Implementation Guidance for the Idaho Copper Criteria for Aquatic Life

Using the Biotic Ligand Model

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Abbreviations, Acronyms, and Symbols

AU	assessment unit
BLM	biotic ligand model
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DEQ	Idaho Department of Environmental Quality
DOC	dissolved organic carbon
EPA	US Environmental Protection Agency
FMB	Fixed Monitoring Benchmark
IR	integrated report
IWQC	instantaneous water quality criteria
µg/L	micrograms per liter
mg/L	milligrams per liter
NPDES	National Pollutant Discharge Elimination System
RPA	reasonable potential analysis
RPTE	reasonable potential to exceed
TU	toxic unit
USGS	US Geological Survey

1 Introduction

The toxicity of metals to aquatic life is highly variable and depends on physical and chemical factors within a water body. Hardness has long been acknowledged as one such factor and is reflected in the Idaho Department of Environmental Quality's (DEQ's) current hardness-dependent criteria, whereby the acute and chronic criteria are determined based on the total hardness of the receiving water body.

Hardness-dependent copper criteria do not take into account the effects of other physicochemical properties that affect toxicity, leading to hardness-dependent copper criteria being either overprotective or under protective of aquatic life. The biotic ligand model (BLM) based criteria outlined in the US Environmental Protection Agency's (EPA's) revised national recommended freshwater aquatic life criterion for copper takes into consideration copper toxicity influenced by a wide variety of water characteristics. Therefore, DEQ has updated the copper criteria for aquatic life to the EPA-recommended 304(a) criteria (EPA 2007a).

This action was identified in both the National Marine Fisheries Service and US Fish and Wildlife Service's biological opinions on EPA's action on Idaho's criteria for toxic substances to support aquatic life (NMFS 2014; FWS 2015). These biological opinions concluded that the hardness-dependent copper criteria (as well as other toxics criteria) were under protective of aquatic life support and would jeopardize the continued existence of species listed under the Endangered Species Act and adversely modify their designated critical habitat. The reasonable and prudent alternative from these opinions directed EPA to ensure new acute and chronic criteria that are no less stringent than EPA's 2007 copper criteria are effective for Clean Water Act purposes. EPA's 2007 copper criteria uses the BLM to predict water body-specific criteria by taking into account other physicochemical properties of the water (e.g., pH, dissolved organic carbon).

This guidance provides background on copper toxicity and the BLM and will detail how DEQ will implement the copper criteria for aquatic life. It discusses data requirements, spatial and temporal representation, options for reconciling multiple time-variable criteria from a single location, and procedures for estimating criteria when data are limited. It also outlines how to derive criteria for permitting and assessment purposes.

1.1 Purpose

The purpose of this document is to provide guidance to DEQ staff, the regulated community, and the general public (hereafter referred to as users) for calculating the copper criteria for aquatic life using the BLM.

This guidance addresses the following issues associated with implementation of the BLM:

- Using site-specific water chemistry data to derive BLM copper criteria
- Accounting for spatial and temporal variability when using the BLM
- Choosing methods for estimating or deriving protective copper criteria when BLM input data are not available

- Reconciling multiple instantaneous water quality criteria (IWQCs) to derive water quality criteria for developing water quality-based effluent limits or identifying impairments for the integrated report

This guidance was developed in coordination with the Idaho Pollutant Discharge Elimination System Program and is limited to developing copper criteria; it does not detail procedures for development of National Pollutant Discharge Elimination System (NPDES) permits or general policies and procedures for Clean Water Act assessments. For more information on development of permit limits, please see DEQ's most recent version of *Effluent Limit Development Guidance* (DEQ 2017a). For more information on listing and assessment methodologies, please see DEQ's most recent version of *Water Body Assessment Guidance* (DEQ 2016).

1.2 Sources of Copper in the Environment

Copper is a natural element that occurs in the earth's crust at low levels. Natural processes, such as air deposition and erosion of parent material containing copper, contribute to the presence of copper in surface waters. In addition, human activities (e.g., mining operations, agriculture) may lead to increased erosion or sediment transport, which could result in higher copper concentrations than would occur from natural weathering alone (ATSDR 2004).

Other anthropogenic activities can lead to elevated levels of copper in the aquatic environment. Anthropogenic sources of copper in surface waters include domestic wastewater, urban stormwater runoff, active milling and mining, abandoned mine runoff, electroplating operations, corrosion of copper in plumbing and construction materials, effluents from power plants that use copper alloys in the heat exchangers of their cooling systems, leachate from municipal landfills, and direct addition of copper sulfate to surface waters as an algaecide (ATSDR 2004).

1.3 Effects of Copper on Aquatic Life

Copper is an essential micronutrient for plants, animals, and humans. However, at concentrations above the recommended levels, copper can become acutely toxic, especially to aquatic organisms (Scannell 2009; Eisler 1998).

Chronic effects of copper 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, migration, changes in metabolism and organ or cellular damage, and changes in olfactory responses in freshwater fish species (Eisler 1998; Sommer et al. 2016).

1.3.1 Effects of Physical and Chemical Properties on the Toxicity of Copper

Copper toxicity in aquatic environments depends on the ability of copper to bind to a biological receptor or cell surface of an organism (e.g., the gill surface of a fish). This receptor is known as a biotic ligand and is the location where interactions with metals occur. Copper that is free to bind to the receptor is considered bioavailable copper. Bioavailability of copper in freshwater is related to the following:

- Chemical species or forms of copper (such as Cu^{2+})

- Complexation of copper with organic ligands[1]
- Complexation of copper with inorganic ligands

Several physicochemical properties can affect copper speciation and the availability of ligands for complexation with copper. The most important of these factors are the concentration of dissolved organic carbon (DOC), which complexes with copper, and pH, which controls copper speciation.

In addition, other cations compete with copper for binding at the biotic ligand. The most common major cations present in surface waters are calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and hydrogen (H^{+}). Therefore, to reliably estimate concentrations of copper available to exert toxicity at any given sampling location, it is necessary to account for these factors.

Figure 1 presents a conceptual framework for how these processes affect the ability for a free copper to bind to a biotic ligand such as the gill surface.

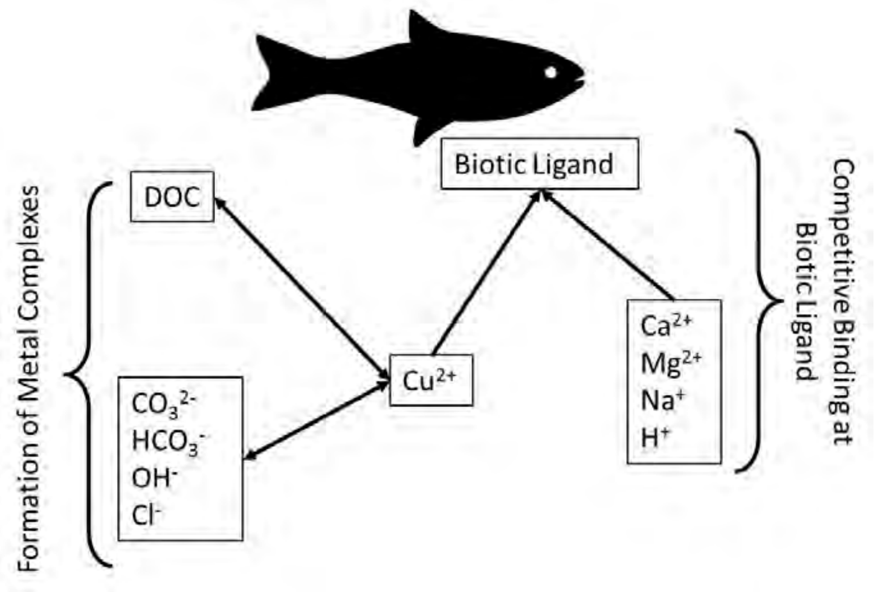

Figure 1. Conceptual model of how chemical speciation, metal complexation, and competition of other cations with copper for binding at biotic ligands affect metal bioavailability. Free metal ion (Me^{2+}) complexes with DOC and inorganic ligands. In addition, cations such as Ca^{2+} and Mg^{2+} compete with the remaining free metal to bind to the biotic ligand, limiting the effects of the metal on the organism (source: adapted from Windward 2015).

In general, copper is most bioavailable in waters with low DOC, low pH, and low hardness. As DOC, pH, and hardness increase, the bioavailability and thus toxicity of copper decreases.

1.4 Impaired Waters and TMDLs

DEQ relies heavily on biological monitoring to determine impairments; direct measures of the aquatic community are used to determine support of aquatic life uses (Jessup 2011; DEQ 2016).

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[1] A ligand is a complexing chemical (ion, molecule, or molecular group) that interacts with a metal like copper to form a larger complex (EPA 2007a).

Waters that have aquatic communities modified by human activities beyond the natural range of reference conditions are considered impaired and are subjected to additional monitoring and analysis to determine the cause or causes of impairment. Impairment listings are then refined to reflect the actual cause of the impairment. Waters may also be sampled for pollutants like copper, for example when associated with Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or when that type of assessment is needed for regulatory activities.

Currently, there are very few waters in Idaho where copper has been identified as impairing aquatic life. The 2014 Integrated Report (IR)—the most recent approved IR—identified 50 miles of stream and river where copper was impairing aquatic life (DEQ 2017b). This represents 0.05% of the 95,119 stream and river miles discussed in the 2014 IR. Figure 2 shows the scope and location of waters that have been identified as impaired for aquatic life by copper.

