria[10] recommendations using the BLM[11] to account for the water chemistry that affects toxicity. Inorganic complexes with bicarbonate and carbonate can also affect Cu bioavailability. Using an equilibrium geochemical modeling framework, the BLM incorporates the competition of the free metal ion with other naturally occurring cations (e.g., $Ca^{2+}$,$Na^{+}$,$Mg^{2+}$, $H^{+}$), together with complexation by abiotic ligands [e.g., dissolved organic matter (DOM)), chloride, and carbonates], for binding with the biotic ligand (Niyogi and Wood, 2004). The quantification of DOM in environmental samples is by the measurement of dissolved organic carbon (DOC), and so the model uses DOC as an input variable rather than DOM for convenience.

**Figure 1**: Schematic of the Biotic Ligand Model (Smith, Balistrieri, Todd, 2015)



[10] EPA's 2007 nationally recommended approach for Cu criteria using the BLM revises previously published recommendations for Cu criteria that were based solely on hardness (e.g. EPA 1980, 1985, 1986, 1996).
[11] https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table




## 3.1 BLM and Water Quality Criteria

BLM[12] software calculates IWQC for Cu based on the model's required chemical inputs. BLM-derived criteria do not necessarily provide more stringent criteria than those derived from hardness-based or similar models. IWQC from multiple sampling events can be used to demonstrate the range of critical conditions likely to be present in water body when establishing regulatory limits (i.e. water quality criteria) in various water pollution control programs.

### 3.1.1 Instantaneous Water Quality Criteria (IWQC)

The phrase "instantaneous water quality criterion" refers to a criterion value based on a singular sampling event and associated model inputs. Therefore, an IWQC is protective at that location and that instant in time. Therefore, an IWQC is only protective at that location and that instant in time and does not account for variability over time. In order to be useful over time, as described below, a series or range of IWQC are analyzed to determine protectiveness of the waterbody over time.

The BLM calculates acute and chronic IWQC by accounting for the influences of several water quality parameters which become the water quality input data set. The BLM uses the input data to first generate a final acute value (FAV) based on EPA's 1985 guidance, then divides the FAV by two to generate the IWQC. The FAV represents the 5$^{th}$ percentile concentration of the acute genus sensitivity distribution (GSD) dataset. The GSD for Cu used in the BLM was established in the EPA 2007 criteria document. The chronic IWQC is then calculated by dividing the FAV by an acute-to-chronic ratio (ACR), which for Cu was also established in the EPA 2007 criteria document.

[12] Biotic Ligand Model software version 2.2.3 serves as the basis for EPA's 2007 Cu criteria.

Water chemistry is time variable, and therefore any IWQC will also be time variable whether it is based on a hardness equation or a BLM calculation. For a single-variable approach, such as the hardness equation, it is relatively straightforward to evaluate the time-variability and select an appropriate hardness value and corresponding WQC. For criteria approaches that reference multiple water quality parameters, such as the BLM, calculations can be complicated by the covariation between input parameters. Rather than considering how each parameter varies independently, and thereby ignoring co-variances between parameters, it is preferable to examine the variability of IWQC values since the co-variation between parameters is thereby preserved. Once a series of site and time-specific IWQC are determined, that account for the variability of the BLM input parameters at the site of interest, a general WQC can be calculated. WQCs must protect the waterbody and its designated aquatic life uses under a variety of circumstances (e.g., daily pH swings, seasonal conditions, high and low flows). If there are clear seasonal patterns to the variation in IWQC, that information could be used to define the critical condition or most bioavailable period at a given location and point in time. A protective WQC could then be based on the range of IWQC that occur during this critical condition (see section 5.3.4). A more generic methodology that takes time variability into account is the fixed monitoring benchmark or FMB.

### 3.1.2 Fixed Monitoring Benchmark (FMB)

The fixed monitoring benchmark or FMB is a probabilistic approach that considers time-variability of both IWQC and Cu to determine a single number that can be used in place of IWQC values in developing permitted effluent limits (EPA, 2012; Ryan et al, 2018). The FMB produces an acute and chronic limit that are each defined such that if the permitted discharges do not exceed the FMB then they will also not exceed the time-variable IWQC more frequently than a specified exceedance frequency (EF) – typically once in three years as suggested by EPA (1996). The use of the FMB can simplify the interpretation of time variable IWQC, without requiring that a critical period (i.e., the period in which Cu is most bioavailable for uptake by aquatic species via the biotic ligand) is defined, or that a set percentile of IWQC values be used. Of course, the monitoring data should be sufficient to include a critical period if one exists. Case studies have shown that the corresponding percentile of IWQC values that match the FMB can vary tremendously depending on the relative variance of metal concentrations, IWQC values, and the correlation between them (Ryan *et al.*, 2018).

The use of the FMB can avoid complications associated with defining "critical condition". For example, should the critical condition be defined as the season or flow condition when IWQC values are low, or when Cu concentrations are high? If there are strong seasonal changes in flow, for example because of snow melt events, those periods may have low IWQC but also low Cu because of the dilution associated with high flow. A period when IWQC is regularly low, therefore, may not be the most critical condition from the standpoint of Cu exposure. The FMB uses the time variability of both IWQC and Cu to determine a value that is protective when criteria exceedances are most likely to occur. There may be situations where the critical period can be defined, and the consideration of critical conditions can be a useful approach. The FMB is simply another approach that can be considered for determining a protective effluent limit when conditions and IWQC values are time variable.

The mathematics behind the calculation of FMBs are like that of waste load allocations and other probabilistic analysis used to develop regulatory limits (Ryan *et al.*, 2018). The calculation of FMBs have been integrated into the BLM output in version 2.2.4 and later (EPA, 2012) and are automatically provided in BLM output (see section 11 for illustrative case studies). Refer to Ryan et al (2018) for a full description of the methods, but briefly: to calculate the FMB, the toxic unit (TU) is first calculated as the quotient of the ambient metal concentration (represented as *Me* in the following equations) to the coincident IWQC at each time point, *i*:

$$TU_i = \frac{Me_i}{IWQC_i}$$

The probability distribution of TU values is used to evaluate the TU at the EF of once in 3 years or 1095 days or roughly 99.9% of the time:

$$TU_{EF} = 10^{[Z_{EF} \times s_{TU} + \log_{10}(TU_{mean})]}$$

where $Z_{EF}$ is the z-score, or number of standard deviations that the EF is from the mean using a standard normal distribution (2.996 with an EF of 1 in 1095 days and a Hazen plotting position), $s_{TU}$ is the standard deviation of the log-transformed TU values, and $TU_{mean}$ is the geometric mean TU. This value of $TU_{EF}$ is used to calculate the adjustment factor, *AF*[13], that must be applied to the metal distribution to obtain the distribution with the highest geometric mean possible while still attaining the IWQC. This can be applied directly to the geometric mean of the distribution:

