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Cover Photo

Monoosnoc Brook, Leominster, MA (left and top right) and Great Pond, Weymouth, MA (bottom right), courtesy of David S. Armstrong, U.S. Geological Survey, Daniel A. Davis, MassDEP, and Richard O. Carey, MassDEP, respectively.

Notice of Availability

This report is available on the Massachusetts Department of Environmental Protection website: https://www.mass.gov/regulations/314-CMR-4-the-massachusetts-surface-water-quality-standards

Massachusetts Department of Environmental Protection

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Watershed Planning Program

The Watershed Planning Program is a statewide program in the Division of Watershed Management, Bureau of Water Resources, at MassDEP. We are stewards of the water resources of Massachusetts. Together with other state environmental agencies, we share in the duty and responsibility to protect, enhance, and restore the quality and value of the waters of the Commonwealth. We are guided by the federal Clean Water Act and work to secure the environmental, recreational, and public health benefits of clean water for the residents of Massachusetts. The Watershed Planning Program is organized into five Sections that each have a different technical focus under the Clean Water Act: (1) Surface Water Quality Standards; (2) Surface Water Quality Monitoring; (3) Data Management and Water Quality Assessment; (4) Total Maximum Daily Load; and (5) Nonpoint Source Management.

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Disclaimer

References to trade names, commercial products, manufacturers, or distributors in this report constituted neither endorsement nor recommendation by MassDEP.

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List of Acronyms

AWQC	Ambient Water Quality Criteria
ATU	Acute Toxic Units
BLM	Copper Biotic Ligand Model v. 2.2.3
CRADA	EPA's Metals Cooperative Research and Development Agreement
CCC	Criterion Continuous Concentration
CMR	Code of Massachusetts Regulations
CMC	Criterion Maximum Concentration
CWA	Clean Water Act
DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
EPA	United States Environmental Protection Agency
FAV	Final Acute Value
GAM	Generalized Additive Model
IWLS	Iteratively Reweighted Least Squares
LMS	Laboratory Matrix Spike
MassDEP	Massachusetts Department of Environmental Protection
MRL	Minimum Reporting Limit
NPDES	National Pollutant Discharge Elimination System
NWIS	USGS National Water Information System
NWQL	USGS National Water Quality Laboratory
POTW	Publicly-owned Treatment Works
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPD	Relative Percent Difference
SU	Standard Units (pH)
SuAsCo	Sudbury, Assabet and Concord (or Concord) River Basin
SWD	Surface Water Discharge
SWQS	Surface Water Quality Standards
TMF	Toxicity Modifying Factors
USGS	United States Geological Survey
WTF	Water Treatment Facility
WTP	Water Treatment Plant
WWTF	Wastewater Treatment Facility

Abstract

Water quality data were collected at 11 water and wastewater treatment facilities (WTFs and WWTFs¹, respectively) from April 2018 through May 2019 in Massachusetts in a joint project by the United States Geological Survey (USGS) and Massachusetts Department of Environmental Protection (MassDEP). The aim of the study was to support the Massachusetts implementation of revised nationally recommended ambient water quality criteria (AWQC) for aluminum and copper in freshwater from the US Environmental Protection Agency (EPA). MassDEP adopted both the revised aluminum and copper criteria into the Massachusetts Surface Water Quality Standards (MA SWQS; 314 CMR 4.00) regulation in 2021. EPA approved these amendments to the MA SWQS, which are now in effect for Clean Water Act (CWA) purposes.

A previously published report for the MassDEP and USGS study focused on data collection considerations to generate example site-dependent aluminum criteria values (Armstrong et al., 2022b). The present report supplements the previous aluminum report by presenting results to demonstrate the application of EPA's copper Biotic Ligand Model (BLM) to generate site-dependent copper criteria values. Water quality results include comparisons among ambient stations for dissolved copper concentrations and the 10 measured input parameters for the BLM (pH, alkalinity, temperature, dissolved organic carbon, dissolved cations (calcium, magnesium, potassium, sodium) and dissolved anions (chloride, sulfate). Although effluent data are not used as input to the BLM, facility effluent discharge concentrations are also shown for each parameter and compared among the eleven facilities. Considerations for laboratory detection limits, data rounding, and quality control procedures are outlined as well.

Example site-dependent copper criteria values varied over a wide range amongst the 11 facilities, despite their geographic proximity in Massachusetts. The results emphasize the importance of collecting water quality data that are appropriate to reflect intra- and inter-annual variability in local water chemistry. The key drivers of site-dependent copper criteria variability in this study were pH and DOC; however, weaker albeit significant relationships were also found between copper criteria values and alkalinity, chloride, sulfate, and potassium.

The site-dependent copper criteria calculated in this study are for demonstration purposes only. MassDEP's implementation guidance includes collection of representative water chemistry data that capture local variability beyond the one year of this study to ensure appropriate application of the BLM to calculate site-dependent freshwater copper criteria values for implementation purposes in Massachusetts (e.g., National Pollutant Discharge Elimination System (NPDES) and Surface Water Discharge (SWD) permits; MassDEP, 2021a). Furthermore, this report provides a relevant case study for other states considering adoption of the BLM.

¹ WWTF is synonymous with Publicly-owned Treatment Works (POTW), the acronym used for these facilities in the MA SWQS regulation (314 CMR 4.00) as defined in the Surface Water Discharge Permit Program regulation (314 CMR 3.00).

1. Introduction

Copper is an abundant trace element found in the earth's crust, and is naturally present in the environment, including surface waters (Nriagu, 1979; U.S. ATSDR, 2022). Anthropogenic inputs of copper can derive from mining, leather and leather products, fabricated metal products and electrical equipment, effluents, pesticides, or antifouling paint (Patterson et al., 1998). While copper is an essential micronutrient necessary for human and animal function, excess uptake in aquatic species can cause mortality or adverse effects on survival, growth, reproduction, brain function, enzyme activity, blood chemistry, and metabolism (U.S. EPA, 2007a). Copper can enter surface waters through soil runoff or weathering, copper sulfate use (algaecide), sewage effluent, urban runoff, agricultural runoff, atmospheric input (e.g., rainwater or aerosols), domestic wastewater, landfill leachate, or small discharges from active mining and milling operations (U.S. ATSDR, 2022).

In surface waters, metal bioavailability is determined by the concentration of soluble metal that is transferred from the environment to a specified location in an aquatic organism. Chemical speciation (or form) can change the relative uptake rate and concentration of chemical species (U.S. EPA, 2007a). Furthermore, bioavailability impacts the potential for bioaccumulation, leading to increased toxicological effects (Magalhaes et al., 2015). Copper bioavailability is impacted by physicochemical factors that affect copper speciation, including temperature, organic matter, suspended particles, pH, and various inorganic cations and anions, such as those influencing hardness and alkalinity (Adams et al., 2020; Paquin et al., 2002).

In 2007, the U.S. Environmental Protection Agency (EPA) updated the 1996 national recommended ambient water quality criteria (AWQC) for acute and chronic copper aquatic life exposure in freshwater by publishing *Aquatic Life Ambient Freshwater Quality Criteria – Copper* (U.S. EPA, 2007a). EPA recommended using the Biotic Ligand Model (BLM) to calculate instantaneous acute and chronic dissolved copper criteria values using a suite of physicochemical input parameters (e.g., pH, temperature, alkalinity, organic matter, and the ionic composition of the water). The BLM is based on the principle that metal toxicity is related to the amount of metal that can bind to a biochemical receptor on an organism, or "biotic ligand", such as the gill surface membrane on a fish (U.S. EPA, 2007a).

In 2021, the Massachusetts Department of Environmental Protection (MassDEP) amended the Massachusetts Surface Water Quality Standards (MA SWQS; 314 CMR 4.00) (MassDEP, 2021b). The amendments included adoption of EPA's 2007 AWQC guidance for copper in freshwater (i.e., the BLM version 2.2.3), which does not reflect fixed acute and chronic criteria values that are independent of site characteristics. Use of the BLM as adopted in the MA SWQS will produce site-dependent copper criteria values that vary across different waterbodies. However, these variable site-dependent criteria values would be protective of aquatic life due to the influence of waterbody characteristics on copper bioavailability and toxicity.

MassDEP published a guidance document for the design and implementation of Quality Assurance Project Plans (QAPPs) for generating the minimum required data to calculate 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 (MassDEP, 2021a). In this guidance, if appropriate data are available to generate site-dependent criteria values using the BLM, these values would supersede the hardness-dependent criteria for use in permits.

1.1 Purpose and Scope

The purpose of this report is to provide guidance to supplement the recently adopted copper criteria in the MA SWQS regulation, <u>314 CMR 4.00</u>. The data presented here provide an example of the collection and use of site-dependent water chemistry data as inputs for the BLM. The data are used in the BLM to calculate site-dependent instantaneous acute (criterion maximum concentration, CMC) and chronic (criterion continuous concentration, CCC) values for ambient waters near eleven water-treatment facilities (WTFs) and wastewater-treatment facilities (WWTFs)¹ in eastern and central Massachusetts. From the instantaneous CMC and CCC values, this report presents the calculation of the minimum, 5th, and 10th percentile CMC and CCC values to demonstrate calculation of final site-dependent acute and chronic copper criteria values, respectively.

This report also supplements the previously published MassDEP/USGS aluminum report (Armstrong et al., 2022b) and associated data release (Armstrong et al., 2022a). The aluminum report and associated data release support implementation of the revised aluminum criteria for protection of aquatic life in Massachusetts. During the study, data were simultaneously collected to support the calculation of site-dependent copper water quality criteria using the BLM for the same 11 facilities.

Thus, the specific aims of this report are to:

- 1. Summarize discrete water quality data from ambient monitoring stations in receiving waterbodies near 11 WTFs and WWTFs, and
- 2. Use the discrete water quality data from selected ambient monitoring stations near each facility to demonstrate application of the BLM (U.S. EPA, 2007a) to calculate site-dependent acute and chronic copper criteria values for surface waters.

The copper criteria values calculated using the BLM are included in this report as application examples for the BLM. The criteria values are not regulatory effluent limits for facilities included in this study or other facilities. The formal implementation of any site-dependent copper criteria is subject to requirements outlined in the federal Clean Water Act (CWA; 33 U.S.C. §1251 et seq. (1972)) and federal Water Quality Standards Regulation (40 CFR 131), as well as the Massachusetts SWQS (314 CMR 4.00), Massachusetts Permit Procedures (314 CMR 2.00), and Massachusetts SWD Permit Program (314 CMR 3.00) regulations. MassDEP (2021a) includes specific guidance on the implementation of the BLM for NPDES and SWD permits.

The previously published aluminum report (Armstrong et al., 2022b) outlined the study design, including the approach used to select monitoring stations and the methods for water sample collection. Therefore, the study design will not be described in detail here. This study considers the same facilities, monitoring stations, and sample collection methods as the aluminum report. Additionally, the results for continuous data (pH and temperature) are included in the aluminum report and will not be duplicated here. The previously published aluminum report and the results presented in this report for copper will be collectively referred to hereafter as the 2018-2019 MassDEP/USGS study.

2. Methods

2.1 Study Site and Sampling Locations

MassDEP selected seven water treatment and four wastewater treatment facilities (WTFs and WWTFs, respectively) in central and eastern Massachusetts to participate in the 2018-2019 MassDEP/USGS study for collection of water quality parameters to support calculation of site-dependent aluminum and copper water quality criteria values (**Figure 1; Table 1**). The aluminum parameters were used to calculate site-dependent aluminum criteria values for each of the 11 facilities, and these results were previously reported in the aluminum report (Armstrong et al., 2022b), including publication of a data release with time series plots (Armstrong et al., 2022a). A second associated data release included total and dissolved organic carbon (TOC and DOC, respectively) data from this study (DeSimone and Armstrong, 2022).

Armstrong *et al.* (2022b) provide a thorough description of the study design and selection of sampling locations for the study, including site descriptions and sample collection methods for the monitoring stations (see Appendix 1 in Armstrong et al., 2022b). Briefly, all four WWTFs are located on the Assabet River in Westborough, Marlborough, Hudson, and Maynard (ordered from upstream to downstream). These WWTFs were chosen in the same drainage basin to quantify the variability in water quality conditions that may occur within a single basin, such as possible effects from upstream effluent discharges. The WTFs are in five of Massachusetts' major drainage basins, including the Nashua River Basin (Fitchburg WTF and Leominster WTF), Sudbury-Assabet-Concord ("SuAsCo" or "Concord") River Basin (Westborough WTF), Ipswich River Basin (Wilmington WTF), Boston Harbor Drainage Area (Weymouth WTF), and South Coastal Drainage Area (Cohasset WTF and Hanover WTF).

Each facility had a minimum of three monitoring stations where water samples were collected in the river or stream both upstream and downstream of the effluent discharge, with one station for the treatment plant effluent discharge itself. Where the effluent discharged to a pond, ambient water samples were taken at near-surface (shallow; ~1.5 ft) and near-bottom (deep; ~3-12 ft) stations near the deepest area (deep hole) of the pond. If possible, this pair of stations was established near the upgradient end, with an additional pair of stations (shallow and deep) established near the pond outlet. If this was not possible (e.g., effluent discharge was near the pond inlet), stations were established at locations outside of the immediate effect of the effluent discharge (i.e., water quality conditions indicated no effect). A map of the 11 facilities is shown in **Figure 1**, with details of the sources and receiving waterbodies for each facility shown in **Table 1**.

Detailed maps of all sampling locations in relation to each facility are provided in Figures 3-13 in the aluminum report (Armstrong et al., 2022b). Armstrong *et al.* (2022b) also describe each facility in detail, including a description of the receiving waterbody for the effluent discharge, source of water for water treatment facilities, any impacts to streamflow (e.g., reservoirs, dams, withdrawals), and the monitoring stations associated with each facility.



Figure 1. Map of the 2018-2019 MassDEP/USGS study location, including major drainage basin boundaries and seven water treatment facilities (WTFs) and four wastewater treatment facilities (WWTFs) in eastern and central Massachusetts (reproduced with permission from Armstrong et al., 2022b). Facility numbers correspond to the map number shown in Table 1.

Table 1. Summary of site locations used in the calculation of copper criteria values for seven water treatment facilities (WTFs)
and four wastewater treatment facilities (WWTFs) in central and eastern Massachusetts (modified from Table 1 of Armstrong et
al., 2022b).

Figure 1 Map Number	Facility Name	Facility Type	Source of WTF water	Receiving Waterbody	Receiving Waterbody type
1	Westborough WWTF	WWTF	NA	Assabet River	Stream
2	Marlborough WWTF	WWTF	NA	Assabet River	River
3	Hudson WWTF	WWTF	NA	Assabet River	River

Figure 1 Map	Facility Name	Facility Type	Source of WTF water	Receiving Waterbody	Receiving Waterbody
Number					type
4	Maynard WWTF	WWTF	NA	Assabet River	River
5	Cohasset WTF	WTF	Surface water	Lily Pond	Pond
6	Fitchburg WTF	WTF	Groundwater	Wyman Pond	Pond
7	Westborough WTF	WTF	Groundwater and surface water	Hocomonco Pond	Pond
8	Hanover WTF	WTF	Groundwater	Third Herring Brook	Stream
9	Leominster WTF	WTF	Surface water	Monoosnoc Brook	Stream
10	Weymouth WTF	WTF	Surface water	Mill River ²	Stream
11	Wilmington WTF	WTF	Groundwater	Maple Meadow Brook	Stream

2.2 Collection and Processing of Water Quality Samples

Discrete samples were collected by USGS staff at 38 monitoring stations near the 11 facilities during 2018-2019. Of these, only samples for 18 monitoring stations upstream of effluent discharge locations or pond sites outside of the immediate effect of the effluent discharge were used in the BLM for calculation of site-dependent copper criteria values, consistent with the approach for calculation of site-dependent aluminum criteria values (Armstrong et al., 2022b). Sampling station details for each facility are listed in **Table 2**, with those stations where data were specifically used for the BLM shown in bold.

Data collection and processing methods for discrete samples are described in detail in Armstrong *et al.* (2022b). Briefly, discrete water samples were collected monthly for 10 to 13 months, from April 2018 through May 2019. No discrete samples were collected from December 21, 2018 through January 28, 2019 due to a lapse in U.S. Government appropriations. After January 28, 2019, samples were collected only at ambient (upstream) stations and selected pond stations. Sampling was conducted only during "dry-weather" conditions to minimize the impact of stormwater runoff on water quality (i.e., rainfall was <0.1 inch in a 1-3 day period prior to sampling). Sampling for all sites associated with a single facility were conducted on the same day.

Mean daily streamflow data from the USGS gaging station on the Assabet River near Maynard, MA (Station No. 01097000) were used to compare conditions during the study to historical streamflow conditions. Streamflow conditions during sampling were found to be normal or above normal, with the exception of June and July 2018 when streamflow conditions were below normal (see Figure 14 in Armstrong *et al.*, 2022b).

As part of the 2018-2019 MassDEP/USGS study, continuous data were also collected at select stations to capture seasonal, diel, and event-driven fluctuations in water temperature and pH. These data are described in Armstrong *et al.* (2022b). The continuous measurements did not have corresponding water samples taken at the location of the sensors; therefore, the continuous data were not used as inputs to the BLM to calculate copper criteria values. However, continuous measurements from the aluminum report showed diel variations in pH at all sites measured, which were largest in low-gradient and

² The Mill River is the EPA-designated receiving water for the Weymouth WTF effluent discharge; however, the effluent discharges directly into an embayment of Great Pond that flows into a control structure at the dam near Randolph Street, then down a small tributary for approximately a half mile prior to confluence with the Mill River.

impounded rivers or ponds with an open canopy and algae and/or vegetation. Diel variations were also largest during the growing season (April to October) (Armstrong et al., 2022b). While Armstrong et al. (2022b) did not use the continuous pH data to calculate aluminum criteria values, the report noted that the measured variability in pH values could potentially affect 10th percentile aluminum CMC and CCC values. Thus, as pH is a key driver of copper criteria values calculated by the BLM, it is important to characterize the range of pH accurately and fully for the waterbody of interest. Further information on the use of continuous sensors for temperature and pH is provided in the MassDEP guidance for application of the copper BLM to NPDES and SWD permits (MassDEP, 2021a).

A quality assurance program was included in the 2018-2019 MassDEP/USGS study to evaluate the accuracy and precision of water quality data collected. Methods used for quality assurance (QA) and quality control (QC) are described in detail in Armstrong *et al.* (2022b), including blank samples, replicate samples and laboratory matrix spike (LMS) samples.

Samples were filtered and acidified (for preservation) at the USGS laboratory in Northborough, Massachusetts, then shipped to the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado, for analysis. Samples were analyzed for the suite of water quality parameters required for input to the BLM. The relevant parameters are shown in **Table 3**, including details of the analysis methods and minimum reporting limits (MRLs) for each analyte.

Table 2. Water quality monitoring stations for discrete sampling near 11 water and wastewater treatment facilities (WTF andWWTFs, respectively) in central and eastern Massachusetts, 2018–19 (modified from Table 2 of Armstrong et al., 2022b). Datacollected from stations in bold were used in the Biotic Ligand Model (BLM) to calculate site-dependent copper criteria values.