Of the 50 miles of impaired stream and rivers, 22 are covered under the approved *Lower Clark Fork River Subbasin Assessment and Total Maximum Daily Load* (DEQ 2007). According to that report, the source of copper impairment is mine wastes in the Clark Fork River watershed in Montana, including sources within the Milltown Reservoir/Clark Fork River Superfund Site. Thus, the Montana Department of Environmental Quality is responsible for reducing copper to meet the criteria at the Idaho border (DEQ 2017b).

Additionally, 15 miles of impaired streams and rivers are in areas that are impacted by the Blackbird Mine and are under active CERCLA remediation (DEQ 2017b).

A 6-mile reach of Prichard Creek, a tributary to the North Fork Coeur d'Alene River, is also impaired due to copper. The Prichard Creek watershed is located within the Coeur d'Alene Mining District. Similar to the adjacent Bunker Hill Mining and Metallurgical Superfund Site, the Prichard Creek watershed contains multiple historic mine and mill sites. Cleanup of priority historical sources (e.g., mill sites) has occurred in the watershed under CERCLA. Additional water quality improvement work, including ecological restoration under the Natural Resources Damage Assessment and Restoration Program, is being planned.

A 7-mile reach of Deep Creek, a tributary to the Snake River in Hells Canyon, is impaired due to copper attributed to historic mining activities in the area. Monitoring results show dissolved copper concentrations exceeding both the acute and chronic water quality criteria for aquatic life (DEQ 2017b).

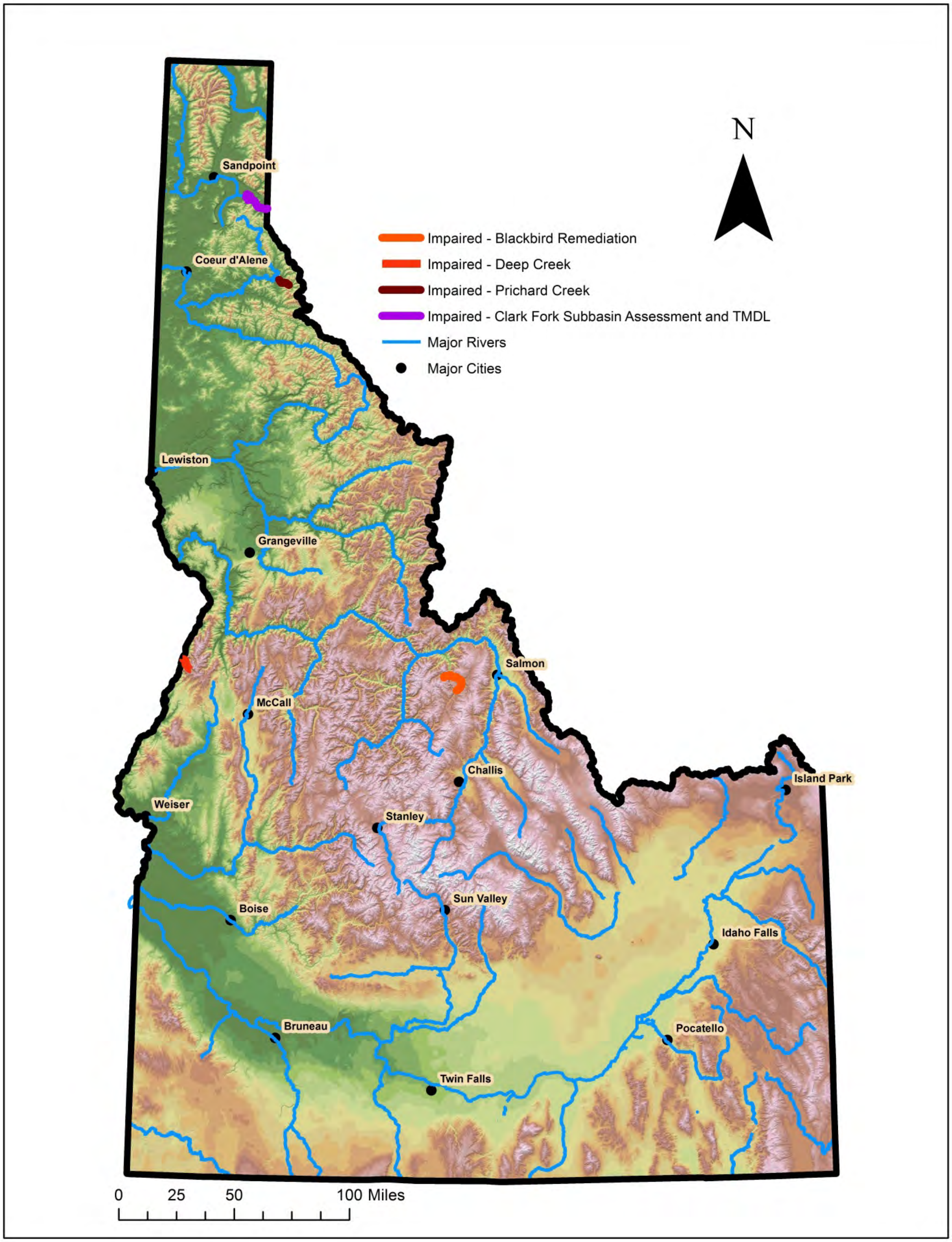


Figure 2. Map of Idaho showing the limited scope of waters where aquatic life is impaired by copper.

1.5 NPDES Permits in Idaho

There are presently relatively few point source dischargers in Idaho that have copper effluent limits. As of the date of this guidance, there are approximately 390 municipal, industrial, commercial, and aquaculture dischargers with NPDES permits in Idaho. Twenty of these dischargers have copper effluent limits: 8 mines, 10 municipal wastewater treatment plants, and 2 fish hatcheries (Figure 3).

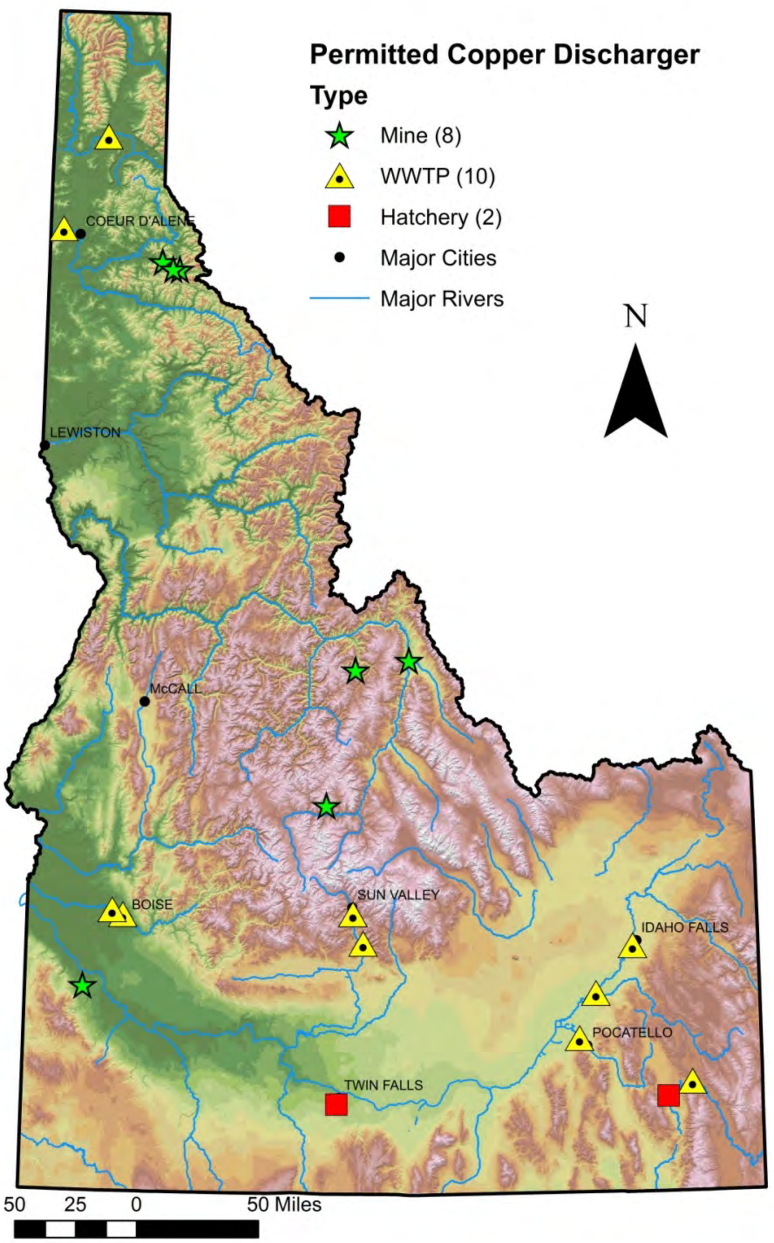
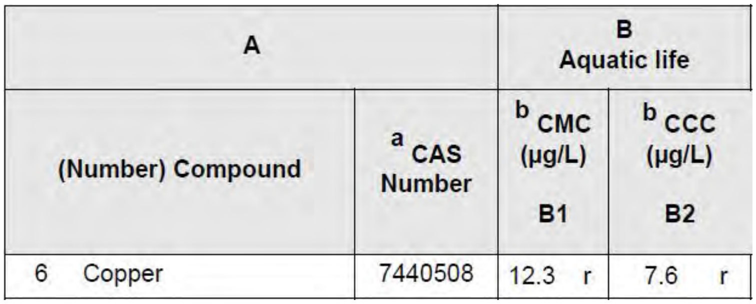


Figure 3. Map of Idaho showing the location and type of dischargers with copper effluent limits.