$$Me_{Mean,\max distribution} = AF \times Me_{Mean}$$

where $Me_{Mean}$ is the geometric mean of the ambient metal[14] concentrations, and $Me_{Mean,\ max\ distribution}$ is the highest geometric mean of metal concentrations that would still attain the IWQC. Finally, the FMB is calculated as the metal concentration from this max distribution that would occur once in three years:

$$FMB = 10^{[Z_{EF} \times s_{Me} + \log_{10}(Me_{Mean,\max distribution})]}$$

Where $s_{Me}$ is the standard deviation of the log-transformed ambient metal concentrations, and $Z_{EF}$ and $Me_{Mean,\ max\ distribution}$ as previously defined. The above is for an acute FMB; to calculate a chronic FMB, the standard deviations must be adjusted to reflect that the ambient metal concentration would be a 4-day average. To do this, an effective sample size, $n_e$, is calculated:

$$n_e = \frac{n^2(1-\rho)^2}{n(1-\rho^2) - 2\rho(1-\rho^n)}$$

where $\rho$ is the serial correlation coefficient, which is by default set to 0.8 (a reasonable assumption for relatively small streams), *n* is the number of days over which the values are averaged (4 in this case), yielding $n_e$ = 1.29199 in this case. The standard deviations for the metal concentrations and TUs are then adjusted with this $n_e$ value to yield the standard deviations relevant to the 4-day average concentrations ($s_{Me,\ 4\text{-}d}$ and $s_{TU,\ 4\text{-}d}$, respectively):

13 AF = 1/$TU_{EF}$

14 "Metal" in this context refers to copper concentrations.

$$s_{Me,4-d} = \sqrt{\ln\left(1 + \frac{\exp(s_{Me}^2) - 1}{n_e}\right)}$$

and,

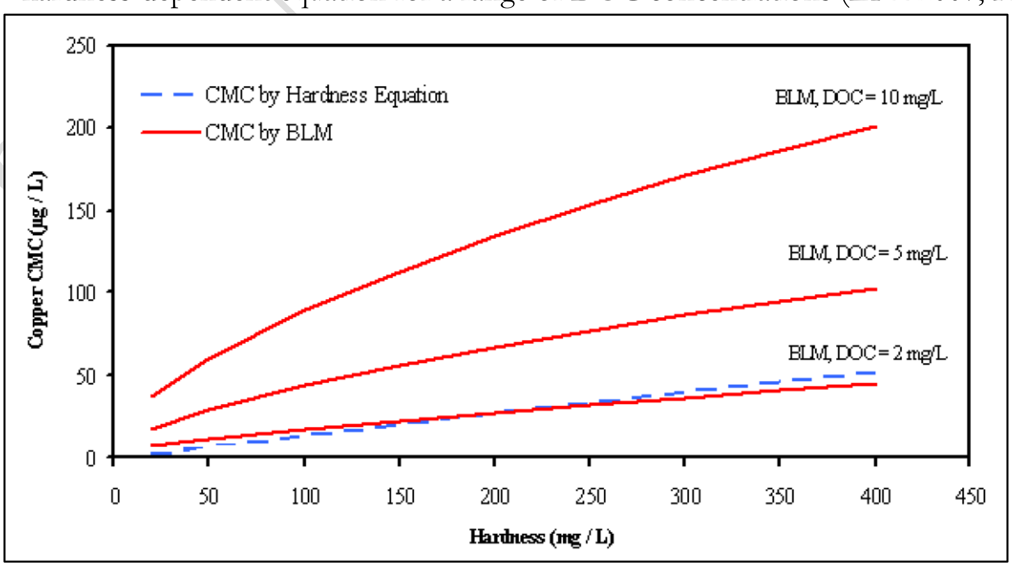
$$s_{TU,4-d} = \sqrt{\ln\left(1 + \frac{\exp(s_{TU}^2) - 1}{n_e}\right)}$$

These adjusted standard deviations are used in the $TU_{EF}$ and FMB equations above instead of their unadjusted counterparts, and of course the chronic IWQC is used to calculate the TU rather than the acute IWQC, when calculating the chronic FMB.

### 3.2 Comparison with Hardness-dependent Approach

It was observed several decades ago that metal toxicity often varies when water hardness was varied and other parameters were held constant, and so EPA's nationally recommended ambient water quality criteria (AWQC) for metals[15] are typically derived as a mathematical function of hardness (Stephan *et al.,* 1985). In Figure 2, the correlation between hardness, pH, and alkalinity is preserved to mimic how these three variables typically vary in natural waters. Under these conditions, the BLM produces IWQC values that are very similar to the hardness equation at low DOC but can be considerably higher (less stringent) in waters with higher DOC concentrations. In waters with very low DOC (i.e., < 2 mg/L), the BLM will produce IWQC values that are lower (more stringent) than that of the hardness equation. The BLM can also calculate lower IWQC for waters where the correlation between hardness, pH, and alkalinity breaks down. For example, waters impacted by acid rock drainage[16] can have high hardness but low pH and alkalinity.

**Figure 2.** Comparison of BLM-based acute (Criterion Maximum Concentration (CMC) and hardness-dependent equation for a range of DOC concentrations (EPA 2007, Figure 5)




[15] The EPA's 304(a) criteria recommendations for Cu were also hardness-based until EPA updated the Cu criteria recommendations to the BLM in 2007.

[16] Acid rock drainage refers to water that has been in contact with sulfide minerals.

### 3.3 Comparison with Water Effect Ratio (WER) Approach

To address the modifying effects of site-specific water quality conditions beyond hardness considerations, EPA issued guidance in the early 1980s on the water-effect ratio (WER) method (Carlson *et al.,* 1984; EPA, 1983, 1992, 1994). The WER is "a biological method to compare bioavailability and toxicity in receiving waters versus laboratory test waters" (EPA, 1992). The WER approach calculates a ratio by dividing toxicity measured in site water with that measured in laboratory water adjusted to similar hardness. The hardness-based acute metal criterion is multiplied by this resultant ratio to yield a site-specific metal criterion (i.e., site water LC50/lab water LC50); then the geometric mean of multiple WERs is typically used to adjust to a hardness-based AWQC (Tobiason *et al.,* 2009).

Application of the BLM does not necessarily reduce uncertainty relative to empirical (e.g. WER) data (EPA 2000)- the BLM in essence is the computational equivalent of the WER (Niyogi and Wood, 2004) since both approaches are using site-specific information to refine criteria to consider bioavailability. The chemistry data needed to run the BLM is relatively easy to obtain and can be incorporated in routine monitoring efforts that can consider spatial and temporal variability. It is far more difficult to provide similar spatial and temporal resolution with toxicity tests that would be needed for a WER analysis. The ability of the BLM to predict potentially toxic conditions over a wide range of environmental settings makes the BLM a more versatile and effective tool for deriving site-specific WQC compared to the WER (EPA, 2000).

