Blackstone River Water Quality Monitoring Program

2022 Sampling Season Report

Prepared for

Karla Sangrey, Director

Upper Blackstone Clean Water

by

Marie-Françoise Hatte and Cameron Richards

Water Resources Research Center, University of Massachusetts

Zachary Eichenwald

CDM Smith

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Authors: Marie-Françoise Hatte and Cameron Richards
Massachusetts Water Resources Research Center

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Front cover photo: Blackstone River at the R116 sampling site in Pawtucket, RI, August 10, 2022. Photo by Denise Prouty.

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1.0 Introduction

In 2012, Upper Blackstone Clean Water (Upper Blackstone) initiated a voluntary water quality monitoring program to evaluate the impact of treatment plant upgrades and subsequent treatment process optimization. This report presents water quality data collected on behalf of Upper Blackstone along the mainstem of the Blackstone River between April and November 2022. It includes a brief overview of trends in total phosphorus, total nitrogen, and chlorophyll-a data observed since the start of the sampling program.

Sampling, sample handling, and laboratory analyses were unchanged from previous years, and chlorophyll filtering and aliquot splitting were done in a separate lab at the Upper Blackstone plant, as was done in the past couple of years. Sampling sites remained at the same locations as in 2021. More detailed technical information regarding the sampling program is available in the 2022 Field Sampling Plan (Appendix D) and the Quality Assurance Project Plan (QAPP, Appendix E) for this project.

Water quality reports for each sampling season are available upon request. The Blackstone River water quality data collected as part of Upper Blackstone's monitoring program are publicly available by request to Karla Sangrey (email: ksangrey@ubcleanwater.org) or via download through the Consortium of Universities for the Advancement of Hydrologic Science, Inc. (CUAHSI, www.cuahsi.org) Hydrologic Information System (HIS) database and servers (data.cuahsi.org), which are sponsored by the National Science Foundation (through 2019) and via the new EPA Water Quality Portal (https://www.waterqualitydata.us/) starting with 2020 data.

2.0 Background

The Blackstone River watershed encompasses an area of approximately 480 mi^2 in central Massachusetts and northern Rhode Island. The watershed lies within EPA's Nutrient Ecoregion XIV, subregion 59, the Eastern Coastal Plain. The river flows from its headwaters in the hills above Worcester, MA, through Woonsocket, RI, and finally joins the Seekonk River in Pawtucket, RI, just below the Slater Mill Dam. The Seekonk River discharges into the Providence River, which flows into Narragansett Bay. Six major tributaries (the Quinsigamond, Mumford, West, Mill, Peters, and Branch rivers) as well as many smaller tributaries join the mainstem of the Blackstone River. The watershed includes over 1,300 acres of lakes and ponds. Reservoirs in the northwest portion of the basin are used for the City of Worcester water supply.

Several U.S. Geological Survey (USGS) streamflow gaging sites are located in the watershed, and hourly precipitation data is available for several locations in and near the watershed from the National Weather Service (NWS) National Centers for Environmental Information (NCEI). This report uses USGS gages in Millbury, MA (gage 01109730), and Woonsocket, RI (gage (01112500) for flow data, and precipitation data is obtained from the National Weather Service's Worcester Regional Airport (KORH) station.

The Blackstone River is one of the largest contributors of freshwater to Narragansett Bay, providing on average almost one quarter of the freshwater flow to the Bay (Ries, 1990), and plays an important role in the health of the Bay.

The Blackstone River Valley is acknowledged as the "Birthplace of the American Industrial Revolution." Over its 48-mile run towards Narragansett Bay, the Blackstone River drops approximately 440 feet (Shanahan, 1994). The Blackstone River and its watershed were transformed from a farming area in colonial days into one of the 19th century's great industrial areas due to this hydraulic potential, starting with the first mill dam built by Samuel Slater at the outlet of the river in 1793. Water-powered textile mills proliferated up and down the river, and at one point, the river had almost one dam for every mile along its run. The historical significance of the river has been recognized at both local and federal levels. In 1986, an Act of Congress established the John H. Chafee Blackstone River Valley National Heritage Corridor. In 1998, the Blackstone was designated as an American Heritage River. In 2002, it was one of eight rivers included in an urban river restoration pilot study led by the U.S. Environmental Protection Agency (EPA) and the U.S. Army Corps of Engineers. In 2014, the Blackstone River Valley National Historical Park was established as the 402nd park in the national park system.

There are nine wastewater treatment facilities (WWTFs) that discharge into the Blackstone River and its tributaries, **Table 1**. The largest, in terms of volume, is the Upper Blackstone (UB). There are twenty named dams remaining along the mainstem of the Blackstone River. The locations of the WWTFs and remaining dams along the mainstem of the Blackstone River are shown in **Table 1** based on river mile. The outlet of the Blackstone River in Pawtucket, RI, is denoted as river mile zero, with river mile increasing in the upstream direction. The locations of federally regulated and controlled (licensed by the Federal Energy Regulatory Commission [FERC]) and minor dams along the river elevation profile are depicted in **Figure 1**. The industrial past of the Blackstone River, urbanization, and a high population density have resulted in a legacy of complex water quality issues.

In 2003, Upper Blackstone requested the Massachusetts Water Resources Research Center (MaWRRC) at UMass Amherst and CDM Smith initiate a watershed assessment study to improve its understanding of these complex dynamics. The study included river monitoring in 2005 and 2006, historical data analysis, and modeling to evaluate trends in river quality as well as management opportunities for improving water quality and aquatic habitat throughout the basin. Upper Blackstone supported additional water quality data collection in 2010 and 2011, and since 2012 has supported consistent annual water quality monitoring at several sampling locations along the mainstem Blackstone River to support the assessment of the river's response to reduced nutrient concentrations in the wastewater treatment plant effluent. While Upper Blackstone's monitoring program has always followed strict sample collection and analysis procedures, sampling was conducted under a Quality Assurance Project Plan (QAPP) approved by the Massachusetts Department of Environmental Protection (MassDEP) from 2014 – 2016 (UMass et al., 2015). A new approved QAPP covered sampling in 2017 – 2019 (UMass et al., 2017), and the latest QAPP covers sampling from 2020 through 2022 (UMass and CDM Smith, 2020). Having the approved QAPP in place allows MassDEP to use the data in the agency's watershed assessments.