2 Idaho Aquatic Life Criteria for Copper

Idaho’s numeric copper criteria for aquatic life are found in IDAPA 58.01.02.210. Derivation of the Idaho aquatic life criteria for copper requires the use of the BLM version 3.1.2.37 (Windward 2015) to calculate acute and chronic copper criteria. An excerpt of the relevant IDAPA table and footnotes are presented in Figure 4.



A		B Aquatic life	
(Number) Compound	[a] CAS Number	[b] CMC (µg/L) B1	[b] CCC (µg/L) B2
6 Copper	7440508	12.3 r	7.6 r

Table Footnotes
r. Aquatic life criteria for copper shall be derived in accordance with Subsection 210.03 c.v. For comparative purposes only, the example values displayed in this table correspond to the Biotic Ligand Model output based on the following inputs: temperature = 14.9°C, pH = 8.16, dissolved organic carbon = 1.4 mg/L, humic acid fraction = 10%, Calcium = 44.6 mg/L, Magnesium = 11.0 mg/L, Sodium = 11.7 mg/L, Potassium = 2.12 mg/L, Sulfate = 46.2 mg/L, chloride = 12.7 mg/L, alkalinity = 123 mg/L $CaCO_3$, and Sulfide = $1.00e^{-8}$ mg/L. *Footnote r is not effective for CWA purposes until the date EPA issues written notification that the revisions adopted under Rule Docket No. 58-0102-1502 have been approved.*

Figure 4. Excerpt from Idaho water quality standards denoting relevant table and footnotes referencing the use of the BLM to derive copper criteria for aquatic life.

Additional rule language regarding applicability of the copper criteria for aquatic life is found in IDAPA 58.01.02.210.03.c and is as follows:

> v. Copper Criteria for Aquatic Life.
>
> (1) Aquatic life criteria for copper shall be derived using:
>
> > (a) Biotic Ligand Model (BLM) software that calculates criteria consistent with the “Aquatic Life Ambient Freshwater Quality Criteria – Copper”: EPA-822-R-07-001 (February 2007); or
> >
> > (b) An estimate derived from BLM outputs that is based on a scientifically sound method and protective of the designated aquatic life use.
>
> (2) To calculate copper criteria using the BLM, the following parameters from each site shall be used: temperature, pH, dissolved organic carbon (DOC), calcium, magnesium, sodium, potassium, sulfate, chloride, and alkalinity. The BLM inputs for humic acid (HA) as a proportion of DOC and sulfide shall be based on either measured values or the following default values: 10% HA as a proportion of DOC, 1.00 x 10^{-8} mg/L sulfide. Measured values shall supersede any estimate or default input.
>
> (3) BLM input measurements shall be planned to capture the most bioavailable conditions for copper.

> (4) A criterion derived using BLM software shall supersede any estimated criterion. Acceptable BLM software includes the "US EPA WQC Calculation" for copper in BLM Version 3.1.2.37 (October 2015), available at www.deq.idaho.gov/58-0102-1502.
>
> (5) Implementation Guidance for the Idaho Copper Criteria for Aquatic Life. The "Implementation Guidance for the Idaho Copper Criteria for Aquatic Life" describes in detail methods for implementing the aquatic life criteria for copper using the BLM. This guidance, or its updates, will provide assistance to the Department and the public for determining minimum data requirements for BLM inputs, and how to estimate criteria when data are incomplete or unavailable. The "Implementation Guidance for the Idaho Copper Criteria for Aquatic Life" is available at the Department of Environmental Quality, 1410 N. Hilton, Boise, Idaho 83706, and on the DEQ website at www.deq.idaho.gov.

These example values found in the criteria table at IDAPA 58.01.02.210 are not intended to represent default criteria values; the locally applicable criteria will depend on local values of input parameters to the BLM.

3 General Implementation for Aquatic Life Criteria

The following general implementation requirements for aquatic life criteria, found in Idaho water quality standards (IDAPA 58.01.02.210.03) shall be applicable when implementing the copper criteria for aquatic life:

- When a mixing zone is authorized, the BLM-derived copper criteria will apply at the boundary of any regulatory mixing zone (IDAPA 58.01.02.210.03.a).
- Water quality-based effluent limits shall be based on criteria exceedances only occurring during low-flow conditions that meet the following criteria: the lowest 1-day flow with a 10-year occurrence (1Q10) for acute copper criteria or based on an allowable exceedance occurring no more than once every 3 years (1B3). For chronic criteria, these are the lowest 7-day average low flow with a 10-year recurrence (7Q10) or based on an exceedance for 4 consecutive days occurring no more than once every 3 years (4B3) (IDAPA 58.01.02.210.03.b).
- The copper criteria for aquatic life will be expressed as a concentration of dissolved copper (IDAPA 58.01.02.210.03.c.iii).
- Acute criteria are criteria not to be exceeded for a 1-hour average more than once in 3 years. Chronic criteria are not to be exceeded for a 4-day average more than once in 3 years (IDAPA 58.01.02.210.03.d.i).

In addition, the following implementation tools shall be available when implementing the Idaho copper criteria for aquatic life:

- Flow-tiered NPDES permit limitations may be provided for dischargers with copper limits in accordance with IDAPA 58.01.02.400.05.
- Intake credits for water quality-based effluent limitations may be allowed in accordance with IDAPA 58.01.02.400.06.

All other water quality standards and Idaho Pollutant Discharge Elimination System rules and regulations (IDAPA 58.01.25) shall apply when implementing the Idaho copper criteria for aquatic life.

4 Biotic Ligand Model

The BLM is a model that predicts toxicity of metals by estimating the bioavailability of the metal to bind to the biological receptor, or biotic ligand, such as the gill surface.

In contrast to hardness-based criteria, which only account for competitive binding at biotic ligand sites by calcium and magnesium cations, the BLM also accounts for binding at biotic ligand sites by other cations, as well as metal speciation and complexation with DOC and other inorganic ligands (Figure 1). EPA's 2007 recommended aquatic life criteria for copper replaces the previously recommended hardness-based equation with the BLM.

4.1 Overview of BLM Version 3.1.2.37

Version 3.1.2.37 is the most recent version of the BLM available at this time. The BLM version 3.1.2.37 and associated user's guide can be downloaded from *www.windwardenv.com/biotic-ligand-model/* or from DEQ's website (*www.deq.idaho.gov*). More information can be found in the BLM user's guide (Windward 2015).

Users must ensure they are using the BLM to return results consistent with EPA's 2007 nationally recommended criteria. In version 3.1.2.37, users must select the "US EPA WQC" radio button and select "Cu" from the dropdown from the "Metal/Organism Selection" shortcut menu (Figure 5 and Figure 6).

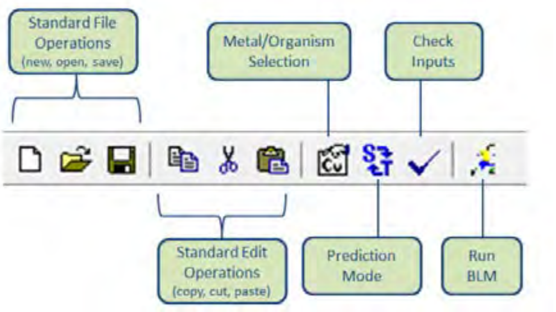
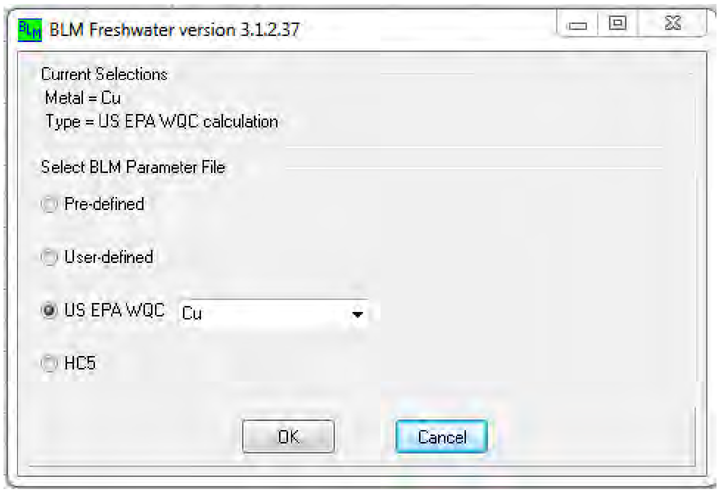


Figure 5. Shortcut toolbar key for BLM version 3.1.2.37, indicating location of the Metal/Organism Selection shortcut (source: Windward 2015).


BLM Freshwater version 3.1.2.37

Current Selections
Metal = Cu
Type = US EPA WQC calculation

Select BLM Parameter File
○ Pre-defined
○ User-defined
● US EPA WQC Cu
○ HC5

Figure 6. Select US EPA WQC and Cu to return results consistent with EPA's 2007 criteria.

Users must also use the complete site chemistry; simplified site chemistry is not sufficient for calculating criteria under this guidance. The BLM estimates copper concentrations that would result in acute and chronic effects to aquatic life in a water body based on the values of the following site-specific physical and chemical parameters:

- Temperature
- pH
- Copper
- DOC
- Calcium
- Magnesium
- Sodium
- Potassium
- Sulfate
- Chloride
- Alkalinity
- Sulfide
- Humic acid

Each parameter is discussed in more detail in section 5.1.

