Aquatic Life Water Quality Criteria for Freshwater Copper: Application of the Biotic Ligand Model (BLM) for National Pollutant Discharge Elimination System (NPDES) and Massachusetts Surface Water Discharge (SWD) Permits

Massachusetts Department of Environmental Protection

Commonwealth of Massachusetts
Executive Office of Energy and Environmental Affairs
Kathleen Theoharides, Secretary
Massachusetts Department of Environmental Protection
Martin Suuberg, Commissioner

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Table of Contents

List of Tables

List of Acronyms

AWQC	Ambient Water Quality Criteria
BLM	Biotic Ligand Model
CMR	Code of Massachusetts Regulations
DOC	Dissolved Organic Carbon
EPA	United States Environmental Protection Agency
MassDEP	Massachusetts Department of Environmental Protection
NPDES	National Pollutant Discharge Elimination System
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
SOP	Standard Operating Procedures
SWD	Surface Water Discharge
TOC	Total Organic Carbon
USGS	United States Geological Survey
WER	Water Effect Ratio

1.0 Introduction

In aquatic systems, metal bioavailability refers to the concentration of soluble metal that adsorb onto, or absorb into and across, membranes of living organisms. The greater the bioavailability, the greater the potential for bioaccumulation, leading to increased toxicological effects (de Paiva Magalhães et al., 2015). Increased metal bioavailability may be beneficial to aquatic organisms; some metals, like copper, are essential micronutrients. Increased copper bioavailability beyond required levels, however, can cause sub-lethal or lethal effects (Eisler, 1998; Scannell, 2009). Elevated copper concentrations in aquatic species can cause growth impacts, metabolic inhibition, photosynthetic issues, reduced feeding, reduced reproduction, gill damage in aquatic invertebrates, olfactory response changes in freshwater fish species, and adverse behavioral effects (Eisler, 1998; Sommer et al., 2016). Copper enters surface waters through atmospheric deposition, weathering, discharges, and other anthropogenic activities (ATSDR, 2004). Copper bioavailability is affected by numerous water chemistry parameters, including pH, total hardness, and dissolved organic carbon (DOC). For example, as DOC increases, the bioavailability of copper decreases (Santore et al., 2001).

In 2007, the U.S. Environmental Protection Agency (EPA) updated the 1996 national recommended ambient water quality criteria (AWQC) for acute and chronic copper exposure in fresh water by releasing the *Aquatic Life Ambient Freshwater Quality Criteria - Copper* (USEPA, 2007). The recommended AWQC for copper are protective of surface waters if the acute 24-hour average is not exceeded more than once every three years and the chronic four-day concentration is not exceeded more than once every three years. The revised guidance is based on the *Biotic Ligand Model* (BLM), a metal bioavailability model that calculates instantaneous acute and chronic dissolved copper criteria values using water chemistry parameters (temperature, pH, DOC, calcium, magnesium, sodium, potassium, sulfate, chloride, and alkalinity) as inputs. Instantaneous copper criteria values generated by the BLM will therefore vary by site because water chemistry affects copper accumulation at biochemical receptors on the surface of aquatic organisms and can lead to toxicity (USEPA, 2007).

The Massachusetts Department of Environmental Protection (MassDEP) amended the Massachusetts Surface Water Quality Standards (314 CMR 4.00) in 2021. The amendments to the Surface Water Quality Standards included adoption of EPA's 2007 AWQC guidance for copper in fresh water (BLM version 2.2.3). This document provides guidance for the design and implementation of Quality Assurance Project Plans (QAPPs) for generating minimum required data for calculating site-dependent copper criteria values using the BLM, directions to calculate instantaneous criteria values using the BLM, and information on how final site-dependent criteria values based on the BLM will be calculated to determine acute and chronic copper effluent limits in National Pollutant Discharge Elimination System (NPDES) and Massachusetts Surface Water Discharge (SWD) permits. If appropriate existing[1] or new[2] data are not available to generate site-dependent criteria values based on the BLM, copper criteria values calculated using hardness-dependent equations will be used in the permitting process. Any adjustments to the hardness-dependent criteria values, such as through the use of a Water Effect Ratio (WER), are subject to MassDEP approval and a separate promulgation process required for listing in

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[1] As defined in Section 4.0.

[2] As defined in Section 5.0.

Table 28, *Site-Specific Criteria*, in the Massachusetts Surface Water Quality Standards (314 CMR 4.00). If both hardness-dependent and BLM instantaneous criteria values are calculated or are able to be calculated for a waterbody, then the site-dependent criteria values generated from the BLM supersede the hardness-dependent criteria for use in NPDES and SWD permits.

2.0 Site Information / Definition

Throughout this document, a site is defined as a segment of a waterbody that receives effluent discharge(s) and includes, where applicable, ambient upstream water, effluent discharge(s) incompletely mixed with ambient water (i.e., "mixing zone"), and completely mixed ambient downstream water. Site determination and sampling locations must capture the spatial and temporal variability of water quality parameters in the waterbody for the duration of data collection. Site-dependent criteria values calculated using the BLM must provide protection for the entire site and further downstream waters across the range of water quality conditions that can increase copper bioavailability at that site. Both site determination and sampling locations will depend on several factors, such as the number of known effluent discharges, location(s) of effluent discharges, waterbody type, and other hydrological features. Additional information regarding sampling location selection can be found in the template QAPP in Appendix C, Section 8.0.

3.0 Determining Applicable Criteria

Facilities that do not have sites with appropriate existing water quality data (See Section 4.0) to calculate site-dependent copper criteria values using the BLM, and are not planning to collect new data, are subject to the hardness-dependent criteria in the Massachusetts Surface Water Quality Standards (314 CMR 4.00).

Facilities that have sites for which appropriate and sufficient water quality data are available to calculate site-dependent copper criteria values using the BLM are ineligible to use hardness-dependent criteria. Only the final copper criteria values for acute and chronic copper exposure calculated by MassDEP and EPA permit writers will apply to these facilities. Regardless of how copper criteria are determined, the frequency and duration components of the copper criteria as specified in the Massachusetts Surface Water Quality Standards (314 CMR 4.00; Table 29a) apply.

If using the BLM, MassDEP and EPA permit writers will determine permit effluent limits using data from one of three options to calculate site-dependent final criteria values: (1) previously collected (existing) data that meet MassDEP requirements; (2) new data collected under a MassDEP-approved QAPP; or (3) previously collected data in conjunction with additional, new sampling data under a MassDEP-approved QAPP. See Appendix A for a decision tree outlining this process. If sufficient[3] data are available at the time of permit development for use in the BLM, then those data will be used to calculate site-dependent criteria to determine permit effluent limits. If sufficient[3] data are not available, hardness-dependent equations for respective acute and chronic exposure will be used to calculate copper criteria and permit effluent limits.

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[3] As defined in Section 4.0 and Section 5.0.

4.0 Use of Existing Data

Existing data include ambient upstream sampling by facilities collected and reported as part of NPDES and SWD permit requirements, water quality data collected by MassDEP, and water quality data collected under a MassDEP-approved sampling plan and QAPP. To calculate site-dependent final criteria values based on the BLM to determine permit effluent limits, MassDEP and EPA permit writers will use existing facility-reported data that meet the following MassDEP requirements:

a. Data cannot be older than 10 years from the anticipated permit start or renewal date.
b. There must be at least 5 continuous years of data for all 10 BLM-required input parameters (listed in Table 1*).
c. Site-dependent criteria values calculation will include only the 5 most recent years of data.
d. There must be at least 20 sampling events[4] in the 5 most recent years of data (i.e., at least quarterly sampling) that capture temporal variability in the waterbody.
e. Data must be from locations that are representative[5] of water quality conditions in the waterbody.
f. Data must have been collected under normal facility operations.

These requirements will establish data currency, representativeness, and appropriate use in the development of site-dependent copper criteria values using the BLM.

*In some cases, facilities may only have previously collected total organic carbon (TOC) data and not dissolved organic carbon (DOC), which is required for the BLM software. In these scenarios, a TOC-to-DOC conversion will be used. The United States Geological Survey (USGS) developed a TOC-to-DOC conversion for surface waters in Massachusetts (Equation 1) (Armstrong et al., *in-prep*). Facilities that wish to collect new data under MassDEP-approved QAPPs must measure DOC and therefore will not require a TOC-to-DOC conversion.

Equation 1. TOC-to-DOC conversion (Armstrong et al., *in-prep*).

$$DOC\ (\frac{mg}{L}) = 0.858 * TOC(\frac{mg}{L}) - 0.196$$

5.0 New Data Collection

If appropriate existing water quality data (see Section 4.0) are not available for calculating site-dependent copper criteria values using the BLM, a sampling QAPP can be developed and implemented by a facility to collect appropriate new water quality data. If a facility chooses to collect new data, the data collection process must be completed prior to issuance of a new permit or renewal of an existing permit.

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[4] A sampling event consists of all samples collected during the same calendar day (i.e., a sampling day).

[5] As defined in Section 5.0 and Appendix C, Section 8.0.

To characterize spatial variability at stream and river sites, sampling will be conducted at in-river upstream and effluent point of discharge locations. For discharges into a lake or reservoir, sampling will be conducted in locations that are representative[5] of water quality conditions in the waterbody, outside the influence of effluent discharge(s), and, where possible, away from outflow(s). Facilities must coordinate with MassDEP on site selection prior to the start of sample collection.

Where possible, a minimum of 20 sampling events[6] over two years spaced at least monthly apart must occur to capture temporal variability. In addition to the input parameters (Table 1) required to generate site-dependent criteria values using the BLM, MassDEP also recommends the collection of dissolved copper using appropriate (e.g., EPA Method 1669) clean techniques for metals sampling.

All sampling must occur under normal facility operations with dry[7] hydrological conditions. Due to potential spatial and temporal variability, multiple sampling locations, sampling at multiple depths within the water column, more frequent sampling, or more samples than the minimum may be required for representative water quality data. See Appendix C, Section 8.0 for further details regarding required sampling procedures.

6.0 Quality Assurance Project Plan

The draft and final QAPPs shall be submitted to MassDEP for review and approval prior to initiation of monitoring. The QAPP must describe the data collection study to be undertaken by a facility or facilities for development of site-dependent criteria values for copper using the BLM software. The QAPP should be formatted to an industry standard (e.g., EPA QA/R-5) and include the following elements:

a. Project organization, distribution, and relevant agency approvals.
b. Project / Task overview, definition, background, and schedule.
c. Training, certifications, documents, and records.
d. Facility description and effluent characteristics, including effluent copper levels.
e. Data quality objectives and performance criteria.
f. Sample design, requirements, procedures, handling, and tracking.
g. Field and laboratory analytical method requirements and procedures.
h. Instrument and equipment calibration, testing, inspection, and maintenance.
i. Quality assurance and quality control requirements.
j. Data acquisition, management, verification, validation, and usability requirements and procedures.
k. Assessment and response actions.
l. Project evaluation and reporting procedures.
m. Field standard operating procedures, including clean metals sampling for both in-river and effluent sampling.
n. Laboratory quality assurance plans and standard operating procedures.

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[6] A sampling event consists of all samples collected during the same calendar day (i.e., a sampling day).

[7] There shall be no wet weather sampling; antecedent dry is defined as less than 0.1 inches of rain for 72 hours prior to sampling.

o. Consultation summary of communication with MassDEP during the design and approval process of the QAPP.

A QAPP template (Appendix C) and Standard Operating Procedure (SOP) examples (Appendices D and E) are included in this document. The QAPP template and SOP examples are intended to aid the development of facility-specific QAPPs for data collection required to generate site-dependent criteria values using the BLM software.