Facility	Station Name	USGS Station No.	Station type
Westborough	Westborough wastewater-treatment plant	421651071381401	Effluent
WWTF	effluent		
	Assabet River near Westborough, Mass.	01096603	Ambient
			(Upstream)
	Assabet River DS from Westborough water-	421700071381901	Ambient
	treatment plant at Route 9		(Downstream)
Marlborough	Marlborough wastewater-treatment plant	422034071365601	Effluent
WWTF	effluent		
	Assabet River at Boundary Street near	01096720	Ambient
	Northborough, Mass.		(Upstream)
	Assabet River, DS Marlborough wastewater-	01096725	Ambient
	treatment plant		(Downstream)
Hudson WWTF	Hudson wastewater-treatment plant effluent	422406071323401	Effluent
	Assabet River at Cox Street near Hudson,	01096870	Ambient
	Mass.		(Upstream)
	Assabet River near Hudson-Stow town line	01096875	Ambient
			(Downstream)
Maynard WWTF	Maynard wastewater-treatment plant effluent	422627071262301	Effluent
	Assabet River, US Maynard wastewater-	01097021	Ambient
	treatment plant		(Upstream)
	Assabet River, DS Maynard wastewater-	01097023	Ambient
	treatment plant		(Downstream)
Cohasset WTF	Cohasset water-treatment plant backwash	421334070490601	Effluent
	effluent		

Facility	Station Name	USGS Station No.	Station type
	Lily Pond deep hole (shallow)	421326070485802	Ambient
			(Pond)
	Lily Pond deep hole	421326070485801	Ambient
			(Pond)
Fitchburg WTF	Fitchburg water-treatment plant backwash	423215071534101	Effluent
0	effluent		
	Wyman Pond, Leino Park Road, shallow,	423132071523401	Ambient
	Westminster, Mass.		(Pond)
	Wyman Pond, Leino Park Road, deep,	423132071523402	Ambient
	Westminster, Mass.		(Pond)
	Wyman Pond shallow, Westminster, Mass.	423211071524701	Ambient
			(Pond)
	Wyman Pond deep, Westminster, Mass.	423211071524702	Ambient
			(Pond)
Westborough	Westborough water-treatment plant backwash	421627071392401	Effluent
WTF	effluent		
	Hocomonco Pond shallow, Westborough,	421622071385701	Ambient
	Mass.		(Pond)
	Hocomonco Pond deep, Westborough, Mass.	421622071385702	Ambient
			(Pond)
	Hocomonco Pond near Otis Street,	421628071384501	Ambient
	Westborough, Mass.		(Pond)
Hanover WTF	Hanover water-treatment plant backwash	420754070495801	Effluent
	effluent		
	Third Herring Brook Pond Street near	011058065	Ambient
	Third Herring Brook Pond Street near Hanover, Mass.	011058065	Ambient (Upstream)
	Third Herring Brook Pond Street near Hanover, Mass. Third Herring Brook, DS water-treatment	011058065 011058075	Ambient (Upstream) Ambient
	Third Herring Brook Pond Street near Hanover, Mass. Third Herring Brook, DS water-treatment plant, near Hanover, Mass.	011058065 011058075	Ambient (Upstream) Ambient (Downstream)
Leominster WTF	Third Herring Brook Pond Street near Hanover, Mass. Third Herring Brook, DS water-treatment plant, near Hanover, Mass. Leominster water-treatment plant backwash	011058065 011058075 423258071480701	Ambient (Upstream) Ambient (Downstream) Effluent
Leominster WTF	Third Herring Brook Pond Street near Hanover, Mass. Third Herring Brook, DS water-treatment plant, near Hanover, Mass. Leominster water-treatment plant backwash effluent	011058065 011058075 423258071480701	Ambient (Upstream) Ambient (Downstream) Effluent
Leominster WTF	Third Herring Brook Pond Street near Hanover, Mass. Third Herring Brook, DS water-treatment plant, near Hanover, Mass. Leominster water-treatment plant backwash effluent Monoosnoc Brook, US Leominster water-	011058065 011058075 423258071480701 01094420	Ambient (Upstream) Ambient (Downstream) Effluent Ambient
Leominster WTF	Third Herring Brook Pond Street near Hanover, Mass. Third Herring Brook, DS water-treatment plant, near Hanover, Mass. Leominster water-treatment plant backwash effluent Monoosnoc Brook, US Leominster water- treatment plant	011058065 011058075 423258071480701 01094420	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream)
Leominster WTF	Third Herring Brook Pond Street near Hanover, Mass. Third Herring Brook, DS water-treatment plant, near Hanover, Mass. Leominster water-treatment plant backwash effluent Monoosnoc Brook, US Leominster water- treatment plant Monoosnoc Brook, DS Leominster water-	011058065 011058075 423258071480701 01094420 01094422	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient
Leominster WTF	Third Herring Brook Pond Street near Hanover, Mass. Third Herring Brook, DS water-treatment plant, near Hanover, Mass. Leominster water-treatment plant backwash effluent Monoosnoc Brook, US Leominster water- treatment plant Monoosnoc Brook, DS Leominster water- treatment plant	011058065 011058075 423258071480701 01094420 01094422	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Downstream)
Leominster WTF	Third Herring Brook Pond Street nearHanover, Mass.Third Herring Brook, DS water-treatmentplant, near Hanover, Mass.Leominster water-treatment plant backwasheffluentMonoosnoc Brook, US Leominster water-treatment plantMonoosnoc Brook, DS Leominster water-treatment plantWeymouth water treatment plant effluent	011058065 011058075 423258071480701 01094420 01094422 420959070580401	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Downstream) Effluent
Leominster WTF	Third Herring Brook Pond Street near Hanover, Mass. Third Herring Brook, DS water-treatment plant, near Hanover, Mass. Leominster water-treatment plant backwash effluent Monoosnoc Brook, US Leominster water- treatment plant Monoosnoc Brook, DS Leominster water- treatment plant Weymouth water treatment plant effluent Mill River near Randolph Street, South	011058065 011058075 423258071480701 01094420 01094422 420959070580401 01105587	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Downstream) Effluent Ambient
Leominster WTF	Third Herring Brook Pond Street near Hanover, Mass. Third Herring Brook, DS water-treatment plant, near Hanover, Mass. Leominster water-treatment plant backwash effluent Monoosnoc Brook, US Leominster water- treatment plant Monoosnoc Brook, DS Leominster water- treatment plant Weymouth water treatment plant effluent Mill River near Randolph Street, South Weymouth, Mass.	011058065 011058075 423258071480701 01094420 01094422 420959070580401 01105587	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream)
Leominster WTF	Third Herring Brook Pond Street near Hanover, Mass. Third Herring Brook, DS water-treatment plant, near Hanover, Mass. Leominster water-treatment plant backwash effluent Monoosnoc Brook, US Leominster water- treatment plant Monoosnoc Brook, DS Leominster water- treatment plant Weymouth water treatment plant effluent Mill River near Randolph Street, South Weymouth, Mass. Great Pond near outlet, shallow, South	011058065 011058075 423258071480701 01094420 01094422 420959070580401 01105587 421004070580201	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Pond)
Leominster WTF Weymouth WTF	Third Herring Brook Pond Street nearHanover, Mass.Third Herring Brook, DS water-treatmentplant, near Hanover, Mass.Leominster water-treatment plant backwasheffluentMonoosnoc Brook, US Leominster water-treatment plantMonoosnoc Brook, DS Leominster water-treatment plantWeymouth water treatment plant effluentMill River near Randolph Street, SouthWeymouth, Mass.Great Pond near outlet, shallow, SouthWeymouth, Mass.	011058065 011058075 423258071480701 01094420 01094422 420959070580401 01105587 421004070580201	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Pond)
Leominster WTF Weymouth WTF	Third Herring Brook Pond Street near Hanover, Mass. Third Herring Brook, DS water-treatment plant, near Hanover, Mass. Leominster water-treatment plant backwash effluent Monoosnoc Brook, US Leominster water- treatment plant Monoosnoc Brook, DS Leominster water- treatment plant Weymouth water treatment plant effluent Mill River near Randolph Street, South Weymouth, Mass. Great Pond near outlet, shallow, South Weymouth, Mass. Great Pond near outlet, deep, South	011058065 011058075 423258071480701 01094420 01094422 420959070580401 01105587 421004070580201 421004070580202	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Pond) Ambient (Pond)
Leominster WTF Weymouth WTF	Third Herring Brook Pond Street near Hanover, Mass. Third Herring Brook, DS water-treatment plant, near Hanover, Mass. Leominster water-treatment plant backwash effluent Monoosnoc Brook, US Leominster water- treatment plant Monoosnoc Brook, DS Leominster water- treatment plant Weymouth water treatment plant effluent Mill River near Randolph Street, South Weymouth, Mass. Great Pond near outlet, shallow, South Weymouth, Mass. Great Pond near outlet, deep, South Weymouth, Mass.	011058065 011058075 423258071480701 01094420 01094422 420959070580401 01105587 421004070580201 421004070580202	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Pond) Ambient (Pond)
Leominster WTF Weymouth WTF	Third Herring Brook Pond Street nearHanover, Mass.Third Herring Brook, DS water-treatmentplant, near Hanover, Mass.Leominster water-treatment plant backwasheffluentMonoosnoc Brook, US Leominster water-treatment plantMonoosnoc Brook, DS Leominster water-treatment plantWeymouth water treatment plant effluentMill River near Randolph Street, SouthWeymouth, Mass.Great Pond near outlet, shallow, SouthWeymouth, Mass.Great Pond near outlet, deep, SouthWeymouth, Mass.Wilmington water-treatment plant backwash	011058065 011058075 423258071480701 01094420 01094422 420959070580401 01105587 421004070580201 421004070580202 423200071100201	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Pond) Ambient (Pond) Effluent
Leominster WTF Weymouth WTF Wilmington WTF	Third Herring Brook Pond Street nearHanover, Mass.Third Herring Brook, DS water-treatmentplant, near Hanover, Mass.Leominster water-treatment plant backwasheffluentMonoosnoc Brook, US Leominster water-treatment plantMonoosnoc Brook, DS Leominster water-treatment plantWeymouth water treatment plant effluentMill River near Randolph Street, SouthWeymouth, Mass.Great Pond near outlet, shallow, SouthWeymouth, Mass.Great Pond near outlet, deep, SouthWeymouth, Mass.Wilmington water-treatment plant backwasheffluent	011058065 011058075 423258071480701 01094420 01094422 420959070580401 01105587 421004070580201 421004070580202 423200071100201	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Pond) Ambient (Pond) Effluent
Leominster WTF Weymouth WTF Wilmington WTF	Third Herring Brook Pond Street nearHanover, Mass.Third Herring Brook, DS water-treatmentplant, near Hanover, Mass.Leominster water-treatment plant backwasheffluentMonoosnoc Brook, US Leominster water-treatment plantMonoosnoc Brook, DS Leominster water-treatment plantWeymouth water treatment plant effluentMill River near Randolph Street, SouthWeymouth, Mass.Great Pond near outlet, shallow, SouthWeymouth, Mass.Great Pond near outlet, deep, SouthWeymouth, Mass.Wilmington water-treatment plant backwasheffluentSawmill Brook at Chestnut Street,	011058065 011058075 423258071480701 01094420 01094422 420959070580401 01105587 421004070580201 421004070580202 423200071100201 01101296	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Pond) Effluent Effluent Ambient (Pond)
Leominster WTF Weymouth WTF Wilmington WTF	Third Herring Brook Pond Street nearHanover, Mass.Third Herring Brook, DS water-treatmentplant, near Hanover, Mass.Leominster water-treatment plant backwasheffluentMonoosnoc Brook, US Leominster water-treatment plantMonoosnoc Brook, DS Leominster water-treatment plantWeymouth water treatment plant effluentMill River near Randolph Street, SouthWeymouth, Mass.Great Pond near outlet, shallow, SouthWeymouth, Mass.Great Pond near outlet, deep, SouthWeymouth, Mass.Wilmington water-treatment plant backwasheffluentSawmill Brook at Chestnut Street,Wilmington, Mass.	011058065 011058075 423258071480701 01094420 01094422 420959070580401 01105587 421004070580201 421004070580202 423200071100201 01101296	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Pond) Effluent Effluent Ambient (Pond)
Leominster WTF Weymouth WTF Wilmington WTF	Third Herring Brook Pond Street nearHanover, Mass.Third Herring Brook, DS water-treatmentplant, near Hanover, Mass.Leominster water-treatment plant backwasheffluentMonoosnoc Brook, US Leominster water-treatment plantMonoosnoc Brook, DS Leominster water-treatment plantMonoosnoc Brook, DS Leominster water-treatment plantMonoosnoc Brook, DS Leominster water-treatment plantMonouth water treatment plant effluentMill River near Randolph Street, SouthWeymouth, Mass.Great Pond near outlet, shallow, SouthWeymouth, Mass.Great Pond near outlet, deep, SouthWeymouth, Mass.Wilmington water-treatment plant backwasheffluentSawmill Brook at Chestnut Street,Wilmington, Mass.Maple Meadow Brook, Wilmington, Mass.	011058065 011058075 423258071480701 01094420 01094422 420959070580401 01105587 421004070580201 421004070580202 123200071100201 01101296 01101294	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Pond) Effluent Ambient (Pond) Effluent Ambient (Upstream) Ambient
Leominster WTF Weymouth WTF Wilmington WTF	Third Herring Brook Pond Street near Hanover, Mass. Third Herring Brook, DS water-treatment plant, near Hanover, Mass. Leominster water-treatment plant backwash effluent Monoosnoc Brook, US Leominster water- treatment plant Monoosnoc Brook, DS Leominster water- treatment plant Weymouth water treatment plant effluent Mill River near Randolph Street, South Weymouth, Mass. Great Pond near outlet, shallow, South Weymouth, Mass. Great Pond near outlet, deep, South Weymouth, Mass. Wilmington water-treatment plant backwash effluent Sawmill Brook at Chestnut Street, Wilmington, Mass. Maple Meadow Brook, Wilmington, Mass.	011058065 011058075 423258071480701 01094420 01094422 420959070580401 01105587 421004070580201 421004070580202 01101296 01101294	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Pond) Effluent Ambient (Pond) Effluent Ambient (Upstream) Ambient (Upstream)
Leominster WTF Weymouth WTF Wilmington WTF	Third Herring Brook Pond Street near Hanover, Mass. Third Herring Brook, DS water-treatment plant, near Hanover, Mass. Leominster water-treatment plant backwash effluent Monoosnoc Brook, US Leominster water- treatment plant Monoosnoc Brook, DS Leominster water- treatment plant Weymouth water treatment plant effluent Mill River near Randolph Street, South Weymouth, Mass. Great Pond near outlet, shallow, South Weymouth, Mass. Great Pond near outlet, deep, South Weymouth, Mass. Wilmington water-treatment plant backwash effluent Sawmill Brook at Chestnut Street, Wilmington, Mass. Maple Meadow Brook, at Middlesex Canal,	011058065 011058075 423258071480701 01094420 01094422 420959070580401 01105587 421004070580202 423200071100201 01101296 01101294 01101298	Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Downstream) Effluent Ambient (Upstream) Ambient (Pond) Effluent Ambient (Pond) Effluent Ambient (Upstream) Ambient (Upstream) Ambient

Table 3. Water quality analytes and minimum reporting levels for discrete samples collected for the purpose of using the Biotic Ligand Model (BLM) for calculation of site-dependent copper criteria values at and near 11 water and wastewater treatment facilities (WTFs and WWTFs, respectively) in Massachusetts, 2018–19. Minimum Reporting Limit (MRL) is for analysis completed by the National Water Quality Laboratory (NWQL).

Analyte	Units	USGS	Analysis	USGS	Method Citation	Minimum
		Parameter	Туре	Method		Reporting
		Code		Code		Limit (MRL)
Alkalinity,	mg/L as	29801	Lab	TT040	USGS: I-2030-85	4
filtered	CaCO₃				(Fishman and Friedman, 1989)	
Calcium,	mg/L	00915	Lab	PLA11	USGS: I-1472-87	0.022
filtered					(Fishman, 1993)	
Chloride,	mg/L	00940	Lab	IC022	Standard Method: 4110 B-2011	0.02
filtered					USGS: I-2057-90	
					(Standard Methods Committee	
					of the APHA, AWWA, and WEF,	
					2018a)	
Organic	mg/L	00681	Lab	CMB15	Standard Method: 5310B	0.23
Carbon,					(Clesceri, L.S. et al., 1998)	
filtered						
Magnesium,	mg/L	00925	Lab	PLA11	USGS: I-1472-87	0.011
filtered					(Fishman, 1993)	
рН	SU	00400	Field	PROBE	USGS: NFM 6.4	NA
					(USGS, 2021)	
Potassium,	mg/L	00935	Lab	PLO02	Standard Method: 3120 ICP	0.004
filtered					(Standard Methods Committee	
					of the APHA, AWWA, and WEF,	
					2018b)	
Sodium,	mg/L	00930	Lab	PLA11	USGS: I-1472-87	0.4
filtered					(Fishman, 1993)	
Sulfate,	mg/L	00945	Lab	IC022	Standard Method: 4110 B-2011	0.02
filtered					USGS: I-2057-90	
					(Standard Methods Committee	
					of the APHA, AWWA, and WEF,	
					2018a)	
Temperature	°C	00010	Field	THM01	USGS: NFM 6.1	NA
					(USGS, 2006)	
Copper,	μg/L	01040	Lab	PLM10	USGS: I-2020-05	0.4
filtered ³					(Garbarino et al., 2006)	

2.3 Data Acquisition

Data from the 2018-2019 MassDEP/USGS study were acquired directly from the USGS on May 13, 2022.⁴ Both "rounded" and "unrounded" datasets were obtained. The rounded data were rounded according to the National Water Information System (NWIS) database default, and this dataset was used in the

³ Copper is not an input to the BLM; however, copper data were collected for comparison to criteria values calculated from the BLM.

⁴ The ambient station water quality data used in this study are also available for download from the National Water Information System (NWIS) database using the dataRetrieval package (DeCicco and Hirsch, 2022) in the software application R (R Core Team, 2020).

aluminum report for calculation of the aluminum CMC and CCC values (Armstrong et al., 2022b). The unrounded data are simply data as stored in the database up to the maximum display of eight digits.

MassDEP guidance recommends reporting limits for each analyte required as input for the BLM (MassDEP, 2021a). These are intended as minimum recommendations, and if justified more precise data can be used (e.g., where appropriate laboratory instrument precision and detection limits exist). The rounded dataset fulfills the minimum recommended criteria in the MassDEP guidance. Copper criteria values generated from the BLM using unrounded versus rounded data were compared. Additionally, the impact of using a full detection limit value was considered in comparison to using a half detection limit value for instances where data values were below the laboratory limit of detection. Note, only one BLM input parameter (alkalinity) had values below the detection limit, for only one facility (Leominster WTF).

2.4 Biotic Ligand Model (BLM)

The copper BLM v. 2.2.3 was used for calculation of the final acute value (FAV), criterion maximum concentration (CMC), criteria chronic concentration (CCC), and acute toxic units (ATU). The BLM incorporates metal speciation and the protective effects of competing cations to predict metal bioavailability and toxicity (HydroQual, Inc., 2007). ATUs are the ratio of the ambient copper concentration to the instantaneous water quality criterion (WQC) value for that water sample. An ATU greater than 1 indicates that the ambient copper concentration exceeds the instantaneous copper criterion value (HydroQual, Inc., 2007).

The parameters required for the BLM and their acceptable input ranges are summarized in Table 4. There are 12 required input parameters for the BLM: temperature, pH, dissolved organic carbon (DOC), humic acid, calcium, magnesium, sodium, potassium, sulfate, chloride, alkalinity, and sulfide. Ten of these parameters were measured in this study, while two constituents (humic acid and sulfide) were estimated following recommendations in the BLM manual (HydroQual, Inc., 2007). The distribution of humic and fulvic acids in the organic matter present is not routinely characterized by laboratories, thus, in the absence of measured data, the default recommended value of 10% for natural waters was used as the BLM input for all samples. The composition of the dissolved organic matter content is not considered an especially critical parameter for the BLM, and little benefit is anticipated to be achieved by characterizing the distribution of humic and fulvic acids (HydroQual, Inc., 2007). A sensitivity analysis with variable % humic acid inputs to the BLM would allow for assessment of the impact of this parameter on the copper criteria values, however this is not within the remit of the present study. Sulfide can persist in freshwaters, particularly those impacted by wastewater treatment plant effluents, and sulfide can impact metal speciation and bioavailability. However, in v. 2.2.3 of the BLM, coppersulfide interaction is not incorporated into the model, and sulfide is included as a "placeholder" for future inclusion. Thus, sulfide concentrations input to the BLM do not have an effect on the calculated copper criteria values. Thus, a nominal input value of 1x10⁻¹⁰ mg/L (HydroQual, Inc., 2007) was used for sulfide in the model to calculate criteria values.

All chemical constituents are the dissolved, or filtered, fraction only. Note that the copper concentration at the time of sampling is not required for criteria calculations when using the BLM. However, if dissolved copper concentrations are entered, these data are used to calculate ATUs.

The BLM was set to "Instantaneous Water Quality Criteria Calculation" mode, and the Dissolved Inorganic Carbon (DIC) input option selected was "Closed System, Input Alkalinity". Input parameters

were checked within the model software prior to running the simulation. If input parameter values were outside the corresponding BLM range, the nearest acceptable input parameter value was automatically used (i.e., the lower or upper limit). Data were flagged where parameters were outside of the acceptable range for the BLM. For this dataset (n=209), there were 96 occasions where temperature data were flagged as outside of the acceptable BLM range (10-25 °C), three occasions where chloride data were above the maximum of the BLM range (0.32 - 279.72 mg/L), and one occasion where both temperature and chloride were outside of the BLM range.

A summary table of all BLM input data and instantaneous site-dependent copper criteria calculations are shown in **Appendix A**.

Table 4. Range of acceptable inputs for each parameter in the Biotic Ligand Model (BLM) for calculation of site-dependent copper criteria values. All chemical constituents should be measured as the dissolved fraction only.

Input Parameter	Units	BLM Range
Temperature	°C	10 – 25
рН	Standard Units (SU)	4.9 – 9.2
Dissolved Organic Carbon (Organic Carbon, filtered)	mg/L	0.05 – 29.65
Humic Acid	% ⁵	10 - 60
Calcium	mg/L	0.204 - 120.24
Magnesium	mg/L	0.024 - 51.9
Sodium	mg/L	0.16 - 236.9
Potassium	mg/L	0.039 – 156
Sulfate	mg/L	0.096 – 278.4
Chloride	mg/L	0.32 – 279.72
Alkalinity	mg/L of CaCO₃	1.99 – 360
Sulfide	mg/L ⁶	
Copper	μg/L ⁷	

2.5 Calculation of Final Acute and Chronic Site-dependent Criteria Values

For calculation of instantaneous copper CMC and CCC values, 18 of the 27 total ambient stations were used in the BLM (those stations in bold in **Table 2**). These 18 ambient stations were on the receiving waterbody and upstream of effluent discharges (for streams or rivers) or outside of the immediate effect of effluent discharges (for ponds). The stations used for calculation of copper criteria values are consistent with those used for the aluminum report (Armstrong et al., 2022b).

Additionally, there were eight discrete monthly samples from the 18 ambient stations that were not used in the calculation of copper criteria values. Samples that were removed include one sample collected after a storm event, and seven monthly pond samples that were collected at different locations from the established stations because of unsafe ice conditions. These eight samples were

⁵ Humic acid content is typically not measured; therefore, it is recommended that a default value of 10% is used for natural waters (HydroQual, Inc., 2007).

⁶ Sulfide is not measured, nor is it incorporated into the BLM v. 2.2.3; however, a sulfide value is required to run the model. Thus, it is recommended that a near-zero value is used (HydroQual, Inc., 2007).

⁷ Copper (dissolved) is not an input parameter for calculation of site-dependent copper criteria values using the BLM.

removed from the analysis because water quality conditions at these sites may have differed due to variable site conditions. These same eight samples were also removed from calculation of aluminum criteria in Armstrong *et al.* (2022b) and are summarized in **Table 5**. At each station, results for the BLM parameters from coincident samples were used as inputs to the model, resulting in instantaneous CMC and CCC criteria values for each sampling event.

Facility	Site Name	USGS Station No.	Date	Rationale for Removal	
Marlborough	Assabet River at	01096720	July 27, 2018	Storm event	
WWTF	Boundary St. near Northborough, MA				
Cohasset WTF	Lily Pond Deep Hole (Shallow)	421326070485802	December 11, 2018 February 2, 2019 March 8, 2019		
Westborough	Hocomonco Pond	421622071385701	February 12, 2019	Samples collected	
WTF	Shallow, Westborough, MA		March 6, 2019	through ice at nearby location	
Fitchburg WTF	WYMAN POND SHALLOW, WESTMINSTER, MA	423211071524701	December 10, 2018 February 12, 2019		

Table 5. Samples removed from calculation of site-dependent copper criteria using the Biotic Ligand Model (BLM).

All instantaneous criteria were used to calculate the 10th percentile of CMC and CCC values, resulting in final site-dependent copper acute and chronic criteria values, respectively, for each of the 18 ambient stations representing a facility, consistent with MassDEP recommendations for NPDES and SWD permits (MassDEP, 2021a). Percentiles are statistical metrics that indicate the value below which a given percentage of observations in the dataset falls. For example, a 10th percentile final criterion value is the value below which 10% of all instantaneous criteria values in the dataset occur and is therefore protective of aquatic life 90% of the time.

The 5th percentile and minimum CMC and CCC were also calculated and presented here for completeness and consistency with the aluminum report (Armstrong et al., 2022b).