The model calculates both acute and chronic criteria based on these inputs, and provides the ratio of measured copper concentration to these criteria, or toxic unit (TU). The criteria calculated from a single set of inputs are referred to as an IWQC. The IWQC represents the criteria that would be protective of aquatic life at the time that the data were collected. However, the input data are variable over time and space, so any single IWQC is time- and location-specific and will not necessarily be protective of aquatic life at any given site; if site chemistry changes, individual IWQCs will change. The same applies to the current hardness-based criteria.

For any given sample, a TU≥1.0 indicates that a copper concentration exceeds the associated IWQC and that aquatic life may be impaired at the time of that sample.

4.2 Comparison to Hardness-Based Criteria

Because the BLM incorporates copper speciation and complexation in addition to competitive binding at biotic ligand sites by cations, it better predicts the toxic effects of exposure to dissolved copper in the aquatic environment than the hardness-based criterion equation. The BLM produces more accurate predictions of toxic effects from copper in a variety of natural waters than the hardness-based criterion equation, which has been found to produce highly variable and often inaccurate predictions of actual toxicity (NMFS 2014).

While the BLM does provide more accurate and precise predictions of toxic effects from a given copper concentration, it is important to note that the BLM does not always provide more stringent criteria.

For example, when waters have relatively high DOC concentrations, such as downstream from a municipal wastewater treatment facility, BLM-derived criteria will likely be less stringent than those derived from the hardness-based criterion equation. Conversely, in areas with very limited organic inputs, or with more acidic conditions (lower pH), BLM-derived criteria may be more stringent than criteria derived from the hardness-based criteria equation.

Figure 7 shows comparisons of acute and chronic criteria derived from both the hardness-based criterion equation and the BLM for 189 stream sites monitored for the *Statewide Monitoring for Inputs to the Copper Biotic Ligand Model* (DEQ 2017c). Of the 189 sites, 82 (44%) had BLM-derived criteria that were less stringent than those derived from the hardness-based criterion equation.

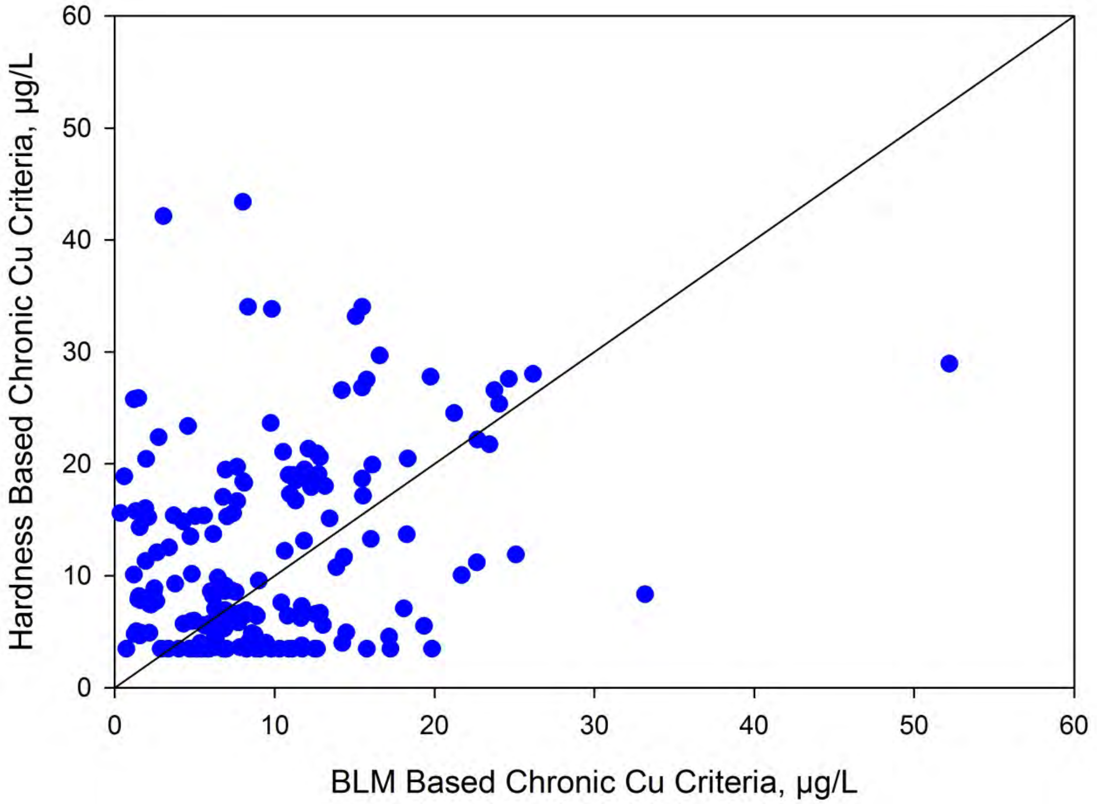


Figure 7. Comparison of BLM-derived to hardness-based criteria calculated from sites monitored as part of the *Statewide Monitoring for Inputs to the Copper Biotic Ligand Model* (DEQ 2017c). The solid black line is the 1:1 line; sites above the line have BLM criteria that are more stringent than the hardness-based criteria, and sites below the line have BLM criteria that are less stringent. Idaho's hardness-based criteria included a minimum hardness floor of 25 mg/L.

Even at a single location, the relative stringency of the BLM- and hardness-based criteria will change over time, with one type of criteria being more stringent during certain times of year while the other is more stringent during other times (Figure 8).

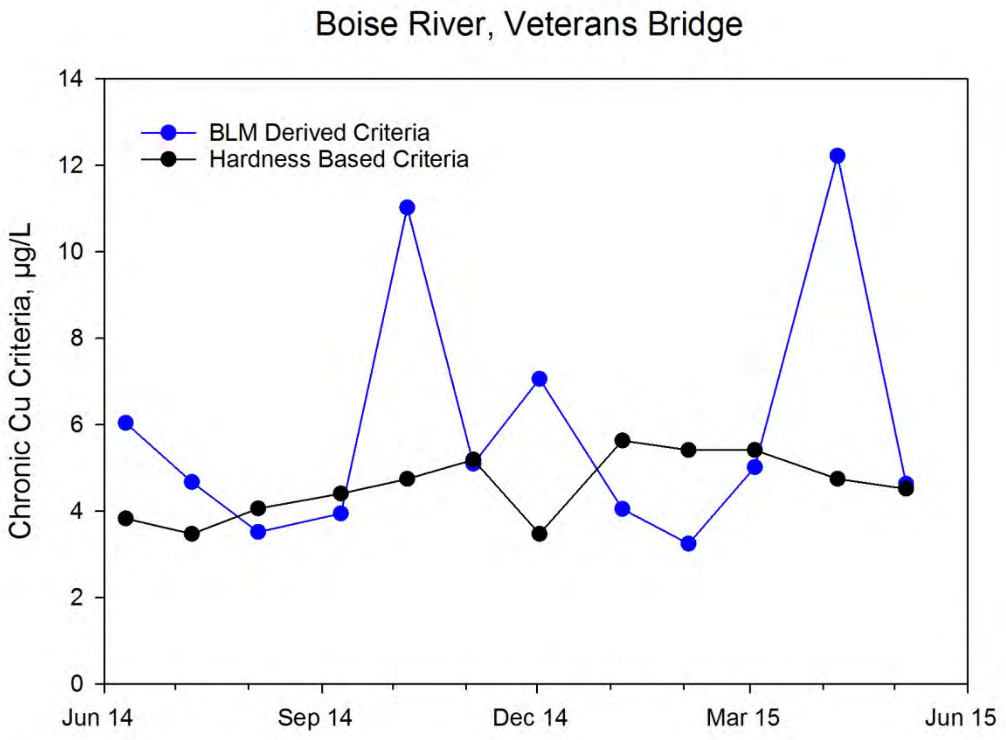


Figure 8. BLM-derived and hardness-based criteria calculated from a single location on the Boise River from June 2014 to June 2015. The BLM-derived criterion is more stringent during certain times of year, while the hardness-based criterion is more stringent during other times (source: unpublished city of Boise data).

This disparity is related to the seasonality of the BLM inputs and their influence on the BLM criteria. As discussed previously, though the concentration of cations is a factor in the calculation of BLM criteria, the BLM is most sensitive to DOC and pH. However, the lowest concentrations of DOC in a stream usually coincide with the highest concentrations of cations, meaning that when hardness-dependent criteria predict that copper is least bioavailable, the BLM-derived criteria will predict the greatest copper bioavailability and toxicity (Figure 9).

