Monitoring for Inputs to the Biotic Ligand Model—Draft Monitoring Plan

Problem Statement

In 2015, the Idaho Department of Environmental Quality (DEQ) initiated rulemaking to update the existing hardness-dependent copper criteria by using the US Environmental Protection Agency's (EPA's) 2007 304(a) copper criteria, which uses other physicochemical properties of the water (e.g., pH, dissolved organic carbon) to predict water-body specific criteria using the Biotic Ligand Model (BLM). This update is a reasonable and prudent alternative identified in the National Oceanic and Atmospheric Administration's (NOAA's) biological opinion (BiOp) on Idaho's criteria for toxic substances to support aquatic life. To derive copper criteria using the BLM, inputs for the following physical and chemical characteristics of the water must be measured: temperature, pH, alkalinity, and the concentration of copper, dissolved organic carbon (DOC), calcium, magnesium, sodium, potassium, sulfate, and chloride.

While some data are available from state and national monitoring efforts, it is not geographically representative. In addition, there are very little DOC data available in Idaho. Therefore, when evaluating and implementing the BLM, DEQ will need to have some information on basic defaults that can be used when data are unavailable for a site. EPA and Oregon have recommended a regional approach to default inputs based on data collected from other locations. In its BiOp, NOAA recommends using critical default BLM criteria derived from data collected during the critical time period (late summer to early fall).

Like all equation- or model-based criteria, BLM-derived criteria are site and time specific. However, because the BLM is particularly sensitive to DOC and pH, it is possible to identify the critical time period for copper toxicity (i.e., when DOC is expected to be at its lowest concentrations). In the intermountain west, DOC is generally at its lowest during late summer baseflows. Therefore, by monitoring in late summer or early fall, we can identify critical BLM criteria for waters throughout the state.

The goal of this monitoring effort is to inform guidance development by identifying critical BLM criteria for copper that can be used for implementing the copper criteria when site-specific data are not available. The following questions will be addressed:

- What are the current copper and BLM conditions at locations throughout the state?
- Can Idaho waters be classified into regions based on physical and chemical properties, and can existing classifications be used to group waters (e.g., terrestrial ecoregions, freshwater ecoregions, basins and stream order, etc.)?
- Can critical BLM conditions be identified for each classification, and can these be used in place of derived BLM criteria when site-specific data are missing?

Intended Usage of Data

Data will be used to investigate classification of Idaho waters and to derive critical copper concentrations to inform guidance development. Possible classification systems to be explored may include EPA ecoregions, Idaho bioassessment site classes, or hydrological basins.

General Overview of Project

Sites will be monitored for the following physical and chemical parameters:

Physical Parameters	Chemical Parameters		
Temperature (°C)	Ca	Mg	Na
pH	K	SO_4	Cl
Specific conductance[a]	Alkalinity	DOC	Cu
Dissolved oxygen[a]	TN* (TKN+NO_3+NO_2)	TP*	

[a] Not a BLM parameter

Physical parameters will be measured with a calibrated probe. Chemical parameters will be collected as a grab sample from a well-mixed area of the water body. Samples will be analyzed by the contract laboratory.

Project Timetable

All sites will be sampled between August 15 and October 15, 2016. Monitoring results will be available for analysis by November 30, 2016. Reporting will be completed by January 31, 2017.

Selection of Sampling Sites

Site selection will be targeted to address likely data deficiencies in areas where changes to the copper criteria are likely to be implemented.

There are 140 minor dischargers in Idaho. Monitoring will occur downstream and upstream of minor industrial and municipal discharge facilities and upstream and downstream of dischargers with current copper limits. This monitoring will provide DEQ with both ambient and mixed effluent water quality information at each facility, and can be used to provide data necessary for analysis and possible permit development after criteria are updated to the BLM. In addition, upstream ambient data can be used to estimate BLM IWQCs for upstream waters and to provide the basis for site classification.