7.0 Quality Assurance / Quality Control

Throughout the sampling and reporting process, quality assurance (QA) and quality control (QC) must be documented. Standard methods must be employed, and QA/QC procedures must be included in the submitted QAPP to MassDEP. Suggested QA/QC procedures for field sampling and laboratory analyses can be found in Appendix C, Sections 7.0 through 13.0.

8.0 Report Requirements

After data collection and analyses are complete, facilities will submit draft and final reports to MassDEP that must include background information, sampling and analysis information, results of QC sampling, and any other deliverables as defined in the approved QAPP. MassDEP recommends the reports follow the outline below:

Background Information

a. Name and location of the discharger(s)
b. Description of the effluent and receiving water
c. Identity of the samplers and laboratory
d. Detailed description of the site, including a map with sampling locations clearly defined

Quality Assurance Planning

a. Consultation summary of communication with MassDEP during the design and approval process of the QAPP

Sampling and Analysis Description

a. Identification and description of each sampling location
b. Date and time of each sampling event of the upstream and effluent point of discharge location(s)
c. Procedures used to obtain, transport, and store the samples
d. Any pretreatment (e.g., filtration) of the effluent and site water samples
e. Effluent flow during each sampling event
f. Meteorological conditions, including rainfall, from the preceding two weeks
g. Testing methods for field and laboratory analyses
h. Field and laboratory equipment calibration and maintenance logs

Quality Control Sample Results

a. Field blanks and duplicates data (raw, final, and summary)
b. Laboratory blanks and duplicates data (raw, final, and summary)
c. Discussion of field and laboratory results and data quality

Sample Results

a. Raw, final, and summary sampling data for upstream and effluent point of discharge locations

In the reports, all final data must have units as noted in Table 1. Once submitted for approval, MassDEP and EPA will review the sampling data, run the BLM software, and calculate the final site-dependent copper criteria values for acute and chronic exposure based on the procedure described in Section 9.0. Only the final site-dependent copper criteria values calculated by MassDEP and EPA permit writers will be used to determine permit effluent limits for copper.

Table 1. Parameters required for the copper BLM.

Analyte	Units	Recommended Reporting Resolution	Recommended Minimum Reporting Limit[8]
Alkalinity, Total	mg/L as $CaCO_3$	1 digit after decimal	1.0
Calcium, Dissolved	mg/L	1 digit after decimal	0.5
Chloride, Dissolved	mg/L	1 digit after decimal	0.5
Dissolved Organic Carbon	mg/L	1 digit after decimal	0.5
Magnesium, Dissolved	mg/L	2 digits after decimal	0.05
pH	SU	1 digit after decimal	N.A.
Potassium, Dissolved	mg/L	1 digit after decimal	1.0
Sodium, Dissolved	mg/L	1 digit after decimal	0.5
Sulfate, Dissolved	mg/L	2 digits after decimal	0.10
Temperature	°C	1 digit after decimal	N.A.

9.0 Site-Dependent Criteria Development

MassDEP and EPA will calculate final site-dependent copper criteria values using appropriate[9] data from upstream sites submitted by the facility in their final report. Site-dependent criteria values based on water chemistry are generated using the BLM software, which is available on MassDEP's website (https://www.mass.gov/regulations/314-CMR-4-the-massachusetts-surface-water-quality-standards).

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[8] Facilities can report data using a lower Minimum Reporting Limit (MRL); however, the MRL should, if possible, not be higher than the recommendations listed in Table 1.
[9] As defined in Sections 4.0 and 5.0.

The BLM software provides instantaneous dissolved copper criteria values for each set of input parameters (i.e., a sampling event that includes all ten parameters listed in **Table *1***). Thus, 20 sampling events will result in 20 instantaneous criteria values for both acute and chronic criteria. When determining the final site-dependent criteria values for acute and chronic copper exposure using the BLM, the values must be protective of the waterbody (i.e., its designated use for aquatic life) under a variety of circumstances (e.g., flow differences, seasonal variation, etc.), and must not be exceeded more than once every three years. Thus, the 10th percentile of acute and chronic instantaneous criteria values generated from the BLM software will be used to calculate the final site-dependent acute and chronic copper criterion values, respectively. If there are endangered species (as defined in the federal Endangered Species Act or Massachusetts Endangered Species Act) within the watershed, the 5th percentile shall be used. See Appendix A for a flowchart on the process to generate site-dependent criteria values and Appendix B for application of the BLM using hypothetical site data.

If there are applicable data to calculate criteria values for a site using the BLM, then the site-dependent criteria values calculated from the BLM shall be used for the site. If both hardness-dependent and BLM criteria values are calculated or are able to be calculated for a site, the BLM criteria values will apply.

10.0 References

Agency for Toxic Substances and Disease Registry (ATSDR). 2004. Toxicological Profile for Copper. U.S. Department of Health and Human Services, Public Health Service, Division of Toxicology/Toxicology Information Branch.

Armstrong, D.S., Savoie, J.G., DeSimone, L., Laabs, K., and R.O. Carey. *In-prep*. Surface-Water-Quality Data to Support Implementation of Revised Freshwater Aluminum Water-Quality Criteria in Massachusetts, 2018-19. United States Geological Survey (USGS).

Eisler, R. 1998. Copper hazards to fish, wildlife, and invertebrates: a synoptic review. Biological Science Report 1997-0002. United States Geological Survey.

de Paiva Magalhães D., da Costa Marques M.R., Baptista D.F., and D.F. Buss. 2015. Metal bioavailability and toxicity in freshwaters. Environmental Chemistry Letters. Volume 13(1): 69-87.

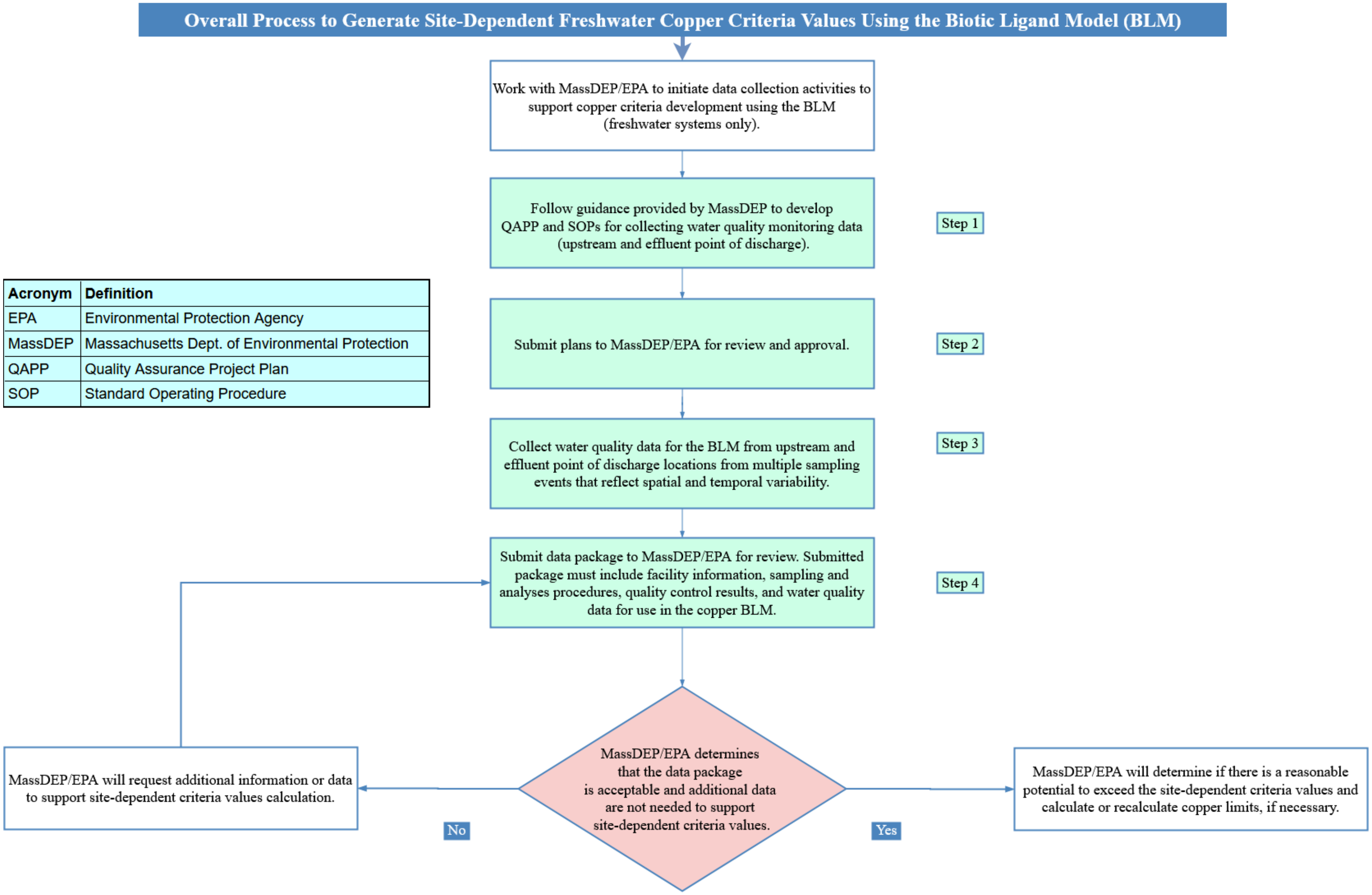
Santore, R.C., Di Toro, D.M., Paquin, P.R., Allen, H.E., and J.S. Meyer. 2001. Biotic Ligand Model of the Acute Toxicity of Metals. 2. Application to Acute Copper Toxicity in Freshwater Fish and *Daphnia*. Environmental Toxicology and Chemistry. Volume 20(10): 2397-2402.

Scannell, P.W. 2009. Effects of Copper on Aquatic Species: A review of the literature. Alaska Department of Fish and Game, Division of Habitat. Technical Report No. 09-04.

Sommers, F., Mudrock, E., Labenia, J., and D. Baldwin. 2016. Effects of salinity on olfactory toxicity and behavioral responses of juvenile salmonids from copper. Aquatic Toxicology. Volume 175: 260-268.

United States Environmental Protection Agency (USEPA). 2007. Aquatic Life Ambient Freshwater Quality Criteria – Copper. Office of Water. EPA-822-R-07-001.

Appendix A: Data Collection Decision Process



Overall Process to Generate Site-Dependent Freshwater Copper Criteria Values Using the Biotic Ligand Model (BLM)

Acronym	Definition
EPA	Environmental Protection Agency
MassDEP	Massachusetts Dept. of Environmental Protection
QAPP	Quality Assurance Project Plan
SOP	Standard Operating Procedure

Appendix B: Example Criteria Values Calculation Process

The BLM accepts input values for each parameter within a range that reflects lower and upper limits (Table 2). If input parameter values are outside the corresponding BLM range, the nearest acceptable input parameter value will be used (i.e., the lower or upper limit).

Table 2. Range of acceptable inputs for each parameter in the BLM.

Input Parameter	BLM Range
Temperature (°C)	10 – 25
pH (SU)	4.9 – 9.2
Cu (µg/L)[1]	--
DOC (mg/L)	0.05 – 29.65
Humic Acid (%)[2]	10 – 60
Ca (mg/L)	0.204 – 120.24
Mg (mg/L)	0.024 – 51.9
Na (mg/L)	0.16 – 236.9
K (mg/L)	0.039 – 156
SO_4 (mg/L)	0.096 – 278.4
Cl (mg/L)	0.32 – 279.72
Alkalinity (mg/L of $CaCO_3$)	1.99 – 360
Sulfide (mg/L)[3]	--

[1] Copper is not required for criteria value calculations, as the BLM will predict the metal concentration that results in acute toxicity (HydroQual, Inc., 2005).
[2] Humic acid content is typically not measured; therefore, a default value of 10% is used (HydroQual, Inc., 2005).
[3] Sulfide is not measured, nor is it incorporated into the BLM through the software; therefore, a near-zero value is used (HydroQual, Inc., 2005).