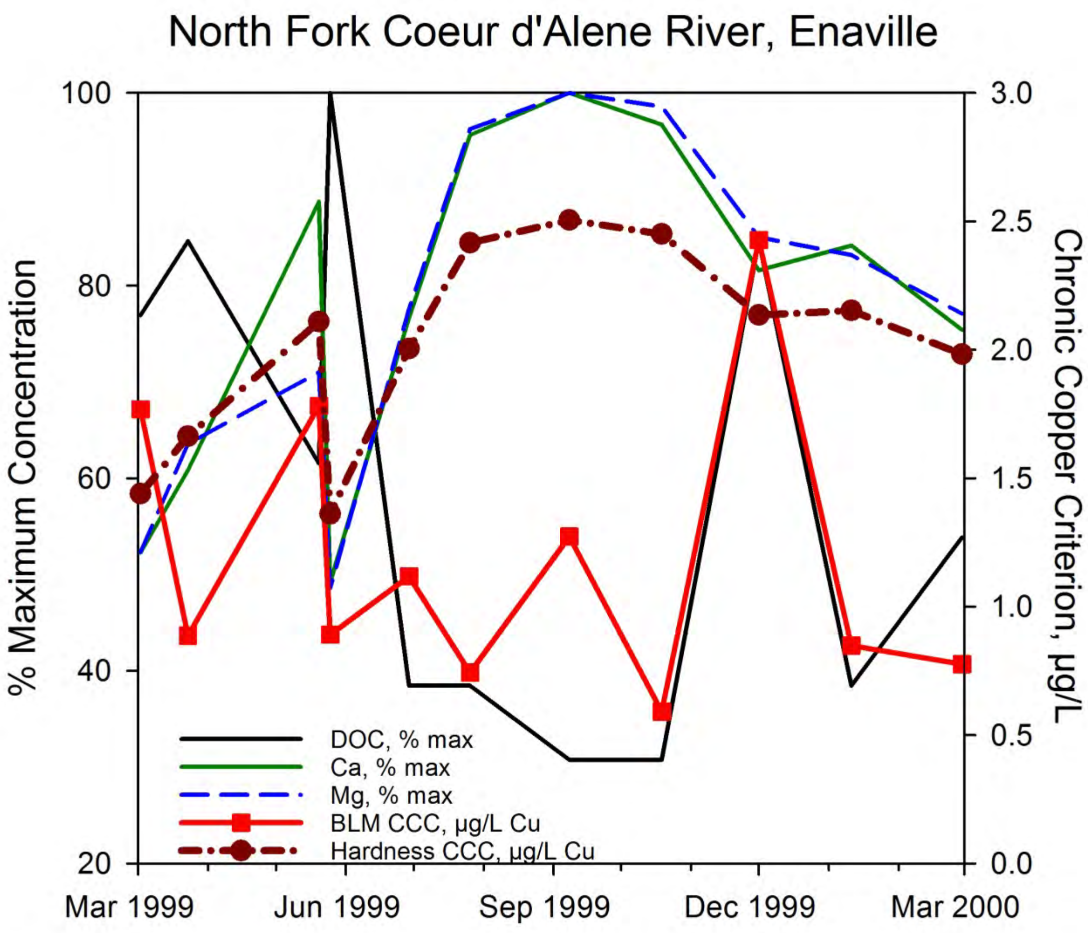


Figure 9. Temporal variability of major cation and DOC inputs to the BLM, BLM-derived chronic copper criterion (CCC), and hardness-based chronic copper criterion, from the North Fork Coeur d'Alene River, showing that DOC is at its lowest concentration when major cations (and hardness) are at their maximum and that BLM-derived copper criterion closely follows DOC, while hardness-based copper criterion closely follows major cations.

5 Data Requirements for Application of the BLM

As described in section 4.1, the BLM requires users to enter site chemistry to generate acute and chronic IWQCs. The following sections describe the minimum data requirements for generating IWQCs using the BLM, each parameter and how it is measured, and the BLM's relative sensitivity to the different input parameters.

5.1 General Data Requirements of the BLM

The required input parameters and associated measurement units are provided below.

- **Temperature** is an important physical characteristic of surface water and affects rates of chemical reactions. Temperature should be measured in situ at the time of sample collection. The BLM allows temperature to be entered in the following units: °C, °F, and K.

- Chemical speciation is controlled in part by ambient **pH**. Therefore, the BLM for copper is highly sensitive to changes in pH. Like temperature, pH can be highly variable and should be measured in situ in the field at the time of sample collection.
- Dissolved **copper** concentrations are not required to derive BLM criteria. However, the model does require that users input a copper concentration in order to give valid results. Dissolved copper concentrations can be entered as µg/L or mg/L. In the absence of specific data, users can enter any non-zero concentration as a default.
- **DOC** mitigates the effects of copper by complexing with free copper. It affects copper speciation and bioavailability. The BLM for copper is highly sensitive to changes in DOC. The BLM allows DOC concentrations to be entered in the following units: mg C/L and mmol C/L.
- The **major cations** (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) compete with copper at the biotic ligand site and affect copper toxicity. Of the major cations used in the BLM, Ca^{2+} and Na^{+} are the most important for copper toxicity. The major cations can be entered as dissolved concentrations in the following units: µg/L, mg/L, g/L, µmol/L, mmol/L, and mol/L.
- **Major anions** (SO_4^- and Cl^-) affect ionic strength and charge balance. Concentrations of these ions can be entered in the following units: µg/L, mg/L, g/L, µmol/L, mmol/L, and mol/L.
- **Alkalinity** is a measure of the buffering capacity of a sample. In natural surface waters, carbonate and bicarbonate ions are usually the largest contributor to alkalinity. These ions form complexes with free copper, reducing copper bioavailability. Alkalinity can be entered as mg/L $CaCO_3$.
- **Sulfide** can affect copper bioavailability by affecting speciation. However, sulfide is very uncommon in natural waters; therefore, users should use a default value of near zero (e.g., 1.0×10^{-8} mg/L).
- **Humic acid fraction** can be measured directly but is not critical to the BLM calculation. In the absence of specific data, users should enter a default of 10% for humic acid fraction of DOC.

Work by EPA (2012) and the Oregon Department of Environmental Quality (ODEQ 2016) indicates that the BLM is most sensitive to changes in DOC and pH. When using the BLM to implement the Idaho copper criteria for aquatic life, a sample refers to a complete set of BLM input parameters as described in Table 1, collected at a single place and time. Section 6 details options for estimating criteria when a sample is incomplete (i.e., when not all required parameters have been measured).

Table 1. BLM parameters required to constitute a complete sample, plus recommended analytical methods, preservative, holding times, and minimum laboratory reporting limits.

Parameter	Analytical Method	Preservative	Holding Time	Reporting Limit
Temperature and pH	Measured in situ, using properly calibrated equipment	N/A	N/A	N/A
Dissolved Ca, Mg, Na, K	EPA 200.7	Cool to ≤4 °C. Filter with 0.45-µm filter as soon as practical. Acidify to pH <2 after filtration.	28 days unpreserved 6 months preserved	0.1 mg/L
Dissolved copper	EPA 200.8	Cool to ≤4 °C. Filter with 0.45-µm filter as soon as practical. Preserve with nitric acid within 2 weeks.	2 weeks unpreserved 6 months preserved	0.001 mg/L
Sulfate	EPA 300.0	Cool to ≤4 °C.	28 days	10 mg/L
Chloride	EPA 300.0	Cool to ≤4 °C.	28 days	0.1 mg/L
Alkalinity	SM 2320 B	Cool to ≤4 °C.	14 days	10 mg/L
DOC	SM 5310 B	Cool to ≤4 °C. Filter with 0.45-µm filter within 48 hours. Acidify to pH <2 after filtration.	7 days	0.2 mg/L

Notes: mg/L = milligrams per liter; N/A = not applicable; SM = standard method; sulfide is a BLM parameter but is input as a default, near-zero value, and is not required to be analyzed

5.2 Special Considerations for Monitoring pH and DOC

It is well known that pH and temperature vary cyclically throughout a single day, and these cycles can be dramatic. The BLM is highly sensitive to pH, and daily pH cycles could result in dramatic changes in the BLM-derived criteria. Therefore, when designing monitoring programs or assessing data for derivation of BLM criteria, users should consider using continuous pH data to capture the daily variability of pH at a given site or collecting samples early in the day when temperatures and pH are generally at their lowest. When continuous data are available, the timing of sampling should coincide with minimum daily pH values. DOC samples are especially susceptible to contamination from sample bottles and sample filtration. To ensure that DOC samples are not affected, it may be necessary to filter an adequate volume of sample or flush filters with deionized water prior to sampling for DOC. Monitoring results from DEQ (2017c) suggest that many of the problems associated with meeting precision requirements from field replicates can be allayed by filtering samples in an analytical laboratory, rather than in the field as required by 40 CFR 136 for NPDES compliance monitoring.