# DEC Performance-based Approach for Deriving Water Quality Criteria – Required Project Elements

## 4.0 Site Definition and Temporal Applicability

In the context of this document, a “Site” is defined as the location where a permitted discharge from a wastewater treatment facility, as referenced in the permit fact sheet, is authorized (i.e., end-of-pipe, zone of instantaneous mixing, or edge of a regulatory mixing zone)Hardness-based criteria for Cu (aquatic life) referenced in the *Alaska Water Quality Manual for Toxic and Other Deleterious Organic and Inorganic Substances* apply upstream and downstream of the boundaries of “the Site” used to develop the BLM IWQCs and applicable WQC.

Site boundaries should be characterized in a manner that ensures:

- Water quality data will be collected from the physical location(s) where the discharge is authorized;;
- hardness-dependent criteria to be met downstream (40 CFR 131.10(b));
- water quality data to be collected in a manner that minimizes spatial and temporal variability of IWQC or input parameters (i.e., DOC & pH); and
- representativeness of the range of conditions expected to occur within the site..

### 4.1 Seasonal Application

Sites that consistently demonstrate seasonable variability may be eligible for seasonal WQC using the approach outlined in the PBA. Such criteria calculations should include evaluations of the effect of climatic and flow variability on bioavailability. To consider seasonal criteria, sufficient data must be available and must demonstrate seasonal variations are consistent with a statistical confidence value of 90%. This evaluation may require up to 24 monthly samples, although additional sampling may be required to sufficiently demonstrate seasonal variability (e.g., new sample data fall within the 90% confidence range of previously collected data for a time and location).

## 5.0 BLM Data Requirements

It is recommended that interested parties consult with DEC staff in advance of any data collection efforts to evaluate BLM data requirements and approach (e.g., reconciliation of IWQCs) when undertaking WQC development using the BLM.

The following data requirements reference the documentation for BLM model version 3.41.2.45.[17] Only versions of the BLM based on the toxicity database and models used in EPA's 2007 Cu criteria shall be used. EPA WQC tab provided in updated versions of the BLM, including version 3.41.2.45. As technical updates occur, newer versions of the BLM are expected to evolve and input requirements may vary. Data requirements to run the BLM will depend on the BLM version; referring to the associated User Guide will provide more information on the parameters associated with the model inputs.

### 5.1 Work Plan

All projects proposing to apply this methodology for the purpose of deriving SSC will provide DEC with a work plan that includes, at a minimum, the following elements:

a) Description of the proposed work and need for a BLM-derived WQC;
b) Description of the discharge facility and its effluent characteristics including effluent Cu levels, potential sources, and previous efforts to address source control (e.g., applicable technology-based effluent limits for Cu);
c) Brief description of historic water quality and flow data that may inform the project;
d) The route of discharge flow and design low flows for the receiving water;
e) The description of the site where the BLM-WQC would be applied;
f) The proposed sampling location(s);
g) Temporal representativeness given water quality conditions and site characterization: sampling data collection protocols that cover daily variability and seasonality;
h) Spatial representativeness given spatial water quality conditions and site characterization: spatial data collection protocol and distribution.
i) Description of other details for the proposed work, such as flow measurement, number of proposed sampling events, list of proposed sampling parameters, and QA/QC protocols; and
j) Summary of consultation with Alaska Department of Environmental Conservation in order to assure the proposed work will address site specific facility and receiving water concerns.

[17] Version available as of 09/13/2022. https://www.windwardenv.com/biotic-ligand-model/

DEC will require a more detailed quality assurance and protection plan (QAPP) and sampling and analysis plan (SAP) in addition to the Work Plan. The QAPP should clearly describe the BLM and how data will be collected to inform the model and its IWQC outputs, demonstrate how concerns for pH cycling and DOC data quality will be addressed, describe how monitoring will target the most bioavailable conditions for Cu, and methods for the collection and analysis of water quality samples. For additional information about the quality assurance/quality control process, see section 7.

## 5.2 General Chemistry Data Requirements

The BLM requires 12 different water quality parameter inputs, shown in Table 1 (sulfide and humic acid percentage typically use default values as these are not generally sampled). Although Cu concentrations do not influence the IWQC, they should be supplied to the model to allow calculation of exceedances. Furthermore, if FMB calculations will be considered, then the collection of ambient Cu data is required . Though measured input parameters are preferred, default inputs may be used in certain circumstances. Refer to section 6.0 of this document for further guidance on missing parameters. All model inputs, whether measured, default or estimated, should be accounted for in a QAPP and subsequent SAP.

Measurements of pH and temperature must be done in situ to avoid extended holding times or other potential bias. For example, sample temperatures measured on receipt at laboratories can be checked for sufficient chilling by ice used for preservation during transit but should not be used in the BLM.

| **Table 1: BLM Input Parameters** | |
|---|---|
| **pH** | **Sodium (Na)** |
| **Dissolved Organic Carbon (DOC)** | **Potassium (K)** |
| **Calcium (Ca)** | **Sulfate (SO4)** |
| **Magnesium (Mg)** | **Chloride (Cl)** |
| **Alkalinity** | **Sulfide (S)** |
| **Temperature** | **Humic Acid (%)** |
| | |

* Ambient copper data is required for the FMB method to be considered.

## 5.3 Representativeness of Water Quality Data

A "sample" refers to the collection and analysis of a complete set of the BLM input parameters as shown in Table 1. The collection, transport, handling, and storage of samples will be identified in the QAPP. All sampling events should collect sufficient volumes of water/effluent so that some can be stored for additional testing or analysis if unusual results occur. Samples should be stored at 0 to 4°C in the dark with no air space in the sample container. Sampling of effluent should capture all effluent parameters that are required to be reported in APDES/State Permit Discharge Monitoring Reports to provide information on the representativeness of the sample(s).

### 5.3.1 Spatial Representation

The applicant should be prepared to demonstrate the physical and chemical characteristics within the Site where the BLM is expected to apply to ensure the derived criteria are protective of the designated uses within the area of application. Depending on the complexity of the project, multiple sample locations may be necessary. The project proponent must provide information pertaining to the influences of groundwater, riparian condition, braided riverine systems, geologic features and/or anthropogenic influences that may affect data collection. Application to multiple reaches of a waterbody is subject to further discussion with DEC to determine whether additional or an expansion of site-specific criteria per 18 AAC 70.235 is required.