The following example in

Table ***3*** uses hypothetical site data and is intended for informative use only. Instantaneous acute and chronic copper criteria values are calculated for each sampling event, with the final criteria values determined by percentile calculations. Percentiles are statistical measures indicating the value below which a given percentage of observations in a group falls. For example, a 10th percentile final criterion value is greater than 10% of all instantaneous criteria values in a dataset.

Table 3. Example instantaneous criteria value calculations using the BLM and a hypothetical upstream dataset (monthly sampling over two calendar years).

Date of Concurrent Sampling	Temp. (°C)	pH (SU)	Cu[1] (µg/L)	DOC (mg/L)	Humic Acid[2] (%)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO_4 (mg/L)	Cl (mg/L)	Alkalinity (mg/L of $CaCO_3$)	S[3] (mg/L)	Acute Criterion (µg/L)	Chronic Criterion (µg/L)
1/5/2019	2.0	8.0	2.5	3.9	10.0	110.0	23.00	110.00	8.0	180.0	140.0	232.0	1E-10	34.8	21.6
2/5/2019	1.0	7.3	2.0	6.7	10.0	91.0	20.00	73.00	7.0	120.0	77.0	256.0	1E-10	28.0	17.4
3/5/2019	3.5	8.5	1.7	4.5	10.0	91.0	22.00	110.00	8.0	160.0	130.0	208.0	1E-10	55.5	34.5
4/5/2019	19.0	9.0	1.4	4.8	10.0	65.0	21.00	120.00	8.0	160.0	140.0	240.0	1E-10	113.9	70.7
5/5/2019	22.0	8.3	1.9	4.5	10.0	73.0	24.00	130.00	7.0	180.0	160.0	173.0	1E-10	69.4	43.1
6/5/2019	24.0	8.8	3.5	4.6	10.0	55.0	21.00	110.00	7.0	140.0	130.0	142.0	1E-10	105.3	65.4
7/5/2019	20.0	8.0	2.6	6.0	10.0	39.0	10.00	46.00	6.0	61.0	53.0	116.0	1E-10	52.4	32.6
8/5/2019	32.0	8.5	2.4	5.4	10.0	43.0	18.00	84.00	8.0	100.0	92.0	124.0	1E-10	111.7	69.4
9/5/2019	22.5	8.8	1.7	4.7	10.0	75.0	21.00	130.00	9.0	160.0	180.0	194.0	1E-10	108.9	67.6
10/5/2019	18.0	9.1	1.7	5.2	10.0	68.0	20.00	120.00	9.0	150.0	140.0	187.0	1E-10	124.6	77.4
1/5/2020	5.0	8.9	1.4	4.1	10.0	86.0	22.00	120.00	8.0	160.0	140.0	236.0	1E-10	66.0	41.0
2/5/2020	1.0	8.6	1.9	4.1	10.0	80.0	21.00	110.00	7.0	160.0	120.0	226.0	1E-10	51.3	31.9
3/5/2020	10.0	8.9	1.1	4.8	10.0	83.0	22.00	110.00	8.0	160.0	120.0	232.0	1E-10	85.6	53.1
4/5/2020	19.0	9.0	1.4	4.8	10.0	65.0	21.00	120.00	8.0	160.0	140.0	240.0	1E-10	113.8	70.7
5/5/2020	21.0	8.8	1.3	5.0	10.0	54.0	19.00	120.00	7.0	140.0	130.0	180.0	1E-10	108.6	67.4
6/5/2020	23.5	8.8	1.5	5.1	10.0	50.0	18.00	98.00	8.0	140.0	100.00	150.0	1E-10	112.3	69.8
7/5/2020	29.0	8.1	3.1	6.0	10.0	48.0	9.00	27.00	8.0	56.0	25.00	148.0	1E-10	65.9	40.9
8/5/2020	24.5	8.5	1.9	5.1	10.0	60.0	13.00	68.00	9.0	100.0	74.00	146.0	1E-10	87.1	54.1
9/5/2020	24.0	7.9	1.6	7.0	10.0	29.0	5.00	9.00	5.0	20.0	7.00	106.0	1E-10	47.9	29.7
10/5/2020	17.0	8.3	1.9	4.3	10.0	55.0	11.00	48.00	9.0	84.0	49.00	144.0	1E-10	49.1	30.5

Date of Concurrent Sampling	Temp. (°C)	pH (SU)	Cu[1] (µg/L)	DOC (mg/L)	Humic Acid[2] (%)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO_4 (mg/L)	Cl (mg/L)	Alkalinity (mg/L of $CaCO_3$)	S[3] (mg/L)	Acute Criterion (µg/L)	Chronic Criterion (µg/L)
10th Percentile	--	--	--	--	--	--	--	--	--	--	--	--	--	**46.6**	**28.9**

[1] Copper is not required for criteria value calculations, as the BLM will predict the metal concentration that results in acute toxicity (HydroQual, Inc., 2005).

[2] Humic acid content is typically not measured; therefore, a default value of 10% is used (HydroQual, Inc., 2005).

[3] Sulfide is not measured, nor is it incorporated into the BLM through the software; therefore, a near-zero value is used (HydroQual, Inc., 2005).

In this hypothetical example, 20 concurrent measurements of temperature, pH, DOC, calcium, magnesium, sodium, potassium, sulfate, chloride, and alkalinity were reported to MassDEP from a facility located within a watershed with no federal or state-listed endangered species. Using the BLM software (version 2.2.3) and default humic acid and sulfide values of 10% and $1*10^{-10}$, respectively, 20 acute and chronic instantaneous criteria values were generated from the dataset. As described in Section 9.0 and Appendix A, 10th percentile calculations are used to calculate final copper criteria values for this example dataset. Thus, the final site-dependent acute criterion value is 46.6 µg/L (the 10th percentile value from all 20 acute instantaneous criteria values), and the final site-dependent chronic criterion value is 28.9 µg/L (the 10th percentile value from all 20 chronic instantaneous criteria values).

References

HydroQual, Inc. 2005. The Biotic Ligand Model Windows Interface, Version 2.2.3: User's Guide and Reference Manual. Mahwah, New Jersey.

Appendix C: Quality Assurance Project Plan Template

TEMPLATE

QUALITY ASSURANCE PROJECT PLAN

Water Quality Monitoring for Site-Dependent Application of the Copper Biotic Ligand Model (BLM)

[Owner]

QUALITY ASSURANCE PROJECT PLAN

Water Quality Monitoring for Site-Dependent Application of the Copper Biotic Ligand Model (BLM)

Signature Page

____
____ (Date)

Project Manager

____
____ (Date)

Project QA Officer

____
____ (Date)

Monitoring Coordinator

____
____ (Date)

____
____ (Date)

____
____ (Date)

MassDEP Reviewer
Richard F. Chase
MassDEP Division of Watershed Management, Watershed Planning Program
8 New Bond St., Worcester, MA, 01606
508-767-2859; Fax: 508-791-4131; richard.f.chase@mass.gov

HOW TO USE THIS TEMPLATE:

This Quality Assurance Project Plan (QAPP) template is intended to guide and assist POTWs in developing site-dependent project plans for the collection of water quality data that can be used in applying the Biotic Ligand Model for freshwater copper.

- Yellow-shaded areas denote parts of the QAPP that require project-specific information. Suggested text is provided in some cases in highlighted areas, but the entirety of the final QAPP must reflect the actual project specifications. Edit these areas as needed.

- *Red italicized text* denotes directions to the user (and should be removed for the final QAPP).

- Unmarked text contained herein that is not applicable to the project for whatever reason MUST be deleted as appropriate, in order to adjust the template/final QAPP to the specific project requirements, tasks, and activities.

- Submit the draft QAPP to MassDEP for review and approval prior to beginning work. Communication during development of the QAPP with MassDEP is highly recommended and encouraged.

- Update the final QAPP as needed as changes become necessary (addendums/as-built).

DISCLAIMERS:

There is no requirement to use this template. It is intended to provide guidance and assistance where needed but is not intended to replace more detailed or alternate quality assurance (QA) planning that may take place for specific projects. References to any trade names, commercial products, and/or manufacturers do not constitute endorsement. Web links are provided for convenience and may not function if the URL address has changed.

2.0 TABLE OF CONTENTS (by QAPP Element)

Appendices:

APPENDIX A: In-River Sampling for “Clean” Metals Standard Operating Procedure (SOP) (separate cover)
APPENDIX B: Effluent Sampling for “Clean” Metals SOP (separate cover)
APPENDIX C: Misc. Sampling SOPs
APPENDIX D: Project Forms
APPENDIX E: Laboratory Quality Assurance Plan(s) and Standard Operating Procedures
APPENDIX F: Summary of consultation and communication with MassDEP during the design and approval process of the project plan.

3.0 QAPP DISTRIBUTION AND APPROVAL

The following persons have received a draft review copy and a final copy of this Quality Assurance Project Plan (QAPP):

[insert names, affiliations, contacts information]

4.0 PROJECT ORGANIZATION

4.1 Organization Chart:

[insert organizational structure and related information for the project]

4.2 Responsible Persons, Qualifications, and Training:

See Table 1 for specific descriptions of project staff roles and responsibilities for this project.

For each field monitoring survey event, each crew member will have the following qualifications:

- Familiarity with this QAPP and the sampling SOP(s);
- Completion of field safety/sampling/quality control (QC) training;
- Prior field experience taking samples; and
- Be physically able to access the stations, carry equipment and samples, and perform the sampling.

Table 1. Personnel Responsibilities and Training

Project Personnel, Title and Affiliation	Responsibility	Training	Training Date/ Instructor(s)	Location of Training Records
		CPR-AED and First Aid		
		Health & Safety		
		Multi-probe Use		
		Water quality sampling (general)		
		“Clean” metals sampling		
		Other (as applicable)		

5.0 PROJECT DEFINITION

In 2007, the Environmental Protection Agency (EPA) updated the 1996 national recommended ambient water quality criteria for copper by releasing the *Aquatic Life Ambient Freshwater Quality Criteria - Copper* (USEPA, 2007). As bioavailability for copper is water chemistry-dependent, criteria recommendations in the updated 2007 guidance were developed using the biotic ligand model (BLM) that included 10 input parameters. The updated 2007 copper criteria consider site-dependent water chemistry and remains ecologically protective of aquatic life.

This QAPP outlines quality assurance objectives and procedures that are intended to produce robust input parameter data sets of known and documented quality for potential use with the copper BLM.

This project is intended to generate water quality data for the parameters listed in Table 2 for ambient waters and effluents. These constituents can be used in applying the copper BLM for site-dependent criteria values calculation.

Table 2. Project Analytes

Cu BLM Application (analytes):
Temperature
pH
Dissolved organic carbon (DOC)
Alkalinity, Total
Calcium, Dissolved
Magnesium, Dissolved
Sodium, Dissolved
Potassium, Dissolved
Sulfate, Dissolved
Chloride, Dissolved

6.0 PROJECT OVERVIEW AND SCHEDULE

See Table 3 for the specific project schedule.

Table 3. Project Schedule

Activity	Approx. Date of Initiation	Approx. Date of Completion	Deliverable	Deliverable Due Date
QAPP submittal/review, coordination with labs, and survey preparation			Final QAPP	
Training			Training records	
Field sampling			COC forms, field notes, etc.	
Sample analysis by ________________ laboratories			Lab reports	

Activity	Approx. Date of Initiation	Approx. Date of Completion	Deliverable	Deliverable Due Date
Draft Project Report			Technical Report (draft)	
Submittal of final report to MassDEP			Technical Report (final)	
Submittal of final data to MassDEP external data portal			EDD	

Note: Any modifications to this QAPP will be described in an addendum to this document.