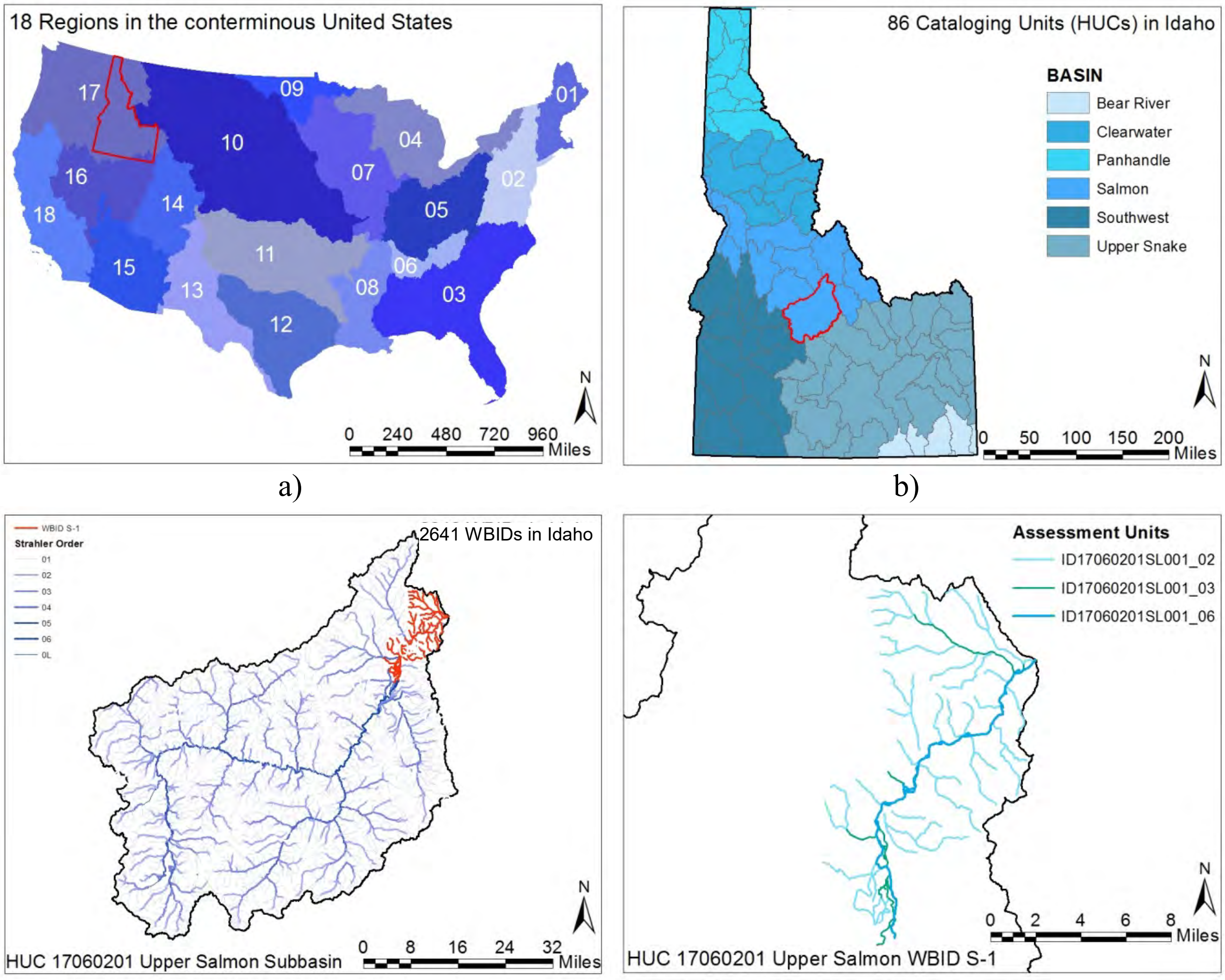
Quality assurance project plans and monitoring plans for collection of BLM input parameters should clearly demonstrate how concerns for pH cycling and DOC data quality will be addressed and describe how monitoring will target the most bioavailable conditions for copper. The most bioavailable conditions for copper can be estimated by identifying critical daily conditions (such as when pH is at its lowest daily value) as well as critical seasonal conditions (such as when DOC concentrations are at their lowest seasonal concentrations).

5.3 Spatial Representation

Physical and chemical parameters can be highly spatially variable. However, when implementing any criteria that are based on site-specific conditions, any single sample location must be considered representative of a larger stream segment. How DEQ interprets spatial representation when implementing the copper criteria for aquatic life will depend upon how the data are to be used, whether monitoring results are intended to determine compliance with water quality standards for the IR and TMDL development or for development of effluent limits and determining compliance with NPDES permits. In flowing waters, spatial representation is generally ensured by sampling well-mixed portions of the flow (i.e., sampling from the thalweg and avoiding confluences or other obvious lateral inputs).

5.3.1 Ambient Monitoring for IR and TMDL Development

When monitoring and assessing waters for IR or TMDL development, DEQ applies monitoring results and listing decisions from a single location or relatively short reach to a collection of waters with similar land uses known as an assessment unit (AU). All waters within an AU can be reasonably expected to have the same ambient water quality and background water chemistry. AUs are numbered systematically and are based on stratification of water body units identified in Idaho's water quality standards (IDAPA 58.01.02.109) by land use and stream order (Figure 10).



a) b)

c) d)

Figure 10. Relationship between hydrologic unit codes (HUCs), water body units, and AUs: (a) Level 1 regions in the nation; (b) 86 Level 4 HUCs in Idaho (the highlighted HUC is 17060201—Upper Salmon River subbasin in central Idaho); (c) HUC 17060201, Upper Salmon River subbasin, with water body unit S-1 highlighted in red; and (d) water body unit S-1 subdivided into three different AUs (source: DEQ 2016).

AUs can be added or deleted as new information suggests a single AU should be split into multiple AUs due to changes in land use or other factors such as mapping errors or suggests separate AUs should be grouped into a single AU.

Currently, there are 5,754 AUs in Idaho representing 95,119 miles of rivers and streams (DEQ 2017b). More detailed discussions of AUs can be found in the most recent version of the IR (DEQ 2017b) as well as the *Water Body Assessment Guidance* (DEQ 2016).

When conducting ambient copper and BLM monitoring for IR or TMDL development, field crews must collect samples at locations that are considered representative of the entire AU being assessed. If multiple locations within an AU have been monitored, assessors should consider if locations are representative before combining data.

Many distinct 1st- and 2nd-order tributaries that drain different areas may be lumped together into one AU. DEQ uses data collected from specific sampling sites to infer water quality throughout an AU. It is possible that differences in activities and discharges exist within an AU and all water within the AU may not be of the same quality as found at the sampled sites. DEQ typically samples the most downstream extent of an AU, where it is expected that water quality will reflect the effects of all upstream activities. Even in larger streams, the location of a sampling site could reflect better or worse water quality than the bulk of the AU. When determining the representativeness of a location to an AU, DEQ assessors will consider differences in activities and discharges within the AU. If data are not considered representative, DEQ will provide sufficient rationale to describe why the sampling location is not representative and that the data do not apply to the AU. If some or all of the sampling sites are not representative of the water, then DEQ may opt to use none of the data or only use data from those sampling sites that do represent the AU. Decisions regarding representativeness of sample results to an AU and any decision to exclude data for assessment purposes would be subject to public comment and EPA approval through the IR approval process.

5.3.2 Monitoring to Identify Criteria for Use in Effluent Limit Development

While it is appropriate to sample at locations representative of an AU for IR and TMDL purposes, this is generally not acceptable for determining applicable criteria for effluent limit development. For effluent limit development, it is instead necessary to characterize site-specific conditions within the effluent’s receiving water.

Monitoring to determine effluent limits should occur downstream of discharge points and below any regulatory mixing zones, where fully mixed conditions are expected to occur. This will ensure that monitoring results used to derive criteria for developing effluent limits are specific to waters affected by the effluent discharge. Monitoring locations should represent the conditions for the receiving water as affected by the specific discharge being considered. If there are multiple points of discharge within a relatively short distance, then a single site below all points of discharge may be necessary for characterizing conditions.

In some instances, it may be necessary or advisable to collect samples upstream of points of discharge to capture baseline conditions.

Monitoring results collected to identify criteria for use in effluent limit development may be used for IR assessment and TMDL development purposes, provided they are determined to be representative of the AU to which they belong.

5.4 Temporal Representation

In addition to determining the spatial extent that a sample represents, it is important to properly capture the temporal variability of the physical and chemical parameters that are used as inputs for the BLM. As described in section 5.1, many of the input parameters can be highly variable, both short term (such as temperature and pH) and seasonally (such as DOC and major cations) (Figure 9). This leads to highly variable IWQCs derived from a site (Figure 8).

5.4.1 Temporal Variability of BLM Parameters

Temperature and pH can have seasonal as well as diel variability. In particular, diel pH variability has been shown to affect concentrations of metals (Brick and Moore 1996). It is important that monitoring programs consider the timing of sampling events to address this variability, particularly when evaluating acute effects (section 5.2). Nearly all the BLM input parameters exhibit some seasonal variability. The degree of variability, and the relative predictability of seasonal variability, can be site specific.

Generally, 24 consecutive, monthly IWQCs calculated over the course of 2 years would be considered appropriate to characterize seasonal variability for any single location. However, users should consider any site-specific factors, such as flood or drought conditions, that may require additional sampling to fully capture site variability.

Comparison of flow data from the time of sample collection to the historical flow record may be used to demonstrate that sampling efforts appropriately captured the temporal variability and range of expected long-term flow conditions and that sampling less than 24 months is appropriate. Similarly, in some water bodies, calculation of more than 24 monthly IWQCs may be necessary to appropriately characterize seasonal variability at a site. Whenever data are available, users should use longer datasets to fully capture temporal variability at any given site.

Monthly sampling may not be possible at some sites in Idaho due to accessibility and safety considerations. For locations where monthly sampling is not practical, effort should be made to minimize the time period when there are no samples collected.

5.4.2 Critical Time Period

In many instances, the critical period of the year when copper is expected to have its greatest bioavailability can be predicted and tied to seasonal variations of DOC. DOC is usually at its lowest concentrations in late fall in Idaho, based on data that is considered representative of streams supporting anadromous fish (Appendix C of NMFS 2014). This is consistent with other observed trends, where BLM-derived IWQCs were usually at their most stringent in fall and winter (EPA 2007b).

5.5 Reconciling Multiple IWQCs

When evaluating time-specific results, users can compare a copper concentration to the BLM-derived IWQC calculated from the same sample. However, because IWQCs can be highly variable over time, it may sometimes be necessary for users to reconcile many different IWQCs to apply a single, consistent criterion, such as when determining the need for water quality-based effluent limits.