Downstream monitoring will occur far enough below the outfall to allow for sufficient mixing of effluent with the receiving water.

Sampling Procedure

Do not handle sunscreen, insect repellant, or any other possible contaminant prior to sampling. Be careful not to disturb the area upstream of where sample is to be collected.

Samples must be delivered to the contract laboratory within 48 hours of collection. Crews must make arrangements to have samples either hand delivered or shipped accordingly and must coordinate with the laboratory to receive and preserve samples upon receipt.

The following procedure will be followed at each sampling location:

1. Navigate to sample location and identify well-mixed portion of stream for sample collection.
2. Record SiteID, Site Name, Date and Time of Collection, Name of Collector, and GPS Coordinates on field form.
3. Describe location, including directions to site, how to access site, and any other relevant information regarding accessing sampling location (e.g., "waded out from boat launch").
4. Take photos of sampling location and other important features.
5. Using pencil or indelible marker, pre-label all sample containers with the following:
   - SiteID
   - Site name
   - Date and time of sample collection
   - Preservative (if used)
   - Name or initials of collector
6. Put on nitrile gloves.
7. Facing upstream, hold calibrated multiparameter probe or sonde at 0.5 m depth in well-mixed portion of the stream. Allow measurements to equilibrate (may take over 2 minutes), then record temperature (°C), specific conductance, and pH.
8. Facing upstream, hold labeled copper bottle from the base. Invert bottle, remove cap from sample container, and plunge into water to a depth of approximately 15 cm. Tip mouth upward toward surface. Allow bottle to fill completely, remove from the water, then cap tightly. Place the sample into a zip-sealed plastic bag, then place into cooler with wet ice.
9. Repeat with labeled DOC sample bottle.
10. Pull corners of labeled cubitainer to inflate—**do not blow into cubitainer** to inflate. Rinse three times with stream water. Collect sample from a depth of approximately 15 cm below surface. Fill cubitainer completely, with no headspace. Screw cap tightly into place, then seal with black electrical tape wrapped clockwise around base of cap. Place cubitainer into cooler with wet ice.
11. Decontaminate any wading gear following the decontamination procedure outlined in the BURP field manual for streams (*www.deq.idaho.gov/media/60176695/burp-field-manual-streams.pdf*). Rinse decontaminated gear with copious amounts of distilled water before sampling at next site.

Quality Assurance/Quality Control

The following table presents the sampling container, parameter, analytical method, preservative, and holding times for water chemistry samples. Raw samples will be delivered to the contract laboratory within 48 hours. The laboratory will filter and preserve aliquots of the raw sample upon receipt.

Sample Container	Parameter	Analytical Method	Preservative	Holding Time
1L Cubitainer	Ca, Mg, Na, K	EPA 200.7	4 °C Filter with 0.45 µm filter within 48 hrs Acidify to pH <2 after filtration	6 months preserved
	Total phosphorus	SM 4500 PF	4 °C Acidify to pH <2	48 hours
	Total nitrogen ($TKN+NO_3+NO_2$)	SM 4500 NO/F	4 °C	7 days
	SO_4, Cl	EPA 300.0	4 °C	28 days
	Alkalinity	SM 2320 B	4 °C	14 days
250-mL amber glass with TFE septa	DOC	SM 5310 B	4 °C Filter with 0.45µm filter within 48 hrs Acidify to pH <2 after filtration	7 days
500-mL plastic bottle	Copper	EPA 200.8	Filter with 0.45µm filter within 48 hrs 4 °C Nitric acid within 2 weeks	6 months preserved

Data quality will be assessed through measurement of accuracy and precision. The following table presents the type, frequency, and data quality objective (DQO) for measures of accuracy and precision.

Measure	Frequency	Type	DQO
Accuracy	10% of all samples	Laboratory control samples or matrix spikes	%Recovery ±25%
Precision	10% of all samples	Field duplicates	Relative Percent Difference ±25%
	10% of all samples	Lab duplicates	Relative Percent Difference ±25%