To ensure projects capture the range of water quality present in the physical vicinity of the discharge, sample collection must occur at a minimum of three locations; upstream of the point of discharge yet close enough to be representative of water quality anticipated to occur absent the influence of effluent discharge, end-of-pipe, and downstream of the zone of rapid mixing and complete mixing is to occur as demonstrated through modelling software such as CORMIX and sampling data. DEC will also consider the results of a composite of upstream and effluent that corresponds to the dilution provided by the 7Q10 flow should it be determined that sample collection at the "downstream" location is compromised by geophysical and hydrodynamic conditions (that can impact access, safety of collection). DEC may require sample collection at additional locations depending on the geophysical and hydrodynamic complexity of the waterbody in relation to the point of discharge.

### 5.3.2 Temporal Representation

Data used in development of BLM IWQC must be representative of a the full range of temporal conditions expected to occur at the Site. In general, DEC requires a minimum of 20 monthly samples be collected over the course of two years to characterize water quality conditions (e.g., including the most toxic and bioavailable condition) that are likely to occur. Monthly sample collection coupled with some hourly sampling to represent the most bioavailable times of the day will assist with identifying the temporal (e.g., diurnal and seasonal) representation of the Site.

The sample design will be defined in the Workplan and associated project documentation. Additional sampling may be required should regular sampling fail to capture seasonal environmental events (e.g., spring ice breakup, wet weather conditions) but should not target rainfall/runoff conditions. If weather conditions prevent the collection of samples (e.g., flooding, ice cover), supplemental sampling may occur during open water months but oversampling or a lack of winter data could result in statistical anomalies and/or concerns about the data being representative of "critical" conditions.

Effluent samples must be taken under the following conditions:

- Normal operating conditions (not influenced by sudden loading change(s), and when
- Biochemical oxygen demand (BOD) and/or other measures of organic loading (e.g., carbonaceous biochemical oxygen demand or CBOD, chemical oxygen demand or COD) and suspended solids concentrations are within permit limits or benchmarks.
- pH is within the allowable range in applicable water quality standards, permit limits, and/or benchmarks.

If the receiving water is expected to experience significant temporal variations to both temperature and pH within the course of a day, these variations should be considered during the development of a sampling plan. Temperature and pH are important input parameters and significant variations may affect the representativeness of the IWQC dataset.

Any anticipated sampling complications should be identified in the project QAPP.

### 5.3.3 Hydrologic Representation

Sampling will occur over the range of flow conditions that are likely to occur over the course of a season.[18] All sampling events must characterize stream flow and meteorological information pertinent to that time period. Sampling is not to occur during or immediately after rainfall events (i.e., 24 hours) to ensure samples are not representative of episodic events, unless these are the hydrologic conditions specific to the permit conditions (*i.e.,* stormwater permittee).A rainfall event is defined as one that significantly (e.g., 5% above the preceding 30-day average flow) increases receiving water stream flow.

Flow data may be required to demonstrate complete mixing below the effluent discharge location/regulatory mixing zone. This information will be used to demonstrate downstream protection calculation.

The number of sampling locations will depend on the stream's hydrologic features and point sources that have the potential to change the water quality. If flow data are unavailable, flow conditions may be determined using data from similar watersheds within the region.

### 5.3.4 Identification of Critical Conditions

The application of the BLM requires the user to identify the *critical* condition of the Site. The critical condition is defined, for the purposes of this document, as the period when Cu is most bioavailable. It is the project proponent's responsibility to adequately characterize the Site and demonstrate that the range of spatial, temporal and hydrologic conditions have been adequately identified and sampled, and that the resulting BLM IWQC are determined to be protective of the designated use at critical conditions. Project proponents may need to hold additional sampling events to ensure the dataset is representative of the entire range of conditions present at the Site.

## 6.0 General Treatment of Missing Parameters

If site-specific data for a BLM input parameter is not available, substitution of an estimated input parameter value or default value may be considered. DEC strongly recommends that efforts be expended to collect measured values rather than substituting BLM-values via the following approach(es).

At the time this guidance document was drafted, there are two estimation methods (EPA, 2016; State of Oregon, 2016) which DEC draws upon; however, DEC recognizes that the BLM has been updated with ability to generate default criteria for pH, DOC, and hardness. The following represents DEC's current guidance on the treatment of missing parameters. It is important to consider that if missing parameters are estimated using conservative values, the BLM is more likely to result in a more conservative IWQC than using measured data.

[18] Season describes a defined period of time. Sampling seasons will differ and need to be identified (i.e. Southeast Alaska will vary to that of Central Alaska due to temperature variations). The timing of sampling events should be discussed with WQS staff during the development of a Quality Assurance Project Plan.

1) **Dissolved Organic Carbon (DOC),** DOC values may not be estimated. Since total organic carbon (TOC) data are collected more frequently than DOC, DEC may accept measured TOC data multiplied by a site-specific adjustment factor to estimate dissolved organic carbon (DOC) value. This is not DEC's preferred approach but in instances where insufficient data exist or is not available for a site, this procedure may be considered. TOC values are not recommended in place of DOC for water from estuaries, wetlands, or higher order streams unless data are included that indicate such data is a reliable indicator of actual DOC values. For technical assistance, please refer to Appendix C-2. *Dissolved, Particulate, and Estimated Total Organic Carbon for Streams and Lakes by State* (as presented in EPA Document #822-B-98-005).

2) **pH,** If concurrent pH data are missing from the sample dataset, a representative pH value may be derived using a monthly mean pHfrom proximate samples collected within the most recent ten year period should it be determined that little variability (e.g., <10%) of pH over the same time period is present. Case-by-case consideration may be given to using pH data from monitoring locations where conditions (such as type of water body, stream flow and geology) are similar to the site. DEC strongly encourages the collection of all pH data in situ as pH values can change between collection time and laboratory analysis.

3) **Cu,** The BLM does not require Cu as input data to derive IWQCs, but the collection of Cu data will inform the decision-making process and potential concerns regarding the protection of downstream designated uses. If the project proponent intends to use the FMB application of the BLM, Cu data must be collected because instream Cu concentrations are needed to calculate TU values.. For additional information see Sections 3.1.2 and 9.0.

4) **Temperature,** If concurrent water temperature data are missing from the sample dataset, DEC may consider use of a monthly mean temperature based on the most recent ten years of climate data available for the site or proximate monitoring locations where conditions (such as type of water body and stream flow) are similar to the site. DEC strongly encourages the collection of all temperature data in situ.

5) **Humic Acid,** If sufficient data on the percentage of humic acid as a proportion of DOC is available for a site, DEC expects measured values to be used for BLM inputs. However, if this data is not available DEC will accept the default value of 10% used in its place for BLM inputs.