3. Water Quality Results

A total of 421⁸ discrete monthly water quality samples were collected for 38 monitoring stations near the 11 WTF and WWTFs from April 2018 to May 2019. This included 115⁸ effluent samples from 11 effluent monitoring stations, and 306 ambient samples from 27 monitoring stations in streams, rivers, or

⁸ The aluminum report (Armstrong et al., 2022b) incorrectly states that 420 discrete water samples and 114 effluent samples were collected in the study due to the inadvertent omission of an effluent sample from April 24, 2018 (Maynard Wastewater Treatment Plant Effluent, Station No. 422627071262301). This resulted from an error in the public-access coding for this sample in the USGS National Water Information System (NWIS), which was discovered after the report and data release were published. However, this omission has no effect on the site-dependent aluminum criteria values calculated in the study. As such, revisions to include this sample in the aluminum report and associated data release were not pursued.

ponds. Of the ambient samples, 209 samples from 18 monitoring stations were used to calculate sitedependent copper criteria values using the BLM (see **Appendix A**).

Data from effluent stations were not used as inputs to the BLM for the purpose of calculating sitedependent copper criteria values. Therefore, the water quality results for discrete monthly samples collected at effluent discharge stations are summarized in **Appendix B**.

Time series plots for all ambient stations (streams/rivers and ponds) and effluent stations for each facility are provided in **Appendix C**, including relevant field observations for interpretation where additional environmental samples were taken. The time series plots include all stations, with no outliers removed.

A legend is shown in **Figure 2** for the interpretation of all boxplots presented here, including the median, mean, percentiles, and outliers for the combined station data.



Figure 2. Boxplot legend for interpretation of relevant figures presented throughout.

3.1 Comparisons of Water Quality Among Ambient Stations

Boxplots of monthly discrete water quality parameters in **Figure 3** to **Figure 13** show the parameter values for the upstream ambient stations and pond stations outside the immediate effect of the effluent discharges (i.e., only those stations used for calculation of site-dependent copper criteria values using the BLM; bold stations in **Table 2**). For facilities with multiple ambient stations (upstream or pond), boxplots were developed using the combined data from those stations. These facilities include Wilmington WTF, Cohasset WTF, Fitchburg WTF, and Westborough WTF.

Summaries of the water quality results, and comparisons of each parameter among the ambient stations used for criteria calculations, are reported below. The reported minimum, median, and maximum values were calculated from all discrete water quality samples from all ambient stations (upstream, pond, and downstream). For the statistics, no values were removed as outliers (i.e., those samples listed in **Table 5**), which is consistent with the aluminum report (Armstrong et al., 2022b). Seasonal patterns in monthly discrete water quality parameters are also discussed below. Note that water quality results at all ambient stations (including upstream, pond, and downstream) for each facility will not be discussed here, as the focus of this report is on those data used for calculation of site-dependent copper criteria values with the BLM.

Overall, a similar pattern was evident for upstream and pond sites associated with the facilities for several chemical parameters: alkalinity, calcium, chloride, copper, magnesium, potassium, sodium, and sulfate. For these parameters, typically higher concentrations were reported for the Assabet River (particularly Marlborough, Hudson, and Maynard WWTFs) and Wilmington and Weymouth WTFs. In contrast, DOC, pH, and temperature indicated a clear seasonal pattern, more likely affected by climate and seasonal events.

3.1.1 Alkalinity

Alkalinity values (mg/L as CaCO₃) at all ambient stations varied over a wide range from below the limit of detection (<4 mg/L) to 93 mg/L, with median alkalinity ranging from 4.35 mg/L (Leominster WTF) to 34.9 mg/L (Marlborough WWTF). Of the stations used for calculating copper criteria values, the highest alkalinity values were typically reported at the upstream ambient stations in the Assabet River (Westborough WWTF, Marlborough WWTF, Hudson WWTF and Maynard WWTF), Hocomonco Pond (Westborough WTF), Mill River (Weymouth WTF), Sawmill Brook, and Maple Meadow Brook (Wilmington WTF), while lower alkalinity was measured at the pond or stream stations associated with Cohasset, Fitchburg, Hanover, and Leominster WTFs (**Figure 3**).

Monthly median alkalinity concentrations for upstream and pond stations tended to be highest in July to September (26.8 - 35.3 mg/L), and lowest in April and June (9.65 and 10.45 mg/L, respectively). Downstream alkalinity concentrations demonstrated apparent seasonality, with the highest median alkalinity in the summer months (June to September: 34.2 - 44.6 mg/L) and the lowest alkalinity in the winter (January to February: 16.4 - 21.9 mg/L). For all ambient stations, monthly median alkalinity was highest in July (36 mg/L) and lowest in April (14.9 mg/L).



Figure 3. Boxplot of alkalinity, filtered (mg/L as calcium carbonate), from discrete samples taken at selected ambient stations (upstream or pond) at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019. Data include only those from selected ambient stations used for copper criteria value calculations in the Biotic Ligand Model (BLM).

3.1.2 Calcium

Calcium concentrations at all ambient stations ranged from 1.47 to 152 mg/L, with median concentrations of 2.1 to 30 mg/L. Of those stations used as inputs to the BLM, the highest median calcium concentrations were reported on the upstream Assabet River stations associated with Marlborough, Hudson, and Maynard WWTFs, as well as Hocomonco Pond (Westborough WTF), and the upstream stations associated with Weymouth and Wilmington WTFs. Low median calcium concentrations (<10 mg/L) were reported at upstream and pond stations associated with Cohasset, Fitchburg, and Leominster WTFs (**Figure 4**).

The monthly median upstream and pond calcium concentration was highest in September (26.4 mg/L) and lowest in June (6.4 mg/L), while the median downstream concentration was highest in June (30 mg/L) and lowest in December and January (15.9 mg/L). At all ambient stations, the monthly median calcium concentration was slightly higher in July and September (24.1-26.4 mg/L) and lower in the winter months (November to February: 12.4-16.7 mg/L).



Figure 4. Boxplot of calcium, filtered (mg/L), from discrete samples taken at selected ambient stations (upstream or pond) at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019. Data include only those from selected ambient stations used for copper criteria value calculations in the Biotic Ligand Model (BLM).

3.1.3 Chloride

Chloride concentrations at ambient stations ranged from 14.9 to 609 mg/L during the study period, while median concentrations ranged from 26.6 to 184 mg/L. Of the stations used to calculate copper criteria values, higher chloride concentrations were typically found in the upstream stations on the Assabet River associated with Marlborough, Hudson, and Maynard WWTFs, in addition to stations upstream of Hanover, Weymouth, and Wilmington WTFs, while lower concentrations were reported at the ambient upstream or pond stations near Westborough WWTF, and Cohasset, Fitchburg, and Leominster WTFs (**Figure 5**).

No seasonality was apparent for upstream and pond chloride concentrations. However, at downstream stations the highest monthly median chloride concentrations were reported from April to July (152-218 mg/L) with the lowest concentration in November (91.9 mg/L). There was no apparent seasonal trend for all ambient stations, with the highest monthly median chloride concentration measured in July (146 mg/L) and the lowest median concentration in June (74.8 mg/L).



Figure 5. Boxplot of chloride, filtered (mg/L), from discrete samples taken at selected ambient stations (upstream or pond) at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019. Data include only those from selected ambient stations used for copper criteria value calculations in the Biotic Ligand Model (BLM).

3.1.4 Copper

Copper concentrations at all ambient stations associated with the facilities ranged from below the limit of detection (<0.4 μ g/L) to 7.3 μ g/L. Median copper concentrations ranged from the limit of detection (0.4 μ g/L at Fitchburg and Westborough WTFs) to 1.6 μ g/L (Marlborough WWTF). At the ambient stations used in the BLM, the highest upstream median copper concentrations were recorded at Marlborough, Hudson, and Maynard WWTFs on the Assabet River, and the Mill River near Weymouth WTF. Low median copper concentrations were reported in Wyman Pond (Fitchburg WTF) and in the Assabet River upstream of Westborough WWTF, while concentrations at both shallow and deep locations in Hocomonco Pond (Westborough WTF) were consistently below the limit of detection (<0.4 μ g/L; **Figure 6**).

Monthly median upstream or pond copper concentrations were $\leq 1 \ \mu g/L$ throughout the year, with some occasional higher values recorded from May through September. Downstream monthly median copper concentrations were slightly higher throughout the year ($\leq 1.3 \ \mu g/L$) as compared to upstream, with the highest values reported in June to September. At all ambient stations, the monthly median copper concentration was highest in May (0.99 $\mu g/L$) and lowest in August (<0.4 $\mu g/L$).



Figure 6. Boxplot of copper, filtered (μ g/L), from discrete samples taken at selected ambient stations (upstream or pond) at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019. Data include only those from selected ambient stations used for copper criteria value calculations in the Biotic Ligand Model (BLM).

3.1.5 Magnesium

Concentrations of magnesium at all ambient stations ranged from 0.354 to 12.2 mg/L, with median concentrations of 0.466 to 5.28 mg/L. Of the upstream and pond stations used to calculate copper criteria values, the highest median magnesium concentration was observed in Mill River upstream of Weymouth WTF, with very low median concentrations reported in samples from the Wyman Pond stations (Fitchburg WTF) and Monoosnoc Brook upstream of Leominster WTF (**Figure 7**).

There was no apparent pattern of seasonality evident for magnesium concentrations in upstream or pond ambient stations. Downstream concentrations of magnesium were typically higher in summer months and lower in winter months, with the highest monthly median concentration in May (5.72 mg/L) and the lowest median concentration in November (2.66 mg/L). At all ambient stations, the highest monthly median magnesium concentration occurred in July (5.47 mg/L), while the lowest median concentration was in November (2.66 mg/L).



Figure 7. Boxplot of magnesium, filtered (mg/L), from discrete samples taken at selected ambient stations (upstream or pond) at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019. Data include only those from selected ambient stations used for copper criteria value calculations in the Biotic Ligand Model (BLM).

3.1.6 Dissolved Organic Carbon

At all ambient stations, concentrations of DOC ranged from 1.07 to 18.9 mg/L, with median DOC ranging from 3.09 to 11.1 mg/L. Of the stations used in the BLM, DOC was typically higher at the Lily Pond (shallow and deep) stations associated with Cohasset WTF, and the median DOC concentration was also high upstream of Hanover WTF in Third Herring Brook. All other upstream or pond stations had relatively low median DOC concentrations (\leq 5.32 mg/L; **Figure 8**).

DOC concentrations were typically lower in the winter to early spring (January to March median: 2.96 – 3.29 mg/L) and higher in October (median: 5.89 mg/L) for all ambient stations. A similar seasonality occurred at the upstream and pond stations, with median DOC lowest in March (2.96 mg/L) and highest in October (5.86 mg/L). Slightly higher monthly median DOC values were recorded at downstream stations, with the lowest median DOC concentration in January (3.31 mg/L) and the highest median DOC concentration observed in October and November (5.89 mg/L).

These observations are consistent with the comparison of DOC concentrations among ambient stations as reported in Armstrong *et al.* (2022b).



Figure 8. Boxplot of organic carbon, filtered (dissolved organic carbon (DOC); mg/L), from discrete samples taken at selected ambient stations (upstream or pond) at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019. Data include only those from selected ambient stations used for copper criteria value calculations in the Biotic Ligand Model (BLM).

3.1.7 pH

All ambient station pH values ranged from 4.9 to 8.6 SU, with median pH ranging from 6.1 SU (Cohasset WTF) to 7.2 SU (Maynard WWTF). Of the stations used as input to the BLM, a similar range of higher pH values was reported for the upstream ambient stations on the Assabet River (Westborough WWTF, Marlborough WWTF, Hudson WWTF and Maynard WWTF), while lower pH values were recorded for the pond stations associated with Cohasset and Fitchburg WTFs and Monoosnoc Brook near Leominster WTF (**Figure 9**).

Monthly median upstream and pond pH values tended to be highest in March to May (6.8-7.0 SU), and lowest in September to October (6.4 SU). Downstream monthly median pH values were highest in April, June, and July (6.9-7.1 SU), and lowest in October and February (6.4 SU). For all ambient stations, median pH values were highest in January and March (7.0 SU), and lowest in September to October (6.4 SU).

These observations are consistent with the comparison of pH among ambient stations as reported in Armstrong *et al.* (2022b).



Figure 9. Boxplot of pH (standard units; SU) from discrete samples taken at selected ambient stations (upstream or pond) at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019. Data include only those from selected ambient stations used for copper criteria value calculations in the Biotic Ligand Model (BLM).

3.1.8 Potassium

Potassium concentrations ranged from 0.41 to 75.8 mg/L at all ambient stations, with median potassium concentrations between 0.61 and 6.91 mg/L. For those stations used in the BLM only, higher potassium concentrations were typically measured in the upstream Assabet River sites (associated with Marlborough, Hudson, and Maynard WWTFs), and consistently low values (medians <1 mg/L) were reported at the ponds associated with Cohasset and Fitchburg WTFs and Monoosnoc Brook, upstream of Leominster WTF (**Figure 10**).

No apparent seasonal pattern was evident for potassium concentrations at upstream or pond sites, with all monthly median values ≤ 3.56 mg/L. At downstream ambient stations, the median potassium concentration was elevated in April, June, and September (5.71, 5.94, and 6.64 mg/L, respectively) with high outlier concentrations observed in July, August, September, and December (all on the Assabet River). At all ambient stations, potassium concentrations typically varied over a narrow range (monthly medians: 1.99-3.73 mg/L) and there was no apparent seasonality.



Figure 10. Boxplot of potassium, filtered (mg/L), from discrete samples taken at selected ambient stations (upstream or pond) at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019. Data include only those from selected ambient stations used for copper criteria value calculations in the Biotic Ligand Model (BLM).

3.1.9 Sodium

At all ambient stations, sodium concentrations ranged from 10.1 to 210 mg/L, with a wide range of median values reported for each facility (18.4 – 98.8 mg/L). For upstream and pond stations used in the BLM, sodium concentrations were typically highest on the Assabet River upstream of Marlborough, Hudson, and Maynard WWTFs, and upstream of Hanover, Weymouth, and Wilmington WTFs (**Figure 11**). Concentrations of sodium were closely linked with those of chloride, likely due to their co-occurrence in natural waters as ions from a dissolved salt (NaCl).

The monthly median sodium concentration ranged from 34 mg/L (November) to 66.8 mg/L (March) at upstream and pond stations. At downstream stations an apparent seasonal pattern was evident, with the highest monthly median concentration occurring in June (121 mg/L) and the lowest in November (51.9 mg/L). For all ambient stations, the highest monthly median was reported in July (75 mg/L), with the lowest in November (38.8 mg/L).



Figure 11. Boxplot of sodium, filtered (mg/L), from discrete samples taken at selected ambient stations (upstream or pond) at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019. Data include only those from selected ambient stations used for copper criteria value calculations in the Biotic Ligand Model (BLM).

3.1.10 Sulfate

Sulfate concentrations at all ambient stations ranged from 1.72 to 56.2 mg/L, with facility median concentrations reported from 3.14 to 13.3 mg/L. Of the stations used as input for the BLM, the highest concentrations were measured in the Assabet River upstream of Marlborough, Hudson, and Maynard WWTFs, with high concentrations also recorded in Sawmill Brook and Maple Meadow Brook (upstream of Wilmington WTF). The lowest median sulfate concentration was measured at Fitchburg WTF (**Figure 12**).

Upstream median sulfate concentrations were always <20 mg/L, with the highest median concentrations reported in January to March (9.57-12.0 mg/L) and the lowest in August (3.53 mg/L). Downstream monthly median sulfate concentrations showed less variability, although higher median values were reported in July-September (13.0-15.2 mg/L) with three outlier concentrations (>30 mg/L) during this period. Sulfate concentrations at all ambient stations showed little seasonal variability, and monthly median concentrations ranged from 4.37 to 12.1 mg/L.



Figure 12. Boxplot of sulfate, filtered (mg/L), from discrete samples taken at selected ambient stations (upstream or pond) at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019. Data include only those from selected ambient stations used for copper criteria value calculations in the Biotic Ligand Model (BLM).

3.1.11 Temperature

Water temperatures at all ambient stations varied over a wide range from 0.2 to 31.5 °C, and median temperatures were between 12.2 and 20 °C. Of the stations used to calculate site-dependent copper criteria values, median temperatures were highest in Wyman Pond (Fitchburg WTF) and lowest in the Assabet River upstream of Hudson WWTF, and the streams associated with Hanover and Leominster WTFs (Third Herring Brook and Monoosnoc Brook, respectively).

Water temperatures showed apparent seasonal variability. Across all ambient stations, the highest median temperature was recorded in July (25.2 °C), and the lowest median temperature occurred in January (0.3 °C). An identical seasonal pattern was observed at upstream/pond and downstream stations, with median temperatures ranging from 0.2 to 25.2 °C and 0.4 to 25.8 °C, respectively. Marginally warmer median temperatures were recorded at the downstream stations as compared to upstream.



Figure 13. Boxplot of temperature (°C) from discrete samples taken at selected ambient stations (upstream or pond) at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019. Data include only those from selected ambient stations used for copper criteria value calculations in the Biotic Ligand Model (BLM).

3.2 Quality Assurance and Quality Control Results

The accuracy and precision of data collected in this study were assessed using QA and QC measurements from each monitoring station, as described in Armstrong *et al.* (2022b). These included samples for equipment and field blanks, replicates, and laboratory matrix spikes. Results from the QA and QC data collected during this study are summarized below.

3.2.1 Blanks

Field and equipment blank samples were randomly collected at monitoring stations over the study period. Blank samples are intended to identify contamination from sampling and processing procedures, therefore introducing biased or artificially high results.

A total of 48 blank samples (approximately 11% of total samples) were collected and analyzed during this study, comprising 15 field and 33 equipment blanks. Values for blanks were compared to the laboratory reporting limit and environmental concentrations collected for ambient and effluent samples.

Analytes in all blanks were almost all low or below the limit of detection for all parameters measured in this study. A single potassium result was measured at the limit of detection (0.004 mg/L), and one sodium result (0.47 mg/L) was marginally above the limit of detection (0.40 mg/L). Five blank samples showed DOC concentrations slightly above the detection limit of 0.23 mg/L (0.25-0.36 mg/L); however, all of these were substantially lower than the DOC concentration detected in the corresponding samples.

3.2.2 Replicates

Replicate samples were collected to quantify variability in the sampling or analysis procedures and allow evaluation of reproducibility for sample collection or analytical techniques. In this study, replicates were collected either concurrently or sequentially immediately following the first sample using the same protocol (i.e., field replicate), or the sample was split into two subsamples (i.e., laboratory replicate).

A total of 27 replicate samples (approximately 6% of total samples) were collected and analyzed during this study. Most replicates were within an acceptable variability with relative percent difference (RPD) for all parameters typically less than 10%. The exceptions included two samples for potassium (RPD = 12.5 and 11.9%) and two copper samples (11.9 and 17.1%). As the RPDs for these exceptions were only marginally above 10%, and considering copper is not an input parameter to the BLM, these samples had minimal impact to the final copper criteria values in this study.

3.2.3 Laboratory Matrix Spikes

A laboratory matrix spike (LMS) sample is used to assess whether the sample matrices (i.e., non-sample components) affect the laboratory analysis of the sample. This can determine if there was any interference of the matrix on analytical recovery that could cause biased results. It is recommended that LMSs are performed when specific conductance of a sample is near or >2,500 μ S/cm.

In this study, four LMS samples were prepared using a portion of the sample and adding a measured volume of known concentration of filtered copper. This "spiked" sample was compared to the "parent sample", and the relative percent differences were calculated to obtain copper spike recovery. The spiked samples included three from the Westborough WWTF effluent (Station No. 421651071381401) and one from the Maynard WWTF effluent (Station No. 422627071262301).

Copper spike recovery ranged from 88-98% for three of the four spiked samples. This indicates that when specific conductance in a sample is greater than 1,000 μ S/cm (as in the spiked samples), matrix suppression of copper can result and may negatively bias the laboratory measured concentrations. Approximately 10% of the samples (13 ambient samples and 34 effluent samples) had specific conductance values greater than 1,000 μ S/cm. We note that for one of the spiked samples from Westborough WWTF effluent (August 1, 2018), the sample was spiked after dilution, while the parent environmental sample was not diluted. Therefore, the result for this sample was deemed invalid due to the inconsistency in dilution.

4. Site-Dependent Copper Criteria Values for Receiving Waterbodies Near 11 WTFs in Eastern and Central MA

Site-dependent copper criteria values (CMCs and CCCs) were calculated for each facility using the BLM, according to the method described in Section 2.5. The impact of the detection limit approach and rounding of the dataset are described, with the final copper criteria presented below.

4.1 Impact of Detection Limits

Considering the input parameters for the BLM, only one parameter (alkalinity, mg/L as CaCO₃) for one facility (Leominster WTF) had values below the laboratory limit of detection. In this case, seven samples (of 13 total samples) were below the detection limit for alkalinity (<4 mg/L). Values below the detection

limit were assigned either half the detection limit (2 mg/L) or the detection limit itself (4 mg/L) for the purposes of comparing impacts to site-dependent copper criteria values. The 10th percentile CMC and CCC outputs were both marginally lower by 0.001 mg/L (i.e., more conservative) when using half of the detection limit value as compared to using the detection limit itself. This was a result of lower instantaneous criteria values for these samples when half the detection limit was employed for alkalinity. Therefore, for samples that were below the detection limit, the value representing half the detection limit was used for a more conservative approach.

4.2 Impact of Rounded versus Unrounded Datasets

Two datasets (unrounded and rounded) were used with the BLM for all facilities. The impact on the 10^{th} percentile CMC and CCC values was minimal, with a maximum difference between the unrounded and rounded criteria of 0.29 µg/L and 0.18 µg/L for CMC and CCC, respectively (Maynard WWTF). The 10^{th} percentile criteria were higher using the rounded dataset as compared to the unrounded for six facilities, while they were lower for five facilities. Thus, there appears to be no systematic difference to using rounded versus unrounded data. Given this, the rounded data were used here to generate copper criteria values from the BLM to be consistent with the approach in the aluminum report (Armstrong et al., 2022b).

4.3 Final Site-Dependent Copper Criteria Values

Site-dependent copper criteria values were calculated using the BLM software. Concurrent input data from the selected ambient upstream (or pond) sites for each facility (see **Table 2** for the list of stations) were used to calculate pairs of instantaneous CMCs and CCCs for each sampling event (n=209). Data for all input parameters and the associated instantaneous copper criteria values calculated using the BLM are shown in **Appendix A**.