7.0 DATA QUALITY OBJECTIVES AND PERFORMANCE CRITERIA

Monitoring data for this project are intended to meet the specific data quality objectives (DQOs) outlined in Table 4. A brief summary of DQOs for this project is as follows:

7.1 Accuracy

Accuracy is determined by how close a reported result is to the true or expected value. For this project, estimates of laboratory accuracy for metals will be determined by following the policy and procedures provided in the _______________ laboratory's Quality Assurance Plan, generally using estimates of percent recoveries for known internal metal standards, matrix spikes, and performance evaluation samples, as well as evaluation of blank contamination. Accuracy criteria have been defined in terms of percent recovery percentages (e.g., 80-120 % recovery of matrix spike/PE sample).

7.2 Precision

Precision is a measure of the degree of agreement among repeated measurements and is estimated through sampling and analysis of replicate samples. For this project, laboratory precision will be determined by following the policy and procedures provided in the ____________________laboratory's Quality Assurance Plan and individual analytical SOPs for the use of laboratory split (duplicate) samples. Overall precision objectives using relative percent difference (RPD) or standard deviation (SD) of field replicate (sequential, same location) samples were set to less than or equal to 20%.

7.3 Representativeness

Representativeness refers to the extent to which measurements actually represent the true environmental condition. For this project, sampling stations have been selected to ensure that the samples taken represent typical field conditions at the time of sampling, and not anomalies due to site-dependent conditions. For this project, the locations and sampling schedules have been selected to achieve typical/average conditions during baseflow periods.

7.4 Completeness

Completeness refers to the amount of valid data collected using a measurement system. It is expressed as a percentage of the number of valid measurements that should have been collected based on planning for the complete project. For this monitoring, the completeness criterion is 90%.

7.5 Comparability

Comparability refers to the extent to which the data from this study are comparable to other studies. For this project, EPA guidelines and analytical methods for clean metals shall be followed. The data generated in this project may be comparable to data generated by others using clean techniques and approved analytical methods. Given the likelihood of sample contamination from field and/or lab error using non-clean techniques, this project's data should not be compared to data generated using non-clean-technique methods.

7.6 Detection Limits

In general, the smallest amount of analyte that can be detected above signal noise and within certain confidence levels. Typically, Method Detection Limits (MDL) are calculated in the laboratory by analyzing a minimum of seven low-level standard solutions using a specific method. Table 4 shows the MDLs (and RDLs, reporting detection limits) for each analyte.

7.7 Holding Times

Standard holding times (maximum allowed time from collection to analysis) from sample collection to analysis of samples are established to ensure analytical accuracy.

7.8 Performance Auditing

Proficiency testing of laboratory analytical accuracy and precision will be performed for the following project analytes. These are single- and/or double-blind lab quality control (QC) checks using purchased QC check standards or samples. Audit results are compared to "true" values/results, evaluated against acceptance limit criteria and used to help validate the data. Results may also be provided to lab analysts, survey coordinators and data users.

Table 4. Data Quality Objectives

Analyte	Analytical Method(s)	Units	Expected Range (site-dependent)	Method Detection Limit (MDL)	Minimum Reporting Limit (MRL)	Accuracy (+/-)	Overall Precision (RPD or other)
Cu BLM Application:							
Example: Sulfate	*EPA 300.0*	*mg/l*	*0-10*	*0.07*	*0.15 est.*	*80-120 % recovery for QC std., lab fortified blank and matrix*	*20% RPD*
Temperature							
Dissolved Organic Carbon (DOC)							
pH							
Sulfate, Dissolved							
Alkalinity, Total							
Calcium, Dissolved							
Magnesium, Dissolved							
Potassium, Dissolved							
Chloride, Dissolved							
Sodium, Dissolved							
Copper, Dissolved							

8.0 SAMPLING DESIGN

The following sampling strategy is intended to provide sufficient data in terms of location, frequency, type, quantity, timing, and quality to meet project goals for the __________________ facility. Both in-river and effluent water quality will be sampled.

The number of sampling locations will depend on hydrological features and point sources that are expected to change water quality.

For situations where the discharge is to a lake or reservoir, select sampling locations consistent with the objectives outlined below for river sampling and coordinate with MassDEP as needed to ensure appropriate sampling of ambient waters.

For facilities in close hydrologic proximity to one another, there may be advantages to combining data collection efforts for greater economy and cost efficiency. In these situations, the resulting data are applied to individual facilities as applicable, and close coordination with MassDEP is highly recommended.

The **IN-RIVER SAMPLING** is planned as followed:

A) Sampling Locations:

Locations have been selected to characterize water quality upstream of the facility. Upstream locations have been carefully selected to be representative of ambient water conditions, mid-river, fully-mixed/homogenous within cross-section, and outside any mixing zones or interferences/contamination from metal surfaces or objects. See Figure ______ for in-river sampling locations.

B) Sampling Conditions During Sampling:

a. All river sampling will be conducted under average dry weather conditions (i.e., no wet weather sampling; antecedent dry is defined as less than 0.1 inches of rain for 72 hours prior to sampling).
b. Water quality is not impacted by relatively higher nonpoint source inputs of organic matter and suspended solids.
c. Samplers shall attempt to locate grab sampling locations away from any metal surfaces and excessive atmospheric particle fallout (e.g., vehicular traffic, bridges).
d. The discharge facility should be under normal operating conditions (i.e., not influenced by sudden load change).

C) Sampling Frequency and Duration:

In general, sampling will be conducted monthly for 20 consecutive months. The sampling will be simple monthly grabs. Where feasible, continuous pH probes will be installed to provide pH variability data.

D) Type and Number of River Samples:

Cu BLM Application (grabs):	Total # of Samples (min.): UPSTREAM (excluding QC samples)
Temperature	20
pH	20
Dissolved organic carbon (DOC)	20
Alkalinity, Total	20
Calcium, Dissolved	20
Magnesium, Dissolved	20
Sodium, Dissolved	20
Potassium, Dissolved	20
Sulfate, Dissolved	20
Chloride, Dissolved	20

E) Sample Types:

The majority of river samples will be simple discrete "grab" samples. The use of continuous loggers for temperature and pH may also be employed to provide a more robust dataset for in-stream variability. Field meters will be used daily for temperature and pH data.

F) Sampling Methodologies:

Sample collection will follow the river sampling SOP (Appendix #). For metals sampling, Clean Hands (CH)/Dirty Hands (DH) sampling procedures will be employed for every metals sample. All sample handling and analysis will also employ clean techniques to avoid sample contamination. Grab sampling will be via *wade-in/boat sampling (select). If boat sampling employed, describe boat sampling logistics.*

G) Field QA/QC Sampling:
   a. QC Screening Evaluation for Survey #1: QC results for the first survey will be expedited and evaluated prior to the second survey. If acceptable, sampling will continue. If any results indicate unacceptable error (e.g., high copper in field blanks), corrective action will be taken to resolve the problem for future surveys.
   b. Trip blanks: See Section 13.
   c. Field blanks: One per analyte per survey or 20%, as appropriate. The source of field blank water will be deionized water (DIW) from the _______________ lab water purification system. This water will be transported to the project site, where it will be used to pour field blanks. For 4-day metals surveys, one day will be selected for field blank sample collection. Note: The field blank samples are NOT trip blanks. Blanks for filtered analytes will be filter blanks.
   d. Field duplicates: One per analyte per survey or 20%, as appropriate. Field duplicates will be collected simultaneously or sequentially (one after another) at the same location and as close in time as possible. For 4-day metals surveys, one day will be selected for field duplicate sample collection.
   e. QC readings for continuous data loggers: Periodic checks adjacent to deployed data loggers will be collected (as applicable) to assess accuracy.

H) Sample Handling & Preservation:
   a. All samples will be preserved on ice (< 6 deg. C) following collection. See also Table __ for detailed sample preservation requirements.
   b. For dissolved copper, grab samples will be filtered in the field (0.45µ capsule filters) within 15 minutes after collection and before acidification, then placed in plastic bags in the cooler on ice and acidified at the lab ASAP (within 8 hours).
   c. DOC samples will be filtered in the field (preferred)/lab (*select one*) and preserved with HCl as required by the method.

I) Field Sampling Equipment and Materials:
   Samples for dissolved copper (and DOC) will be filtered by … (*describe*) (e.g., using 60 mL plastic (no metal) syringes and 0.45µ disk or capsule filters under clean field/lab sampling protocols).

J) Sample Bottles:
   New, pre-cleaned sample containers will be used for all samples. For metals samples, certified, trace-clean amber glass or HDPE sample bottles will be used. Any re-used glass bottles will be hot water rinsed and acid-washed and DIW-rinsed prior to reuse.

The **EFFLUENT SAMPLING** is planned as followed:

A) Sampling Location(s):
See Figure ______ for effluent sampling location(s) that is (are) representative of the discharge(s) into the receiving water. Samples will be collected where specified in the permit, unless no site is specified in the permit, in which case sampling will be done at the most representative effluent location furthest downgradient of all wastewater inflows prior to discharge into the receiving water. The location(s) actually sampled will be documented in the sampling records. For multiple effluent discharge pipes, flow-weighted composite samples will

be collected in order to characterize overall effluent quality.

B) Sampling Conditions During Sampling:
   a. All effluent sampling will be conducted under average dry weather conditions (i.e., no wet weather sampling; antecedent dry is defined as less than 0.1 inches of rain for 72 hours prior to sampling).
   b. Samplers shall attempt to locate grab sampling locations away from any metal surfaces and excessive atmospheric particle fallout (e.g., vehicular traffic, bridges).
   c. The discharge facility should be under normal operating conditions (i.e., not influenced by sudden load change).
   d. Carbonaceous biochemical oxygen demand and total suspended solid concentrations are within permit limits.

C) Sampling Frequency and Duration:

Sampling will be conducted monthly for 20 consecutive months on the same days as the IN-RIVER sampling.

D) Number of Samples:

Cu BLM Application:	Total # of Samples (min.): EFFLUENT (excluding QC samples)
Temperature	20
pH	20
Dissolved organic carbon (DOC)	20
Alkalinity, Total	20
Calcium, Dissolved	20
Magnesium, Dissolved	20
Sodium, Dissolved	20
Potassium, Dissolved	20
Sulfate, Dissolved	20
Chloride, Dissolved	20

E) Sample Types:

All samples will be 24-hour composites (manual or automated) or grab samples, where appropriate. For this QAPP, it is assumed that all samples will be “clean” regardless of whether taken through grab sampling, manually, or via automated sampling. Field meters will be used for in-situ pH data.

F) Sampling Methodologies:

Sample collection for the effluent will follow the effluent sampling SOP (Appendix #). For metals sampling, Clean Hands (CH)/Dirty Hands (DH) sampling procedures will be employed. All sample handling and lab analyses will also employ clean techniques to avoid sample contamination.

G) Field QA/QC Sampling:
   a. QC Screening Evaluation for Survey #1: QC results for the first survey will be expedited and evaluated prior to the second survey. If acceptable, sampling will continue. If any results indicate unacceptable error (e.g., high copper in trip/field blanks), corrective action will be taken to resolve the problem for future surveys.
   b. Trip blanks: See Section 13.

   c. Field blanks: One per analyte per survey or 20%, as appropriate. The source of field blank water will be deionized water (DIW) from the _______________ lab water purification system. This water will be transported to the project site, where it will be used to pour field blanks. Note: The field blank samples are NOT trip blanks. Blanks for non-filtered samples will be equipment-only (autosampler) blanks and blanks for filtered analytes will be equipment + processing (sampler & filtration step) blanks.
   d. Field duplicates: One per analyte per survey or 20%, as appropriate. Field duplicates will be collected simultaneously or sequentially (one after another), at the same location and as close in time as possible.