The following sections describe possible approaches that may be used to reconcile multiple IWQCs from a single site when it is impractical to use individual IWQCs.

5.5.1 Minimum of IWQCs

The simplest approach to reconciling multiple IWQCs from a single site is to take the minimum of the IWQCs developed from the site. When using the minimum IWQC, users would need to demonstrate that critical conditions have been captured. This demonstration may rely on information from nearby sites, historical flow records, or other data sources.

This approach is the most conservative. However, it is most appropriate when there are relatively few data points (e.g., fewer than 24 monthly samples, or samples do not represent the annual hydrograph) and, therefore, lower confidence that the site's temporal variability has been sufficiently characterized.

5.5.2 Distribution of IWQCs

One common approach to reconciling time-variable criteria is to select a relatively conservative value from the distribution of criteria. When sufficient data are available to fully characterize the seasonal variability of IWQCs (e.g., at least 24 consecutive, monthly samples), then a conservative percentile of all IWQCs should be used. Users must demonstrate that the selected percentile will be protective of aquatic life and will not lead to a frequency of copper exceedance of individual IWQCs at the site more than once in 3 years. This can be accomplished by demonstrating that copper concentrations at the selected percentile will not lead to TU≥1.0 more than once every 3 years.

5.5.3 Other Statistical Approaches

Other, more sophisticated statistical approaches can be used to reconcile multiple IWQCs from a single location. For example, the Fixed Monitoring Benchmark (FMB) may be used to evaluate compliance with time-variable criteria. The FMB uses the relationship of copper and individual IWQCs and their variability at a given site to derive a benchmark concentration that would comply with the frequency of exceedance component water quality criteria. For more information on the FMB, see EPA (2012). Users may choose to use statistical approaches, such as the FMB, when sufficient data are available to fully characterize the variability of IWQCs and the relationship of IWQCs to copper concentrations. In some cases, it may require up to 3 or more years of monthly samples for all BLM input parameters as well as copper to fully characterize the variability of flows and water quality within a water body.

5.5.4 Seasonal Criteria

For waters with predictable seasonal variability of IWQCs, seasonal criteria may be developed. For example, in waters with sufficient IWQC data, it may be possible to derive dry season criteria based on the distribution of IWQCs during low-flow conditions, and wet season criteria based on the distribution of IWQCs during high flow. To consider seasonal criteria, sufficient data must be available and demonstrate predictable seasonality. This would generally require at least 36 consecutive monthly samples and may require multiple years of monthly samples to fully capture the variability and flood cycle.

6 Estimating Criteria When Data Are Absent

The BLM requires complete samples to derive criteria. However, data may be limited at times, with either incomplete samples with certain parameters missing or no samples available for a specific water body. In these cases, users may choose to estimate criteria based on available data.

While it may be possible to estimate conservative concentrations of geochemical ions and DOC based on statistical approaches (e.g., EPA 2016), it may be overly conservative. For example, a minimum BLM chronic criterion of 3.25 micrograms per liter (µg/L) was calculated from monthly samples for the Boise River at Glenwood Bridge. According to Appendix B of the missing parameters document (EPA 2016), the 2.5th percentile of BLM IWQCs is sufficient for protection of aquatic life; the 2.5th percentile of BLM chronic IWQCs at the Boise River at Glenwood Bridge site was 3.38 µg/L. By contrast, using the recommended 10th percentile of geochemical ions and DOC inputs as recommended by EPA (2016), and a conservative pH of 7, would result in a BLM chronic criterion of 1.35 µg/L. This is less than half of the minimum IWQCs calculated at that site (Figure 11).

Additionally, using lower percentile values from each of the inputs to the BLM may ignore the lack of synchronicity in natural seasonal variability of these parameters; for example, DOC is often at its lowest concentration during low-flow conditions. However, during these conditions, many of the geochemical ions are at their highest concentrations (Figure 9). Ignoring such realities and taking low-end inputs across the board can result in overly stringent criteria.

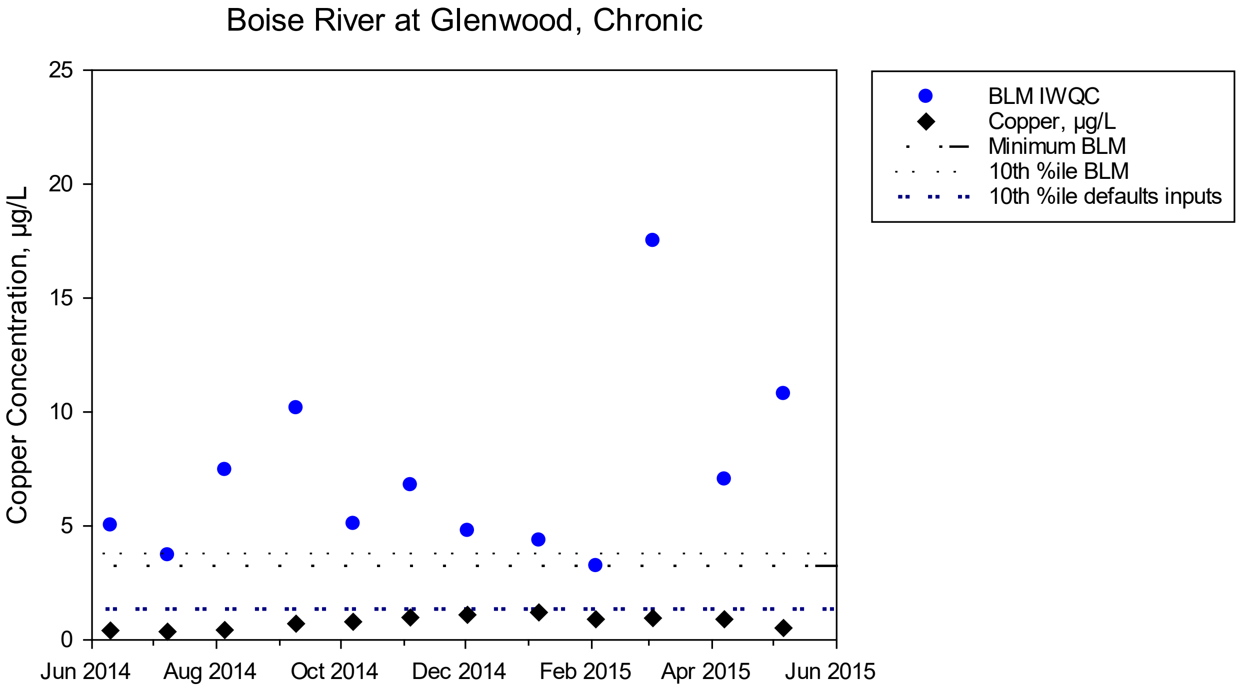


Figure 11. BLM-calculated chronic criteria for the Boise River at Glenwood Bridge (June 2014–June 2015). Reference lines demonstrate the criterion that would be calculated from the 10th percentile and minimum IWQC calculated from these data, and the criterion calculated using the EPA (2016) recommended default inputs (source: unpublished city of Boise data).

A more realistic approach than using conservative default inputs values would be to calculate BLM-derived IWQCs for geographical regions and then recommend default criteria. This would more accurately reflect water quality at a given site at a given time and would be easier for DEQ to implement.

It may be possible to estimate conservative criteria based on data collected during the critical time period when IWQCs are expected to be at their minimum.

6.1 Estimating Conservative Criteria

When no data are available, DOC or pH data are absent, or available data are determined not to adequately characterize critical conditions, conservative criteria estimates should be used to estimate critical conditions of a water body or AU and ensure estimated criteria are protective of aquatic life.

In late summer and fall 2016, DEQ collected full BLM input data from 189 sites throughout the state. BLM criteria were generated from each sample. Sites were grouped according to the following regional classification systems:

- Idaho administrative basins as described in Idaho water quality standards, hereafter referred to as basins (IDAPA 58.01.02.109–160)
- Level III ecoregions, hereafter referred to as ecoregions (EPA 2013)
- Stream order
- Water body assessment guidance site classes, hereafter referred to as site class (Jessup 2011; DEQ 2016b)
- Site class combined with stream size, where rivers are any water with stream order ≥5 and streams are any water with stream order <5, hereafter referred to as site class + river/stream

Conservative criteria can be estimated for a site by applying the lowest of the 10th percentile criteria calculated from the five regional classifications (DEQ 2017c). Table 2 presents potential conservative criteria estimates for each regional classification system.

Table 2. Potential conservative criteria estimates.

Regional Classification		Estimated Copper Criteria 10th Percentile Acute (µg/L)	Estimated Copper Criteria 10th Percentile Chronic (µg/L)
Basins	Bear River	7.9	4.9
	Clearwater	7.6	4.7
	Panhandle	1.1	0.7
	Salmon	3.9	2.4
	Southwest	9.3	5.8
	Upper Snake	2.6	1.6
Ecoregions	Blue Mountains	10.1	6.3
	Central Basin and Range	14.3	8.9
	Columbia Plateau	7.2	4.5
	Idaho Batholith	3.9	2.4
	Middle Rockies	8.4	5.2
	Northern Basin and Range	13.0	8.1
	Northern Rockies	1.4	0.9
	Snake River Plain	3.2	2.0
	Wasatch and Uinta Mountains	9.0	5.6
	Wyoming Basin	38.6	24.0
Stream order	1	5.2	3.2
	2	3.7	2.3
	3	4.0	2.5
	4	1.6	1.0
	5	8.9	5.5
	6	2.3	1.4
	7	10.1	6.3
	8	7.6	4.7
	Unassigned	9.0	5.6
Site class	Mountains	1.4	0.9
	Foothills	6.3	3.9
	Plains, Plateaus, and Broad Valleys (PPBV)	5.3	3.3
Site class + river/stream	Foothills River	9.7	6.0
	Foothills Stream	4.7	2.9
	Mountains River	3.9	2.4
	Mountains Stream	1.0	0.6
	PPBV River	5.0	3.1
	PPBV Stream	5.5	3.4

Note: Values represent the 10th percentile of BLM criteria derived from statewide monitoring (DEQ 2017c).