Table 1: Dams, sampling sites, and tributaries on the Blackstone River mainstem
(adapted from Wright et al., 2001)

Mile	Description	Mile	Description
0	Slater Mill Dam	27.8	Below Rice city Pond Sluice Gates, Hartford St., Uxbridge, MA (W1779)
0	Slater Mill Dam, Pawtucket, RI (RMSD)	29.2	Northbridge WWTF
0.8	Pawtucket Hydro Dam	31.9	Riverdale Hydro Dam
1.8	Abbot Run	33.4	USGS gage at Sutton St. Bridge, Northbridge, MA (W0767)
2	Central Falls Dam	35.4	Grafton WWTF
4.1	Lonsdale Dam	35.6	Farnumsville Hydro Dam
6.3	Rte 116 Bikepath Bridge, Pawtucket, RI (R116)	36.3	Route 122A, Grafton, MA (W1242)
6.8	Ashton Dam	36.5	Fisherville Dam
8.2	Albion Dam	36.6	Quinsigamond River
9.9	Manville Dam	38	Depot St., Sutton, MA (Depot)
12.4	Woonsocket WWTF	38.7	Saundersville Dam
12.8	Hamlet Ave. Dam	39.2	Wilkinsonville Dam
13.1	Peters River	39.8	Singing Dam
13.1	USGS gaging station 01112500	41	Millbury Electric Dam
15.5	Thundermist Hydro Dam	40.8	Former Millbury WWTP
15.5	State Line, RI (RMSL)	42.1	Riverlin Street
16.5	Blackstone Dam	42.7	Central Cemetery, Millbury, MA (W1258)
17.4	Branch River	43.9	McCracken Rd Dam
17.8	Tupperware Dam	44.4	Upper Blackstone WWTF
19.2	Mill River	44.6	Below confluence with UB effluent (UBWPAD2)
22	Uxbridge WWTF	45.2	New Millbury St. Bridge, Worcester, MA (W0680)
24.2	West River	46.4	Worcester CSO
25.9	Mumford River	46.6	Mill Brook/Middle River Confluence
27.8	Rice City Pond Dam	46.6	USGS Gaging Station 01109730

Sampling sites, Tributaries, WWTFs, FERC dams, Minor dams/ impoundments, USGS gaging stations

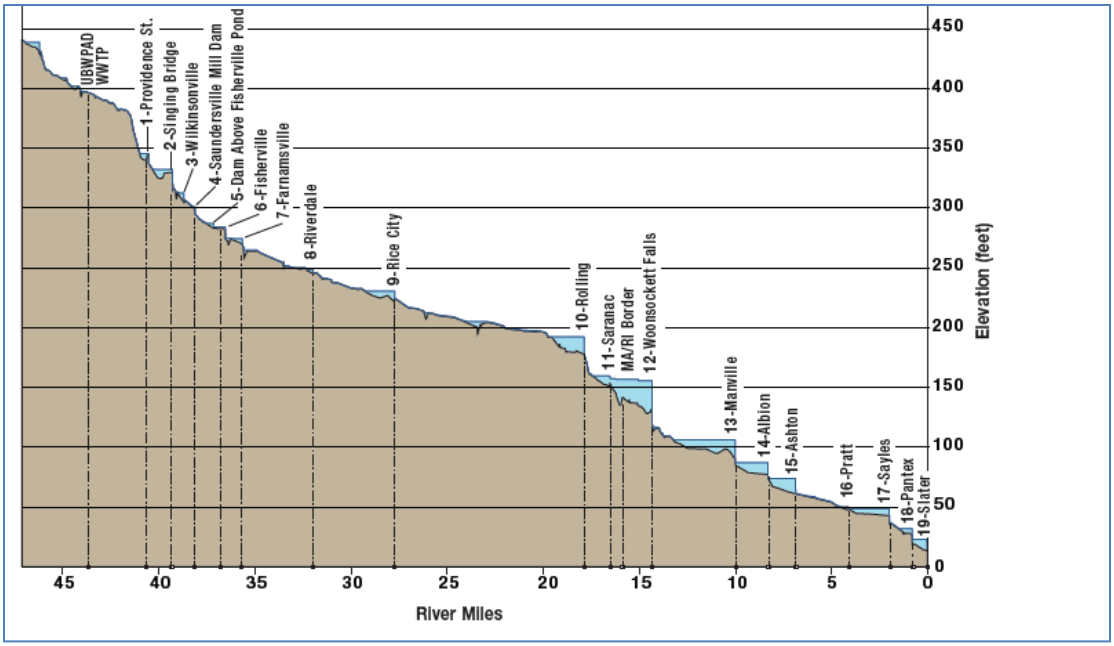


Figure 1: River elevation profile

3.0 Blackstone Water Quality Sampling Program

In 2022, the river monitoring program included monthly water quality sampling for nutrients, chlorophyll-a, and field parameters (dissolved oxygen, temperature, conductivity, and pH) from April through November. The three Rhode Island sites were co-sampled with the Narragansett Bay Commission (NBC) each month except in October, when NBC and this project sampled on different days.

Sampling locations for routine nutrient/chlorophyll-a monitoring and continuous dissolved oxygen monitoring were selected based on several criteria, in order to:

- Provide reference data for the river above and below the confluence with Upper Blackstone's effluent channel;
- Correspond with locations monitored by MassDEP in 2008;
- Correspond with long-term monitoring locations maintained by NBC;
- Build upon Upper Blackstone sampling efforts that were first initiated in 2004;
- Provide information on both run-of-river and impounded sites along the river;
- Provide information on both the nutrient and chemical status of the river; and
- Build a database to facilitate identification of temporal trends in water quality within the river.

Although this is Upper Blackstone's monitoring program, the data collected as part of this water quality-monitoring program are generally denoted "UMass 2022 data" in graphs and tables to avoid potential confusion with 1) the location where Upper Blackstone effluent enters the Blackstone River, and 2) the river monitoring location immediately downstream of this confluence. A brief overview of Upper Blackstone's monitoring programs is presented in the sections below. Detailed descriptions of sampling methods, quality control measures, and additional technical details are available in yearly field sampling plans and the project QAPP (Appendices D and E, respectively).

3.1 Overview

Monitoring locations and data collection type are summarized in **Table 2** and on **Figure 2**. Monthly water quality sampling for nutrients and chlorophyll-a were conducted from April through November every three or four weeks at nine sites along the mainstem of the Blackstone River, including three Rhode Island sites that are co-sampled with NBC. Continuous data loggers were placed at four river sites between June 30 and July 15, and remained in place through November 8. The four loggers were placed to examine gradients in water quality between W1258 and Depot Street observed during previous monitoring years.

Table 2: Blackstone River 2022 sampling sites

Site ID#	Site Name	Lat.	Long.	River Mile[2]	HSPF Reach[2]	Sampling Details[3]
RSMD[1]	Slater Mill Dam, Pawtucket, RI	41.877	-71.382	0.0	200	N
R116[1]	Rte 116 Bikepath Bridge, Pawtucket, RI	41.938	-71.434	6.3	228	N
RMSL[1]	State Line, RI	42.010	-71.529	15.5	268	N
W1779	Below Rice City Pond Sluice Gates, Hartford St., Uxbridge, MA	42.097	-71.622	27.8	326	N
W0767[6]	Sutton St. Bridge, Northbridge, MA	42.154	-71.653	33.4	348	N
W1242	Route 122A, Grafton, MA	42.177	-71.688	36.3	360	N
Millbury WWTP	Former Millbury WWTP, Millbury, MA	42.187	-71.743	40.8	382	DO
Riverlin St.	Riverlin Street, Millbury, MA	42.193	-71.754	42.1	386	DO
W1258	Central Cemetery, Millbury, MA	42.194	-71.766	42.7	392	NDO
UBWPAD2[4]	Confluence Site, Millbury, MA	42.206	-71.781	44.6	402	NDO
W0680[5]	New Millbury St. Bridge, Worcester, MA	42.228	-71.787	45.2	414	N

[1] Locations of co-sampling with NBC

[2] Corresponding river mile and model reach in Blackstone River HSPF model: *Blackstone River HSPF Water Quality Model Calibration Report* (UMass and CDM Smith, August 2008) and the *Blackstone River HSPF Water Quality Model Calibration Report Addendum* (UMass and CDM Smith, October 2011).