The minimum, 5th, and 10th percentile values were calculated for each facility from the instantaneous CMC and CCC values to obtain final acute and chronic criteria values, respectively. The 10th percentile values are protective of aquatic life 90% of the time, the 5th percentile values are protective 95% of the time, and the minimum criteria values are protective at all times. The final site-dependent copper criteria values for each facility are presented in **Table 6**.

The instantaneous criteria are summarized as boxplots in **Figure 14A** and **B**. Where a facility had more than one ambient station used for calculation of the site-dependent copper criteria values, the instantaneous criteria for all stations were combined for the boxplot.

Overall, the instantaneous site-dependent copper criteria values varied at each site, according to the changes in the local water chemistry. The largest range of criteria was reported for Maynard WWTF (CMC = $5.7-77 \ \mu g/L$; CCC = $3.6-48 \ \mu g/L$), while the criteria values for Leominster WTF varied over the narrowest range (CMC = $0.26-4.7 \ \mu g/L$; CCC = $0.16-2.9 \ \mu g/L$). The highest minimum, 5th percentile, and 10^{th} percentile CMC and CCC values were calculated for Hudson WWTF, whereas the lowest criteria were calculated for Leominster WTF.

There were apparent seasonal trends in the instantaneous criteria values, with the lowest criteria values typically occurring during the fall and winter months, and the highest criteria values occurring during the spring and summer months. This highlights the importance of collecting representative data throughout the year, and across years, to capture the full intra- and inter-annual variability in local water chemistry data at sites. Consistent with this finding, MassDEP guidance for application of the BLM for NPDES and

SWD permits recommends a minimum of 20 sampling events over two years, spaced at least monthly, to capture a representative dataset for use in the BLM (MassDEP, 2021a).

The site-dependent criteria values are described below for each facility and compared to the measured copper concentrations downstream of each facility, where possible. Time-series plots of the monthly copper CMC and CCC values for each station are available in **Appendix D**.

Table 6. Minimum, 5th, and 10th percentile statistics for site-dependent acute (criterion maximum concentration, CMC) and chronic (criterion continuous concentration, CCC) values calculated using the Biotic Ligand Model (BLM) for stations near seven water treatment facilities and four wastewater treatment facilities in eastern and central Massachusetts, 2018-2019. Final CMC and CCC values are rounded to two significant figures, as in Stephen et al. (1985).

Facility	USGS Station No.	Upstream	Min (µg/l)		5 th percentile		10 th percentile	
		or Pond			(µg/l)		(µg/l)	
			СМС	CCC	CMC	CCC	СМС	CCC
Westborough	01096603	Upstream	5.5	3.4	5.5	3.4	5.6	3.5
WWTF								
Marlborough	01096720	Upstream	6.4	4.0	6.8	4.2	7.8	4.8
WWTF								
Hudson WWTF	01096870	Upstream	7.1	4.4	7.6	4.7	8.3	5.2
Maynard WWTF	01097021	Upstream	5.7	3.6	6.0	3.7	6.5	4.0
Cohasset WTF	421326070485802	Pond	0.55	0.34	0.57	0.35	0.75	0.47
	421326070485801							
Fitchburg WTF	423132071523401	Pond	0.31	0.19	0.48	0.30	0.51	0.32
	423132071523402							
	423211071524701							
	423211071524702							
Westborough	421622071385701	Pond	1.4	0.86	1.8	1.1	2.1	1.3
WTF	421622071385702							
	421628071384501							
Hanover WTF	11058065	Upstream	5.3	3.3	5.6	3.5	5.8	3.6
Leominster WTF	01094420	Upstream	0.26	0.16	0.28	0.17	0.30	0.19
Weymouth WTF	01105587	Upstream	2.1	1.3	2.6	1.6	3.0	1.8
Wilmington WTF	01101296	Upstream	3.7	2.3	5.8	3.6	6.1	3.8
	01101294							



Figure 14. Boxplots of instantaneous site-dependent (A) acute (criterion maximum concentration, CMC) and (B) chronic (criterion continuous concentration, CCC) values for dissolved copper (µg/L) calculated using the Biotic Ligand Model (BLM) for stations near seven water treatment facilities (WTFs) and four wastewater treatment facilities (WWTFs) in eastern and central Massachusetts, 2018-2019.

4.3.1 Westborough WWTF

Instantaneous site-dependent copper criteria were calculated for the Assabet River near Westborough WWTF using water quality data collected at the ambient (upstream) station, Assabet River near Westborough, MA (Station No. 01096603). The CMC values for this station ranged from 5.5 to 16 μ g/L, and the CCC values ranged from 3.4 to 9.8 μ g/L. Monthly CMC and CCC values were lowest in September and highest in November. The CMC minimum, 5th percentile, and 10th percentile values were 5.5, 5.5, and 5.6 μ g/L, respectively, and the CCC minimum, 5th percentile, and 10th percentile values were 3.4, 3.4, and 3.5 μ g/L, respectively.

Copper concentrations at the Assabet River downstream from the Westborough WTP at Route 9 (Station No. 421700071381901) ranged from 1.3 to 7.3 μ g/L. The minimum, 5th percentile, and 10th percentile copper CMC values were exceeded at the downstream station on a single occasion (July 13th, 2018), while the minimum, 5th percentile, and 10th percentile CCC values were exceeded on two occasions (June 8th, 2018 and July 13th, 2018) over the study period.

4.3.2 Marlborough WWTF

The site-dependent copper criteria values near Marlborough WWTF were calculated for the Assabet River from water quality data collected at the ambient (upstream) station, Assabet River at Boundary St. near Northborough, MA (Station No. 01096720). The CMC values upstream ranged from 6.4 to 25 μ g/L, while CCC values ranged from 4.0 to 16 μ g/L. Monthly copper criteria values (CMC and CCC values) were lowest in February but highest in June. The CMC minimum, 5th percentile, and 10th percentile values were 6.4, 6.8, and 7.8 μ g/L, respectively, and the CCC minimum, 5th percentile, and 10th percentile values were 4.0, 4.2, and 4.8 μ g/L, respectively.

Copper concentrations at the Assabet River, downstream of the Marlborough WWTF (Station No. 1096725), ranged from 1 to 3.4 μ g/L, and did not exceed the minimum, 5th percentile, or 10th percentile copper CMC and CCC values on any occasion.

4.3.3 Hudson WWTF

Water quality data collected at the ambient (upstream) station, Assabet River at Cox St near Hudson, MA (Station No. 01096870), were used to calculate the site-dependent copper criteria values for Hudson WWTF. The CMC values at this station ranged from 7.1 to 21 μ g/L, and the CCC values ranged from 4.4 to 13 μ g/L. The instantaneous CMC and CCC values were lowest in December and highest in June. The minimum, 5th percentile, and 10th percentile CMC values were 7.1, 7.6, and 8.3 μ g/L, respectively, while the minimum, 5th percentile, and 10th percentile CCC values were 4.4, 4.7, and 5.2 μ g/L, respectively.

Copper concentrations were measured downstream at the Assabet River near Hudson-Stow Town Line (Station No. 1096875) and ranged from 0.94 to 4.8 μ g/L. The minimum, 5th percentile, and 10th percentile copper CMC values were not exceeded on any occasion. However, the minimum and 5th percentile CCC values were both exceeded in a single sample (July 30th, 2018).

4.3.4 Maynard WWTF

The instantaneous copper criteria were calculated for the Assabet River upstream of Maynard WWTF from water quality data collected at the ambient (upstream) station, Assabet River, US Maynard Wastewater Treatment Plant (Station No. 01097021). The CMC values at the upstream station ranged from 5.7 to 77 µg/L, and the CCC values ranged from 3.6 to 48 µg/L. The lowest monthly CMC and CCC
values were reported in February, while the highest values occurred in July. The CMC minimum, 5^{th} percentile, and 10^{th} percentile values were 5.7, 6.0, and 6.5 µg/L, respectively, while the CCC minimum, 5^{th} percentile, and 10^{th} percentile values were 3.6, 3.7, and 4.0 µg/L, respectively.

Copper concentrations were measured at the Assabet River downstream of the Maynard WWTF (Station No. 1097023). At this station, copper concentrations ranged from 0.77 to 1.7 μ g/L, and the CMC and CCC minimum, 5th percentile, and 10th percentile values were not exceeded on any sampling occasion during the study period.

4.3.5 Cohasset WTF

The instantaneous criteria values for Cohasset WTF were calculated using water quality data collected at two ambient (pond) stations in Lily Pond: Lily Pond Deep Hole (Station No. 421326070485801) and Lily Pond Deep Hole (Shallow) (Station No. 421326070485802). The CMC values at these two stations ranged from 0.55 to 72 μ g/L, and the CCC values ranged from 0.34 to 45 μ g/L. Monthly CMC and CCC values were lowest in November and highest in October. The CMC minimum, 5th percentile, and 10th percentile values were 0.55, 0.57, and 0.75 μ g/L, respectively, while the CCC minimum, 5th percentile, and 10th percentile values were 0.34, 0.35, and 0.47 μ g/L, respectively. The low copper criteria values calculated for Cohasset WTF were likely a result of the relatively low pH range (5-7.9 SU) measured at the two stations in Lily Pond.

Pond sites were specifically selected to be outside of the immediate effect of the effluent discharge. Therefore, no pond sites were measured within the immediate effect of the Cohasset WTF effluent discharge. However, copper concentrations in Lily Pond at the two ambient stations [Lily Pond Deep Hole (Station No. 421326070485801) and Lily Pond Deep Hole (Shallow) (Station No. 421326070485802)] ranged from <0.4 to $1.5 \mu g/L$. The minimum and 5th percentile copper CMC values were exceeded in 18 of 23 samples, while the 10^{th} percentile CMC value was exceeded in 14 of 23 samples. The minimum, 5th percentile, and 10^{th} percentile CCC values were all exceeded in 19 out of 23 samples.

4.3.6 Fitchburg WTF

The instantaneous copper criteria were calculated for Wyman Pond near Fitchburg WTF using water quality data collected at four ambient (pond) stations: Wyman Pond, Leino Park Rd, Shallow, Westminster MA (Station No. 423132071523401); Wyman Pond, Leino Park Rd, Deep, Westminster, MA (Station No. 423132071523402); Wyman Pond Shallow, Westminster, MA (Station No. 42312071524701); and Wyman Pond Deep, Westminster, MA (Station No. 423211071524702). The CMC values for the four Wyman Pond stations ranged from 0.31 to 5.9 µg/L, and the CCC values ranged from 0.19 to 3.7 µg/L. There was no apparent seasonal pattern in monthly CMC and CCC values, however the highest criteria value occurred in April, while the lowest criteria values were reported for September and November. The CMC minimum, 5th percentile, and 10th percentile values were 0.31, 0.48 and 0.51 µg/L, respectively, while the CCC minimum, 5th percentile, and 10th percentile values were 0.19, 0.30, and 0.32 µg/L, respectively. The low copper criteria values calculated for Fitchburg WTF were likely a result of the relatively low pH range (5.5-7.3 SU) and low DOC concentrations (1.68-4.71 mg/L) measured in Wyman Pond.

There were no pond sites within the immediate effect of the Fitchburg WTF effluent discharge, and all four ambient sites in Wyman Pond were used as input to the BLM. However, copper concentrations at

the four ambient stations ranged from <0.4 to 0.72 μ g/L. The CMC minimum value was below the copper limit of detection (0.4 μ g/L), therefore copper concentrations in all 43 samples from the four stations in Wyman Pond exceeded the minimum CMC. However, copper concentrations were below the limit of detection in over half of the samples collected at the four stations in Wyman Pond (23 of 43 samples). The 5th percentile CMC value was exceeded in 8 samples, while the 10th percentile CMC value was exceeded in 4 of the 43 samples collected at the four sampling locations in Wyman Pond. The exceedances of the 5th and 10th percentile CMC values occurred mainly in May and June at all four stations, except for one exceedance in February that occurred at a single station (Wyman Pond, Leino Park Rd, Shallow, Westminster, MA). The CCC minimum, 5th, and 10th percentile values were all below the copper laboratory detection limit (< 0.4 μ g/L), thus copper concentrations exceeded the calculated criteria values on all sampling occasions.

4.3.7 Westborough WTF

Instantaneous site-dependent copper criteria were calculated for each sampling occasion in Hocomonco Pond near Westborough WTF. Data from three ambient (pond) stations were used as input to the BLM, including: Hocomonco Pond Shallow, Westborough MA (Station No. 421622071385701), Hocomonco Pond Deep, Westborough MA (Station No. 421622071385702) and Hocomonco Pond near Otis St, Westborough MA (Station No. 421628071384501). For all stations combined, the CMC values ranged from 1.4 to 17 μ g/L, and the CCC values ranged from 0.86 to 11 μ g/L. Monthly CMC and CCC values were highest in July, and lowest in October. The CMC minimum, 5th percentile and 10th percentile values user 1.4, 1.8 and 2.1 μ g/L, respectively, while the CCC minimum, 5th percentile and 10th percentile values were 0.86, 1.1 and 1.3 μ g/L, respectively.

There were no sites in Hocomonco Pond considered within the immediate effect of the Westborough WTF effluent discharge, and data from all three stations were used as input to the BLM to calculate sitedependent copper criteria. At all three ambient stations [Hocomonco Pond Shallow, Westborough MA (Station No. 421622071385701), Hocomonco Pond Deep, Westborough MA (Station No. 421622071385702) and Hocomonco Pond near Otis St, Westborough MA (Station No. 421628071384501)], concentrations of copper were consistently below the limit of detection (<0.4 μ g/L). All copper criteria were higher than the limit of detection, therefore there were no exceedances of the minimum, 5th percentile and 10th percentile copper CMC and CCC values on any occasion.

4.3.8 Hanover WTF

The instantaneous copper criteria values were calculated for Third Herring Brook near Hanover WTF using water quality data collected at the ambient (upstream) station, Third Herring Brook Pond St near Hanover, MA (Station No. 011058065). The CMC values upstream ranged from 5.3 to 50 μ g/L, and the CCC values ranged from 3.3 to 31 μ g/L. Monthly CMC and CCC values were lowest in March and highest in December. The CMC minimum, 5th percentile, and 10th percentile values were 5.3, 5.6, and 5.8 μ g/L, respectively, while the CCC minimum, 5th percentile, and 10th percentile values were 3.3, 3.5, and 3.6 μ g/L, respectively.

Copper concentrations were measured at Third Herring Brook, downstream of the WTF, near Hanover, MA (Station No. 11058075). Copper concentrations at this station ranged from 0.53 to 1.7 μ g/L over the study period; thus, the minimum, 5th percentile, and 10th percentile copper CMC and CCC values were not exceeded on any occasion.

4.3.9 Leominster WTF

Site-dependent copper criteria values were calculated for Leominster WTF using water quality data from the ambient (upstream) station, Monoosnoc Brook, US Leominster Water Treatment Plant (Station No. 01094420). At this station, CMC values ranged from 0.26 to 4.7 μ g/L, and the CCC values ranged from 0.16 to 2.9 μ g/L. Monthly CMC and CCC values were lowest in December and highest in July. The CMC minimum, 5th percentile, and 10th percentile values were 0.26, 0.28, and 0.30 μ g/L, respectively, and the CCC minimum, 5th percentile, and 10th percentile values were 0.16, 0.17, and 0.19 μ g/L, respectively. Leominster WTF had the lowest criteria values of all facilities, likely a result of the low pH range in Monoosnoc Brook (5.2 to 6.9 SU); however, the other BLM input parameters were also consistently low.

Copper concentrations in Monoosnoc Brook were also measured downstream of the Leominster WTF (Station No. 1094422). Concentrations ranged from 0.46 to 0.8 μ g/L and consistently exceeded the minimum, 5th percentile, and 10th percentile copper CMC and CCC values, as all criteria values were below the limit of detection for copper (< 0.4 μ g/L).

4.3.10 Weymouth WTF

Instantaneous copper criteria were calculated for Mill River near Weymouth WTF, using water quality data collected at the ambient (upstream) station, Mill River near Randolph St, South Weymouth, MA (Station No. 01105587). CMC values calculated from water quality data at this station ranged from 2.1 to 9.2 μ g/L, while CCC values ranged from 1.3 to 5.7 μ g/L. The lowest monthly CMC and CCC values were recorded in August, while the highest criteria occurred in April. The CMC minimum, 5th percentile, and 10th percentile values were 2.1, 2.6 and 3.0 μ g/L, respectively, and the CCC minimum, 5th percentile, and 10th percentile values were 1.3, 1.6, and 1.8 μ g/L, respectively.

Copper concentrations were measured downstream at Great Pond near Outlet, Shallow, South Weymouth, MA (Station No. 421004070580201) and Great Pond near Outlet, Deep, South Weymouth, MA (Station No. 421004070580202)⁹. Concentrations of copper in samples from the Great Pond shallow and deep stations ranged from <0.4 to 0.59 μ g/L, and were consistently below the minimum, 5th percentile and 10th percentile copper CMC and CCC values.

4.3.11 Wilmington WTF

Water quality data for input to the BLM were collected at two ambient stations upstream of Wilmington WTF: Maple Meadow Brook, Wilmington, MA (Station No. 01101294) and Sawmill Brook at Chestnut St, Wilmington, MA (Station No. 01101296). The instantaneous CMC values for the upstream stations ranged from 3.7 to 15 μ g/L, and the CCC values ranged from 2.3 to 9.1 μ g/L. Criteria were typically higher for the Sawmill Brook as compared to Maple Meadow Brook. Monthly CMC and CCC values were lowest in August and December and highest from May to June. The CMC minimum, 5th percentile, and 10th percentile values were 3.7, 5.8, and 6.1 μ g/L, respectively, while the CCC minimum, 5th percentile, and 10th percentile values were 2.3, 3.6, and 3.8 μ g/L, respectively.

⁹ Note that although the Mill River is the EPA-designated receiving water for the Weymouth WTF effluent discharge, the effluent discharges directly into an embayment of Great Pond that flows into a control structure at the dam near Randolph Street, and then down a small tributary for ~0.5 miles prior to confluence with the Mill River.

Copper concentrations were measured downstream at Maple Meadow Brook, at Middlesex Canal, Wilmington MA (Station No. 1101298) and ranged from <0.4 to 1.1 μ g/L over the study period. All measured downstream concentrations were below the site-dependent criteria.

5. Relationships Between Water Quality Parameters and Site-Dependent Copper Criteria

A multiple nonlinear regression of the instantaneous site-dependent copper criteria values (acute and chronic) as a function of the water quality parameter inputs for the BLM allowed an assessment of the relationships between a criterion and the respective water quality constituent. The objective of this analysis was to identify the most influential input parameters for the BLM. All 10 BLM input parameters measured in this study were included in the analysis: pH, DOC, temperature, alkalinity, calcium, magnesium, sodium, potassium, sulfate, and chloride. A generalized additive model (GAM) was developed using an iteratively reweighted least squares (IWLS) method in the 'mgcv' package in R software (R Core Team, 2020; Wood, 2006). GAMs allow for parameters to vary non-linearly with the response variable by fitting data with smooths, or splines.

The key drivers of variability in the site-dependent acute and chronic copper criteria values were identified using the summary output of the GAM, which identifies the significance of the smooth terms for each parameter using an analysis of variance (ANOVA). The ANOVA F-statistic is the ratio of the variance of the means between groups to the within group variance (i.e., the higher the F-statistic, the greater the importance of the variable to the GAM). Statistical significance was determined by using a 0.05 threshold for the *p*-values associated with the ANOVA F-statistic (i.e., p<0.05 indicates the water quality variable is a statistically significant predictor of the criteria values).

5.1 Generalized Additive Model Results

The GAMs using all ambient station data for all facilities considered in this study explained 96.5% of the variance in acute and chronic criteria values (adjusted $R^2 = 0.965$). Note that the model ANOVA results are the same for both acute and chronic because the BLM chronic criteria values are derived from the final acute values using the acute to chronic ratio (ACR).

The most significant predictors of copper criteria values were pH and DOC (**Table 7**). Weaker, albeit statistically significant, relationships were identified between copper criteria values and alkalinity, chloride, sulfate, and potassium. However, no statistical significance was found between criteria values and sodium, magnesium, calcium, or temperature. The partial effects plots of each BLM input parameter on the criteria values for a GAM for acute (criterion maximum concentration, CMC) and chronic (criterion continuous concentration, CCC) values are shown in **Figure 15** and **Figure 16**, respectively. These plots show the component effect of each of the smooth terms in the GAM assuming all other parameters are constant, which together add up to the overall model prediction for copper criteria values.

Hardness-dependent equations do not take into account pH and DOC, which in this study were found to be the most important parameters for determining copper criteria values using the BLM. This supports the prioritization for copper criteria outlined in the MA SWQS regulation, as follows (314 CMR 4.06(d): *Table 29a*): "If both hardness-dependent and BLM instantaneous criteria values for Fresh Water are

calculated or are able to be calculated for a relevant location, the values calculated using the BLM shall be used."

Table 7. Statistical significance of the 10 measured Biotic Ligand Model (BLM) input parameters as predictors of the acute (criterion maximum concentration, CMC) or chronic (criterion continuous concentration, CCC) values. A Generalized Additive Model (GAM) was used with all input parameters (n=209), and statistical significance was determined using an Analysis of Variance (ANOVA) with p<0.05. Significance symbol codes: p<0.0001 '***', p<0.001 '***', p<0.01 '**', p<0.05 '*'.

BLM Input	GAM Analysis of Variance (ANOVA)									
Parameter	Degrees of	F-statistic	p-value	Significance						
	Freedom									
рН	8.99	327	< 0.0001	****						
DOC	4.35	33.4	< 0.0001	****						
Alkalinity	8.83	3.61	0.000549	***						
Chloride	7.63	3.49	0.00118	**						
Sulfate	6.67	2.62	0.0153	*						
Potassium	1.00	4.44	0.0366	*						
Sodium	1.00	3.89	0.0502							
Magnesium	1.00	1.64	0.203							
Calcium	1.00	0.264	0.608							
Temperature	1.40	0.474	0.670							



Figure 15. Smooth partial effects plots for the Generalized Additive Model (GAM) for acute (criterion maximum concentration, CMC) values as a function of each input parameter to the Biotic Ligand Model (BLM). The y-axis is the smooth or spline function partial effect in response to the respective BLM input parameter. Shaded area indicates the 95% confidence interval for the mean shape of the effect.