H) Sample Handling & Preservation:
   a. All samples will be preserved on ice (< 6 deg. C) following collection. See also Table __ for detailed sample preservation requirements.
   b. For dissolved copper, composite samples collected with an automated sampler will be filtered within 15 minutes after completion of collection and before acidification, then placed in plastic bags in the cooler on ice and acidified at the lab ASAP (within 8 hours).

I) Field Sampling Equipment and Materials:

   Samples for dissolved copper and DOC will be filtered using clean work areas and technique to avoid sample contamination. 0.45µ capsule filters will be used for filtration.

J) Sample Bottles:

   New, pre-cleaned sample containers will be used for all samples. For metals samples, certified, trace-clean amber glass or HDPE sample bottles will be used. Any re-used glass bottles will be hot water rinsed and acid-washed and DIW-rinsed prior to reuse.

Insert Figures _______ for in-river & effluent sampling locations.

9.0 FIELD SAMPLING REQUIREMENTS AND PROCEDURES

9.1 Sampling Methodologies.

See Appendices # and # for in-river and effluent sampling procedures, respectively.

For low level metals, results can be confounded by sample contamination during collection, transport, and laboratory analysis if appropriate steps to avoid contaminant pathways are not taken. Contamination pathways include airborne particulates (dust, vehicle exhaust, human breath, clothing, etc.), cross-contamination between stations, and inadvertent contact with samples. In order to provide a means to generate reliable data at water quality criteria levels, EPA has developed field and analytical methods. EPA Method 1669 provides performance-based guidance for proper field collection of metals samples under a variety of conditions and references EPA analytical methods for determination of specific metal analytes. The sampling procedures outlined in this QAPP are intended to meet the intent of EPA Method 1669 and have been modified based on project logistics. The sampling will be performance-based, and if sample contamination or precision is evident based on QC sampling, corrective actions will be undertaken to resolve the problem.

Sampling equipment/materials to be reused and that will be decontaminated following standard procedures as outlined in Appendices #/# are as follows:

- ..
- ..
- ..

9.2 Field Safety and Training

Survey crews shall use best professional judgment at all times regarding personal safety and follow safety precautions at all times. All sampling personnel have been trained on what to do in the event of an emergency. A fully-stocked first aid kit containing basic first aid equipment shall be available to survey crews at all times. Training in cardiopulmonary resuscitation (CPR)/Automated Electronic Defibrillation (AED) and in basic first aid procedures is recommended. Each crewmember shall bring personal protective gear, such as protective clothing and footgear (i.e., hip boots). At least one cellular phone will be available for all surveys.

9.3 Field Instrument Use

For in-situ pH and temperature measurements, a calibrated __________ meter/probe will be used. Calibration will be performed prior to use and check readings collected following the survey to verify accuracy for survey data.

9.4 Field Documentation

In order to provide a permanent record of field activities and to detect possible sampling error, observations made in the field will be recorded in project notebooks or on standard project field sheets.

- Field Notebooks will be used to record detailed information at each site for each survey, OR Field Sheets will be used at each site and for each survey. Copies of field notes become part of the hard copy file for the project.

- Chain-of-Custody (COC) forms will be filled out for all lab samples with special instruction and/or sample notes made as necessary. COC forms are used to transfer sample custody from survey crews to the analytical labs. The samples received by the lab are then compared with accompanying custody and analysis specification forms to make sure that the paperwork agrees with the labels on each sample container. All individuals who handle samples are required to sign and date the COC forms. Once completed and signed by all involved in the transaction, the completed form(s) become part of the project record.

- Calibration Records: In order to document probe calibrations, adequate recordkeeping will be kept for field and/or lab probe calibrations.

10.0 SAMPLE HANDLING AND TRACKING

10.1 Sample IDs:

Project sample identification numbers have been allocated for individual project samples. Sample labels shall be affixed to sample containers prior to use and clear-taped onto the bottles, if necessary, to prevent loss.

10.2 Sample Transport, Preservation, and Analytical Holding Times:

Coolers will be used to transport all samples on ice. “Clean” metals samples will be kept apart from other samples using plastic bags. Samples requiring filtration will be filtered ASAP following collection consistent with the analytical method. All samples requiring acid-preservation will be preserved at the lab. The analytical holding times for project samples are listed in Table 5.

10.3 Lab Coordination:

Each lab shall be notified several days prior to the survey of the date and estimated time of sample arrival. Appropriate COC forms shall be filled out and signed upon sample receipt by each lab.

Table 5. Container Types and Sample Filtration, Preservation, Holding Time and Method
(Note: some analytes may be grouped into the same bottle in coordination with the lab; bottle size TBD based on groupings)

ANALYTE	BOTTLE TYPE(S)	FILTERING	PRESERVATIVE	HOLDING TIME (DAYS)	ANALYTICAL METHOD
Dissolved organic carbon (DOC)	*Amber glass*	*Yes = STEP 1 (at the lab within 8 hours of collection*	*Yes = STEP 2 (HCl to pH<2 following filtration)*	*28*	*SM 5310-B*
Alkalinity, Total	*HDPE*	*No*	*No*	*14*	*SM 2320-B*
Calcium, Dissolved	*HDPE*	*Yes*	*1:1 HNO3 to pH < 2*	*180*	*EPA 200.7*
Magnesium, Dissolved	*HDPE*	*Yes*	*1:1 HNO3 to pH < 2*	*180*	*EPA 200.7*
Sodium, Dissolved	*HDPE*	*Yes*	*1:1 HNO3 to pH < 2*	*180*	*EPA 200.7*
Potassium, Dissolved	*HDPE*	*Yes*	*1:1 HNO3 to pH < 2*	*180*	*EPA 200.7*
Sulfate, Dissolved	*HDPE*	*Yes*	*No*	*28*	*EPA 300.0*
Chloride, Dissolved	*HDPE*	*Yes*	*No*	*28*	*EPA 300.0*
Copper, Dissolved	*Certified, trace-clean HDPE*	*Yes = STEP 1 (at the lab within 8 hours of collection and before acidification)*	*Yes = STEP 2 (HNO3 to pH<2 after filtration)*	*180*	*EPA 200.8*
Total Hardness (calculated)	---	---	---	---	*SM 2340-B*

11.0 FIELD ANALYTICAL METHOD REQUIREMENTS

11.1 Probe Calibrations and Checks:

For in-situ pH measurements, pH probe calibration will be performed according to manufacturer's instructions and prior to use. Check readings for pH following use will be performed to verify accuracy of survey data.

11.2 Use of Continuous Data Loggers:

For in-situ temperature and pH data collection, continuous data loggers are recommended to evaluate daily variability. The continuous data provides a more robust dataset than discrete grab samples. If used, loggers will be pre-evaluated prior to use for functionality and accuracy. Once deployed, logged pH data will be checked periodically collecting side-by-side readings in the field. Continuous logging for pH can be achieved for short durations prior to recalibration in order to determine typical daily pH ranges in each month.

12.0 LABORATORY METHODS REQUIREMENTS AND PROCEDURES

12.1 ______________________ Laboratory SOPs and Quality Assurance Plans:

All samples will be analyzed using standard lab protocols and in accordance with the _____________ Laboratory's Quality Assurance Plan (QAP). All samples will be analyzed using methods that are consistent with Massachusetts regulations (314 CMR 4.03(6): *Procedures for Sampling and Analyses*).

The ______________ Laboratory has the capability to analyze for low-level metals to ppb levels without sample contamination (i.e., "clean" lab or work stations meeting Federal Standard 209E Class ___ and/or ISO 14644/14698 Class ___). Metals samples will be filtered and acidified using "clean" technique and shall employ ultra-pure HNO_3 for preservation and in the analysis.

Table 6. Field Equipment Calibration, Inspection, and Maintenance

INSTRUMENT	PERSON(S) RESPONSIBLE	FREQUENCY OF CALIBRATION	INSPECTION ACTIVITY AND FREQUENCY	MAINTENANCE ACTIVITY AND FREQUENCY	TESTING ACTIVITY AND FREQUENCY	CORRECTIVE ACTION (CA)	SOP #

INSTRUMENT	PERSON(S) RESPONSIBLE	FREQUENCY OF CALIBRATION	INSPECTION ACTIVITY AND FREQUENCY	MAINTENANCE ACTIVITY AND FREQUENCY	TESTING ACTIVITY AND FREQUENCY	CORRECTIVE ACTION (CA)	SOP #
Example: *pH probe*		*Pre-cal/re-cal prior to and within 24 hours of use* *Post-use QC checks*	*Visual & Electronic; monthly and/or before each use*	*Hardware & Software Repair and maintenance as needed.*	*Pre-survey calibration & post-survey QC checks*	*Re-calibrate as necessary during pre-calibration; censoring or qualifying data if post-survey check indicates excessive drift or inaccuracies in comparison to pre-calibrated readings and standard solutions*	
Temperature Loggers		*Annually, and as needed based on QC checks.*	*Visual & Electronic; Before, during and after each use; if possible, review data while deployed to ensure working order and accuracy*	*NA*	*Annual QC check against NIST-traceable thermometer and PC network clock, per SOP.*	*Replace with working sensor.*	
NIST-traceable thermometer (field)		*Annually, and as needed based on QC checks.*	*Visual & Electronic; Before and after each use*	*As needed*	*Annual comparison to NIST-traceable thermometer*	*Replace unit as needed*	

12.2 Lab Data Reporting

All lab-quality-controlled data will be sent directly to the Project Manager. Quality control sample data shall be included in the laboratory data reports.

12.3 Lab Data Qualifiers

In some instances, qualification of data by the lab(s) may be necessary. If so, appropriate data qualifiers are applied to individual datum and/or sample batches using standard data qualifiers: *check with project lab and insert lab-specific qualifiers here.*

- ND = Not Detected above Reporting limit
- NA = Not Applicable due to high sample dilutions or sample interferences
- NC = Not calculated since analyte concentration is ND.
- J = Estimated value
- J1 = Estimated value due to MS recovery outside acceptance criteria
- J2 = Estimated value due to LFB result outside acceptance criteria
- J3 = Estimated value due to RPD result outside acceptance criteria
- J4 = Estimated value due to LCS result outside acceptance criteria
- E = Estimated value exceeds the calibration range
- L = Estimated value is below the calibration range
- B = Analyte is associated with the lab blank or trip blank contamination. Values are qualified when the observed concentration of the contamination in the sample extract is less than 10 times the concentration in the blank
- R = No recovery was calculated since the analyte concentration is greater than four times the spike level.

13.0 QUALITY CONTROL REQUIREMENTS

Methods employed to verify accuracy and precision of data are performance-based. Alternative procedures may be used provided they result in valid data (e.g., non-detects in metals blanks) with an appropriate level of documentation.