[3] Sampling Types: N = 9 sites, nutrients & chlorophyll-a + handheld meters 1 event/4-weeks; DO = 4 sites, Continuous Data Loggers.

[4] Site replaced original confluence site (UBWPAD) in 2013

[5] W0680 is located between the Worcester CSO discharge and UBWPAD2

[6] In 2019, this site was changed from the bank of the river to the middle of the bridge at those coordinates.

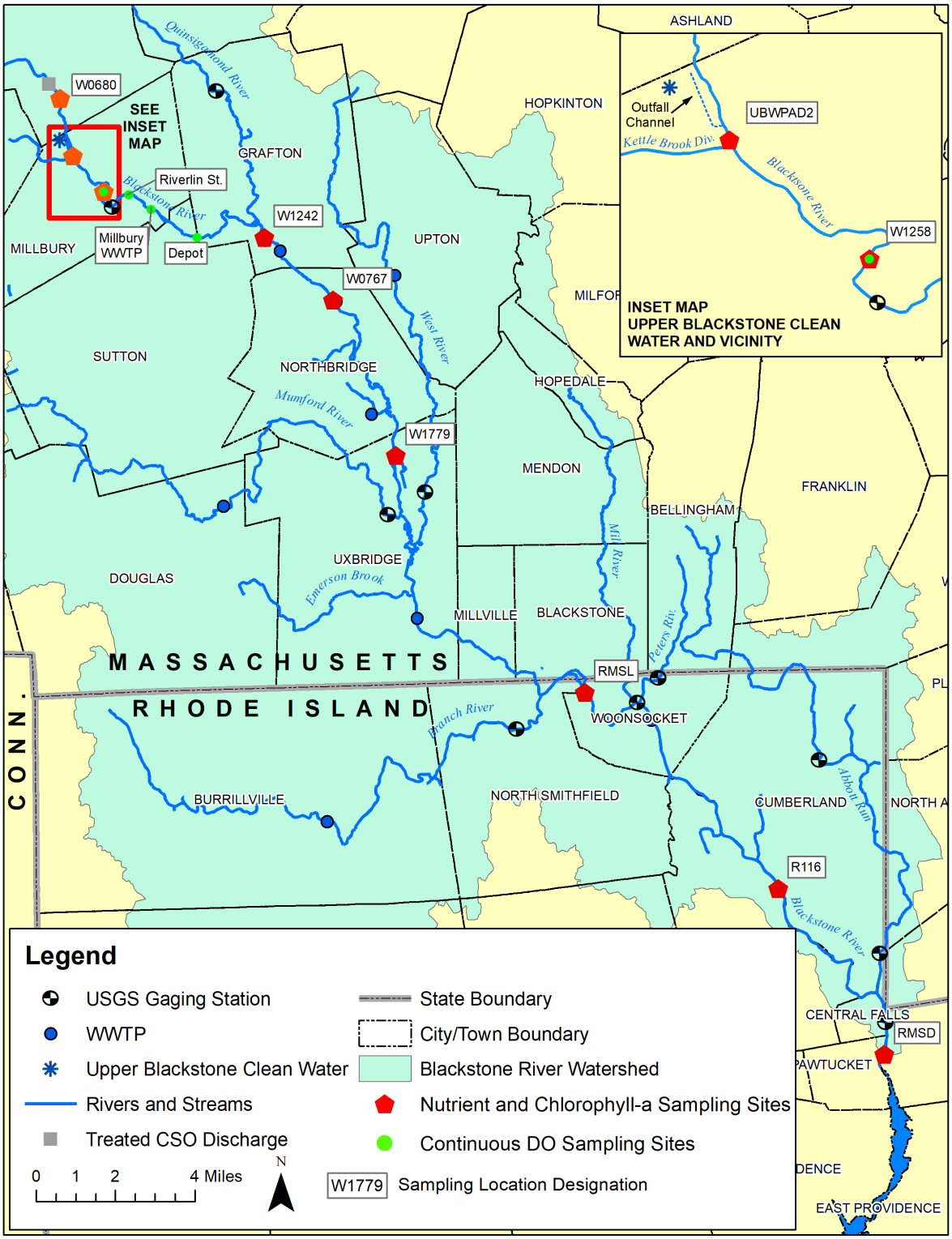


Figure 2: Blackstone River 2022 sampling sites and location of continuous data loggers

3.2 Sampling Dates and Data Collected

2022 sampling dates are summarized in **Table 3.**

Table 3: 2022 river sampling dates

Site ID#	4/20	5/18	6/15	7/13	8/10	9/7	10/17	11/2
RSMD	X	X	X	X	X	X	X	X
R116	X	X	X	X	X	X	X	X
RMSL	X	X	X	X	X	X	X	X
W1779	X	X	X	X	X	X	X	X
W0767	X	X	X	X	X	X	X	X
W1242	X	X	X	X	X	X	X	X
W1258	X	X	X	X	X	X	X	X
UBWPAD2	X	X	X	X	X	X	X	X
W0680	X	X	X	X	X	X	X	X

X: Data collection completed

Samples collected for nutrient analysis are analyzed for total ammonia nitrogen (dNH_4), dissolved nitrite-nitrate nitrogen (dNO_{23}), either total Kjeldahl nitrogen (TKN) or dissolved total nitrogen (dTN) depending on the analysis laboratory, particulate organic nitrogen (PON), total orthophosphate (TOP), total phosphorus (TP), total suspended solids (TSS), and chlorophyll-a (chl-a), **Table 4**. Samples are analyzed at Upper Blackstone's laboratory, NBC's laboratory, the UMass Environmental Analysis Laboratory (EAL), and/or the Coastal Systems Program Lab at UMass Dartmouth (UMD) laboratory depending on the parameter as noted in the table.