Figure 16. Smooth partial effects plots for the Generalized Additive Model (GAM) for chronic (criterion continuous concentration, CCC) values as a function of each input parameter to the Biotic Ligand Model (BLM). The y-axis is the smooth or spline function partial effect in response to the respective BLM input parameter. Shaded area indicates the 95% confidence interval for the mean shape of the effect.

5.1.1 Significance of BLM Input Parameters

pH was the most significant driver of instantaneous copper CMC and CCC values, with a highly significant relationship between criteria and pH (ANOVA F-statistic = 327, p<0.0001; **Table 7**). This result is anticipated, as copper bioavailability decreases with increasing pH due to the increasing degree of complexation of copper with hydroxides and carbonates, and decreasing proton competition with copper at the biotic ligand binding sites (Meyer et al., 2002; Miller and Mackay, 1980; Playle et al., 1992; U.S. EPA, 2007a). Thus, high pH values (i.e., low copper bioavailability) typically generated high CMC and CCC values, while low pH (i.e., high copper bioavailability) resulted in low criteria values. The relationship of pH with criteria values is clearly nonlinear, with the steepest slope in criteria values occurring at pH greater than 7.5 SU (**Figure 15** and **Figure 16**). The impact of pH on criteria values was apparent at facilities such as Leominster WTF, where low pH (median = 5.9 SU) resulted in the lowest criteria values calculated from the BLM (10th percentile CMC and CCC = 0.30 and 0.19 µg/L, respectively) using the example dataset. Similarly low CMC and CCC values were calculated for Cohasset and Fitchburg WTFs ($\leq 0.75 \mu g/L$), where pH was also relatively low (median = 6.2 SU at both facilities).

DOC was also a highly significant predictor of criteria values (ANOVA F-statistic = 33.4, p<0.0001; **Table 7**). DOC binds with copper, thus reducing copper bioavailability (Di Toro et al., 2001; Liao et al., 2019; Sciera et al., 2004). Therefore, the most sensitive conditions for copper toxicity occur when the DOC concentration is low (Peters et al., 2019). In effect, this results in more stringent (i.e., lower) copper criteria values using the BLM when there are low DOC concentrations (**Figure 15** and **Figure 16**). An example of this occurred near Fitchburg WTF, where low DOC concentrations in Wyman Pond (1.68-4.71 mg/L) resulted in low 10th percentile CMC and CCC values (0.51 and 0.32 µg/L, respectively).

There was a significant relationship between alkalinity and criteria values (ANOVA F-statistic = 3.61, p<0.001; **Table 7**). Alkalinity reduces copper toxicity to aquatic organisms due to the formation of copper-carbonate complexes as a function of increasing pH, which reduces the bioavailability of free copper ions (Hyne et al., 2005; Laurén and McDonald, 1986; Wurts and Perschbacher, 1994). Thus, stations with higher alkalinity result in higher copper criteria values calculated using the BLM (**Figure 15** and **Figure 16**). In this study, the impact of alkalinity was evident at stations on the Assabet River, for example, where relatively high alkalinity upstream of the WWTFs (16.8-61.1 mg/L as CaCO₃) corresponded with high 10th percentile CMC and CCC values for these facilities (5.6-8.3 and 3.5-5.2 µg/L, respectively).

Chloride was a significant predictor of copper criteria values, albeit a weaker relationship than found for pH, DOC, or alkalinity (ANOVA F-statistic = 3.49, p<0.01; **Table 7**). As an anion, chloride can bind to copper to form a complex, reduce the concentration of the free copper ion, and thus reduce copper bioavailability (Meyer, 2007; U.S. EPA, 2022). Chloride had a clear negative effect on criteria values, where higher chloride concentrations resulted in lower copper criteria values (**Figure 15** and **Figure 16**).

Sulfate was a weakly significant predictor of copper criteria values in the GAM (ANOVA F-statistic = 2.62, p<0.05; **Table 7**). As with chloride, sulfate is an anion that can form a complex with copper, therefore reducing the concentration of free copper ions available (Meyer, 2007; U.S. EPA, 2022). However, based on the partial effects plots, sulfate does not have a noticeable effect on copper criteria values over the range of sulfate concentrations (**Figure 15** and **Figure 16**).

Potassium was a weakly significant parameter in the GAM (ANOVA F-statistic = 1.00, p<0.05; **Table 7**). Potassium is a cation and can act by competing with copper ions for binding sites on organisms (Meyer, 2007; U.S. EPA, 2022). In this study, there was a slight positive linear relationship, with higher potassium concentrations associated with higher copper criteria values (**Figure 15** and **Figure 16**).

The parameters which were not considered significant predictors of copper criteria values in this study were sodium, magnesium, calcium, and temperature. There was a slight positive relationship between sodium, magnesium, and calcium concentrations and copper criteria values (**Figure 15** and **Figure 16**); however, the relationship was not significant in all cases (Sodium ANOVA F-statistic = 3.89, p = 0.0502; Magnesium ANOVA F-statistic = 1.64, p = 0.203; Calcium ANOVA F-statistic = 0.264, p = 0.608; **Table 7**). There was also no significant relationship found between temperature and copper criteria values (ANOVA F-statistic = 0.474, p=0.670; **Table 7**). The partial effects plots showed no variation in criteria values over the range of temperatures (**Figure 15** and **Figure 16**), indicating that temperature is not a driver of variability in the copper criteria values for this study dataset.

5.1.2 Comparison to Previous Studies

According to the EPA's *Supplementary Training Materials for Aquatic Life Criteria – Copper: Data Requirements*, the copper BLM is generally most sensitive to variations in pH and DOC; however, the sensitivity of the BLM to input parameters can vary depending on site-specific characteristics (U.S. EPA, 2007b, 2002). Furthermore, the EPA's Metals Cooperative Research and Development Agreement (CRADA) Phase I Report outlines the primary toxicity modifying factors (TMFs) for the copper BLM as pH, alkalinity, hardness, and DOC (Appendix C of U.S. EPA, 2022).

The finding in this study of pH and DOC as the key drivers of copper criteria variability is consistent with EPA's sensitivity analysis for the BLM (U.S. EPA, 2007b, 2002) and EPA's Metals CRADA Phase 1 Report (U.S. EPA, 2022). The additional sensitivity of the BLM to alkalinity values was described as a TMF in EPA's Metals CRADA Phase 1 Report only (Appendix C of U.S. EPA, 2022), and other studies have identified alkalinity as a primary factor affecting acute copper toxicity in aquatic environments (Hyne et al., 2005; Wurts and Perschbacher, 1994). In the 2018-2019 MassDEP/USGS study, ambient stations typically had lower alkalinity measurements (median = 4.35 - 34.9 mg/L as CaCO₃) than the dataset used to calibrate the model (median = ~10 - 250 mg/L as CaCO₃) (Appendix A of U.S. EPA, 2007a), which may have influenced the relative significance of alkalinity. Given the mechanism of action for alkalinity is through binding with copper to form copper-carbonate complexes (Hyne et al., 2005; Wurts and Perschbacher, 1994), even low alkalinity values are expected to have an effect on copper bioavailability.

Previous studies have found that the major geochemical cations (calcium, magnesium, sodium, and potassium) and geochemical anions (chloride, sulfate) can impact copper bioavailability as well as reflect favorable or unfavorable ion exchange gradients (Boran, 2020; Erickson et al., 1996; Meyer et al., 2002; Nys et al., 2020; U.S. EPA, 2007a). The statistically significant ions relative to the copper BLM criteria outputs in the 2018-2019 MassDEP/USGS study were chloride, sulfate, and potassium. Sodium, calcium, and magnesium were not significant. However, previous studies have found that hardness is an important factor for copper bioavailability, and in particular higher concentrations of calcium and magnesium ions demonstrate "protective effects" for aquatic life against copper toxicity by competing for binding sites on the biotic ligand (Crémazy et al., 2017; Meyer, 2007; Nys et al., 2020). Sodium has also been associated with decreased copper toxicity through competition at metal binding sites, although sodium ions appear to provide less protection than calcium or magnesium (Meyer, 2007; U.S.

EPA, 2022). Indeed, hardness-dependent equations have been historically recommended by the EPA for calculation of aquatic water quality criteria for various metals, including cadmium, chromium III, lead, nickel, silver and zinc (U.S. EPA, 2022). Nonetheless, the results from the 2018-2019 MassDEP/USGS study show that calcium and magnesium ions do not impact copper criteria values calculated with the BLM as much as other water quality constituents for this dataset.

Similar to alkalinity, calcium (median = 2.1 to 30 mg/L) and magnesium (median = 0.466 to 5.28 mg/L) concentrations at ambient stations in the 2018-2019 MassDEP/USGS study were lower than corresponding median concentrations in the BLM calibration dataset (calcium: ~8-200 mg/L; magnesium: ~0.1- 200 mg/L) (U.S. EPA, 2007a). However, median sodium (18.4 – 98.8 mg/L) and potassium concentrations (0.61 and 6.91 mg/L) at ambient stations were similar to median concentrations in the BLM calibration dataset (sodium = ~5-150 mg/L; potassium = ~0.04-7 mg/L) (U.S. EPA, 2007a). The lower calcium and magnesium concentrations for the 2018-2019 MassDEP/USGS study dataset may explain why these ions had less influence on the copper criteria values calculated with the BLM in this study. In contrast to the complexing action for alkalinity, the mechanism of action for calcium and magnesium is by competition with copper ions at binding sites (Crémazy et al., 2017; Meyer, 2007; Nys et al., 2020). However, at low concentrations of calcium and magnesium, there may be an insufficient concentration of these ions to effectively compete with the copper ions. This would explain why calcium and magnesium have less influence on copper criteria values calculated using the BLM. Indeed, research on juvenile channel catfish exposed to toxic concentrations of copper found that a minimum calcium hardness concentration (between 20 and 250 mg/L) may be required to maintain normal ion metabolism (Wurts and Perschbacher, 1994). Thus, the protective effects of calcium or magnesium may only apply at sufficiently high concentrations of these ions.

As found in this study, previous studies have indicated that temperature is not a key driver of copper toxicity (U.S. EPA, 2022). However, temperature has been shown to have an effect on chronic copper toxicity in *Daphnia magna* (Pereira et al., 2017), although impacts on copper toxicity for other species is limited. It is important to include temperature as a BLM input parameter because it is used along with alkalinity and pH to estimate DIC concentrations in the model (HydroQual, Inc., 2007).

6. Summary

The aim of the 2018-2019 MassDEP/USGS study was to support the implementation of EPA's revised copper and aluminum criteria for protection of freshwater aquatic life in Massachusetts. Revised copper and aluminum criteria were both adopted into the Massachusetts SWQS regulation (314 CMR 4.00) in 2021 (MassDEP, 2021b). The previously published MassDEP/USGS aluminum report (Armstrong et al., 2022b) and associated data release (Armstrong et al., 2022a) provide an example to aid with the implementation of revised aluminum criteria for protection of aquatic life in Massachusetts. To supplement the aluminum report, this report provides an example of how to collect data to calculate site-dependent copper criteria values using the BLM at 11 water and wastewater treatment facilities in Massachusetts, including sample collection and analysis, quality control procedures, use of the BLM, and presentation of the final criteria values (acute and chronic minimum, 5th, and 10th percentile values).

Water quality results and comparisons among ambient stations were presented for each BLM input parameter, and facility effluent discharge concentrations for each parameter were compared among the

11 facilities. Considerations such as laboratory detection limit and the impact of rounded data on the BLM criteria outputs were described. Final site-dependent copper criteria values were presented, with the key drivers of criteria variability explored with a multiple nonlinear regression.

Overall, a similar pattern was evident for ambient stations (upstream and pond sites) associated with the facilities for several chemical parameters, with the highest concentrations typically reported for the Assabet River (particularly Marlborough, Hudson, and Maynard WWTFs) and Wilmington and Weymouth WTFs. DOC, pH, and temperature indicated an apparent seasonal pattern, reflecting the influence of seasonal events. In effluent discharge, alkalinity, copper, and ion concentrations were typically highest at the WWTF stations as compared to the WTF stations, while high pH, temperature, and DOC were often reported at WTF stations.

Site-dependent copper criteria values varied over a broad range amongst the facilities according to changes in local water chemistry, despite their geographic proximity. The highest criteria values were calculated for the WWTFs and the lowest for the WTFs. There were also apparent seasonal trends in the instantaneous criteria values, with the lowest criteria values typically in the fall and winter months, and the highest criteria values occurring during the spring and summer months. This highlights the importance of collecting representative data throughout the year, and across years, to capture the full intra- and inter-annual variability in local water chemistry data at sites¹⁰. The key drivers of variability in the site-dependent copper criteria values were pH and DOC, while weaker, albeit statistically significant, relationships were identified between criteria values and alkalinity, chloride, sulfate, and potassium ions. No statistical significance was found between copper criteria values and sodium, magnesium, calcium, or temperature.

This study comprises a limited range of data collection over a one-year period (April 2018 - May 2019). Therefore, the site-dependent copper criteria calculated herein are for demonstration purposes only. MassDEP's implementation guidance includes collection of representative data to capture local variability in ambient surface water chemistry beyond the one year of this study. The guidance ensures the appropriate application of the BLM to calculate site-dependent freshwater copper criteria values for implementation purposes in Massachusetts (e.g., National Pollutant Discharge Elimination System (NPDES) and Surface Water Discharge (SWD) permits; MassDEP, 2021a). Ultimately, this case study for Massachusetts provides a relevant example for other states considering adoption of the BLM into their surface water quality standards regulations.

¹⁰ MassDEP guidance recommends, where possible, a minimum of 20 sampling events over two years spaced at least monthly apart in order to capture temporal variability in water quality (MassDEP, 2021a).

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Appendix A: Table of BLM Input Data and Instantaneous Site-Dependent Copper Criteria Values

Table A-1.Water quality input data for the Biotic Ligand Model (BLM) for each ambient station near 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-19, and associated BLM outputs of instantaneous acute and chronic copper criteria (FAV, CMC and CCC). BLM Flag indicates where parameters were either absent or outside the acceptable input range and the nearest value was used as input to the BLM. See Figure 2 for list of station names associated with each station number. Any values below the detection limit (DL) were treated as half the DL value for the purposes of the BLM. Temp = Temperature; FAV = Final Acute Value; CMC = Criterion Maximum Concentration; CCC = Criterion Continuous Concentration; WTF = Water Treatment Facility; WWTF = Wastewater Treatment Facility.

Facility	USGS Station No.	Date	Temp (°C)	pH (SU)	Copper, filtered (μg/L)	Organic Carbon, filtered (mg/L)	Calcium, filtered (mg/L)	Magnesium, filtered (mg/L)	Sodium, filtered (mg/L)	Potassium, filtered (mg/L)	Sulfate, filtered (mg/L)	Chloride, filtered (mg/L)	Alkalinity, filtered (mg/L as CaCO₃)	FAV (µg/L)	CMC (µg/L)	CCC (µg/L)	BLM Flag
Westborough WWTF	01096603	4/13/2018	10.3	7.2	0.43	3.97	13.6	3.29	38.8	2.60	8.27	75.8	18.0	24.40	12.20	7.58	
Westborough WWTF	01096603	5/9/2018	21.9	7.1	0.50	5.08	13.9	3.04	34.9	2.45	6.87	69.9	18.5	27.27	13.63	8.47	
Westborough WWTF	01096603	6/8/2018	21.2	7.0	0.42	5.57	15.9	3.47	39.0	2.22	5.04	74.8	26.5	26.39	13.20	8.20	
Westborough WWTF	01096603	7/13/2018	23.0	6.5	0.44	5.54	21.6	4.69	43.2	2.68	4.41	89.7	38.5	11.65	5.82	3.62	
Westborough WWTF	01096603	8/1/2018	25.5	6.5	<0.40	5.61	14.3	3.07	34.1	1.83	3.16	69.0	24.3	11.07	5.53	3.44	High Temp
Westborough WWTF	01096603	9/17/2018	23.5	6.5	<0.40	5.63	14.7	3.19	33.5	2.34	3.31	66.9	26.0	11.05	5.53	3.43	
Westborough WWTF	01096603	10/5/2018	17.1	6.6	0.76	7.56	14.3	3.00	30.0	2.37	3.33	61.1	24.8	17.66	8.83	5.48	
Westborough WWTF	01096603	11/23/2018	0.7	7.0	0.61	7.04	11.6	2.57	29.6	2.57	5.86	55.9	21.4	31.61	15.80	9.82	Low Temp
Westborough WWTF	01096603	12/12/2018	3.5	6.8	0.47	5.32	11.6	2.58	27.0	2.52	7.38	55.0	20.2	16.94	8.47	5.26	Low Temp
Westborough WWTF	01096603	2/11/2019	4.6	7.1	0.42	3.99	12.3	2.64	28.6	2.25	7.85	58.9	20.8	20.02	10.01	6.22	Low Temp
Westborough WWTF	01096603	3/7/2019	3.7	6.9	<0.40	3.15	12.8	2.73	31.6	2.23	8.12	68.7	22.4	11.88	5.94	3.69	Low Temp
Westborough WWTF	01096603	3/28/2019	9.1	7.3	<0.40	3.31	11.3	2.54	34.4	2.06	6.93	65.4	20.0	22.75	11.37	7.07	Low Temp
Westborough WWTF	01096603	5/2/2019	12.6	6.9	0.47	5.19	11.9	2.60	28.3	2.14	5.58	55.6	21.1	19.67	9.84	6.11	
Marlborough WWTF	01096720	5/4/2018	18.7	7.1	1.4	4.90	24.4	4.55	81.7	4.71	12.2	156	32.8	31.51	15.76	9.79	
Marlborough WWTF	01096720	5/25/2018	20.3	7.2	2.0	4.76	32.2	5.23	93.4	6.29	14.3	177	41.7	36.46	18.23	11.32	
Marlborough WWTF	01096720	6/13/2018	19.3	7.6	2.3	3.94	32.8	6.16	98.2	8.16	15.0	194	39.8	50.51	25.26	15.69	
Marlborough WWTF	01096720	7/5/2018	28.2	7.2	2.2	5.81	35.7	5.75	96.6	7.78	12.1	183	51.3	46.91	23.45	14.57	High Temp

Facility	USGS Station No.	Date	Temp	рН	Copper,	Organic	Calcium,	Magnesium,	Sodium,	Potassium,	Sulfate,	Chloride,	Alkalinity,	FAV	СМС	ссс	BLM
			(°C)	(SU)	filtered (µg/L)	Carbon, filtered (mg/L)	filtered (mg/L)	filtered (mg/L)	filtered (mg/L)	filtered (mg/L)	filtered (mg/L)	filtered (mg/L)	filtered (mg/L as CaCO₃)	(µg/L)	(µg/L)	(µg/L)	Flag
Marlborough WWTF	01096720	7/31/2018	23.8	7.2	<2.0	5.15	60.6	5.05	111	23.7	10.9	270	39.0	41.61	20.81	12.92	
Marlborough WWTF	01096720	9/10/2018	16.1	7.3	3.0	3.67	57.7	6.54	120	17.9	18.3	254	61.1	33.69	16.85	10.46	
Marlborough WWTF	01096720	10/9/2018	17.4	7.0	1.6	5.71	34.1	4.33	79.7	9.49	11.0	178	34.3	31.18	15.59	9.68	
Marlborough WWTF	01096720	11/30/2018	3.2	6.7	<1.2	4.50	19.0	3.08	58.4	4.73	11.3	111	22.7	14.25	7.13	4.43	Low Temp
Marlborough WWTF	01096720	12/20/2018	2.2	7.1	0.97	3.65	24.5	4.11	67.8	6.33	14.0	134	31.0	21.62	10.81	6.71	Low Temp
Marlborough WWTF	01096720	2/5/2019	3.0	6.9	0.81	2.84	21.5	3.89	69.3	5.19	13.5	135	26.3	12.77	6.38	3.96	Low Temp
Marlborough WWTF	01096720	3/8/2019	0.2	7.3	1.0	2.80	24.0	4.61	93.1	5.68	15.6	184	30.4	23.34	11.67	7.25	Low Temp
Marlborough WWTF	01096720	3/27/2019	7.0	7.2	0.78	2.92	28.5	3.78	82.8	9.29	13.0	175	26.0	20.72	10.36	6.43	Low Temp
Marlborough WWTF	01096720	5/3/2019	10.1	7.0	0.98	4.31	20.7	3.49	64.6	4.96	10.9	127	27.8	22.25	11.12	6.91	
Hudson WWTF	01096870	4/24/2018	14.1	7.0	1.1	3.94	22.7	4.62	88.5	5.42	13.8	159	23.8	22.32	11.16	6.93	
Hudson WWTF	01096870	5/11/2018	17.8	6.9	1.5	5.03	24.7	5.60	93.4	4.59	13.2	175	31.2	25.18	12.59	7.82	
Hudson WWTF	01096870	6/11/2018	22.3	7.3	1.7	4.46	31.2	7.29	119	6.66	14.8	220	40.3	42.40	21.20	13.17	
Hudson WWTF	01096870	7/30/2018	25.1	7.1	1.8	6.39	30.2	5.87	83.3	8.36	10.8	174	37.8	42.12	21.06	13.08	High Temp
Hudson WWTF	01096870	9/5/2018	24.9	7.2	1.7	4.46	39.4	10.0	117	11.2	19.9	227	56.5	37.37	18.68	11.60	
Hudson WWTF	01096870	10/9/2018	16.2	6.8	1.4	6.00	26.2	5.11	76.6	6.64	11.2	153	32.9	24.26	12.13	7.53	
Hudson WWTF	01096870	10/22/2018	8.9	6.8	1.3	5.40	24.9	5.22	77.2	5.55	12.3	143	32.9	21.81	10.90	6.77	Low Temp
Hudson WWTF	01096870	12/7/2018	1.9	6.8	0.91	4.29	18.3	3.58	59.1	4.54	12.3	115	22.2	16.02	8.01	4.98	Low Temp
Hudson WWTF	01096870	12/20/2018	1.6	6.8	0.94	3.75	19.0	4.33	62.9	4.27	13.6	121	25.4	14.20	7.10	4.41	Low Temp
Hudson WWTF	01096870	1/29/2019	0.2	7.1	0.89	3.27	15.4	3.54	59.6	3.56	12.0	115	21.1	19.04	9.52	5.91	Low Temp
Hudson WWTF	01096870	3/8/2019	0.9	7.3	0.86	2.69	19.9	4.84	85.4	4.19	15.3	177	28.2	22.01	11.01	6.84	Low Temp
Hudson WWTF	01096870	3/28/2019	7.3	7.2	0.77	2.96	23.1	4.27	78.0	6.99	13.1	157	24.7	20.87	10.43	6.48	Low
Hudson WWTF	01096870	5/3/2019	10.5	6.9	1.1	4.27	17.7	3.87	63.9	3.94	10.9	120	25.1	19.15	9.57	5.95	
Maynard WWTF	01097021	4/24/2018	14.5	7.2	1.0	4.18	19.2	4.02	84.1	4.94	12.3	139	20.9	31.14	15.57	9.67	
Maynard WWTF	01097021	5/10/2018	18.9	6.8	1.5	5.44	20.4	4.44	80.7	4.22	11.3	149	28.1	22.59	11.30	7.02	
Maynard WWTF	01097021	6/12/2018	24.1	8.4	1.3	4.57	25.9	5.82	106	5.92	12.2	184	38.5	146.98	73.49	45.65	