For example, the following scenario illustrates how conservative and protective criteria could be estimated for a new discharge permit.

A new permit is proposed in a water body where there are no BLM input data available to determine site-specific copper criteria. The permit writer determines that the site is in the Salmon basin, in the Middle Rockies ecoregion, a 3rd order stream, and in the Foothills site class. Using this information, the permit writer determines that conservative acute and chronic copper criteria estimates would be 3.9 and 2.4 µg/L, respectively (Table 3).

Table 3. Example of conservative criteria estimates based on regional classification systems.

	Estimated Conservative Criteria	
Regional Classification	**Acute (µg/L)**	**Chronic (µg/L)**
Salmon basin	**3.9**	**2.4**
Middle Rockies ecoregion	8.4	5.2
3rd-rrder stream	4.0	2.5
Foothills site class	6.3	3.9
Foothills Stream site class + river/stream	4.7	2.9

Note: Values in bold indicate the minimum of these values and would serve as the estimated criteria in this example.

The permit writer can use these conservative criteria estimates to perform reasonable potential analysis (RPA) to determine if there is a reasonable potential to exceed (RPTE) copper criteria. If the resulting RPA does not indicate RPTE, then no further analysis is necessary. If the RPA indicates RPTE, then the permit writer would use the conservative estimate of criteria to develop water quality-based effluent limits following procedures outlined in the *Effluent Limit Development Guidance* (DEQ 2017a). Additionally, if the reasonable potential analysis indicates reasonable potential to exceed, the discharger should initiate monitoring of BLM input parameters to confirm or refine applicable criteria once sufficient data (e.g., 24 monthly samples) are collected.

Users may propose alternative methods for estimating protective criteria. The proposed estimates must use the BLM to derive criteria, must be based on scientifically sound methods, and must be demonstrated to be protective of aquatic life. Analysis similar to what is found in *Statewide Monitoring for Inputs to the Copper Biotic Ligand Model (BLM*) (DEQ 2017c) would be considered sufficient to demonstrate protectiveness.

6.1.1 Protectiveness of Conservative Criteria Estimates

The conservative criteria estimates presented in Table 2 should be considered protective of the most bioavailable conditions for any given site.

These values are lower than calculated IWQCs at all but 6 of the 189 sample locations from which they were derived. Only 5 of the 189 sites with complete samples had copper concentrations that exceeded BLM IWQC at the time of sampling. Of these 5, only 2 (ID0000167U and ID0027120D) would have met the conservative criteria estimate but would have exceeded the IWQC calculated at the time of sampling. Additionally, these 2 sites had copper concentrations that were detected below the reporting limit for copper (Table 2), meaning that while there was dissolved copper present in the sample the result cannot be quantified (DEQ 2017c).

Table 4. Calculated BLM chronic criteria, estimated conservative criteria, and dissolved copper concentrations for the 5 sample locations where copper exceeded BLM derived IWQCs at the time of sampling.

Site ID	Stream Name	Chronic Criterion, Calculated	Chronic Criterion, Estimated	Dissolved Copper
ID0000167U	Canyon Creek	0.24	0.6	0.25
ID0027120D	Little Wood River	0.35	1.6	0.49
ID0028321D	Big Deer Creek	1.61	0.6	2.86
ID0028321U	Big Deer Creek	2.18	0.6	2.42
SFDeerCKD	South Fork Deer Creek	2.44	0.6	6.65

These results indicate that this approach to estimating conservative criteria should be considered protective of the most bioavailable conditions for any given site.

While data sufficient to calculate BLM criteria in Idaho waters are rare, there are limited independent datasets that can be used to assess the protectiveness of the recommended default criteria presented in Table 2.

US Geological Survey (USGS) data are available from nine sites throughout Idaho with complete BLM data (USGS 2016). Table 5 presents a comparison of how conservative criteria estimates based on the minimum of 10th percentile values calculated for regional site classification systems (based on fall monitoring data) compare to the actual minimum IWQCs calculated from the nine USGS monitoring locations where complete BLM data are available.

In most instances, criteria that represent the most bioavailable condition (defined as the minimum measured IWQC) can be estimated by taking the 10th percentile of chronic criteria from one of the site classification systems. Furthermore, if we take into account reporting limits and consider the reporting limit to be the effective criteria for waters where the BLM-derived criteria are below the reporting limit for dissolved copper, then the minimum of the regional classification 10th percentile values would be considered protective for each site where independent BLM criteria are available.

For example, USGS sites 12413000 and 12413470 both had a minimum chronic copper criterion of 0.6 µg/L. The minimum 10th percentile regional site classification system estimate for these sites is based on the site class (Mountains) and is 0.9 µg/L. Although this is greater than the minimum calculated criterion of 0.6 µg/L, if we consider our ability to quantify dissolved copper, these concentrations are both below the reporting limit of 1 µg/L and could be considered equivalent when determining compliance.

For more details on the derivation of the 10th percentile chronic BLM criteria estimates and comparison to actual IWQCs at USGS sites with complete BLM data, see *Statewide Monitoring for Inputs to the Copper Biotic Ligand Model (BLM*) (DEQ 2017c).

Table 5. Comparison of the minimum chronic IWQC calculated from samples collected at USGS monitoring sites to recommended conservative criteria estimates based on the minimum of the 10th percentile values from regional site classes (DEQ 2017c).

USGS Site ID	Minimum IWQC (µg/L)	Conservative Criteria Estimate (µg/L)
10068500—Bear River at Pescadero	8.9	1.4
12392155—Lightning Creek at Clark Fork, Idaho	1.1	0.7
12413000—North Fork Coeur d'Alene River at Enaville	0.6	0.7
12413470—South Fork Coeur d'Alene River at Pinehurst	0.6	0.7
12413875—St Joe River at Red Ives	3.7	0.7
12419000—Spokane River near Post Falls	1.5	0.7
13056500—Henry's Fork near Rexburg	4.1	1.4
13092747—Rock Creek above Hwy 30/93 Crossing, Twin Falls	10.7	1.6
13154500—Snake River at King Hill	4.9	2.0

7 Identifying Impairments for the Integrated Report

The process of assessing whether a water body fully supports designated and existing beneficial uses is governed by IDAPA 58.01.02.054. DEQ uses the *Water Body Assessment Guidance* (DEQ 2016) as a guide in making assessment decisions.

Under IDAPA 58.01.02.054.05, data used for developing copper criteria for IR assessment purposes should be representative of the AU being assessed (section 5.3.1). It is recommended that copper assessments be based on paired dissolved copper and complete BLM parameter sample results. When copper data are associated with complete BLM parameter results, assessments should be based on direct comparison to the IWQC associated with the dissolved copper sample.

When evaluating copper exceedances, assessors must ensure that the frequency of exceedance requirement is met before listing a water body as impaired. This requires at least two exceedances of an acute or chronic criterion within 3 years. Therefore, a single exceedance of an IWQC is not sufficient for listing. If assessors only have one paired copper and IWQC sample, they must make an effort to collect at least one additional sample to confirm the IWQC exceedance prior to listing the water as impaired.

DEQs approach to ambient water quality monitoring relies heavily on biological monitoring. This approach uses direct measures of the aquatic community (e.g., benthic macroinvertebrates, fish) to assess aquatic life use support and ensures that waters where copper (or any other pollutant) are impairing aquatic life are properly identified as impaired regardless of availability of BLM input parameter data to know the IWQC.

When evaluating copper data to determine compliance with criteria for the IR, DEQ assessors will use the following hierarchical approach:

1. Compare to concurrent IWQC: If copper concentrations exceed the IWQC derived from concurrent sample inputs, then the AU will be listed as impaired. Follow-up monitoring will be required to confirm that the exceedance frequency is greater than

once in 3 years. Subsequent monitoring should target the most bioavailable time period (i.e., late summer/fall through winter).

2. Compare to IWQC from within AU for same season (winter, spring, summer, or fall): If concurrent BLM input parameter data are not available, the assessor should determine if BLM IWQC data are available from a representative reach within the same AU from within the same season when copper data were collected. If copper concentrations exceed the seasonal IWQC from within the AU, the AU will be listed as impaired. Follow-up monitoring will be required to confirm the results.
3. Compare to conservative criteria estimates: If no IWQC data are available, or are not representative of the AU or season that copper data were collected, the assessor will compare copper results to recommended conservative criteria (Table 2). If copper concentrations exceed the conservative criteria estimate, the AU will be listed as impaired. Follow-up monitoring will be required to confirm the results.

8 TMDL Targets

For AUs identified as impaired and needing TMDLs for copper, TMDL targets and subsequent load and wasteload allocations will be based on a conservative percentile of IWQCs derived from 24 monthly samples (section 5.5.2) or an appropriate statistical approach (section 5.5.3). If applicable, seasonal load and wasteload allocations may be developed (section 5.5.4).

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