Table 4: 2022 river sampling program analytes and laboratories

Parameter	Upper Blackstone Lab	NBC Lab	UMass EAL	UMD Lab
Dissolved Ammonia (dNH_4)	--	Apr* – Nov 3 RI Sites	--	Apr – Nov All sites
Dissolved Nitrite/Nitrate (dNO_{23})	--	Apr* – Nov 3 RI Sites	--	Apr – Nov All sites
Total Dissolved Nitrogen (TDN)	--	Apr* – Nov 3 RI Sites	--	Apr – Nov All sites
Total Nitrogen (TN)	--	--	--	Calculated
Particulate Organic Nitrogen (PON)	--	--	--	Apr – Nov All sites
Total Orthophosphate (TOP)	Apr – Nov All sites	--	--	--
Total Phosphorus (TP)	--	--	Apr – Nov All sites	--
Total Suspended Solids (TSS)	Apr – Nov All sites	Apr* – Nov 3 RI Sites	--	--
Chlorophyll-a (chl-a)	--	--	Apr – Nov All sites	--
Dissolved Oxygen (DO)	Apr - Nov All Sites & Continuous Jul-Nov @ 4 sites			
Water Temperature	Apr - Nov All Sites & Continuous Jul-Nov @ 4 sites			
pH	Apr - Nov All Sites			
Specific Conductance (SC)	Jul -Nov All Sites			

*In October 2022, NBC sampled on 10/5 and UMass sampled on 10/17

4.0 Sampling Season Environmental Conditions

Precipitation, temperature, and streamflow influence how the river and bay systems respond to inputs of nutrients. In wet years, the WWTF effluent comprises a smaller fraction of the river volume, and nutrients from WWTF effluent and other sources tend to be flushed from the river system more quickly, reducing the opportunity for algal growth in impoundments. For example, when flows are ~4,000 cfs[1] at Woonsocket, RI, it takes a "drop" of water approximately two days to travel from the Blackstone headwaters at river mile 46.6 to the outlet. Large storm events can also scour the streambed, washing periphyton and macrophytes downstream. Conversely, in dry years, in-stream nutrient concentrations tend to be higher. Shallower stream water depths enhance the penetration of light to the stream

[1] A flow of 4,000 cfs is exceeded ~1% of the time at the Woonsocket stream gaging station

bottom, and lower flows reduce scour, providing conditions more amenable for periphyton growth. The time it takes for water to move from the headwaters to the outlet of the river greatly increases, to approximately 30 days, when river flows are near 85 cfs[2] at Woonsocket, RI, providing conditions that could promote the growth of algae in impoundments. A cold spring season tends to maintain the snowpack and keep river and impoundment temperatures below conditions amenable for algal and periphyton growth. Warmer air temperatures result in higher water temperatures, which in turn promote algal and periphyton growth.

Data describing the 2022 environmental conditions are presented in this section. Precipitation and air temperature data are presented in Section 4.1, followed by a summary of the river streamflow conditions in Section 4.2. Section 4.3 provides a brief summary of the potential relative impacts of these conditions on river quality compared to previous sampling years.

4.1 Precipitation and Air Temperature

Snowfall records are available from the National Weather Service (NWS) since 1892 for Worcester (Worcester Regional Airport, KORH). This 130-year record is summarized in **Figure 3** based on published monthly data. Snowfall accumulations from the winters of 2020 - 2021 and 2021-2022 are highlighted due to their potential influence on the subsequent sampling season results. The ten sampling seasons in the current project span the range of typical snow accumulation, ranging from a total of 47.2 inches (winter of 2012-2016) to 119.8 inches (winter of 2014-2015). The historical ranking of each sampling year in terms of snow accumulation is summarized in **Table 5**. The 2022 sampling season was preceded by the fourth least snowy winter in the past ten years, with 53.6 inches[3] of snowfall (ranked 78th snowiest since 1893).

[2] 85 cfs is the lowest average discharge over a period of seven days that occurs on average once every 10 years (7Q10) at the Woonsocket stream gaging station

[3] The winter snowfall amount is calculated by adding all monthly snowfall totals from July of the previous year to June of the current year

Table 5: Snowfall totals winters 2012-2013 to 2021-2022

	Snow (in)	Rank in 130 years of record (1 = snowiest)
Winter 2012 - 13	108.9	6th
Winter 2013 - 14	85.2	23rd
Winter 2014 - 15	119.8	2nd
Winter 2015 - 16	47.2	90th
Winter 2016 - 17	78.3	30th
Winter 2017 - 18	96.1	13th
Winter 2018 - 19	51.4	82nd
Winter 2019 - 20	44.9	95th
Winter 2020 - 21	76.9	32nd
Winter 2021 - 22	53.6	78th

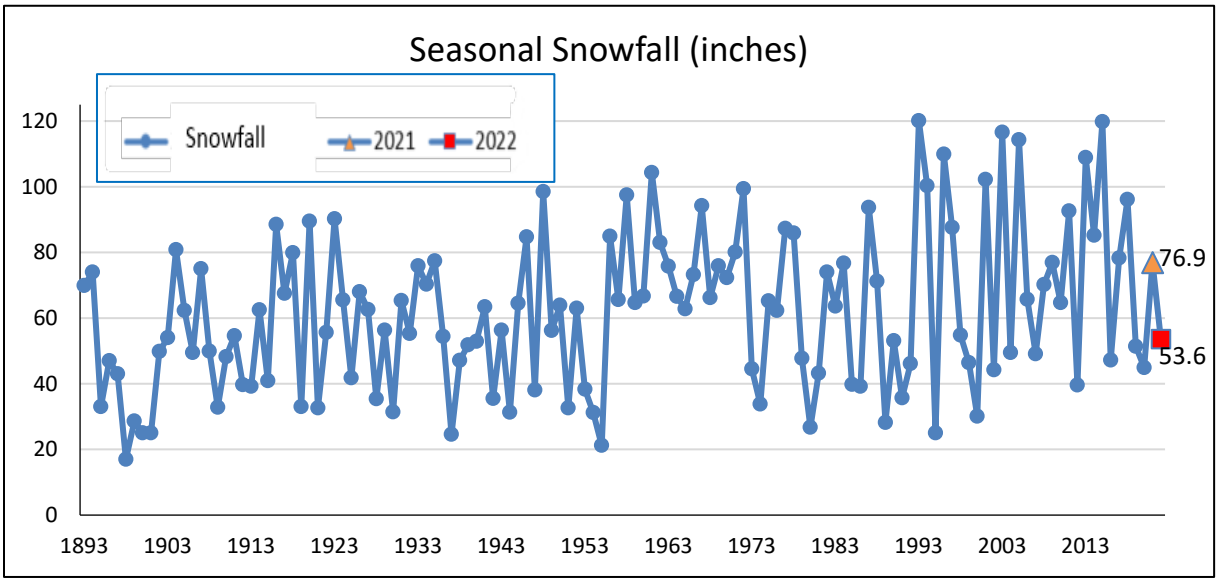


Figure 3: Seasonal snowfall (inches) in Worcester from 1893 through 2022, inclusive

Air temperature data for Worcester are available from the NWS starting in 1948. Monthly average temperature data since 1948 are summarized on **Figure 4** as a box plot, with the data for 2022 shown with blue diamonds. The box plots provide a summary of the distribution of the data, with the box showing the first quartile, median, and third quartile, and the whiskers showing 1.5 times the interquartile range above the upper quartile and below the lower quartile of the data. The small black circles above and below the whiskers represent observed data that are statistically considered "outliers."

Temperatures in 2022 were higher than historical median every month except January. August was particularly hot, with the mean monthly temperature the highest on record. The months when average temperature was close to the historical median temperature were April, June and September.