Facility **USGS Station No.** Date Temp рΗ Copper, Organic Calcium, Magnesium, Sodium, Potassium, Sulfate, Chloride, Alkalinity, FAV СМС CCC BLM (SU) (°C) filtered Carbon, filtered filtered filtered filtered filtered (µg/L) (µg/L) (µg/L) filtered filtered Flag (µg/L) filtered (mg/L) (mg/L) (mg/L) (mg/L) (mg/L) (mg/L as (mg/L) (mg/L) CaCO₃) Maynard WWTF 01097021 7/12/2018 26.2 7.8 1.3 5.70 24.1 5.66 95.0 6.20 11.2 175 43.7 99.96 49.98 31.04 High Temp Maynard WWTF 01097021 7/31/2018 27.3 8.1 1.8 6.46 21.6 75.6 5.40 9.45 146 35.0 153.59 76.80 47.70 4.75 High Temp Maynard WWTF 01097021 9/6/2018 26.6 7.4 5.07 30.1 102 8.95 13.3 188 54.6 54.39 27.19 16.89 1.4 6.22 High Temp 10/10/2018 Maynard WWTF 01097021 17.7 6.9 1.4 6.28 20.7 4.30 70.7 4.94 9.96 132 30.5 29.30 14.65 9.10 01097021 11/30/2018 0.92 4.71 91.4 Maynard WWTF 2.8 6.6 12.4 2.66 51.6 3.08 9.76 16.8 12.39 6.20 3.85 Low Temp 3.47 Maynard WWTF 01097021 12/20/2018 0.8 6.8 1.0 4.08 15.9 57.5 3.82 12.2 107 22.5 15.21 7.61 4.72 Low Temp 01097021 2/5/2019 0.77 4.14 12.5 5.73 Maynard WWTF 0.9 6.8 3.01 16.6 3.85 63.0 114 23.3 11.45 3.56 Low Temp Maynard WWTF 01097021 3/8/2019 1.4 7.5 0.78 2.79 18.5 4.38 88.9 4.25 13.6 165 25.8 29.51 14.76 9.16 Low Temp Maynard WWTF 01097021 3/28/2019 7.1 7.4 0.84 3.00 16.7 3.45 66.8 4.32 11.3 124 22.4 26.59 13.29 8.26 Low Temp 01097021 5/3/2019 11.0 7.0 0.86 4.44 14.8 3.18 58.5 3.46 10.1 110 22.0 22.74 11.37 7.06 Maynard WWTF Cohasset WTF 421326070485802 6/22/2018 25.9 6.5 0.85 11.6 6.34 2.84 38.5 0.89 3.53 66.7 10.7 25.76 12.88 8.00 High Temp Cohasset WTF 421326070485802 7/17/2018 27.0 6.0 0.58 11.3 5.87 2.62 33.3 0.94 3.20 58.7 10.0 7.21 3.60 2.24 High Temp 8/17/2018 3.03 57.2 12.5 10.38 Cohasset WTF 421326070485802 26.3 6.5 0.40 10.0 6.26 2.83 31.5 1.01 20.75 6.45 High Temp Cohasset WTF 421326070485802 10/1/2018 18.0 7.9 0.40 9.54 5.14 2.53 26.1 1.21 5.08 45.6 11.5 143.36 71.68 44.52 25.8 0.90 9.51 45.3 7.2 3.71 Cohasset WTF 421326070485802 10/17/2018 13.0 5.7 0.66 14.3 6.35 3.17 1.85 1.15 Cohasset WTF 421326070485802 11/15/2018 4.7 5.0 1.5 18.9 3.77 1.97 17.6 1.16 4.58 30.6 4.9 1.14 0.57 0.35 Low Temp 4/4/2019 Cohasset WTF 421326070485802 9.4 6.7 0.85 6.99 4.99 2.20 35.0 0.91 5.28 62.1 7.6 21.59 10.80 6.71 Low Temp Cohasset WTF 421326070485802 5/1/2019 0.88 42.4 8.04 4.02 12.7 6.1 1.3 10.4 4.13 1.76 24.1 3.89 8.0 2.50 4/23/2018 < 0.40 2.17 2.90 0.573 16.6 0.82 3.58 27.1 4.9 1.87 0.93 0.58 Fitchburg WTF 423132071523401 11.8 6.2 Fitchburg WTF 423132071523401 5/9/2018 20.5 6.1 0.44 2.44 3.39 0.672 18.6 0.89 3.72 29.8 6.2 1.64 0.82 0.51 6/7/2018 0.764 20.6 3.14 8.3 Fitchburg WTF 423132071523401 20.2 6.2 0.47 3.09 3.94 0.99 33.5 2.78 1.39 0.86 Fitchburg WTF 423132071523401 6/26/2018 22.7 6.1 0.52 3.10 3.80 0.755 21.9 1.23 3.03 35.1 8.2 2.18 1.09 0.68 Fitchburg WTF 423132071523401 7/19/2018 26.3 6.2 0.47 3.43 3.91 0.783 21.6 1.08 2.73 36.1 8.4 3.15 1.57 0.98 High Temp 8/16/2018 Fitchburg WTF 26.1 6.3 < 0.40 3.96 0.711 0.98 1.72 8.6 423132071523401 3.60 20.0 33.1 4.68 2.34 1.45 High Temp 20.6 5.7 0.41 4.71 3.26 0.643 0.97 2.15 27.0 7.4 1.07 0.53 0.33 Fitchburg WTF 423132071523401 9/20/2018 16.4 Fitchburg WTF 423132071523401 10/10/2018 19.1 6.2 < 0.40 3.64 3.12 0.612 15.6 0.80 2.67 25.9 7.3 3.16 1.58 0.98

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Facility	USGS Station No.	Date	Temp (°C)	pH (SU)	Copper, filtered (µg/L)	Organic Carbon, filtered (mg/L)	Calcium, filtered (mg/L)	Magnesium, filtered (mg/L)	Sodium, filtered (mg/L)	Potassium, filtered (mg/L)	Sulfate, filtered (mg/L)	Chloride, filtered (mg/L)	Alkalinity, filtered (mg/L as CaCO₃)	FAV (µg/L)	CMC (µg/L)	CCC (µg/L)	BLM Flag
Fitchburg WTF	423132071523401	11/8/2018	7.9	5.6	<0.40	3.64	2.59	0.560	13.3	0.85	2.98	21.2	6.0	0.61	0.31	0.19	Low Temp
Fitchburg WTF	423132071523401	12/10/2018	3.7	5.9	<0.40	2.60	2.78	0.583	13.8	0.87	3.75	22.6	5.8	0.95	0.48	0.30	Low
Fitchburg WTF	423132071523401	2/12/2019	4.6	6.7	0.72	2.20	2.90	0.583	16.1	0.76	3.64	27.8	6.0	5.90	2.95	1.83	Low Temp
Fitchburg WTF	423132071523401	3/6/2019	4.1	6.0	<0.40	2.07	2.86	0.611	16.1	0.84	4.11	28.8	6.2	1.02	0.51	0.32	Low Temp
Fitchburg WTF	423132071523401	4/2/2019	5.5	7.3	<0.40	1.68	2.77	0.549	16.5	0.69	3.10	28.2	5.3	11.52	5.76	3.58	Low Temp
Fitchburg WTF	423132071523401	4/25/2019	14.8	6.2	<0.40	2.59	2.66	0.530	13.5	0.935	3.28	21.6	5.3	2.18	1.09	0.68	
Fitchburg WTF	423132071523402	5/9/2018	18.0	6.2	0.41	2.46	3.46	0.684	19.0	0.96	3.70	29.6	6.3	2.17	1.09	0.67	
Fitchburg WTF	423132071523402	6/7/2018	20.2	6.2	0.60	3.26	3.83	0.742	20.2	0.95	3.15	33.5	8.5	2.93	1.47	0.91	
Fitchburg WTF	423132071523402	6/26/2018	22.0	6.2	0.48	3.14	3.81	0.757	22.2	1.11	3.01	35.1	8.2	2.90	1.45	0.90	
Fitchburg WTF	423132071523402	7/19/2018	25.8	6.1	0.45	3.62	3.84	0.771	22.0	1.17	2.74	36.1	8.5	2.57	1.28	0.80	High Temp
Fitchburg WTF	423132071523402	8/16/2018	24.8	6.2	<0.40	3.79	3.65	0.722	20.2	0.97	1.81	33.8	8.6	3.46	1.73	1.07	
Fitchburg WTF	423132071523402	9/20/2018	20.6	5.5	0.42	4.65	3.26	0.643	16.4	0.97	2.17	27.1	7.4	0.64	0.32	0.20	
Fitchburg WTF	423132071523402	10/10/2018	18.1	6.1	<0.40	3.57	3.25	0.636	16.3	0.87	2.62	26.7	7.4	2.38	1.19	0.74	
Fitchburg WTF	423132071523402	4/2/2019	5.5	7.3	<0.40	1.72	2.75	0.547	16.5	0.65	3.11	28.2	5.2	11.81	5.91	3.67	Low Temp
Fitchburg WTF	423132071523402	4/25/2019	14.2	6.2	<0.40	2.59	2.64	0.531	13.5	0.91	3.29	21.5	5.2	2.18	1.09	0.68	
Fitchburg WTF	423211071524701	4/23/2018	10.4	6.3	<0.40	2.16	3.41	0.675	19.5	1.03	3.98	31.8	5.7	2.46	1.23	0.76	
Fitchburg WTF	423211071524701	5/9/2018	20.3	6.2	0.42	2.21	3.60	0.727	20.6	1.00	4.08	32.9	6.1	1.97	0.99	0.61	
Fitchburg WTF	423211071524701	6/7/2018	20.5	6.3	0.50	2.90	4.00	0.796	21.9	1.04	3.69	35.3	7.8	3.40	1.70	1.06	
Fitchburg WTF	423211071524701	6/26/2018	22.8	6.2	0.54	2.87	3.88	0.781	22.7	1.08	3.30	36	8.0	2.65	1.32	0.82	
Fitchburg WTF	423211071524701	7/19/2018	26.2	6.2	0.43	3.11	4.06	0.816	22.3	1.12	2.89	37.4	8.7	2.85	1.43	0.89	High Temp
Fitchburg WTF	423211071524701	8/16/2018	25.8	6.3	<0.40	3.31	3.96	0.796	21.7	1.14	2.39	36.3	8.9	3.91	1.95	1.21	High Temp
Fitchburg WTF	423211071524701	9/20/2018	21.0	6.2	<0.40	3.89	3.92	0.769	20.8	1.11	2.23	34.6	9.3	3.56	1.78	1.10	
Fitchburg WTF	423211071524701	10/10/2018	18.7	6.4	<0.40	3.75	3.62	0.712	18.6	1.01	2.60	31.3	8.3	5.51	2.75	1.71	
Fitchburg WTF	423211071524701	11/8/2018	8.3	6.1	<0.40	3.54	3.18	0.671	16.9	1.10	3.15	27.5	7.0	2.38	1.19	0.74	Low Temp
Fitchburg WTF	423211071524702	4/23/2018	8.1	6.5	<0.40	2.17	3.40	0.669	19.2	0.90	4.01	31.9	5.6	3.94	1.97	1.22	Low Temp
Fitchburg WTF	423211071524702	5/9/2018	17.6	6.3	0.51	2.24	3.61	0.735	21.0	0.94	4.12	33.4	6.2	2.59	1.30	0.81	
Fitchburg WTF	423211071524702	6/7/2018	20.0	6.4	0.49	2.78	4.00	0.794	21.6	0.97	3.72	35.4	8.0	4.12	2.06	1.28	
Fitchburg WTF	423211071524702	6/26/2018	22.3	6.2	0.50	2.85	3.90	0.784	22.8	1.03	3.33	36.1	7.9	2.63	1.31	0.82	

Facility	USGS Station No.	Date	Temp	рН	Copper.	Organic	Calcium.	Magnesium.	Sodium.	Potassium.	Sulfate.	Chloride.	Alkalinity.	FAV	СМС	ссс	BLM
			(°C)	(SU)	filtered	Carbon,	filtered	filtered	filtered	filtered	filtered	filtered	filtered	(µg/L)	(µg/L)	(µg/L)	Flag
					(µg/L)	filtered (mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L as CaCO₃)				
Fitchburg WTF	423211071524702	7/19/2018	25.9	6.2	0.43	3.09	4.00	0.804	22.6	1.08	2.89	37.4	8.7	2.85	1.42	0.88	High Temp
Fitchburg WTF	423211071524702	8/16/2018	25.0	6.4	<0.40	3.29	3.99	0.802	21.8	1.07	2.43	36.8	9.2	4.93	2.47	1.53	
Fitchburg WTF	423211071524702	9/20/2018	20.4	5.7	<0.40	4.10	3.98	0.772	21.0	1.23	2.22	34.8	9.3	0.96	0.48	0.30	
Fitchburg WTF	423211071524702	10/10/2018	17.8	6.4	0.43	3.86	3.64	0.719	18.8	1.01	2.62	31.5	8.3	5.69	2.85	1.77	
Fitchburg WTF	423211071524702	11/8/2018	8.1	5.9	<0.40	3.53	3.20	0.673	17.0	1.12	3.15	27.6	7.1	1.36	0.68	0.42	Low
																	Temp
Westborough WTF	421622071385701	4/18/2018	8.4	7.2	<0.40	2.40	19.9	4.53	47.4	3.62	9.87	97.0	27.4	15.07	7.53	4.68	Low Temp
Westborough WTF	421622071385701	5/8/2018	19.2	6.9	<0.40	3.30	22.1	4.67	45.9	3.50	9.03	96.3	29.8	13.65	6.82	4.24	
Westborough WTF	421622071385701	6/14/2018	220.	6.8	<0.40	3.52	25.5	5.45	51.2	3.18	7.17	114	35.7	12.88	6.44	4.00	
Westborough WTF	421622071385701	7/17/2018	27.9	7.5	<0.40	3.29	25.9	5.69	51.3	2.78	6.24	118	35.3	34.35	17.18	10.67	High Temp
Westborough WTF	421622071385701	8/6/2018	27.9	6.8	<0.40	3.38	23.9	5.14	43.5	2.64	4.64	101	34.6	12.05	6.03	3.74	High Temp
Westborough WTF	421622071385701	9/14/2018	19.9	6.6	<0.40	3.16	26.4	5.69	50.4	3.74	6.05	117	35.3	8.25	4.13	2.56	- r
Westborough WTF	421622071385701	10/4/2018	15.9	6.2	<0.40	3.35	21.7	4.78	40.5	3.76	6.91	93.8	28.2	3.65	1.82	1.13	
Westborough WTF	421622071385701	11/5/2018	8.9	6.6	<0.40	3.26	21.5	4.84	38.4	3.80	9.71	89.2	27.7	7.83	3.91	2.43	Low Temp
Westborough WTF	421622071385701	12/4/2018	4.3	6.5	<0.40	3.03	17.9	3.92	34.9	3.24	9.34	75.7	24.7	5.87	2.93	1.82	Low Temp
Westborough WTF	421622071385701	3/29/2019	8.2	7.2	<0.40	2.05	21.8	4.67	46.0	3.47	10.4	98.7	30.4	12.76	6.38	3.96	Low Temp
Westborough WTF	421622071385701	4/25/2019	17	7.0	<0.40	3.46	20.1	4.30	41.2	3.46	8.41	87.2	28.7	16.18	8.09	5.02	
Westborough WTF	421622071385702	4/18/2018	8.4	7.2	<0.40	2.40	20.5	4.56	45.6	3.49	9.89	97.2	27.3	14.92	7.46	4.63	Low Temp
Westborough WTF	421622071385702	5/8/2018	18.5	7.0	<0.40	3.17	21.9	4.62	45.5	3.46	9.05	96.3	29.7	15.17	7.59	4.71	
Westborough WTF	421622071385702	6/14/2018	21.1	6.8	<0.40	3.53	26.0	5.55	51.9	3.51	7.08	113	36.1	12.96	6.48	4.02	
Westborough WTF	421622071385702	7/17/2018	25.6	7.2	<0.40	3.40	25.9	5.62	50.0	2.81	6.18	118	36.0	22.76	11.38	7.07	High Temp
Westborough WTF	421622071385702	8/6/2018	24.6	6.3	<0.40	4.11	24.2	5.10	43.2	3.02	4.09	101	38.7	5.82	2.91	1.81	
Westborough WTF	421622071385702	9/14/2018	18.2	6.4	<0.40	5.17	27.8	5.87	56.4	3.44	5.96	132	35.9	9.58	4.79	2.97	
Westborough WTF	421622071385702	10/4/2018	15.6	6.0	<0.40	4.17	21.2	4.60	40.7	3.47	7.82	94.6	24.8	2.78	1.39	0.86	
Westborough WTF	421622071385702	11/5/2018	8.9	6.6	<0.40	3.04	21.7	4.90	38.8	3.80	9.79	89.7	27.9	7.32	3.66	2.27	Low Temp
Westborough WTF	421622071385702	12/4/2018	4.3	6.5	<0.40	2.88	18.4	3.99	36.6	3.23	9.37	78.8	25.3	5.64	2.82	1.75	Low Temp
Westborough WTF	421622071385702	3/29/2019	8.2	7.2	<0.40	1.92	21.8	4.64	46.0	3.46	10.4	98.6	30.5	11.95	5.97	3.71	Low Temp
Westborough WTF	421622071385702	4/25/2019	16.0	6.9	<0.40	3.77	18.6	4.00	37.9	3.21	8.17	82.9	27.1	14.88	7.44	4.62	
Westborough WTF	421628071384501	4/18/2018	9.1	7.0	<0.40	3.18	18.3	4.00	44.2	3.16	8.67	92.1	23.4	14.94	7.47	4.64	Low Temp

Facility	USGS Station No.	Date	Temp (°C)	pH (SU)	Copper, filtered (μg/L)	Organic Carbon, filtered	Calcium, filtered (mg/L)	Magnesium, filtered (mg/L)	Sodium, filtered (mg/L)	Potassium, filtered (mg/L)	Sulfate, filtered (mg/L)	Chloride, filtered (mg/L)	Alkalinity, filtered (mg/L as	FAV (µg/L)	CMC (µg/L)	CCC (µg/L)	BLM Flag
						(mg/L)							CaCO₃)				
Westborough WTF	421628071384501	5/8/2018	20.4	6.7	<0.40	3.39	21.9	4.61	47.0	3.32	9.04	98.6	29.6	10.25	5.13	3.18	
Westborough WTF	421628071384501	6/14/2018	21.6	6.7	<0.40	3.51	25.4	5.39	51.7	3.22	7.29	113	35.7	10.94	5.47	3.40	
Westborough WTF	421628071384501	7/17/2018	28.6	6.6	<0.40	4.28	26.8	5.72	53.2	2.69	5.28	121	36.1	11.48	5.74	3.56	High Temp
Westborough WTF	421628071384501	8/6/2018	31.4	6.5	<0.40	4.04	21.9	4.58	43.0	2.14	3.89	98.2	29.2	8.50	4.25	2.64	High Temp
Westborough WTF	421628071384501	9/14/2018	19.0	6.3	<0.40	3.69	27.1	5.69	45.9	3.53	3.99	103	43.6	5.36	2.68	1.67	
Westborough WTF	421628071384501	10/4/2018	16.3	6.3	<0.40	2.89	22.7	4.91	42.6	3.65	6.68	96.4	30.7	4.01	2.01	1.25	
Westborough WTF	421628071384501	11/5/2018	8.5	6.6	<0.40	2.83	22.7	5.02	41.3	3.70	10.3	95.4	28.1	6.91	3.46	2.15	Low Temp
Westborough WTF	421628071384501	12/4/2018	4.6	6.5	<0.40	3.10	18.6	3.94	35.6	3.24	9.51	78.7	24.1	6.03	3.02	1.87	Low Temp
Westborough WTF	421628071384501	2/12/2019	4.5	6.4	<0.40	2.03	22.9	4.79	43.3	3.47	12.1	96.8	30.8	3.45	1.72	1.07	Low Temp
Hanover WTF	011058065	5/3/2018	22.9	6.2	1.0	8.33	11.8	4.70	86.3	2.91	8.17	162	12.2	11.76	5.88	3.65	
Hanover WTF	011058065	5/29/2018	21.6	6.3	0.82	9.20	15.4	5.75	103	3.74	5.81	187	15.9	17.35	8.68	5.39	
Hanover WTF	011058065	7/3/2018	25.2	6.6	0.64	9.01	18.6	7.18	116	4.24	5.83	210	19.2	31.22	15.61	9.70	High Temp
Hanover WTF	011058065	7/20/2018	21.8	6.6	0.6	6.75	20.9	8.12	124	4.36	7.46	238	18.9	23.38	11.69	7.26	
Hanover WTF	011058065	10/5/2018	16.5	6.4	1.1	11.3	13.7	5.30	92.9	3.34	6.35	167	15.5	25.62	12.81	7.96	
Hanover WTF	011058065	10/23/2018	9.4	6.3	0.76	11.7	16.4	6.21	101	3.36	6.88	190	16.1	22.04	11.02	6.85	Low Temp
Hanover WTF	011058065	12/6/2018	2.4	7.6	0.73	8.48	8.62	3.61	62.6	2.49	7.22	114	10.2	99.45	49.72	30.88	Low Temp
Hanover WTF	011058065	12/19/2018	0.9	6.4	0.67	7.48	8.74	3.68	64.8	2.45	7.93	120	10.7	14.90	7.45	4.63	Low Temp
Hanover WTF	011058065	2/15/2019	2.9	6.5	0.55	4.58	9.25	4.03	76.8	2.38	9.57	139	11.0	11.51	5.76	3.58	Low Temp
Hanover WTF	011058065	3/7/2019	0.8	6.5	0.52	4.12	10.6	4.58	86.5	2.38	10.1	170	12.1	10.63	5.32	3.30	Low Temp
Hanover WTF	011058065	4/5/2019	7.9	6.7	0.58	5.68	9.21	3.92	76.3	2.56	7.97	142	11.7	20.51	10.26	6.37	Low Temp
Hanover WTF	011058065	5/2/2019	11.1	6.4	0.78	8.81	9.03	3.58	64.6	2.55	5.70	117	15.2	17.72	8.86	5.50	- 1-
Leominster WTF	01094420	4/23/2018	8.3	5.6	0.58	4.37	2.10	0.467	17.6	0.54	4.26	26.1	<4.0	0.80	0.40	0.25	Low Temp
Leominster WTF	01094420	5/15/2018	19.5	5.9	0.64	4.13	2.72	0.565	22.4	0.61	4.56	35.5	4.6	1.74	0.87	0.54	
Leominster WTF	01094420	6/8/2018	NA	6.6	0.64	3.98	3.67	0.668	28.2	0.88	4.58	44.4	7.0	NA	NA	NA	No Temp
Leominster WTF	01094420	7/13/2018	19.0	6.9	0.64	2.00	12.2	1.41	66.8	1.83	7.92	104	28.4	9.40	4.70	2.92	
Leominster WTF	01094420	8/21/2018	17.5	6.8	<1.2	2.21	13.4	1.54	64.8	2.14	9.69	101	32.7	8.74	4.37	2.72	
Leominster WTF	01094420	9/17/2018	21.6	6.2	0.47	4.10	3.27	0.616	22.8	0.79	3.68	34.1	7.6	3.93	1.96	1.22	
Leominster WTF	01094420	10/5/2018	16.6	5.9	0.58	6.29	2.06	0.462	15.2	0.658	3.19	22.8	4.1	2.61	1.30	0.81	