13.1 Field Quality Control:

a) Trip blanks: One per metal analyte for survey #1 to verify clean DI water source for blanks. Following acceptable results for the first survey, then collect at 20% of the remainder of the surveys and as needed if blank contamination is found.
b) Field blanks: Minimum one per analyte per survey. The source of field blank water will be deionized water (DIW) from the _______________ lab water purification system. This water will be transported to the project site, where it will be used to pour field blanks. Note: The field blank samples are NOT trip blanks. Blanks for non-filtered samples will be equipment-only (autosampler) blanks and blanks for filtered analytes will be equipment + processing (sampler & filtration step) blanks.

c) Field duplicates: Minimum one per analyte per survey. Field duplicates will be collected simultaneously or sequentially (one after another), at the same location and as close in time as possible.

d) Performance Evaluation (PE) Samples: At least one set of single- blind (lab knows the sample is for QC purposes, but is unaware of the true concentration)- or double-blind (lab knows neither that the sample is for QC purposes nor the true concentration). Performance Evaluation (PE) samples shall be provided to the lab for selected analytes, including the following (at a minimum):
    - Dissolved Organic Carbon (DOC)
    - Hardness
    - Copper, dissolved

e) QC Screening Evaluation for Survey #1: QC results for the first survey will be expedited and evaluated prior to the second survey. If acceptable, sampling will continue. If any results indicate unacceptable error (e.g., high copper in trip blank and/or field blank), corrective action will be taken to resolve the problem for future surveys.

f) QC readings for continuous loggers (as applicable): Periodic checks adjacent to deployed loggers will be collected to assess logger accuracy.

13.2 Lab Quality Control

Laboratory quality control samples shall include reagent water blanks, lab-fortified blanks, lab-fortified matrix and matrix duplicate samples, and internal quality control samples. Lab QC data shall be provided with the results in the lab reports.

14.0 DATA ACQUISITION REQUIREMENTS

Not applicable (no non-direct data acquisition for this project). *Revise as needed if non-project data are used.*

15.0 DATA MANAGEMENT AND PROJECT DOCUMENTATION

All field (field sheets, notebook, and COC forms) and analytical data for this project will be stored and maintained by the Project Manager. In addition, lab notebooks and data reports shall be kept on file at the respective labs. Field and lab data will be entered into a database for electronic storage. Validated final data will be made available to project partners, as applicable.

Table 7. Project Documentation

SAMPLE COLLECTION RECORDS	HEALTH & SAFETY RECORDS	FIXED LABORATORY RECORDS	DATA AND QA/QC ASSESSMENT RECORDS
Examples: *Field Sheets/Field Notebook*	*MSDS/SDS*	*Chain of Custody (COC) Forms*	*Technical Correspondence regarding data quality*
Chain of Custody (COC) Forms	*Training forms*	*Laboratory Raw Data Reports (including lab QC data)*	*QA/QC section in published reports (e.g. Tech Memos)*
Digital photos	*Corrective Action Forms*	*Electronic Laboratory Data (LIMS, EDD)*	*Database*
Survey-related Correspondence (e.g., e-mail)		*Analytical Instrument Logbooks*	
GPS waypoints		*Laboratory QC Results*	
Probe/logger Raw Data (Hard Copy & digital)		*Reagent Water Control Chart*	
Training forms		*Performance Evaluation Test Results*	
Corrective Action Forms		*Probe Instrument Calibration Logbook, User Reports, and Maintenance Logbook*	
		Automated logger QC data	
		Training forms	

16.0 ASSESSMENT AND RESPONSE ACTIONS

Assessment of raw laboratory data shall be the responsibility of the ________________ lab, using the policy and procedures in the laboratory's Quality Assurance Plan. Subsequently, additional QC review by the Project QA Officer will be conducted as part of data validation and finalizing the data. This review may recommend specific data for qualification or censoring, based on criteria identified in this QAPP and/or SOPs. The review may also result in corrective actions where necessary.

17.0 DATA VERIFICATION AND VALIDATION REQUIREMENTS

Procedures used to verify and validate this project's data will be generally consistent with *Region 1, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses*.

All available field and lab quality control sample data will be reviewed to assess data quality. As needed, project data may be qualified or censored based on the lab data qualification and/or other project QC data that indicate problems and suspect data.

18.0 DATA VERIFICATION AND VALIDATION PROCEDURES

All supporting data and metadata including field sheets, Chain of Custody sheets, laboratory quality control results, outlier analyses, etc. will be used to verify the data. The Project QA Officer shall review the field and laboratory data to determine if the data meet the project's data quality objectives. Data deemed to be suspect or erroneous will be flagged for further review, and qualified or censored as appropriate.

Insert more specific information on how data will be evaluated for the project.

19.0 DATA USABILITY AND PROJECT EVALUATION

The project will be evaluated against the following criteria for success:

1) The generation of usable, validated data meeting the DQOs outlined in this QAPP; and/or
2) Sufficient quantity and quality of data for use in the copper BLM.

"BLM" data will be used directly as input parameters in the BLM software to calculate site-dependent copper criteria.

20.0 PROJECT REPORTING

Final data shall be submitted to MassDEP data portal following the instructions here: http://www.mass.gov/eea/agencies/massdep/water/watersheds/external-data-submittals-for-the-wpp.html.

A final project report will also be generated and will include the raw data, final data, and a discussion of field and lab data quality. This report will be submitted to MassDEP.

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Appendix D: Standard Operating Procedure for Effluent Metals Sampling Example

EXAMPLE

Standard Operating Procedure for Effluent "Clean" Metals Sampling

HOW TO USE THIS EXAMPLE:

This SOP example is intended to guide and assist POTWs in collecting valid metals data using "clean" techniques in sampling, handling and analyses. While generally applicable to most metal analytes, the example focuses on copper.

- Shaded areas denote parts of the SOP that require project-specific information. Suggested text is provided in some cases in highlighted areas, but the entirety of the final SOP must reflect the actual procedures that will be used. Edit, delete, add to the SOP as needed to make it specific to your group.
- *Red italicized text* denotes directions to the user (and should be removed for the final SOP).
- Unmarked text contained herein that is not applicable to the project for whatever reason MUST be deleted as appropriate, in order to adjust the example/final SOP to the specific project procedures.
- Submit the draft SOP to MassDEP for review and approval prior to beginning work.
- Update the final SOP as needed as changes become necessary (addendums/as-built).

DISCLAIMER:

There is no requirement to use this example. It is intended to provide guidance and assistance where needed but is not intended to replace more detailed project-specific procedures that result in metals data based on "clean" techniques. References to any trade names, commercial products, and/or manufacturers do not constitute endorsement. Web links are provided for convenience and may not function if the URL address has changed.

Standard Operating Procedure for Effluent "Clean" Metals Sampling

Background:
Low level metals (e.g., copper) results can be confounded by sample contamination during collection, transport, and laboratory analysis if appropriate steps to avoid contaminant pathways are not taken. Contamination pathways include airborne particulates (dust, vehicle exhaust, human breath, clothing, etc.), cross-contamination between stations, and inadvertent contact of metallic surfaces with sample water. In order to provide a means to generate reliable metals data at water quality criteria levels, EPA has developed specific field and analytical methods. EPA Method 1669, for example, provides performance-based guidance for proper field collection of metals samples under a variety of conditions and references EPA analytical methods for determination of specific metal analytes. The effluent sampling procedures outlined in the document, "Standard Operating Procedure for Effluent "Clean" Metals Sampling," are intended to meet the intent of EPA Method 1669 and have been modified based on project logistics. The sampling, however, will be performance-based. As long as sample contamination, poor precision, and/or unacceptable accuracy can be avoided, the use of alternative, documented procedures is acceptable. Regardless of methodologies used, corrective actions will be undertaken to resolve issue(s) when QC sampling results indicate problems.

Objective:

1) Collect sufficient data on dissolved copper concentrations to aid in interpreting the results of the Biotic Ligand Model (BLM) software for copper.

Quality Assurance Planning:
For related information regarding data quality objectives for metals samples, training requirements, analytical methods, sampling logistics (timing, locations, frequency, number, etc.), and data management, see the project-specific QAPP.

Definitions:

- "Clean" Sampling = Special sampling procedures to prevent contamination of metals samples from sources, such as: improperly cleaned equipment; improper sample-collection techniques that allow dust, dirt, or metallic surfaces to contact samples; contaminated preservatives; and/or atmospheric inputs from dust, dirt and rain (excerpted from USGS; https://water.usgs.gov/owq/FieldManual/chapter5/pdf/5.6.4.B_v1.0.pdf).
- CH = Clean Hands Person
- DH = Dirty Hands Person
- COC = Chain of Custody
- QC = Quality Control
- DIW or DIW Carboy= Deionized water or container filled with deionized water for laboratory use.

Equipment and Supplies:

1. Autosampler (with new clean Teflon tubing). *NOTE: If manually collecting composite samples, adhere to clean technique procedures similar to ambient sampling and follow compositing instructions below.*
2. Trace-clean sample bottles for use in autosampler

3. One sampling kit per sample set. These will be assembled in the lab ahead of time using CH/DH approach. Each kit will consist of the following items placed inside new, clean plastic bags and will be used to collect the lab sample from the autosampler bottle(s).
    - One 500 mL pre-cleaned, certified-clean bottles per site ("DUP" kits will contain 2 bottles per kit), pre-labeled;
    - One pair of "powder free" shoulder length polyethylene gloves; and
    - One pair of "powder free" vinyl gloves in clean plastic bag
4. A bag containing a box of new vinyl gloves (for dirty-hands to glove up)
5. A bag of new large disk or capsule filters
6. A bag of spare sampling kits (if you need an extra item, take it from a spare kit)
7. DI water carboy containing DIW for field equipment blanks
8. One clean "metals"-only cooler to hold dry materials
9. A bag of sealable clean plastic bags to hold filled sample bottles in ice chests
10. A wet-ice chest for preserving/storing samples
11. General equipment: Site logbooks, indelible marker, waterproof pen, field data sheets, chain of custody forms, etc.

Pre-sampling Preparation:

- Determine the number of samples (including QC samples) to be taken and prepare bottle labels, COC, field sheets, etc.
- To affix labels before site work, remove sample bottle(s) from each kit bag to affix survey-specific bottle labels with CH (gloves), then replace bottle(s) inside kit bag. Sharpie-label kit bags with site#, ID#, or other.
- QC samples: see QAPP for frequency
- Samplers should remove metallic jewelry and watches prior to sampling activity

General Guidance for Autosampler Use for Clean Metals Sampling:

NOTE: the following summary is excerpted from USEPA, CA DOT, and TN DEQ; develop site-specific clean metals sampling protocols for your facility.

When collecting a composite sample for the effluent, refer to NDPES permit for sample location. If the sample location is not specified in the permit, collect the sample between the last discharge and the receiving water. Generally, mid-depth, center of the flow, is the best location for the intake line. Unless otherwise specified, collect time-composite samples.

A composite sample is a combined or composited series of discrete, equal samples collected over a temporal or spatial range. Time (temporal) composite samples are made up of a number of discrete samples of equal size collected at equal time intervals into one container. Automatic samplers may be used to collect composite samples either for collecting several aliquots at frequent intervals or to collect continuous samples.

Any automatic sampler meeting the following specifications may be used to collect composite samples:

- Automatic sampler must provide refrigeration either by mechanical means or ice.
- Automatic sampler shall be capable of collecting a large enough sample for all parameter analyses (each aliquot must be at least 100 milliliters).
- Automatic sampler must have adjustable sample volume.

- Automatic sampler must provide at least 20 feet of lift and be capable of purging prior to sample collection.
- Pumping velocity must be at least two feet/second.
- Minimum inside diameter of intake line is ¼ inch.
- No metal parts may come in contact with the sample water (for metals analyses)

Remove contaminated tubing before cleaning and replace with new tubing before the next sample collection. Thoroughly clean the automatic sampler between uses and check for any damage or needed repairs. Inspect the desiccant and batteries and replace if necessary. Test the manual and automatic operation of the automatic sampler to make sure it is operating correctly. Check the pumps function in forward, reverse, automatic, and run the automatic sampler through at least one purge-pump-purge cycle. Compare function against manufacturer's specifications.