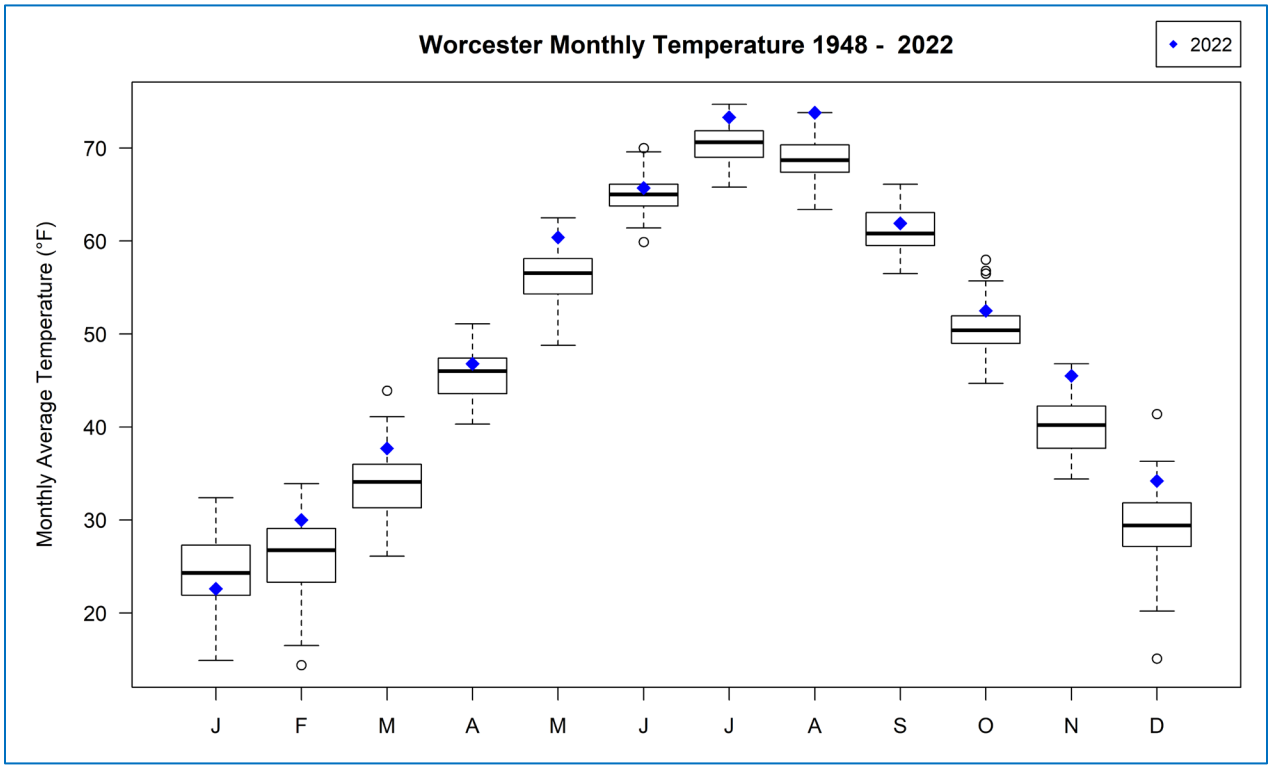
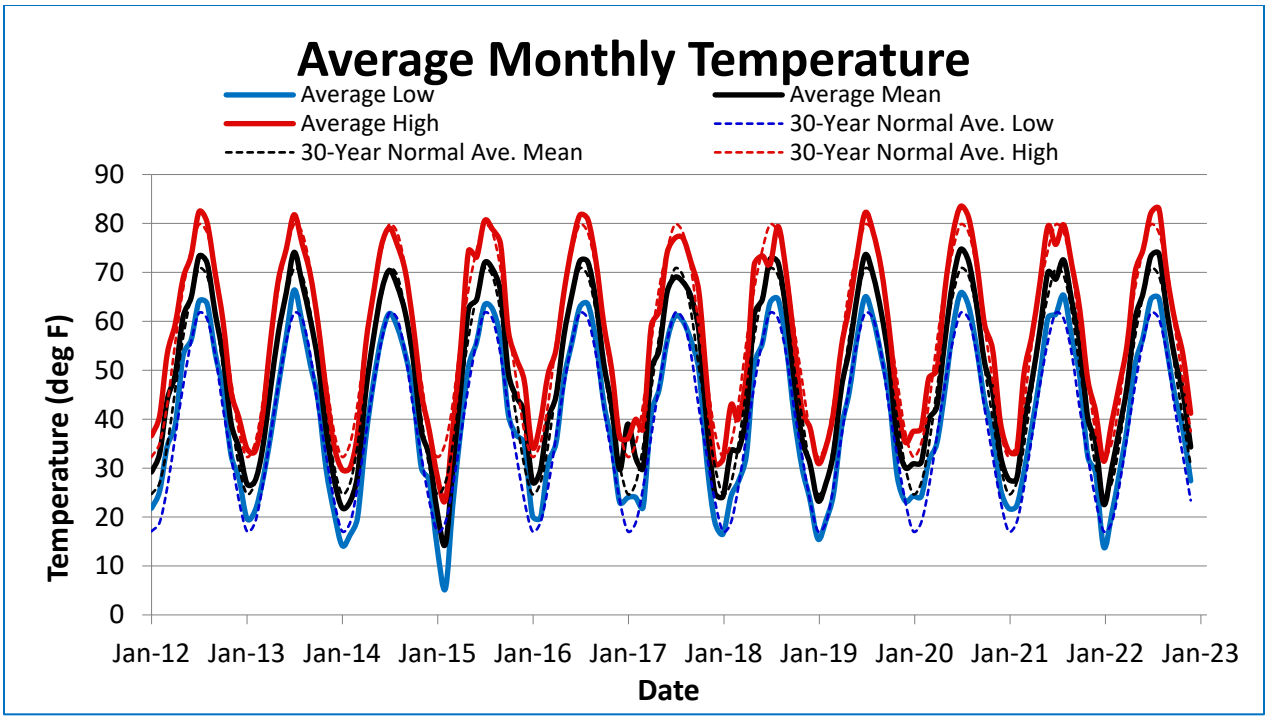


Figure 4: Worcester monthly air temperatures 1948 - 2022

Figure 5 presents three statistics to summarize monthly temperature conditions at the Worcester Regional Airport (KORH) since routine sampling began in 2012. The average mean temperature (black solid line) is determined based on the average daily temperature for each day in the given month. The average low temperature (solid blue line) is determined based on the average of the low temperatures observed on each day in the given month while the average high temperature (solid red line) is determined based on the average of the high temperatures observed each day. These data are plotted against the published normal monthly data for each statistic, based on the 30-year period from 1992 to 2021, shown as a dashed line of the same color. Instances where the solid line falls above the dashed line indicate warmer than typical conditions, whereas instances where the solid line falls below indicate cooler than normal conditions. The 2022 sampling season was generally warmer than those of recent sampling years.