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Massachusetts Using the Biotic Ligand Model Facility **USGS Station No.** Date Temp рΗ Copper, Organic Calcium, Magnesium, Sodium, Potassium, Sulfate, Chloride, Alkalinity, FAV СМС CCC BLM (SU) filtered (µg/L) (µg/L) (µg/L) (°C) Carbon, filtered filtered filtered filtered filtered filtered filtered Flag (µg/L) filtered (mg/L) (mg/L) (mg/L) (mg/L) (mg/L) (mg/L as (mg/L) (mg/L) CaCO₃) Leominster WTF 01094420 11/9/2018 7.7 5.3 0.68 7.37 1.65 0.395 11.6 0.603 3.12 16.8 <4.0 0.78 0.39 0.24 Low Temp Leominster WTF 01094420 12/11/2018 2.1 5.2 0.52 5.92 1.82 0.414 11.8 0.570 3.85 17.8 <4.0 0.51 0.26 0.16 Low Temp 01094420 2/1/2019 1.0 5.4 0.48 4.89 1.47 0.354 10.1 0.451 3.53 14.9 0.59 0.29 0.18 Leominster WTF <4.0 Low Temp 3/7/2019 Leominster WTF 01094420 1.9 6.2 <0.40 4.38 1.71 0.403 13.9 0.528 3.87 22.4 <4.0 4.03 2.02 1.25 Low Temp 01094420 3/27/2019 1.58 0.374 0.52 0.32 Leominster WTF 4.4 5.8 < 0.40 3.55 11.9 0.446 3.61 18.5 <4.0 1.04 Low Temp Leominster WTF 01094420 5/6/2019 12.2 6.2 0.52 4.21 1.72 0.394 13.4 0.522 3.63 20.0 <4.0 3.85 1.92 1.19 01105587 5/3/2018 2.4 7.89 5.74 86.9 3.24 156 35.4 Weymouth WTF 19.2 6.4 19.3 7.26 16.97 8.48 5.27 Weymouth WTF 01105587 5/30/2018 18.6 6.2 1.3 6.37 26.9 8.54 85.2 3.13 7.12 168 42.3 8.99 4.49 2.79 Weymouth WTF 01105587 7/2/2018 20.7 6.1 1.0 5.29 27.4 10.1 75.0 2.99 7.38 158 44.4 5.81 2.91 1.81 Weymouth WTF 01105587 7/20/2018 21.3 6.3 1.1 4.01 25.8 9.00 65.5 2.67 7.53 142 41.3 6.49 3.24 2.01 Weymouth WTF 01105587 8/7/2018 22.3 6.2 <1.2 3.28 27.5 10.4 59.2 2.76 7.33 137 43.6 4.30 2.15 1.33 Weymouth WTF 01105587 9/24/2018 14.9 6.2 2.0 11.1 25.9 8.33 88.6 3.35 7.52 170 46.8 15.99 8.00 4.97 01105587 10/26/2018 7.7 1.4 10.1 19.9 6.55 61.1 2.81 5.15 112 41.3 15.89 7.95 4.94 Weymouth WTF 6.3 Low

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Weymouth WTF

Weymouth WTF

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3/7/2019

4/5/2019

5/2/2019

5/4/2018

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6/21/2018

7/30/2018

8/27/2018

9/21/2018

10/18/2018

11/29/2018

3.4

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2.0

1.5

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10.5

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6.7

6.6

1.6

0.87

0.82

1.0

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3.0

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0.91

1.0

6.71

3.41

3.26

3.63

5.25

6.32

4.20

2.81

2.59

2.60

2.97

4.13

4.50

4.14

16.5

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21.8

22.1

17.6

19.2

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34.9

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36.8

34.5

32.4

28.8

20.1

Surface Water Quality Data (2018-2019) to Support Implementation of Revised Freshwater Copper Ambient Water Quality Criteria in

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Temp

Low Temp

Low Temp

Low Temp

Low

Low Temp

Low Temp

Low Temp

Temp, High Chloride

Facility **USGS Station No.** Date Temp рΗ Copper, Organic Calcium, Magnesium, Sodium, Potassium, Sulfate, Chloride, Alkalinity, FAV СМС CCC BLM (SU) filtered (µg/L) (µg/L) (µg/L) (°C) Carbon, filtered filtered filtered filtered filtered filtered filtered Flag (µg/L) filtered (mg/L) (mg/L) (mg/L) (mg/L) (mg/L) (mg/L) (mg/L as (mg/L) CaCO₃) Wilmington WTF 01101294 12/13/2018 3.8 6.6 0.59 2.54 23.0 3.45 80.9 3.18 15.7 143 37.3 7.46 3.73 2.32 Low Temp Wilmington WTF 01101294 2/11/2019 4.4 7.0 0.64 2.55 20.9 3.10 70.1 2.53 14.0 130 33.5 13.34 6.67 4.14 Low Temp Wilmington WTF 01101294 3/7/2019 7.0 0.62 2.33 20.7 3.08 74.4 2.46 14.1 154 34.0 12.33 6.16 3.83 3.4 Low Temp 01101294 4/5/2019 147 6.47 Wilmington WTF 7.2 6.9 0.59 2.76 23.0 3.42 79.0 2.93 12.7 33.1 12.93 4.02 Low Temp 01101294 5/6/2019 Wilmington WTF 11.5 7.0 0.75 3.33 21.5 3.14 72.3 2.78 11.8 131 32.9 17.74 8.87 5.51 8.91 Wilmington WTF 01101296 5/4/2018 18.7 6.9 1.4 5.31 24.2 4.67 117 3.65 14.2 210 28.2 28.69 14.35 Wilmington WTF 01101296 5/31/2018 11.98 22.6 6.8 1.2 4.71 29.6 5.97 153 4.17 14.4 272 31.3 23.95 7.44 Wilmington WTF 01101296 6/21/2018 23.3 6.7 1.0 6.66 29.4 6.08 157 4.95 11.3 291 36.8 29.43 14.72 9.14 High Chloride Wilmington WTF 01101296 7/30/2018 22.4 6.5 <0.80 4.87 34.3 7.06 190 5.14 12.0 333 35.7 16.53 8.26 High 5.13 Chloride Wilmington WTF 01101296 8/27/2018 20.9 6.5 1.2 3.85 32.2 6.58 154 4.75 16.1 289 38.3 12.03 6.01 3.74 High Chloride Wilmington WTF 01101296 9/21/2018 17.1 6.5 1.5 5.66 28.9 5.47 120 4.47 17.1 221 34.8 16.05 8.02 4.98 Wilmington WTF 01101296 10/18/2018 10.1 6.8 0.60 3.24 32.8 4.79 104 3.90 12.0 189 43.2 14.21 7.10 4.41 Wilmington WTF 01101296 11/29/2018 5.90 3.34 2.90 123 29.0 9.99 6.20 6.4 6.7 1.5 17.7 69.8 14.2 19.98 Low Temp 01101296 <1.2 94.6 16.5 172 29.8 Wilmington WTF 12/13/2018 1.3 6.7 3.78 22.4 4.52 3.19 13.78 6.89 4.28 Low Temp Wilmington WTF 01101296 2/11/2019 2.4 0.78 3.64 2.69 15.2 176 27.4 8.94 6.9 20.9 4.15 91.9 17.88 5.55 Low Temp 01101296 3/7/2019 0.9 7.0 0.83 3.30 139 15.4 249 29.0 10.66 Wilmington WTF 23.4 4.92 3.24 21.33 6.62 Low Temp Wilmington WTF 01101296 4/5/2019 7.1 6.9 0.97 3.67 22.5 4.58 118 3.07 14.2 215 27.6 19.59 9.80 6.08 Low Temp Wilmington WTF 01101296 5/6/2019 11.9 7.0 1.0 4.92 20.2 3.88 90.5 2.81 13.2 164 28.8 28.26 14.13 8.78

Surface Water Quality Data (2018-2019) to Support Implementation of Revised Freshwater Copper Ambient Water Quality Criteria in Massachusetts Using the Biotic Ligand Model

Appendix B: Comparisons of Water Quality Among Effluent Discharge Stations

Water quality results for discrete monthly samples collected at effluent discharge stations are shown as boxplots by facility in **Figure B-1** to **Figure B-11**. Summaries of the water quality results, and comparisons of each parameter at the effluent stations, are reported below. The reported minimum, median, and maximum values were calculated from all discrete water quality samples from each effluent station with no values removed as outliers, consistent with the aluminum report (Armstrong et al., 2022b). Note, data from effluent stations were not used as inputs to the BLM for the purpose of calculating site-dependent copper criteria values.

WWTF effluents can have large impacts on their receiving waters, often controlling hydrological characteristics and nutrient processes (Carey and Migliaccio, 2009). Thus, effluent water quality was considered in this study, although comparisons of effluent samples to upstream versus downstream stations for individual facilities will not be presented here. Time series plots of water quality parameters from effluent and ambient stations are shown in **Appendix C**.

Overall, alkalinity and concentrations of chloride, copper, magnesium, potassium, sodium, and sulfate were typically highest at the WWTF effluent stations as compared to the WTF effluents. However, high alkalinity, pH, and concentrations of calcium, DOC, and sulfate were reported in the Hanover WTF effluent, and high DOC and sulfate concentrations were also measured in the effluent from Wilmington WTF. For pH, values were highest in effluent discharge from the Westborough, Hanover, and Leominster WTFs. DOC was highest in Maynard WWTF, Wilmington WTF, and Hanover WTF effluents. Effluent temperatures varied over a narrower range for the WWTFs as compared to the WTFs, with the highest effluent temperatures recorded at Hanover WTF.

Alkalinity

Alkalinity ranged from 5.4 to 245 mg/L as $CaCO_3$ for all effluent discharge samples (**Figure B-1**). The highest alkalinity and widest range of values was recorded for Hudson WWTF effluent samples (129-245 mg/L; median = 188 mg/L), with high alkalinity also measured at Westborough WWTF, Marlborough WWTF and Hanover WTF effluent stations. The lowest median alkalinity was measured in effluent from the Fitchburg WTF (8.8 mg/L), with low median alkalinity values (\leq 30.8 mg/L) also reported for Maynard WWTF, and Cohasset, Westborough, Leominster, Weymouth, and Wilmington WTFs.



Figure B-1. Boxplot of alkalinity (mg/L as CaCO₃) from discrete samples taken at effluent stations at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019.

Calcium

Calcium concentrations ranged from 1.45 to 254 mg/L in effluent samples (**Figure B-2**). Low median calcium concentrations (< 40 mg/L) were measured in most facility effluent discharges, with higher median concentrations reported for Hanover WTF (63.3 mg/L) and Westborough WWTF (65.5 mg/L). Calcium concentrations in the Westborough WWTF effluent discharge were markedly higher (97-254 mg/L) on four occasions over the study period, with the maximum concentration measured on August 1st, 2018.



Figure B-2. Boxplot of calcium, filtered (mg/L), from discrete samples taken at effluent stations at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019.

Chloride

Concentrations of chloride in effluent samples varied over a wide range over the study period (19.4-991 mg/L; **Figure B-3**). Median chloride values were higher in effluent discharges from the WWTFs (202-317 mg/L) as compared to the WTFs (33.5-129 mg/L). The highest median concentration was reported at Marlborough WWTF (317 mg/L), while the widest range (220-991 mg/L) and highest mean concentration (418 mg/L) were reported at Westborough WWTF. The maximum concentration at Westborough WWTF (991 mg/L) occurred on August 1st, 2018, corresponding with high calcium, potassium, and sodium concentrations in this sample. Leominster and Fitchburg WTFs had consistently low chloride concentrations in effluent samples (\leq 50.2 mg/L).



Figure B-3. Boxplot of chloride, filtered (mg/L), from discrete samples taken at effluent stations at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019.

Copper

Copper concentrations in effluent samples from the 11 facilities ranged from 0.2 to 15 μ g/L over the study period (**Figure B-4**). Effluent concentrations were highest at the WWTFs, and particularly at Hudson WWTF (median = 9.8 μ g/L). Copper concentrations at Hudson WWTF also varied over a wider range (5.7-15 μ g/L) as compared to the other facilities. Relatively low concentrations were typically measured in the WTF effluents (\leq 1.5 μ g/L), except for a single high copper concentration at Weymouth WTF (4.1 μ g/L on May 30th, 2018).



Figure B-4. Boxplot of copper, filtered (μ g/L), from discrete samples taken at effluent stations at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019.

Magnesium

At all facilities, effluent concentrations of magnesium ranged from 0.351 to 51.1 mg/L (**Figure B-5Error! Reference source not found.**). Magnesium concentrations measured at Marlborough WWTF were consistently higher than the other facilities, with a median concentration of 45.6 mg/L. The median concentrations at the other WWTFs (Westborough, Hudson, and Maynard) ranged from 4.94 to 8.11 mg/L, while the median concentrations at the WTFs ranged from 0.484 (Leominster WTF) to 5.75 mg/L (Hanover WTF).



Figure B-5. Boxplot of magnesium, filtered (mg/L) from discrete samples taken at effluent stations at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019.

Dissolved Organic Carbon

DOC concentrations in effluent samples ranged from 1.55 to 7.5 mg/L for all facilities (**Figure B-6**). The widest range in DOC concentrations was observed in samples from Hanover (2.06-6.19 mg/L) and Wilmington WTFs (2.71-7.5 mg/L). The lowest median DOC concentration was recorded for the Westborough WTF effluent station (1.82 mg/L), while the highest median DOC concentration was measured at the Maynard WWTF effluent station (5.38 mg/L).

A comparison of DOC concentrations among effluent stations was also discussed in Armstrong *et al.* (2022b).



Figure B-6. Boxplot of dissolved organic carbon, filtered (mg/L), from discrete samples taken at effluent stations at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019.

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pH values at all effluent stations ranged from 5.8 to 8.7 SU, with median values from 6.25 to 7.5 SU (**Figure B-7**). The pH at WWTF effluent stations varied over a narrow range of values around neutral pH (6.6-7.3 SU), while the pH at WTFs was more variable between facilities (5.8-8.7 SU). The broadest range of pH was measured at Westborough WTF, the facility where the highest pH was recorded in effluent discharge (8.7 SU on September 14, 2018). Median pH was highest in Westborough, Hanover, and Leominster WTFs effluent samples (7.5 SU), while the lowest median pH was reported for effluent from Weymouth and Cohasset WTFs (6.3 SU).

A comparison of pH values among effluent stations was also discussed in Armstrong et al. (2022b).



Figure B-7. Boxplot of pH (SU) from discrete samples taken at effluent stations at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019.

Potassium

For all facility effluents, potassium concentrations ranged from 0.390 to 131 mg/L (**Figure B-8**). As compared to the WTFs, potassium concentrations were consistently higher at the WWTFs, with median concentrations from 17.6 to 34.0 mg/L. Westborough WWTF had the largest range of potassium measured in effluent samples (14-131 mg/L), with the maximum concentration reported on August 1, 2018. The highest median concentration was reported at Hudson WWTF (34.0 mg/L). For WTFs, the highest median concentration occurred at Westborough WTF effluent station (9.12 mg/L), and relatively low concentrations were reported for the other facilities (\leq 4.3 mg/L).



Figure B-8. Boxplot of potassium, filtered (mg/L), from discrete samples taken at effluent stations at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019.

Sodium

At all effluent stations, sodium concentrations ranged from 19.3 to 340 mg/L, with median values of 20.4 to 234 mg/L (**Figure B-9**). As observed with chloride and potassium, median sodium concentrations were higher in the WWTF effluent samples (156-234 mg/L) as compared to the WTF effluents (20.4-69.3 mg/L). The highest median concentration of sodium was reported at Hudson WWTF (234 mg/L), while the lowest concentrations were consistently measured at Fitchburg WTF (19.3-22.2 mg/L). The maximum sodium concentration reported on August 1, 2018, at Westborough WWTF coincided with high calcium, chloride, and potassium concentrations at this effluent station.



Figure B-9. Boxplot of sodium, filtered (mg/L), from discrete samples taken at effluent stations at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019.

Sulfate

Sulfate concentrations varied between 3.66 and 107 mg/L in all effluent samples, with median concentrations ranging from 3.95 to 73.4 mg/L (**Figure B-10**). The WWTF effluent station concentrations ranged from 22.9-62.7 mg/L, with the highest median concentration reported in the effluent discharge from Maynard WWTF (44.0 mg/L). Median sulfate concentrations were typically lower at the WTFs (≤ 18.1 mg/L) except for the Hanover and Wilmington WTFs, where median effluent sulfate concentrations were 73.4 and 60.9 mg/L, respectively.



Figure B-10. Boxplot of sulfate, filtered (mg/L), from discrete samples taken at effluent stations at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019.

Temperature

Water temperatures in effluent discharge ranged from 0.6 to 30.3 °C at all facilities (**Figure B-11**). The temperature in WWTF effluent samples varied over a narrower range than those from WTFs, with the greatest range of temperatures recorded at Cohasset WTF (0.6-29.6 °C). Median temperatures at WWTF effluent stations ranged from 15.2 °C (Hudson WWTF) to 16.8 °C (Maynard WWTF), while median temperatures at WTF stations ranged from 13.4 °C (Weymouth WTF) to 19.1 °C (Hanover WTF).



Figure B-11. Boxplot of temperature (°C) from discrete samples taken at effluent stations at 11 water or wastewater treatment facilities in eastern and central Massachusetts, 2018-2019.

Appendix C: Time-Series Plots of Water Quality Parameters from Effluent and Ambient Stations near 11 water and wastewater treatment facilities in Massachusetts

Table C-1. Field observations made where additional environmental samples were collected (i.e., not replicate samples) at ambient or effluent stations.

Facility	Site Name	Station No.	Date	Comment
Marlborough WWTF	Assabet River at Boundary St. near Northborough, MA	01096720	July 27, 2018	A high flow sample was taken upstream of the WWTF following a rain event, in addition to the sample collected on July 31, 2018. This sample was not included in criteria calculations (see Table 5).
Hanover WTF	Hanover Water Treatment Plant Backwash Effluent	420754070495801	August 8, 2018	Two separate samples were collected at 10:40 and 10:45, as the field crew noted changing effluent discharge conditions while on station. The WTF was running a backflush, causing flows to decrease and visible variations in water quality from the two discharging culverts. The left culvert was discharging dark water (with solids) and the right culvert was discharging clear water. The 10:40 sample was a sweep from both culverts (but was predominantly water from the left culvert), and the 10:45 sample was taken from the right culvert.
Leominster WTF	Leominster Water Treatment Plant Backwash Effluent	423258071480701	June 8, 2018	Two separate effluent samples were collected at 11:05 and 11:13 during low and high flows, respectively.
	Monoosnoc Brook, DS Leominster Water Treatment Plant	01094422	June 8, 2018	Two separate downstream samples were collected at 11:10 and 11:15 during low and high flows, respectively.
Wilmington WTF	Wilmington Water Treatment Plant Backwash Effluent	423200071100201	November 29, 2018	Two separate effluent samples were taken at 10:45 and 11:00. The 10:45 sample was collected with a pump from the concrete well after outflow (darker). The 11:00 sample was collected from flow coming between cracks in the boards (clearer). The 11:00 sample had fewer solids than the 10:45 sample.



Figure C-1. Time series plot of alkalinity, filtered (mg/L as calcium carbonate) from discrete samples taken at effluent and ambient stations near Westborough WWTF, 2018-2019.



Figure C-2. Time series plot of calcium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Westborough WWTF, 2018-2019.


Figure C-3. Time series plot of chloride, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Westborough WWTF, 2018-2019.



Figure C-4. Time series plot of copper, filtered (μ g/L) from discrete samples taken at effluent and ambient stations near Westborough WWTF, 2018-2019.



Figure C-5. Time series plot of magnesium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Westborough WWTF, 2018-2019.



Figure C-6. Time series plot of organic carbon, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Westborough WWTF, 2018-2019.



Figure C-7. Time series plot of pH (SU) from discrete samples taken at effluent and ambient stations near Westborough WWTF, 2018-2019.



Figure C-8. Time series plot of potassium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Westborough WWTF, 2018-2019.



Figure C-9. Time series plot of sodium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Westborough WWTF, 2018-2019.



Figure C-10. Time series plot of sulfate, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Westborough WWTF, 2018-2019.



Figure C-11. Time series plot of water temperature (°C) from discrete samples taken at effluent and ambient stations near Westborough WWTF, 2018-2019.