6) **Alkalinity, Calcium, Chloride, Magnesium, Potassium, Sodium and Sulfate,** If data for any of these BLM input parameters are missing from a particular dataset, the value may be calculated based on:

    (i) the relationship of the ion or alkalinity to specific conductance measurements for that data set using a regression analysis equations in Table 2,[19] or
    (ii) the geometric mean of all measured data for the area of concern.

[19] DEC anticipates the collection of sufficient specific conductance and alkalinity and ion data to statistically validate the expected relationships for the specific site. Specific conductance measurements must be concurrent with the other BLM input parameters dataset. DEC expects that if the relationship is validated, interested parties will monitor specific conductance rather than all the ions.

| Table 2 | |
|---|---|
| **Parameter** | **Regression Equation** |
| Alkalinity | Alk. = exp(0.88·[ln(SpC)] – 0.41) |
| Calcium | Ca = exp(0.96·[ln(SpC)] – 2.29) |
| Chloride | Cl = exp(1.15·[ln(SpC)] – 3.82) |
| Magnesium | Mg = exp(0.91·[ln(SpC)] – 3.09) |
| Potassium | K = exp(0.84·[ln(SpC)] – 3.74) |
| Sodium | Na = exp(0.86·[ln(SpC)] – 2.22) |
| Sulfate | $SO_4$ = exp(1.45·[ln(SpC)] – 5.59 |

Where, "SpC" is a measurement of specific conductance in µmhos/cm, "ln" is the natural logarithm, and "exp" is a mathematical constant that is the base of the natural logarithm.

### 6.1 Total versus Dissolved BLM Parameters

Dissolved concentrations of BLM input parameters are required to run the BLM. If the dissolved measurements are not available, they can be estimated by multiplying the total recoverable concentrations by a site-specific (e.g. waterbody) translator[20] developed using available data and DEC approval.

## 7.0 QA/QC[21]

Quality assurance and quality control (QA/QC) will be documented throughout the sampling and reporting process using the following measures:

1. All water quality analysis will be conducted by a DEC-certified laboratory. Documentation pertaining to laboratory certification requirements will be provided in the QAPP.
2. All analysis will be completed using U.S. EPA-approved methods and guidelines in the EPA's *Standard Methods for the Examination of Water and Wastewater* and *Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act* at 40 CFR 136. The appropriate method(s) of analysis will be determined by the laboratory, project proponent, and DEC prior to project commencement.
3. 10% field sample replicates (i.e., duplicates) will be collected and analyzed as an indicator of sample representativeness and variability of conditions in the stream. Replicate events should be randomly selected prior to initial sample collection.
4. Water samples provided for laboratory analysis will be subject to method-specific quality assurance and quality control as referenced in the project QAPP. The collection of field blanks and equipment blanks will be identified in QAPP and reflect project-specific QA/QC. Replicate samples for each analyte should be randomly selected prior to initial sample collection.
5. For field measurements, precision is assessed by measuring replicate (paired) samples at the same locations and as soon as possible to limit temporal variance in sample results. Overall project precision is measured by collecting blind (to the laboratory) field replicate samples.

[20] EPA's translation guidance and the conversion factors table and relevant information is available at https://www.epa.gov/system/files/documents/2021-07/metals_translator.pdf

[21] DEC has taken the liberty of adapting text from the Iowa Department of Natural Resources *Implementation Procedures for the Site-Specific Application of Copper Biotic Ligand Model* (2017) in this and subsequent sections.

Laboratory precision is determined similarly via analysis of laboratory duplicate samples. For paired and small data sets, project precision is calculated using the following formula:

$$RPD = 100 \times \frac{(A - B)}{\left(\frac{A + B}{2}\right)}$$

Where: RPD= Relative Percent Deviation
A=primary sample
B=replicate field sample or laboratory duplicate sample

All replicate samples will meet a <20% RPD or will be re-collected (field) or re-run (laboratory).

6. Bias (Accuracy) is a measure of confidence that describes how close a measurement is to its "true" value. Methods to determine and assess accuracy of field and laboratory measurements include, instrument calibrations, various types of QC checks (e.g., sample split measurements, sample spike recoveries, matrix spike duplicates, continuing calibration verification checks, internal standards, sample blank measurements (field and lab blanks), external standards), performance audit samples (DMRQA, blind Water Supply or Water Pollution PE samples from American Association for Laboratory Accreditation (A2LA) certified, etc. Bias/ Accuracy is usually assessed using the following formula:

$$Accuracy = \frac{Measured\ Value}{True\ Value} \text{ X } 100$$

7. Completeness is a measure of the percentage of valid samples collected and analyzed to yield sufficient information to make informed decisions with statistical confidence. As with representativeness, data completeness is determined during project development and specified in the QAPP. Project completeness is determined for each pollutant parameter using the following formula:

$$Completeness = \frac{T - (I + NC)}{T} \times (100\%)$$

Where: T= Total number of expected sample measurements.
I= Number of invalid sample results (samples that did not meet quality control measures for temperature, hold times, etc), etc)
NC= Number of sample measurements not completed (e.g., spilled sample, etc.)

An overall completeness goal has been set at 80% for each analytical parameter and field measurement type. If the completeness goal is not met, re-sampling and/or re-analyzing may be conducted. The completeness goals will be stated in the QAPP. Any less than should be justified in the QAPP with approval. A minimum of 20 samples must be collected and analyzed for two years, approximately one from each month with a DEC completeness goal of 80%. DEC will ultimately determine if the dataset is considered to be representative of the range of IWQCs potentially present at the site including during conditions when copper is most bioavailable.

8. Field sampling and Laboratories must report all sample analyses using the units listed in the table below for each analyte.

**Table 3: Field/Lab Reporting Requirements**[22]

| Analyte | Units | Annual Proficiency Test required | Significant figures | Lower bound | Upper bound |
|---|---|---|---|---|---|
| Temperature | °C | No (field sampled) | One digit after decimal | Equipment dependent | 25.0 |
| pH | s.u. | No (field sampled) | One digit after decimal | 4.9 | 9.2 |
| Dissolved Organic Carbon | mg C/L | Yes | Two digits after decimal | 0.05 | 29.65 |
| Calcium | mg/L | Yes | Two digits after decimal | 0.20 | 120.24 |
| Magnesium | mg/L | Yes | Two digits after decimal | 0.02 | 51.90 |
| Sodium | mg/L | Yes | Two digits after decimal | 0.16 | 236.90 |
| Potassium | mg/L | Yes | Two digits after decimal | 0.04 | 156.00 |
| Sulfate | mg/L | Yes | Two digits after decimal | 0.10 | 278.40 |
| Chloride | mg/L | Yes | Two digits after decimal | 0.32 | 279.72 |
| Alkalinity | mg CaCO3/L | Yes | Two digits after decimal | 1.99 | 360.00 |
| Cu (not required for IWQC, but is required for generating a FMB, and generally recommended by DEC) | | | One digit after decimal | --- | --- |

9. All chemical constituents should be filtered and measured as dissolved concentrations. Field filtration will be conducted according to parameter-specific method.
10. 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.