Notes: Observed values for each month (solid lines) are compared to the normal for the month (dashed lines) based on NWS monthly data for Worcester from 1991 – 2020, available online https://www.ncei.noaa.gov/products/land-based-station/us-climate-normals

Figure 5: Average monthly low, mean, and high air temperature values observed since 2012

Annual precipitation totals for Worcester Regional Airport (KORH) from the NWS since 1949 are shown on **Figure 6**, with the years 2021 and 2022 noted with the associated accumulation. The annual precipitation in 2022, 48.33 inches, was lower than in 2021, and close to the average of the observed values since 1949 (48.0 inches).

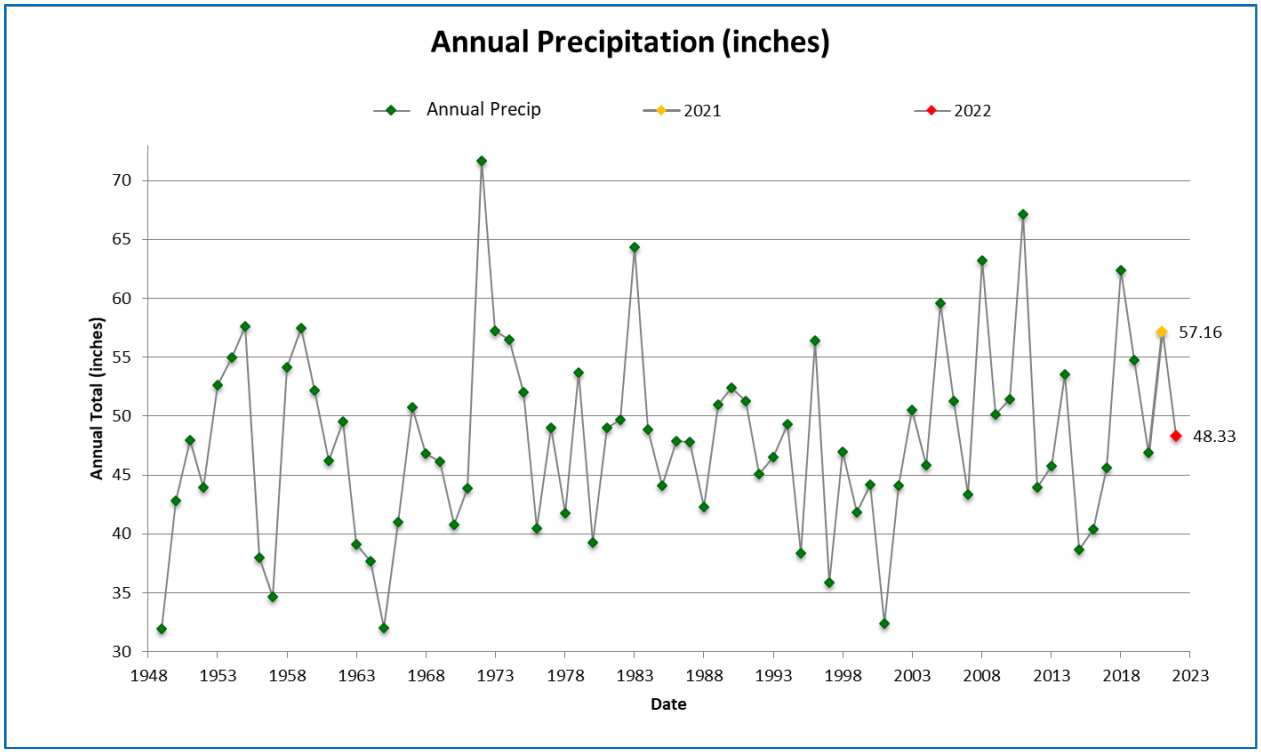


Figure 6: Worcester Annual Total Precipitation, 1949-2022 (KOHR station)

Figure 7 summarizes monthly precipitation conditions based on Worcester Regional Airport data since sampling began in 2012, shown as a solid green line, compared to published normals from the NWS based on the 30-year period 1992 – 2021, shown as a dashed green line. There is significant variability in monthly precipitation year-to-year and month-to-month, but 2022 sampling season generally shows lower precipitation amounts than average, except in September. Note that July and August were especially drier than typical in 2022.

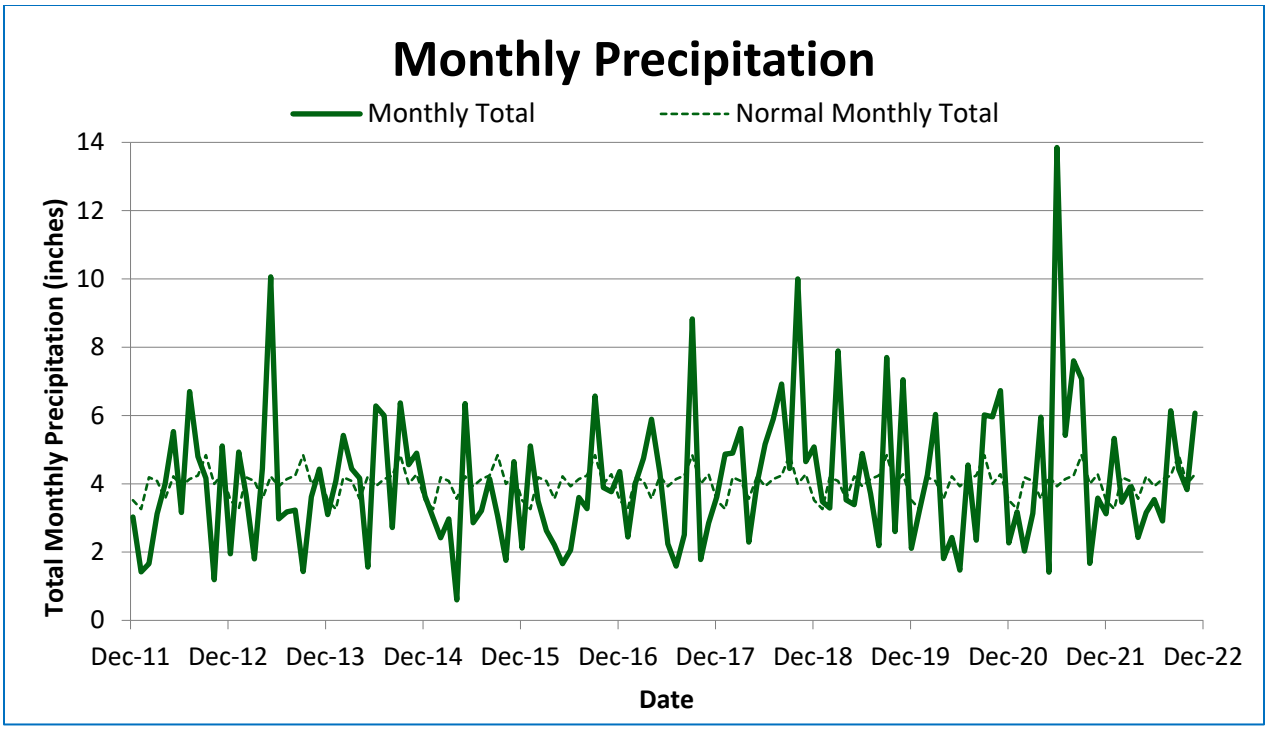


Figure 7: Monthly precipitation totals 2012-2021 compared to normal (1991-2022) monthly totals

Monthly precipitation totals since 1948 for Worcester are summarized using box plots on **Figure 8**. Data for 2022 are represented by blue diamonds. In 2022, monthly precipitation was at or near the historical median, except in February and September when it was much higher, and in May, August and December when it was lower. Monthly precipitation condition data for the 2022 sampling year compared to the NWS 30-year normal are provided in Appendix A.