250 Station - ASSABET RIVER AT BOUNDARY ST. NR NORTHBOROUGH, MA MARLBOROUGH WASTEWATER TREATMENT PLANT EFFLUENT Alkalinity (mg/L as calcium carbonate) 00 00 00 00 00 ASSABET RIVER, DS MARLBOROUGH WWTP 0 Jun-2018 Jul-2018 Sep-2018 Oct-2018 Nov-2018 Dec-2018 Jan-2019 Feb-2019 Mar-2019 May-2019 May-2018 Aug-2018 Apr-2019

Figure C-12. Time series plot of alkalinity, filtered (mg/L as calcium carbonate) from discrete samples taken at effluent and ambient stations near Marlborough WWTF, 2018-2019. Note additional sample collected at Assabet River at Boundary St. near Northborough, MA on July 27, 2018 is not a replicate (see Table C-1 for detail).



Figure C-13. Time series plot of calcium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Marlborough WWTF, 2018-2019. Note additional sample collected at Assabet River at Boundary St. near Northborough, MA on July 27, 2018 is not a replicate (see Table C-1 for detail).



Figure C-14. Time series plot of chloride, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Marlborough WWTF, 2018-2019. Note additional sample collected at Assabet River at Boundary St. near Northborough, MA on July 27, 2018 is not a replicate (see Table C-1 for detail).



Figure C-15. Time series plot of copper, filtered (μ g/L) from discrete samples taken at effluent and ambient stations near Marlborough WWTF, 2018-2019. Note additional sample collected at Assabet River at Boundary St. near Northborough, MA on July 27, 2018 is not a replicate (see Table C-1 for detail).



Figure C-16. Time series plot of magnesium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Marlborough WWTF, 2018-2019. Note additional sample collected at Assabet River at Boundary St. near Northborough, MA on July 27, 2018 is not a replicate (see Table C-1 for detail).



Figure C-17. Time series plot of organic carbon, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Marlborough WWTF, 2018-2019. Note additional sample collected at Assabet River at Boundary St. near Northborough, MA on July 27, 2018 is not a replicate (see Table C-1 for detail).



Figure C-18. Time series plot of pH (SU) from discrete samples taken at effluent and ambient stations near Marlborough WWTF, 2018-2019. Note additional sample collected at Assabet River at Boundary St. near Northborough, MA on July 27, 2018 is not a replicate (see Table C-1 for detail).



Figure C-19. Time series plot of Potassium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Marlborough WWTF, 2018-2019. Note additional sample collected at Assabet River at Boundary St. near Northborough, MA on July 27, 2018 is not a replicate (see Table C-1 for detail).



Figure C-20. Time series plot of Sodium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Marlborough WWTF, 2018-2019. Note additional sample collected at Assabet River at Boundary St. near Northborough, MA on July 27, 2018 is not a replicate (see Table C-1 for detail).



Figure C-21. Time series plot of Sulfate, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Marlborough WWTF, 2018-2019. Note additional sample collected at Assabet River at Boundary St. near Northborough, MA on July 27, 2018 is not a replicate (see Table C-1 for detail).



Figure C-22. Time series plot of water temperature (°C) from discrete samples taken at effluent and ambient stations near Marlborough WWTF, 2018-2019. Note additional sample collected at Assabet River at Boundary St. near Northborough, MA on July 27, 2018 is not a replicate (see Table C-1 for detail).



Figure C-23. Time series plot of alkalinity, filtered (mg/L as calcium carbonate) from discrete samples taken at effluent and ambient stations near Hudson WWTF, 2018-2019.



Figure C-24. Time series plot of calcium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Hudson WWTF, 2018-2019.



Figure C-25. Time series plot of chloride, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Hudson WWTF, 2018-2019.



Figure C-26. Time series plot of copper, filtered (μ g/L) from discrete samples taken at effluent and ambient stations near Hudson WWTF, 2018-2019.



Figure C-27. Time series plot of magnesium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Hudson WWTF, 2018-2019.



Figure C-28. Time series plot of organic carbon, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Hudson WWTF, 2018-2019.



Figure C-29. Time series plot of pH (SU) from discrete samples taken at effluent and ambient stations near Hudson WWTF, 2018-2019.



Figure C-30. Time series plot of Potassium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Hudson WWTF, 2018-2019.



Figure C-31. Time series plot of sodium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Hudson WWTF, 2018-2019.



Figure C-32. Time series plot of sulfate, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Hudson WWTF, 2018-2019.



Figure C-33. Time series plot of water temperature (°C) from discrete samples taken at effluent and ambient stations near Hudson WWTF, 2018-2019.

Maynard WWTF



Figure C-34. Time series plot of alkalinity, filtered (mg/L as calcium carbonate) from discrete samples taken at effluent and ambient stations near Maynard WWTF, 2018-2019.



Figure C-35. Time series plot of calcium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Maynard WWTF, 2018-2019.



Figure C-36. Time series plot of chloride, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Maynard WWTF, 2018-2019.



Figure C-37. Time series plot of copper, filtered (μ g/L) from discrete samples taken at effluent and ambient stations near Maynard WWTF, 2018-2019.



Figure C-38. Time series plot of magnesium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Maynard WWTF, 2018-2019.



Figure C-39. Time series plot of organic carbon, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Maynard WWTF, 2018-2019.



Figure C-40. Time series plot of pH (SU) from discrete samples taken at effluent and ambient stations near Maynard WWTF, 2018-2019.



Figure C-41. Time series plot of potassium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Maynard WWTF, 2018-2019.



Figure C-42. Time series plot of sodium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Maynard WWTF, 2018-2019.



Figure C-43. Time series plot of sulfate, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Maynard WWTF, 2018-2019.



Figure C-44. Time series plot of water temperature (°C) from discrete samples taken at effluent and ambient stations near Maynard WWTF, 2018-2019.

Cohasset WTF



Figure C-45. Time series plot of alkalinity, filtered (mg/L as calcium carbonate) from discrete samples taken at effluent and ambient stations near Cohasset WTF, 2018-2019.



Figure C-46. Time series plot of calcium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Cohasset WTF, 2018-2019.



Figure C-47. Time series plot of chloride, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Cohasset WTF, 2018-2019.



Figure C-48. Time series plot of copper, filtered (μ g/L) from discrete samples taken at effluent and ambient stations near Cohasset WTF, 2018-2019.



Figure C-49. Time series plot of magnesium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Cohasset WTF, 2018-2019.



Figure C-50. Time series plot of organic carbon, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Cohasset WTF, 2018-2019.



Figure C-51. Time series plot of pH (SU) from discrete samples taken at effluent and ambient stations near Cohasset WTF, 2018-2019.



Figure C-52. Time series plot of potassium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Cohasset WTF, 2018-2019.



Figure C-53. Time series plot of sodium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Cohasset WTF, 2018-2019.



Figure C-54. Time series plot of sulfate, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Cohasset WTF, 2018-2019.



Figure C-55. Time series plot of water temperature (°C) from discrete samples taken at effluent and ambient stations near Cohasset WTF, 2018-2019.

Fitchburg WTF



Figure C-56. Time series plot of alkalinity, filtered (mg/L as calcium carbonate) from discrete samples taken at effluent and ambient stations near Fitchburg WTF, 2018-2019.



Figure C-57. Time series plot of calcium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Fitchburg WTF, 2018-2019.



Figure C-58. Time series plot of chloride, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Fitchburg WTF, 2018-2019.



Figure C-59. Time series plot of copper, filtered (μ g/L) from discrete samples taken at effluent and ambient stations near Fitchburg WTF, 2018-2019.



Figure C-60. Time series plot of magnesium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Fitchburg WTF, 2018-2019.



Figure C-61. Time series plot of organic carbon, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Fitchburg WTF, 2018-2019.



Figure C-62. Time series plot of pH (SU) from discrete samples taken at effluent and ambient stations near Fitchburg WTF, 2018-2019.



Figure C-63. Time series plot of potassium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Fitchburg WTF, 2018-2019.



Figure C-64. Time series plot of sodium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Fitchburg WTF, 2018-2019.



Figure C-65. Time series plot of sulfate, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Fitchburg WTF, 2018-2019.



Figure C-66. Time series plot of water temperature (°C) from discrete samples taken at effluent and ambient stations near Fitchburg WTF, 2018-2019.

Westborough WTF



Figure C-67. Time series plot of alkalinity, filtered (mg/L as calcium carbonate) from discrete samples taken at effluent and ambient stations near Westborough WTF, 2018-2019.



Figure C-68. Time series plot of calcium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Westborough WTF, 2018-2019.


Figure C-69. Time series plot of chloride, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Westborough WTF, 2018-2019.



Figure C-70. Time series plot of copper, filtered (μ g/L) from discrete samples taken at effluent and ambient stations near Westborough WTF, 2018-2019.



Figure C-71. Time series plot of magnesium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Westborough WTF, 2018-2019.



Figure C-72. Time series plot of organic carbon, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Westborough WTF, 2018-2019.



Figure C-73. Time series plot of pH (SU) from discrete samples taken at effluent and ambient stations near Westborough WTF, 2018-2019.



Figure C-74. Time series plot of potassium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Westborough WTF, 2018-2019.



Figure C-75. Time series plot of sodium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Westborough WTF, 2018-2019.



Figure C-76. Time series plot of sulfate, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Westborough WTF, 2018-2019.



Figure C-77. Time series plot of water temperature (°C) from discrete samples taken at effluent and ambient stations near Westborough WTF, 2018-2019.

Hanover WTF



Figure C-78. Time series plot of alkalinity, filtered (mg/L as calcium carbonate) from discrete samples taken at effluent and ambient stations near Hanover WTF, 2018-2019. Note additional sample collected at Hanover Water Treatment Plant Backwash Effluent on August 8, 2018 is not a replicate (see Table C-1 for detail).



Figure C-79. Time series plot of calcium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Hanover WTF, 2018-2019. Note additional sample collected at Hanover Water Treatment Plant Backwash Effluent on August 8, 2018 is not a replicate (see Table C-1 for detail).



Figure C-80. Time series plot of chloride, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Hanover WTF, 2018-2019. Note additional sample collected at Hanover Water Treatment Plant Backwash Effluent on August 8, 2018 is not a replicate (see Table C-1 for detail).



Figure C-81. Time series plot of copper, filtered (μ g/L) from discrete samples taken at effluent and ambient stations near Hanover WTF, 2018-2019. Note additional sample collected at Hanover Water Treatment Plant Backwash Effluent on August 8, 2018 is not a replicate (see Table C-1 for detail).



Figure C-82. Time series plot of magnesium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Hanover WTF, 2018-2019. Note additional sample collected at Hanover Water Treatment Plant Backwash Effluent on August 8, 2018 is not a replicate (see Table C-1 for detail).



Figure C-83. Time series plot of organic carbon, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Hanover WTF, 2018-2019. Note additional sample collected at Hanover Water Treatment Plant Backwash Effluent on August 8, 2018 is not a replicate (see Table C-1 for detail).



Figure C-84. Time series plot of pH (SU) from discrete samples taken at effluent and ambient stations near Hanover WTF, 2018-2019. Note additional sample collected at Hanover Water Treatment Plant Backwash Effluent on August 8, 2018 is not a replicate (see Table C-1 for detail).



Figure C-85. Time series plot of potassium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Hanover WTF, 2018-2019. Note additional sample collected at Hanover Water Treatment Plant Backwash Effluent on August 8, 2018 is not a replicate (see Table C-1 for detail).



Figure C-86. Time series plot of sodium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Hanover WTF, 2018-2019. Note additional sample collected at Hanover Water Treatment Plant Backwash Effluent on August 8, 2018 is not a replicate (see Table C-1 for detail).



Figure C-87. Time series plot of sulfate, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Hanover WTF, 2018-2019. Note additional sample collected at Hanover Water Treatment Plant Backwash Effluent on August 8, 2018 is not a replicate (see Table C-1 for detail).



Figure C-88. Time series plot of water temperature (°C) from discrete samples taken at effluent and ambient stations near Hanover WTF, 2018-2019. Note additional sample collected at Hanover Water Treatment Plant Backwash Effluent on August 8, 2018 is not a replicate (see Table C-1 for detail).

Leominster WTF



Figure C-89. Time series plot of alkalinity, filtered (mg/L as calcium carbonate) from discrete samples taken at effluent and ambient stations near Leominster WTF, 2018-2019. Note additional samples collected at Leominster Water Treatment Plant Backwash Effluent and Monoosnoc Brook, DS Leominster Water Treatment Plt on June 8, 2018 are not replicates (see Table C-1 for detail).



Figure C-90. Time series plot of calcium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Leominster WTF, 2018-2019. Note additional samples collected at Leominster Water Treatment Plant Backwash Effluent and Monoosnoc Brook, DS Leominster Water Treatment Plt on June 8, 2018 are not replicates (see Table C-1 for detail).



Figure C-91. Time series plot of chloride, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Leominster WTF, 2018-2019. Note additional samples collected at Leominster Water Treatment Plant Backwash Effluent and Monoosnoc Brook, DS Leominster Water Treatment Plt on June 8, 2018 are not replicates (see Table C-1 for detail).



Figure C-92. Time series plot of copper, filtered (μ g/L) from discrete samples taken at effluent and ambient stations near Leominster WTF, 2018-2019. Note additional samples collected at Leominster Water Treatment Plant Backwash Effluent and Monoosnoc Brook, DS Leominster Water Treatment Plt on June 8, 2018 are not replicates (see Table C-1 for detail).



Figure C-93. Time series plot of magnesium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Leominster WTF, 2018-2019. Note additional samples collected at Leominster Water Treatment Plant Backwash Effluent and Monoosnoc Brook, DS Leominster Water Treatment Plt on June 8, 2018 are not replicates (see Table C-1 for detail).



Figure C-94. Time series plot of organic carbon, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Leominster WTF, 2018-2019. Note additional samples collected at Leominster Water Treatment Plant Backwash Effluent and Monoosnoc Brook, DS Leominster Water Treatment Plt on June 8, 2018 are not replicates (see Table C-1 for detail).



Figure C-95. Time series plot of pH (SU) from discrete samples taken at effluent and ambient stations near Leominster WTF, 2018-2019. Note additional samples collected at Leominster Water Treatment Plant Backwash Effluent and Monoosnoc Brook, DS Leominster Water Treatment Plt on June 8, 2018 are not replicates (see Table C-1 for detail).



Figure C-96. Time series plot of potassium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Leominster WTF, 2018-2019. Note additional samples collected at Leominster Water Treatment Plant Backwash Effluent and Monoosnoc Brook, DS Leominster Water Treatment Plt on June 8, 2018 are not replicates (see Table C-1 for detail).



Figure C-97. Time series plot of sodium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Leominster WTF, 2018-2019. Note additional samples collected at Leominster Water Treatment Plant Backwash Effluent and Monoosnoc Brook, DS Leominster Water Treatment Plt on June 8, 2018 are not replicates (see Table C-1 for detail).



Figure C-98. Time series plot of sulfate, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Leominster WTF, 2018-2019. Note additional samples collected at Leominster Water Treatment Plant Backwash Effluent and Monoosnoc Brook, DS Leominster Water Treatment Plt on June 8, 2018 are not replicates (see Table C-1 for detail).



Figure C-99. Time series plot of water temperature (°C) from discrete samples taken at effluent and ambient stations near Leominster WTF, 2018-2019. Note additional samples collected at Leominster Water Treatment Plant Backwash Effluent and Monoosnoc Brook, DS Leominster Water Treatment Plt on June 8, 2018 are not replicates (see Table C-1 for detail).

Weymouth WTF



Figure C-100. Time series plot of Alkalinity, filtered (mg/L as calcium carbonate) from discrete samples taken at effluent and ambient stations near Weymouth WTF, 2018-2019.



Figure C-101. Time series plot of Calcium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Weymouth WTF, 2018-2019.



Figure C-102. Time series plot of Chloride, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Weymouth WTF, 2018-2019.



Figure C-103. Time series plot of Copper, filtered (μ g/L) from discrete samples taken at effluent and ambient stations near Weymouth WTF, 2018-2019.



Figure C-104. Time series plot of Magnesium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Weymouth WTF, 2018-2019.



Figure C-105. Time series plot of Organic Carbon, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Weymouth WTF, 2018-2019.



Figure C-106. Time series plot of pH (SU) from discrete samples taken at effluent and ambient stations near Weymouth WTF, 2018-2019.



Figure C-107. Time series plot of Potassium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Weymouth WTF, 2018-2019.



Figure C-108. Time series plot of Sodium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Weymouth WTF, 2018-2019.



Figure C-109. Time series plot of Sulfate, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Weymouth WTF, 2018-2019.



Figure C-110. Time series plot of water temperature (°C) from discrete samples taken at effluent and ambient stations near Weymouth WTF, 2018-2019.

Wilmington WTF



Figure C-111. Time series plot of Alkalinity, filtered (mg/L as calcium carbonate) from discrete samples taken at effluent and ambient stations near Wilmington WTF, 2018-2019. Note additional sample collected at Wilmington Water Treatment Plant Backwash Effluent on November 29, 2018 is not a replicate (see Table C-1 for detail).



Figure C-112. Time series plot of Calcium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Wilmington WTF, 2018-2019. Note additional sample collected at Wilmington Water Treatment Plant Backwash Effluent on November 29, 2018 is not a replicate (see Table C-1 for detail).



Figure C-113. Time series plot of Chloride, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Wilmington WTF, 2018-2019. Note additional sample collected at Wilmington Water Treatment Plant Backwash Effluent on November 29, 2018 is not a replicate (see Table C-1 for detail).



Figure C-114. Time series plot of Copper, filtered (μ g/L) from discrete samples taken at effluent and ambient stations near Wilmington WTF, 2018-2019. Note additional sample collected at Wilmington Water Treatment Plant Backwash Effluent on November 29, 2018 is not a replicate (see Table C-1 for detail).



Figure C-115. Time series plot of Magnesium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Wilmington WTF, 2018-2019. Note additional sample collected at Wilmington Water Treatment Plant Backwash Effluent on November 29, 2018 is not a replicate (see Table C-1 for detail).



Figure C-116. Time series plot of Organic Carbon, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Wilmington WTF, 2018-2019. Note additional sample collected at Wilmington Water Treatment Plant Backwash Effluent on November 29, 2018 is not a replicate (see Table C-1 for detail).



Figure C-117. Time series plot of pH (SU) from discrete samples taken at effluent and ambient stations near Wilmington WTF, 2018-2019. Note additional sample collected at Wilmington Water Treatment Plant Backwash Effluent on November 29, 2018 is not a replicate (see Table C-1 for detail).



Figure C-118. Time series plot of Potassium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Wilmington WTF, 2018-2019. Note additional sample collected at Wilmington Water Treatment Plant Backwash Effluent on November 29, 2018 is not a replicate (see Table C-1 for detail).



Figure C-119. Time series plot of Sodium, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Wilmington WTF, 2018-2019. Note additional sample collected at Wilmington Water Treatment Plant Backwash Effluent on November 29, 2018 is not a replicate (see Table C-1 for detail).



Figure C-120. Time series plot of Sulfate, filtered (mg/L) from discrete samples taken at effluent and ambient stations near Wilmington WTF, 2018-2019. Note additional sample collected at Wilmington Water Treatment Plant Backwash Effluent on November 29, 2018 is not a replicate (see Table C-1 for detail).



Figure C-121. Time series plot of water temperature (°C) from discrete samples taken at effluent and ambient stations near Wilmington WTF, 2018-2019. Note additional sample collected at Wilmington Water Treatment Plant Backwash Effluent on November 29, 2018 is not a replicate (see Table C-1 for detail).

Appendix D: Time-Series Plots of Site-Dependent Copper Criteria Values near 11 water and wastewater treatment facilities in

Massachusetts

Westborough WWTF



Figure D-1. Time series plot of site-dependent instantaneous Criteria Maximum Concentration (CMC) and Criteria Continuous Concentration (CCC) values (μ g/L) for ambient stations used in the BLM near Westborough WWTF, 2018-2019.



Marlborough WWTF

Figure D-2. Time series plot of site-dependent instantaneous Criteria Maximum Concentration (CMC) and Criteria Continuous Concentration (CCC) values (μ g/L) for ambient stations used in the BLM near Marlborough WWTF, 2018-2019.

Hudson WWTF



Figure D-3. Time series plot of site-dependent instantaneous Criteria Maximum Concentration (CMC) and Criteria Continuous Concentration (CCC) values (μ g/L) for ambient stations used in the BLM near Hudson WWTF, 2018-2019.

Maynard WWTF



Figure D-4. Time series plot of site-dependent instantaneous Criteria Maximum Concentration (CMC) and Criteria Continuous Concentration (CCC) values (μ g/L) for ambient stations used in the BLM near Maynard WWTF, 2018-2019.

Cohasset WTF



Figure D-5. Time series plot of site-dependent instantaneous Criteria Maximum Concentration (CMC) and Criteria Continuous Concentration (CCC) values (μ g/L) for ambient stations used in the BLM near Cohasset WTF, 2018-2019.



Fitchburg WTF

Figure D-6. Time series plot of site-dependent instantaneous Criteria Maximum Concentration (CMC) and Criteria Continuous Concentration (CCC) values (μ g/L) for ambient stations used in the BLM near Fitchburg WTF, 2018-2019.

Westborough WTF



Figure D-7. Time series plot of site-dependent instantaneous Criteria Maximum Concentration (CMC) and Criteria Continuous Concentration (CCC) values (μ g/L) for ambient stations used in the BLM near Westborough WTF, 2018-2019.

Hanover WTF



Figure D-8. Time series plot of site-dependent instantaneous Criteria Maximum Concentration (CMC) and Criteria Continuous Concentration (CCC) values (μ g/L) for ambient stations used in the BLM near Hanover WTF, 2018-2019.



Leominster WTF

Figure D-9. Time series plot of site-dependent instantaneous Criteria Maximum Concentration (CMC) and Criteria Continuous Concentration (CCC) values (μ g/L) for ambient stations used in the BLM near Leominster WTF, 2018-2019. Note data gap is a result of a missing temperature value for June 8, 2018.

Weymouth WTF



Figure D-10. Time series plot of site-dependent instantaneous Criteria Maximum Concentration (CMC) and Criteria Continuous Concentration (CCC) values (μ g/L) for ambient stations used in the BLM near Weymouth WTF, 2018-2019.



Wilmington WTF

Figure D-11. Time series plot of site-dependent instantaneous Criteria Maximum Concentration (CMC) and Criteria Continuous Concentration (CCC) values (μ g/L) for ambient stations used in the BLM near Wilmington WTF, 2018-2019.