Follow manufacturer's instructions to make any needed repairs or calibration changes. Develop calibration and use SOPs for each brand and/or model of automatic sampler. Keep all calibration and repair records in a bound logbook.

Powder-free nitrile gloves must be worn when installing sampling equipment or collecting samples to avoid contamination of the sample and to provide protection from possible health risks. Nitrile gloves should not be assumed to provide adequate protection from acids or hazardous materials.

Power must be available for the entire sampling event. If accessible, the facility's power may be used. If the facility's power is not available, then generator or battery power must be used. Install new tubing (Silastic®, or equal, in the pump and Tygon®, Teflon®, or equal in the sample train) in the automatic sampler before deployment. Collect an equipment blank on the automatic sampler prior to the surveys to confirm metal analyte(s) not detected.

Before installation, test the rinse, purge-pump-purge cycle at least once. Also, check the pump volume at least twice using a graduated cylinder. Each aliquot must be at least 100 milliliters. Test flow-proportional automatic sampler operation with the flow meter to make certain it is operating properly.

After the automatic sampler and tubing is placed in the proper location, program the sampler. For time composite samples, program the automatic sampler to collect at least 100 milliliters aliquots at the permit specified frequency. For flow proportional samples, program the automatic sampler to collect at least 100 milliliters aliquots at intervals based on the flow.

The final total volume must be sufficient to conduct all required analyses, for either collection method. If possible, install the automatic sampler where specified in the permit and document the location in the sampling records. Position the intake to draw treated wastewater from the mid-channel at mid-depth. If no site is specified in the permit, sample at the most representative site downstream from all entering wastewater streams prior to discharge into the receiving water.

Secure the automatic sampler in such a way as to prevent tampering with the sample. At a minimum, place a lock and signed and dated custody seal on the automatic sampler housing. Some locations may require additional security measures. Custody seals may also be placed on sampling pole and tubing line.

When the compositing period has ended, remove the sample from the automatic sampler and thoroughly mix the composite sample. After the sample is well mixed, pour the composite sample into the appropriate, properly preserved sample container(s), or process as needed depending on sample type. Attach a completed sample tag to each sample bottle and complete the Sample Request Form. Write the Site No. (sample ID), Date, Military Time, Station Location, and Samplers on the sample tag. The primary sampler's name must be on the sample tag. Mark the sample type and whether it contains a preservative. Place the labeled sample bottle in a zip-type bag (optional) and store in a cooler on ice until delivery to the laboratory.

"Clean" Technique using Auto-Sampler:
NOTE: the following summary is excerpted from USEPA, CA DOT, and TN DEQ; develop site-specific clean metals sampling protocols for your facility.

1. During all sampling operations, extreme care must be taken to minimize exposure of the sample and sample collection equipment to human, atmospheric, and other sources of contamination.
2. Clean sampling techniques typically require a two-person sampling team. Upon arrival at the sampling site, one member of the sampling team is designated as "dirty hands"; the second member is designated as "clean hands." All operations involving contact with the sample bottle, sample bottle lid, sample suction tubing, and the transfer of the sample from the sample collection device (if the sample is not directly collected in the bottle) to the sample bottle are handled by "clean hands" wearing clean powder-free nitrile gloves. "Dirty hands" (also wearing clean powder-free nitrile gloves) is responsible for preparation of the sampler (except the sample container itself), operation of any machinery, and for all other activities that do not involve handling items that have direct contact with the sample. "Clean hands" will change into clean gloves as frequently as required to ensure that the gloved hands contacting the sample container, container lid, and laboratory cleaned sampling equipment have not contacted any source of potential contamination.
3. Although the duties of "clean hands" and "dirty hands" would appear to be a logical separation of responsibilities, in fact the completion of the entire protocol may require a good deal of coordination and practice. For example, "dirty hands" must open the box or ice chest containing the sample bottle and unzip the outer bag; "clean hands" must reach into the outer bag, open the inner bag, remove the bottle, collect the sample, replace the bottle lid, put the bottle back into the inner bag, and zip the inner bag. "Dirty hands" must close the outer bag and place the double-bagged sample in an ice-filled ice chest.
4. It is recommended that a third sampling team member be available to direct the team, review the monitoring plan, and complete the necessary sample documentation (e.g., sample location, time, sample number, weather conditions, etc.). If a third sampling team member is not available, "dirty hands" must perform the sample documentation activities.
5. For metal sample collection, rinse the entire automatic sampler with reagent-grade water. Pump about a half-gallon of reagent-grade rinse water through the system and discard.
6. For metal samples, acidification with nitric acid for the collected final metals sample can be performed at the laboratory within 8 hours of sampling completion. If the automatic sampler tubing is attached to a metal conduit pipe, install the intake tubing upstream. Wrap the submerged portion of the conduit pipe with a protective barrier such as duct tape.
7. Composite bottle changing, if required, is conducted using the following steps:

   a. The automated sampling equipment is placed in pause mode prior to the initiation of a composite bottle change. This action is accomplished in the field or by remote monitoring personnel if the monitoring station is equipped with telemetry.
   b. Composite bottle changing requires two field crew members: “clean hands” and “dirty hands.” Both team members wear clean, powder-free nitrile gloves. “Clean hands” only touches suction tubing and Teflon composite bottle lids. Keep extra gloves within easy reach.
   c. Prior to putting on clean gloves, the clean empty sample bottle is placed near the automated sampling unit, and the sampler is opened.
   d. Wearing clean powder-free nitrile gloves, “dirty hands” removes the lid clamps from both the full sample bottle and the clean sample bottle.
   e. “Clean hands” removes the end of the pump tubing from the composite bottle and “dirty hands” places a clean Ziplock bag over the end of the tubing securing it with a rubber band. The inside of the bag should never be touched by sampling personnel.
   f. “Clean hands” switches the bottle lids, putting the solid lid on the full bottle and the perforated lid on the clean empty bottle.
   g. “Dirty hands” installs the lid clamps on both bottles, removes the full bottle from the sampler, replacing it with the clean empty bottle.
   h. “Clean hands” holds the tubing while “dirty hands” removes the Ziplock bag from the end of the pump tubing, being careful not to touch the tubing.
   i. “Clean hands” inserts the tubing through the lid of the clean bottle.
   j. The sampler is closed, and sampling equipment is placed in sample mode. Remote operation personnel are notified as soon as the bottle change is complete.
   k. The sampling team fills out the appropriate information on the label of the full sample bottle.
   l. The full bottle is surrounded with fresh ice or frozen re-freezable ice packets and is secured inside the vehicle for transport.

Sampling Procedure for Equipment Blank (Dissolved Copper prior to automated sample collection):

1. Sampling is done in teams of 2-3. The person taking the sample is designated the “clean hands” person (CH), and the assistant is designated the “dirty hands” person (DH).
2. The DH dons regular powder-free gloves contained in a sealed bag.
3. DH then opens the sample kit, extracts the shoulder-length gloves, allowing the CH to put them on.
4. DH then extracts the bag containing the new vinyl gloves and opens it, allowing the CH to take them out and put them on over the shoulder-length gloves.
5. CH takes the TRA blank sample container out of the bag (opened by DH).
6. Prior to the automated sampling for the composite sample, DH runs autosampler with intake line in DIW carboy.
7. DH purges line for a sufficient time.
8. CH uncaps field blank bottle and DH directs line into the bottle (from above).
9. CH caps bottle and place in plastic bag in the cooler (for delivery to the lab later with the rest of the samples).

Sampling Procedure for Filter Blank (Dissolved Copper) prior to automated sample collection:

1. Sampling is done in teams of 2-3. The person taking the sample is designated the “clean hands” person (CH), and the assistant is designated the “dirty hands” person (DH).

2. The DH dons regular powder-free gloves contained in a sealed bag.
3. DH then opens the sample kit, extracts the shoulder-length gloves, allowing the CH to put them on.
4. DH then extracts the bag containing the new vinyl gloves and opens it, allowing the CH to take them out and put them on over the shoulder-length gloves.
5. CH takes the DA blank sample container out of the bag (opened by DH).
6. Prior to the automated sampling for the composite sample, DH runs autosampler with intake line in DIW carboy.
7. DH purges line for sufficient time.
8. Next, the CH removes the syringe from the kit (DH opens the package if needed, since some syringes are plastic-wrapped).
9. DH directs DIW via intake line in carboy into the syringe and CHP discards the rinse water downstream (to rinse syringe). 2-3 X rinse.
10. Next, the CH takes out and opens the new disk/capsule filter package (bag opened by DH). The CH then removes the filter (and the adaptor if capsule). The syringe is attached to the filter by CH. For capsule filters, the adaptor is screwed onto the capsule filter on the syringe side (so the syringe will fit into it snugly; note the flow arrow on the filter and hook the adaptor up to the filter inlet side---opposite the flow direction).
11. DH then directs DIW via intake line in carboy into the syringe/filter and CH wastes (to rinse filter). 2-3 X rinse. Do not allow the filter to contact any unclean surfaces.
12. Next the DH takes the DA sample bottle from the kit and opens it without touching the inside. The cap is held in one hand (without touching the inside of the cap), and the bottle is capped in-between successive additions.
13. Prior to collecting the sample, rinse inside of sample bottle 1-2X with filtered water. DH directs blank water into the syringe/filter, and CH plunges filtered water into the open bottle held by DH. DH caps, shakes, uncaps, and wastes the rinsate.
14. For sample collection, DH directs blank water into the syringe/filter, and CH plunges filtered water into the open bottle held by DH. Continue to do this until about 200-225 mL is collected (for a 250 mL bottle). <u>Be careful not to drip any unfiltered water from gloves, etc. into the sample bottle!</u>
15. After sufficient volume has been collected, DH caps the sample bottle and places it into the plastic kit bag in the cooler (for delivery to the lab later with the rest of the samples).
16. All waste plastic, including the syringe and filter, is placed in a separate, used plastic bag for later disposal.

Sampling Procedure for <u>Dissolved Copper Sample and Duplicate</u> following automated sample collection:

1. Dissolved Copper samples require field-filtration ASAP in the field.
2. Sampling is done in teams of 2-3. The person taking the sample is designated the “clean hands” person (CH), and the assistant is designated the “dirty hands” person (DH).
3. The DH dons regular powder-free gloves contained in a sealed bag.
4. DH then opens the sample kit, extracts the shoulder-length gloves, allowing the CH to put them on.
5. DH then extracts the bag containing the new vinyl gloves and opens it, allowing the CH to take them out and put them on over the shoulder-length gloves.
6. Next, the CH takes out and opens the new disk/capsule filter package (bag opened by DH). The CH then removes the filter (and the adaptor if capsule). The syringe is attached to the filter by

CH. For capsule filters, the adaptor is screwed onto the capsule filter on the syringe side (so the syringe will fit into it snugly; note the flow arrow on the filter and hook the adaptor up to the filter inlet side---opposite the flow direction).

7. DH retrieves the composited sample from the autosampler, places a clean cap on the bottle and gently swirls to complete mixing.
8. When the composite sample is mixed, DH pours the composite sample into the syringe/filter and CH wastes (to rinse filter). 2-3 X rinse. Do not allow the filter to contact any unclean surfaces.
9. Next the DH takes the DA sample bottle from the kit and opens it without touching the inside. The cap is held in one hand (without touching the inside of the cap) and the bottle is capped in-between successive additions.
10. Prior to collecting the sample, rinse inside of sample bottle 1-2X with filtered sample water. DH pours composite water into the syringe/filter, and CH plunges filtered water into the open bottle held by DH. DH caps, shakes, uncaps, and wastes the rinsate.
11. For sample collection, DH pours composite water into the syringe/filter, and CH plunges filtered water into the open bottle held by DH. Continue to do this until about 200-225 mL is collected (for a 250 mL bottle). Be careful not to drip any unfiltered water from gloves, etc. into the sample bottle!
12. After sufficient volume has been collected, DH caps the sample bottle and places it into the plastic kit bag in the cooler (for delivery to the lab later with the rest of the samples).
13. All waste plastic, including the syringe and filter, is placed in a separate, used plastic bag for later disposal.
14. Alternate “clean” method for filtering samples may be used.