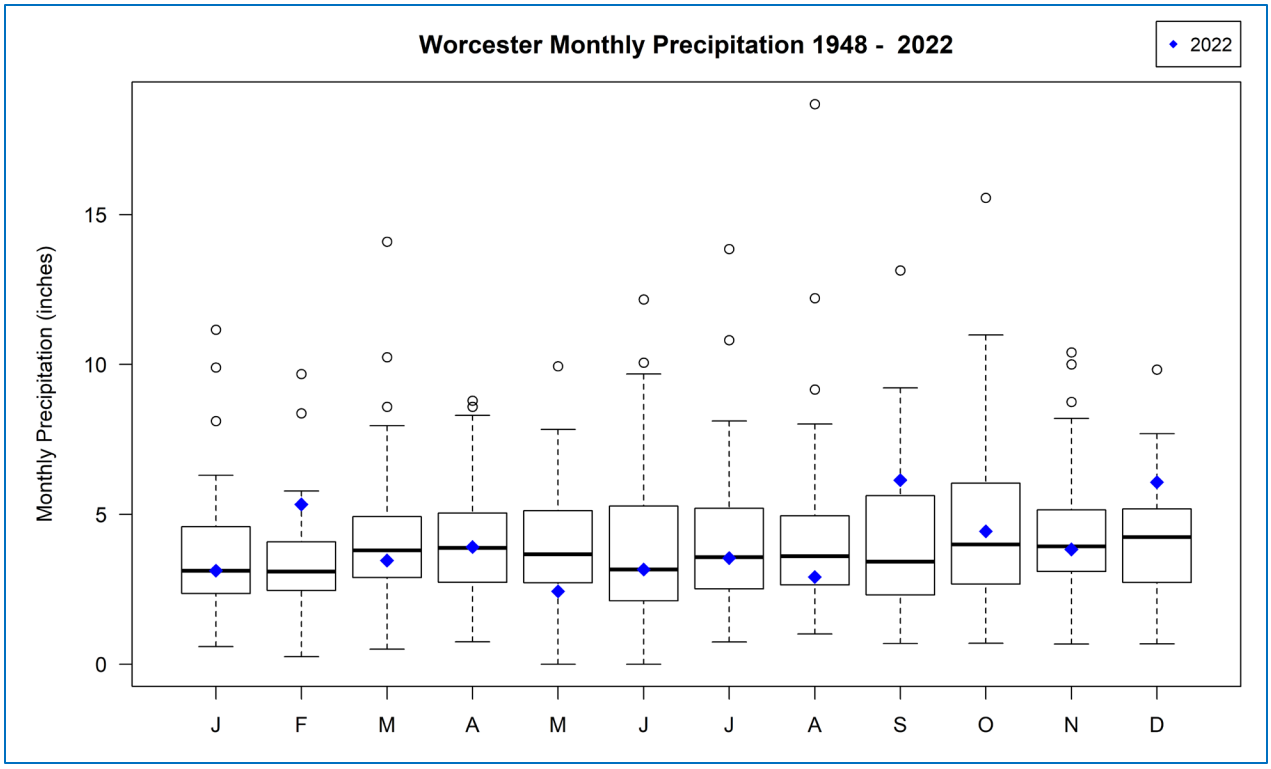


Figure 8: **Worcester monthly precipitation 1948 - 2022**

Daily precipitation data as measured at the Worcester Airport are plotted on **Figure 9** for 2022. The precipitation on sampling dates is highlighted with triangles. Cumulative precipitation for the year is also plotted and compared against the historical data, calculated as the cumulative sum of the 50th percentile cumulative daily normal for Worcester from 1991 – 2020, on the last day of the given month. Total precipitation was 48 inches in 2022. Cumulative rainfall in the 2022 sampling season was lower than the historical cumulative 50th percentile starting in May and stayed low the rest of the sampling period.

The occurrence of precipitation relative to the occurrence of routine sampling can have an impact on the measured levels of in-stream constituents such as nutrients and chlorophyll-a. Sampling day and antecedent precipitation conditions are summarized in **Table 6** for all routine sampling dates in 2022. Most routine sampling in 2022 occurred on days with little to no precipitation, except in July (0.32”) and October (0.6”). Significant rainfall (> 0.5 inches) occurred during the week prior to sampling every month except July and August. In June and September, over 2 inches of rain fell during the week before sampling day (almost 4 inches in September).