## 8.0 Final Reporting Requirements

A final report summarizing the project and its results will be submitted to DEC for approval. Reports will include the following:

1. All information identified in the Work Plan and any situations where deviations were required.

[22] The BLM is currently configured to utilize default values for humic acid and sulfide. This is why these two parameters are not included in this table. The sulfide module is not currently used in the calculation of IWQC for copper, so the model assigns a default value of 1x10-6 mg/L. The humic acid percentage of the DOC is typically set to a default value of 10% because these data are not commonly available. Users may enter measured values where data is available.

2. Documentation pertaining to adherence to DEC-approved QAPPs.
3. Results of all chemical and physical measurements on actual water samples including the relevant input parameters for the BLM, and/or concentrations of total recoverable or dissolved Cu, TSS, etc.
4. Description of BLM IWQC results, identification of outliers and similar statistical anomalies, and uncertainties associated with the data collection and analysis process.
5. Sample information will include the following:
    a. Date and time of each sampling of the Site water;
    b. Sampling location characteristics
    c. Effluent flow during each sampling event;
    d. Upstream flow during each sampling event, either measured directly or estimated from relevant neighboring gauges;
    e. Prior meteorological conditions affecting flow and sampled water quality;
    f. Sample collection methodology, measurements of all chemical concentrations, and testing methods;
6. Summary of all sampling data in an Excel spreadsheet or other format that is compatible with the BLM model.
7. Upstream and downstream sampling data will be provided to the department in a Water Quality Exchange template (provided by the department).

## 9.0 Criteria Derivation

The BLM-derived WQC must protect the water body over the full range of ambient water chemistry conditions, including during critical conditions when copper is most bioavailable and toxic. Two different methods will be used by DEC to derive single-value Cu criteria (both acute and chronic) for a Site based on a representative set of IWQCs:

(1) For those proposals that do not collect Cu concentration data, DEC will apply the lowest 10th percentile of the IWQC distribution to calculate acute and chronic Cu criteria protective of aquatic life, unless a lower percentile is needed to protect the Site when copper is most bioavailable and toxic (e.g., consideration of threatened or endangered species; unexplained variability in IWQCs).

(2) For those proposals that collect Cu concentration data, DEC will consider application of the fixed monitoring benchmark (FMB) value derived from the range of calculated IWQCs to calculate acute and chronic Cu criteria protective of aquatic life when copper is most bioavailable and toxic. The determination whether to use the FMB will take into consideration:
    - Distribution of BLM-input data (normal or lognormal transformed)
    - The presence of temporal Variability of BLM inputs and Cu concentrations

If it is demonstrated that significant spatial differences in instantaneous BLM-derived criteria for a Site are present, data collected from different sampling locations may need to be evaluated independently. The criteria selected must be protective of designated uses within the entire Site.

If a waterbody exhibits significant (e.g., >20% variance) seasonal variations in the BLM input parameters and BLM-derived IWQCs, seasonal criteria may be considered.

## 10.0 Implementation of BLM criteria in APDES/State Permitting process.

Should DEC determine that the project applicant has sufficiently met the conditions outlined in this document, DEC may approve use of the BLM-derived WQC for the purposes of deriving a WQBEL for Cu in APDES and/or state permits. All documentation identified in Section 8.0 of this document will be incorporated into to the permit Fact Sheet and available for consideration per state and federal public notification requirements. In addition, the following conditions will be considered:

- Where BLM-derived WQC are significantly affected by the effluent water chemistry of point source discharges (e.g., effluent dominated streams), this correlation will be considered when establishing the appropriate wasteload allocations under critical design conditions.[23]
- 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 Cu criteria under critical design conditions.
- The implementation of the Cu BLM criteria will also be consistent with all relevant state regulations and department policies and procedures including antidegradation and anti-backsliding regulations.

Effluent monitoring should be consistent with locations at which the BLM-derived IWQCs (e.g., at end-of-pipe, and/or downstream of discharge points and below any regulatory mixing zones[24], where fully mixed conditions are expected to occur). Permittees must continue to collect BLM-related data and update facility-specific records. This will allow DEC to evaluate whether the BLM-derived SSC are appropriately protective of designated uses during the state's triennial review process, and throughout the duration of the associated permit. DEC will re-evaluate WQBELs based on site-specific BLM results at least every five years.



[23] Technical Guidance Manual for Performing Wasteload Allocations, Book VI: Design Conditions Chapter 1: Stream Design Flow for Steady-State Modeling
[24] Additional information regarding regulatory mixing zones may be found at 18 AAC 70.240.

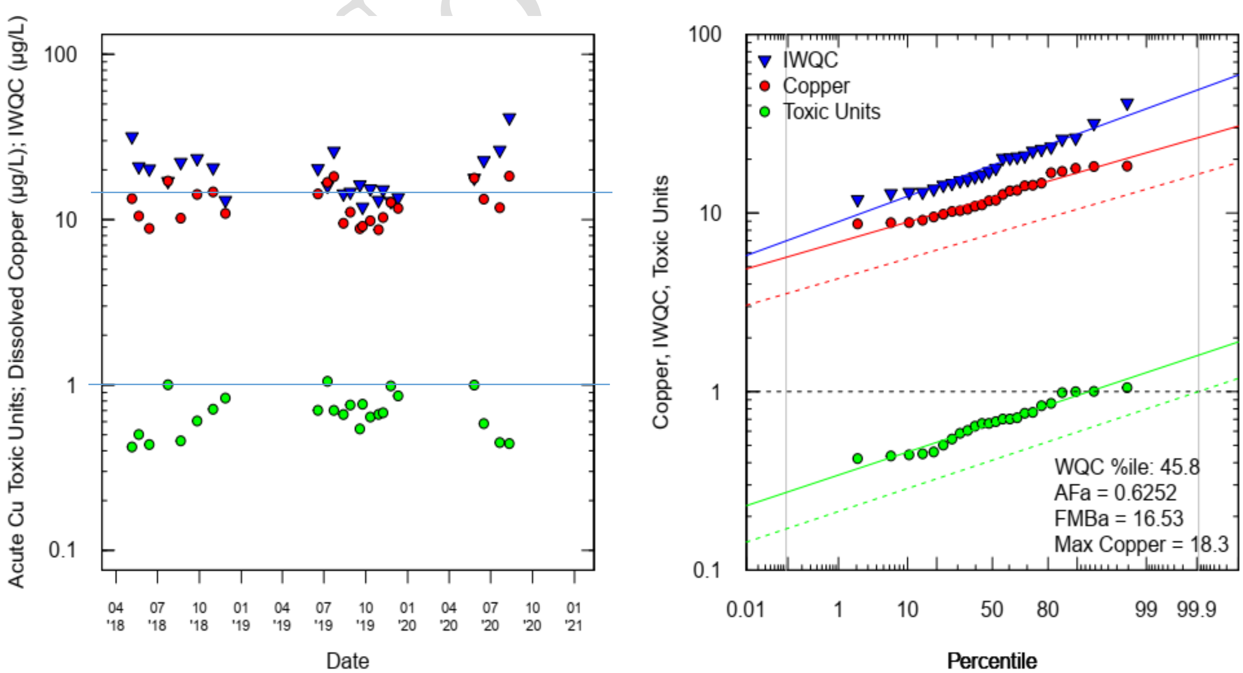
# Appendix A: Illustrative Case Studies of the FMB calculation