Acidification of All Metals Samples (at the lab):

1. All samples are placed in clean plastic bags in wet ice (<6 deg. C) and delivered to the lab the same day for preservation at the lab within 8 hours to pH < 2 using HNO_3. Perform acidification under “clean” conditions to minimize contamination potential.

Filtration of dissolved copper samples (in the field):

Under “clean” field conditions, filter copper samples through a 0.45µ filter ASAP after collection in the field.

Sample Analyses:

The holding time for all samples is 180 days.

- Dissolved Cu samples: Analyze directly using method EPA ###.# (no digestion) following CH/DH filtration

Appendix E: Standard Operating Procedure for In-River Metals Sampling Example

EXAMPLE

Standard Operating Procedure for
In-River "Clean" Metals Sampling

HOW TO USE THIS EXAMPLE:

This SOP example is intended to guide and assist POTWs in collecting valid AMBIENT metals data using "clean" techniques in sampling, handling and analyses. While generally applicable to most metal analytes, the example focuses on copper.

- Shaded areas denote parts of the SOP that require project-specific information. Suggested text is provided in some cases in highlighted areas, but the entirety of the final SOP must reflect the actual procedures that will be used. Edit, delete, add to the SOP as needed to make it specific to your group.
- *Red italicized text* denotes directions to the user (and should be removed for the final SOP).
- Unmarked text contained herein that is not applicable to the project for whatever reason MUST be deleted as appropriate, in order to adjust the example/final SOP to the specific project procedures.
- Submit the draft SOP to MassDEP for review and approval prior to beginning work.
- Update the final SOP as needed as changes become necessary (addendums/as-built).

DISCLAIMER:

There is no requirement to use this example. It is intended to provide guidance and assistance where needed but is not intended to replace more detailed project-specific procedures that result in metals data based on "clean" techniques. References to any trade names, commercial products, and/or manufacturers do not constitute endorsement. Web links are provided for convenience and may not function if the URL address has changed.

Standard Operating Procedure for In-River “Clean” Metals Sampling

Background:
Low level metals (e.g., copper) results can be confounded by sample contamination during collection, transport, and laboratory analysis if appropriate steps to avoid contaminant pathways are not taken. Contamination pathways include airborne particulates (dust, vehicle exhaust, human breath, clothing, etc.), cross-contamination between stations, and inadvertent contact of metallic surfaces with sample water. In order to provide a means to generate reliable metals data at water quality criteria levels, EPA has developed specific field and analytical methods. EPA Method 1669, for example, provides performance-based guidance for proper field collection of metals samples under a variety of conditions and references EPA analytical methods for determination of specific metal analytes. The ambient sampling procedures outlined in this SOP are intended to meet the intent of EPA Method 1669 and have been modified based on project logistics. The sampling, however, will be performance-based. As long as sample contamination, poor precision, and/or unacceptable accuracy can be avoided, the use of alternative, documented procedures is acceptable. Regardless of methodologies used, corrective actions will be undertaken to resolve issue(s) when QC sampling results indicate problems.

Objective:

1. Collect sufficient data on dissolved copper concentrations to aid in interpreting the results of the Biotic Ligand Model (BLM) software for copper.

Quality Assurance Planning:
For related information regarding data quality objectives for metals samples, training requirements, analytical methods, sampling logistics (timing, locations, frequency, number, etc.) and data management, see the project-specific QAPP.

Definitions:

- “Clean” Sampling = Special sampling procedures to prevent contamination of metals samples from sources, such as: improperly cleaned equipment; improper sample-collection techniques that allow dust, dirt, or metallic surfaces to contact samples; contaminated preservatives; and/or atmospheric inputs from dust, dirt and rain (excerpted from USGS; https://water.usgs.gov/owq/FieldManual/chapter5/pdf/5.6.4.B_v1.0.pdf).
- CH = Clean Hands Person
- DH = Dirty Hands Person
- COC = Chain of Custody
- QC = Quality Control
- DIW or DIW Carboy = Deionized water or container filled with deionized water for laboratory use.

Equipment and Supplies:

1. Trace-clean sample bottles (not pre-preserved; non-straight-sided)
2. One sampling kit per sample set. These will be assembled in the lab ahead of time using CH/DH approach. Each kit will consist of the following items placed inside new, clean plastic bags and will be used to collect the lab sample from the autosampler bottle(s):

  - One 500 mL pre-cleaned, certified-clean bottles per site (“DUP” kits will contain 2 bottles per kit), pre-labeled;
  - One pair of “powder free” shoulder length polyethylene gloves; and
  - One pair of “powder free” vinyl gloves in clean plastic bag

3. A bag containing a box of new vinyl gloves (for dirty-hands to glove up)
4. A bag of new large disk or capsule filters
5. A bag of spare sampling kits (if you need an extra item, take it from a spare kit)
6. DI water carboy containing DIW for field equipment blanks
7. DI water blank bottle for drawing blanks
8. One clean “metals”-only cooler to hold dry materials
9. A bag of sealable clean plastic bags to hold filled sample bottles in ice chests
10. A wet-ice chest for preserving/storing samples
11. General equipment: Site logbooks, indelible marker, waterproof pen, field data sheets, chain of custody forms

Pre-sampling Preparation:

- Determine the number of samples (including QC samples) to be taken and prepare bottle labels, COC, field sheets, etc.
- To affix labels before site work, remove sample bottle(s) from each kit bag to affix survey-specific bottle labels with CH (gloves), then replace bottle(s) inside kit bag. Sharpie-label kit bags with site#, ID#, or other.
- QC samples: see QAPP for frequency.
- Samplers should remove metallic jewelry, watches prior to sampling activity.

“Clean” Sampling Procedure for IN-RIVER/AMBIENT SAMPLES:

1. Sampling is done in teams of two. The person taking the sample is designated the “clean hands” person (CH), and the assistant is designated the “dirty hands” person (DH). The CH is not to touch anything except the sample bottles, syringe, filter, and adaptor until sampling is complete. DH minimizes touching anything that might potentially contaminate the samples.
2. **Pre-Survey training & Practice**: Prior to actual sampling, the step-by-step procedures to be used should be practiced in a “dry-run” setting. This will help to avoid/minimize confusion during the real sampling survey.
3. **Sampling Order**: If the metals sampling crew is also involved in other site activities, SAMPLE FOR METALS USING CH/DH FIRST, PRIOR TO OTHER ACTIVITIES, as follows:
    a. Clean metals (field blanks), then
    b. Clean metals (ambient), including field duplicates, then
    c. Other samples
4. **Pre-rinsing**: Ensure that all surfaces that will come into contact with sample water are pre-rinsed prior to sample collection. Discard rinsates.
5. On shore, the DH dons regular powder-free gloves contained in a sealed bag. DH carries the plastic bag sampling kit containing items that are needed.
6. DH then opens the sample kit, extracts the shoulder-length gloves, allowing the CH to put them on.
7. DH then extracts the bag containing the new vinyl gloves and opens it, allowing the CH to take them out and put them on over the shoulder-length gloves.

8. **Ambient blank sampling (dissolved)**: Now (on shore), CH removes the syringe from the kit (DH opens the package if needed, since some syringes are plastic-wrapped), and fills the syringe with DIW water (blank water bottle opened by DH and capped in-between uses) and wastes downstream (to rinse syringe). Repeat. Next, the DH takes out and opens the new capsule filter package. The CH then removes the filter and the adaptor. The adaptor is screwed onto the capsule filter on the syringe side by CH (so the syringe will fit into it snugly; note the flow arrow on the filter and hook the adaptor up to the filter inlet side---opposite the flow direction). *NOTE: At very clean sites, samplers may elect to use a large disk filter (from a separate plastic bag) in lieu of the more expensive capsule filter.* CH then fills the syringe with DIW water, places the tip of it into the adaptor, and empties the syringe contents into the filter (to waste). Repeat 3-4X (~150-200 mL) to thoroughly rinse the filter with DIW (to waste). Do not allow the filter to contact any unclean surfaces. Next the DH takes the dissolved field blank sample bottle from the kit and opens it without touching the inside. The cap is held in one hand (without touching the inside of the cap; bottle is capped in-between successive additions). Prior to collecting the actual sample, rinse inside of sample bottle 1-2X with filtered DIW, as above. DH caps, shakes, uncaps, and wastes the rinsate. Repeat. Finally, CH draws DIW water into the syringe, attaches to filter, and filters site water into the open field blank bottle held by DH to collect the actual sample. When filled to neck, the sample bottle cap is replaced by DH and placed in the inner bag. The DIW filter assembly can be reused for other same-station dissolved samples as long as the entire filter assembly is purged of DIW and pre-rinsed with site water prior to sample collection.
9. **Sampling for Dissolved Copper and co-located/sequential duplicates:** Remaining at a fixed point in-stream, CH removes the syringe from the kit and fills the syringe with ambient water from about 0.2 meters below the surface and wastes downstream (to rinse syringe). 2-3 X rinse. Next, the DH takes out and opens the new capsule filter package. The CH then removes the filter and the adaptor. The adaptor is screwed onto the capsule filter on the syringe side (so the syringe will fit into it snugly; note the flow arrow on the filter and hook the adaptor up to the filter inlet side---opposite the flow direction). *NOTE: At very clean sites, samplers may elect to use a large disk filter (from a separate plastic bag) in lieu of the more expensive capsule filter.* CH then fills the syringe with stream water from about 2-4 inches below the surface, places the tip of it into the adaptor, and empties the syringe contents into the filter (wasted downstream). Do this 3-4X (~150-200 mL) to thoroughly rinse the filter with site stream water. (Do not allow the filter to contact any unclean surfaces). Next the DH takes the sample bottle from the kit and opens it without touching the inside. The cap is held in one hand (without touching the inside of the cap) and the bottle is capped in-between successive additions. Prior to collecting the sample, rinse inside of sample bottle 1-2X with filtered site water. CH draws water into the syringe, attaches to filter, and filters site water into the open bottle held by DH. DH caps, shakes, uncaps, and discharges the rinsate downstream. The CH now draws multiple syringes of water from about 2-4 inches below the surface to filter site water into the open bottle held by DH. Continue to do this until about sufficient volume is collected. Be careful not to drip any unfiltered stream water from gloves, etc. into the sample bottle! DH then caps the sample bottle and places it into the plastic kit bag. FOR QC DUPLICATES, REPEAT PROCEDURE USING THE SAME SYRINGE/CAPSULE FILTER ASSEMBLY TO FILL THE DUPLICATE BOTTLE IMMEDIATELY.
10. All waste plastic, including the syringe and filter, is placed in a separate, used plastic bag for later disposal.
11. Place the sample bottle(s) in the designated plastic bag in the cooler (separate from the other, loose bottles).

Acidification of All Metals Samples (at the lab):

1. All samples are placed in clean plastic bags in wet ice (<6 deg. C) and delivered to the lab the same day for preservation at the lab within 8 hours to pH<2 using ultra-pure HNO_3. Perform acidification under "clean" conditions to minimize contamination potential.

Filtration of dissolved copper samples (in the field):
Under "clean" field conditions, filter dissolved copper samples through a 0.45µ filter ASAP after collection in the field.

Sample Analyses:
The holding time for all samples is 180 days.
Dissolved Cu samples: Analyze directly using method EPA ###.# (no digestion) following CH/DH filtration