This section walks through several examples of calculating the FMB with real site data to develop site-specific water quality criteria. These graphs illustrate the distributions used in the FMB calculations described in Section 3.1.2 and the processes used to obtain the FMB. These calculations are done automatically with each BLM run, and calculating the FMB will not require manual calculation or use of these graphs in the vast majority of situations (the exception being if the monitoring data cannot be run in a single input file – which would mean more than 1000 observations with current software limitations). Nevertheless, these case studies are a good illustration of the process so that it may be understood better.

An illustrative case study that can be used to show how the FMB considers time-variable information is shown in Figure 3. Twenty-five samples were analyzed for the chemical input data and Cu to run the BLM and calculate IWQC values.  The toxic units for each sample were also calculated as the ratio of Cu to IWQC.  As can be seen in Figure 3 (left panel), although the average Cu concentration is lower than the average IWQC, both IWQC and Cu concentrations are time variable and there are four samples where Cu equals or exceeds the IWQC (i.e., the toxic unit is greater than or equal to 1).  The same data are shown in the right-hand panel as a probability plot, where the x-axis is defined as the inverse of the cumulative normal distribution.  The use of this axis allows a direct reading of the probability associated with any value in the plotted data.  For example, the toxic units show values of 1 or less in approximately 80% of the dataset, and this is far more frequent than the target of once in three years.



**Figure 3.** An example dataset for FMB calculations showing acute IWQC, Cu concentrations, and toxic units as either a time-series (left) or probability plot (right).



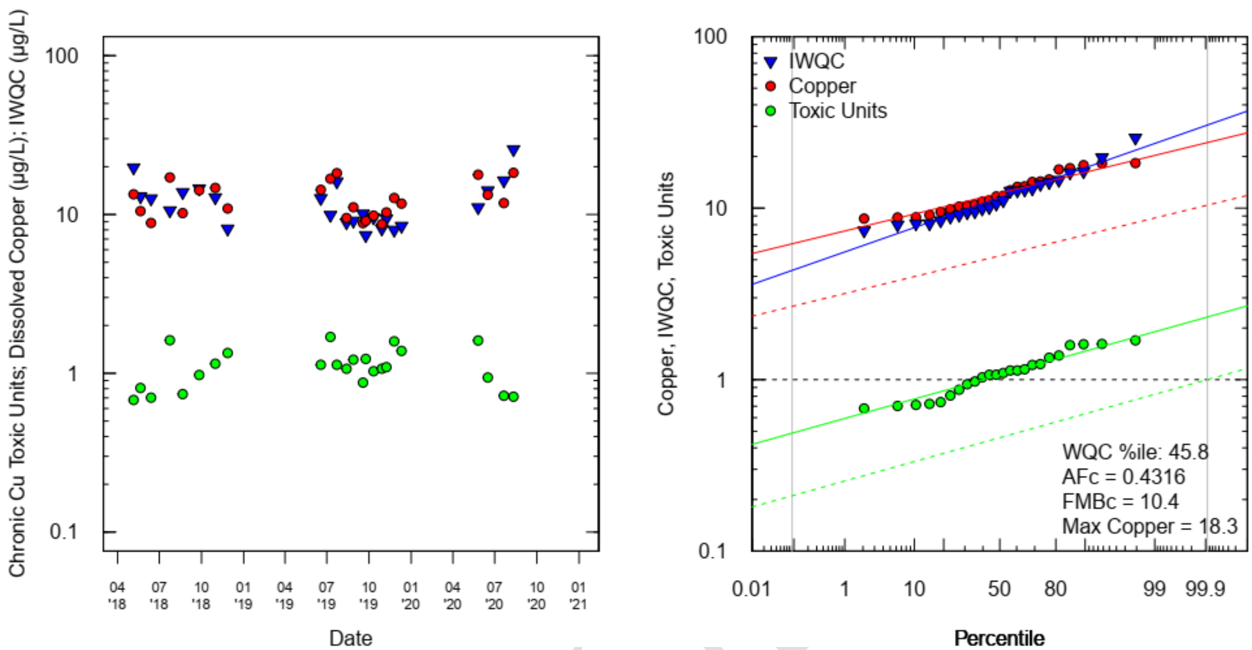
The probability axis also facilitates a display of the properties of the underlying distributions. The log-normal distributions based on the means and standard deviations of IWQC, Cu, and toxic units are shown as solid blue, red, and green lines respectively. The standard deviation determines the slope of these lines, and the mean determines the vertical placement.

A dataset that meets the once in three years exceedance frequency should have toxic units less than 1 for 1094 out of 1095 days (1095 days is three years), or 99.9% of the time. This value is indicated by a vertical gray line at the 99.9-percentile. Since the exceedance frequency of this dataset is greater than once in three years the solid green line corresponding to the toxic unit distribution crosses a value of 1 near 80%, which means that the site exceeds the IWQC more frequently than the once in three years target. It is straightforward to calculate how much the Cu concentrations would need to be reduced in order to exactly meet the target exceedance frequency for the acute IWQCs, and for these data that would require a reduction such that the new Cu concentrations were 62.5% of their current values on average. The Cu and toxic unit distributions of a dataset that would be in compliance with the IWQC are shown with dashed red and green lines respectively. The acute FMB is defined as the Cu concentration from this adjusted distribution that would occur at the 99.9-percentile, or 16.53 μg/L. If Cu concentrations at this site could be reduced so that they did not exceed the acute FMB of 16.53 μg/L, then they would also not exceed the time-variable IWQC more frequently than once in three years. The acute FMB, therefore, could be used to develop an effluent permit that would bring this site into compliance but without needing to consider the time-variability of the IWQC values.

The acute FMB for this site also happens to correspond to the 45.8-percentile of the IWQC values. As demonstrated by Ryan et al. (2018) the FMB can correspond to very low percentiles of the IWQC distribution for some datasets, and high percentiles for others. A single percentile, therefore, risks being either over- or under-protective.

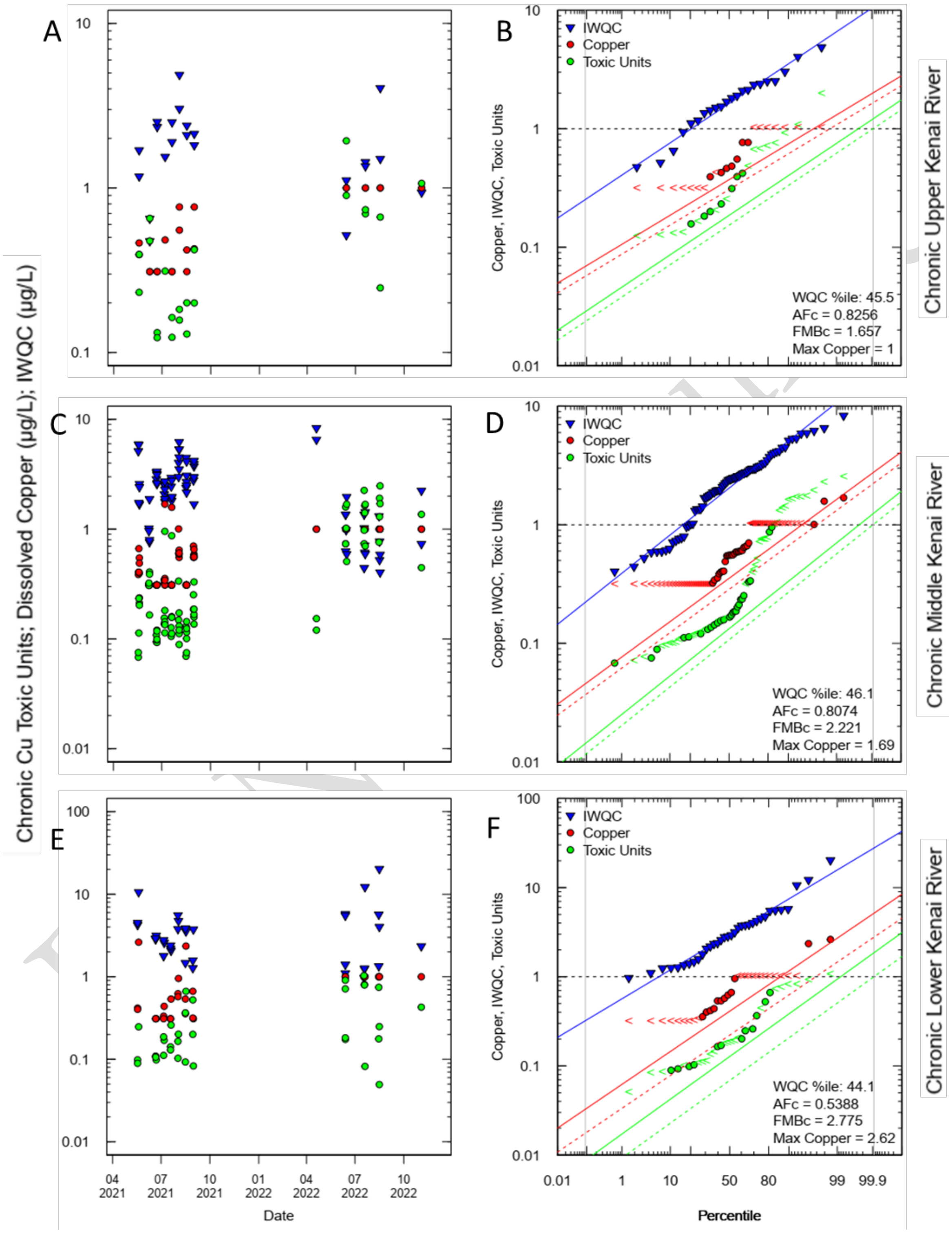
A similar analysis can be conducted with chronic IWQCs as shown in Figure 4. Since the chronic IWQCs should be compared with a four-day average, the Cu distribution based on grab samples is adjusted to consider the four-day averaging (Ryan et al., 2018, supplemental). The layout of the figure for chronic FMBs in Figure 4 is the same as Figure 3, with time series for IWQC, Cu, and toxic units shown in the left panel, and probability plots for the same constituents on the right. Since this site is not in compliance with acute IWQCs, it is not surprising that it is even further out of compliance with chronic IWQCs. The Cu concentrations are less than the IWQCs only about 30% of the time. To meet the target exceedance frequency for the chronic IWQCs, the Cu concentrations would need to be reduced to 43% of their current values on average. Compliance with the chronic IWQCs could be achieved if the four-day average concentrations were no more than the chronic FMB of 10.4 μg/L.

**Figure 4.** An example dataset for FMB calculations showing chronic IWQC, Cu concentrations, and toxic units as either a time-series (left) or probability plot (right).




The case study illustrated in Figures 3 and 4 show the application of the acute and chronic FMBs to a dataset where the detection method for Cu was low enough to quantify the Cu concentrations in all samples. When Cu concentrations are low, it is not uncommon to have some values that are below the analytical detection limit. The FMB procedure built into the BLM can consider values that are below detection. In these cases the distribution is calculated using maximum-likelihood estimation (MLE) (EPA, 2012; Ryan et al, 2018). Another case study showing how the FMB can be applied to datasets that include values below detection is shown for the upper, middle, and lower sections of the Kenai river in Figure 5. Cu concentrations in these samples are frequently below the detection limit. These values are plotted at the detection limit with "<" symbols. Since the toxic unit is the ratio of Cu to the IWQC, when the Cu is below detection (i.e., the true concentration is less than the value shown) then the same is true for the toxic unit value., and the corresponding toxic units are also plotted using "<" symbols. The underlying distributions are calculated using MLE. The high proportion of data that are below detection highlight the importance of using analytical methods with low detection limits. Nevertheless, the FMB procedure can still be used when a portion of the available data are below detection. The Kenai example also shows interesting spatial patterns. The chronic FMBs increase from the upper (1.66 µg/L) to middle (2.22 µg/L) to lower (2.78 µg/L) reaches of the Kenai. But Cu concentrations also increase, so that of the three reaches the lower reach is furthest out of compliance. These examples show how the BLM and FMB can be used to understand temporal and spatial patterns in Cu bioavailability, and compliance with the site-specific criteria.

**Figure 5.** Chronic FMB calculations for the Upper, Middle, and Lower Kenai River. Values below detection limits are plotted as “<” symbols at the detection limit.



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