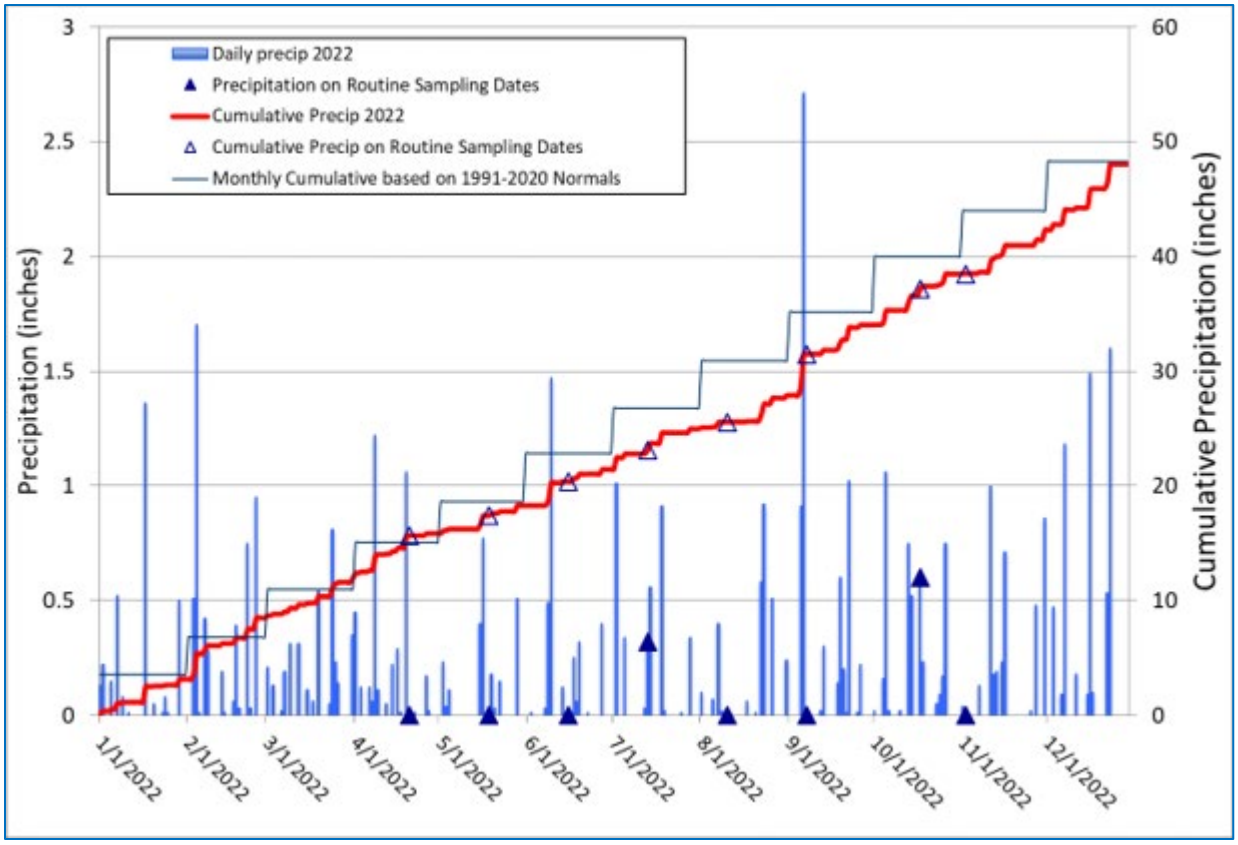


Figure 9: 2022 sampling season daily precipitation at Worcester Airport (KORH) compared against 50th percentile cumulative daily normal precipitation

Table 6: Day-of and antecedent precipitation on routine sampling dates in 2022

Sampling Date	Precipitation in Worcester, MA (NWS Station KORH) - inches			
	Day Of	1-day Prior	Total over 3-days Prior	Total over 7-days Prior
20 April	0.0	1.06	1.07	1.58
18 May	0.0	0.0	1.17	1.17
15 June	0.0	0.0	0.12	2.08
13 July	0.32	0.03	0.03	0.03
10 August	0.0	0.0	0.42	0.49
7 September	0.0	2.71	3.62	3.86
17 October	0.6	0.0	0.52	1.29
2 November	0.0	0.04	0.04	0.79

While it is not possible to fully account for the impacts of rainfall on results, stream sampling results can be summarized and reviewed based on the prevailing streamflow conditions on the sampling days. This issue is addressed further in the next sections.

4.2 Streamflow Conditions

Blackstone River Streamflow conditions during the 2021 sampling season are described in this section. It should be noted that some of the USGS streamflow data were still considered provisional at the time they were accessed for compilation of this report. Data are considered provisional until they undergo a formal review by USGS staff. During the formal review, small adjustments to the data may be made based on the most up-to-date field quality control data, particularly for very high or low streamflows. As a result, the data presented here might vary slightly from the final approved data.

Monthly average streamflow data collected by the USGS at Millbury, MA (01109730) since 2003 are summarized in **Figure 10** as a box plot, with the monthly average data for 2022 depicted with blue diamonds. Data for the USGS gage at Woonsocket, RI (01112500), collected since March 1929, are similarly presented in **Figure 11**. Monthly streamflows for each month of the routine sampling season are compared against the median, average and minimum monthly data for both Millbury and Woonsocket in **Table 7**.

During the 2022 sampling season, streamflows at the Millbury gage were below the median value every month except in September, and were very low in May through August. The mean monthly streamflows were lower than the 2003-2022 average each month except October. At the Woonsocket gage, average sampling season streamflows were low from April through August, but rose to above the historical median starting in September. The mean monthly streamflow was lower than the 2003-2022 average the entire year at the Woonsocket gage.

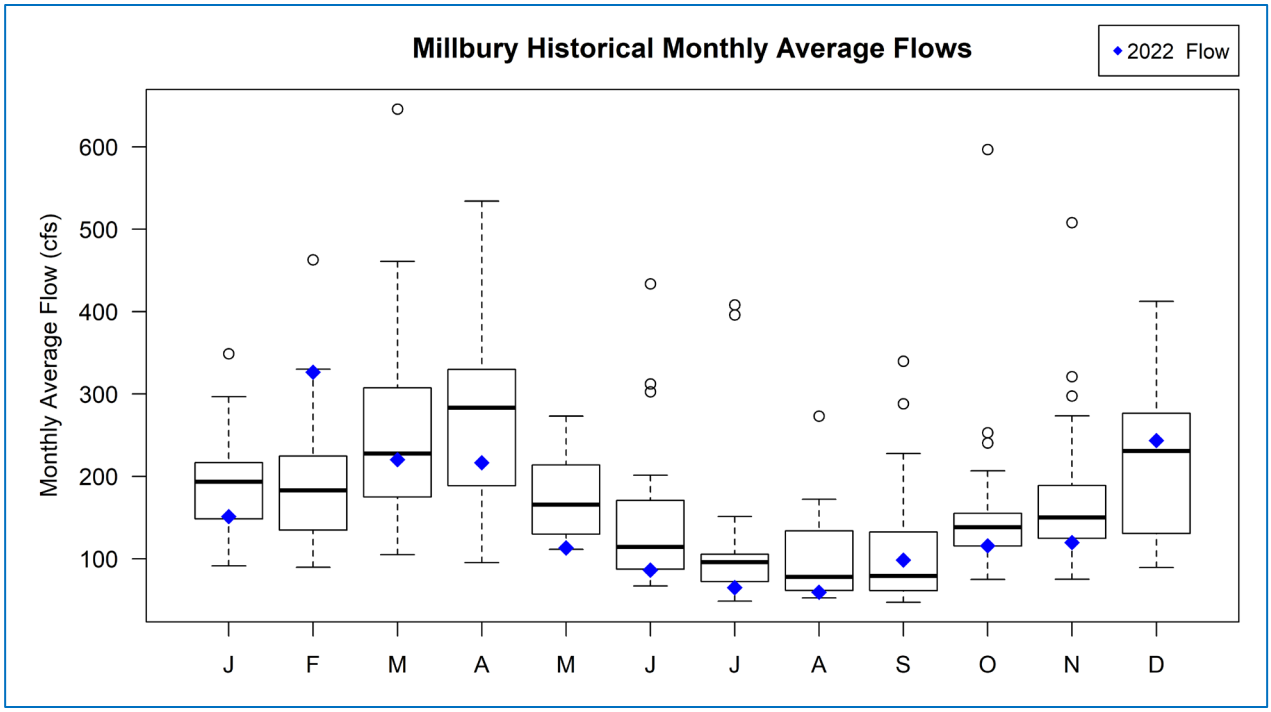


Figure 10: Millbury, MA, USGS gaging station (01109730) historical monthly average streamflows, 2003 - 2022

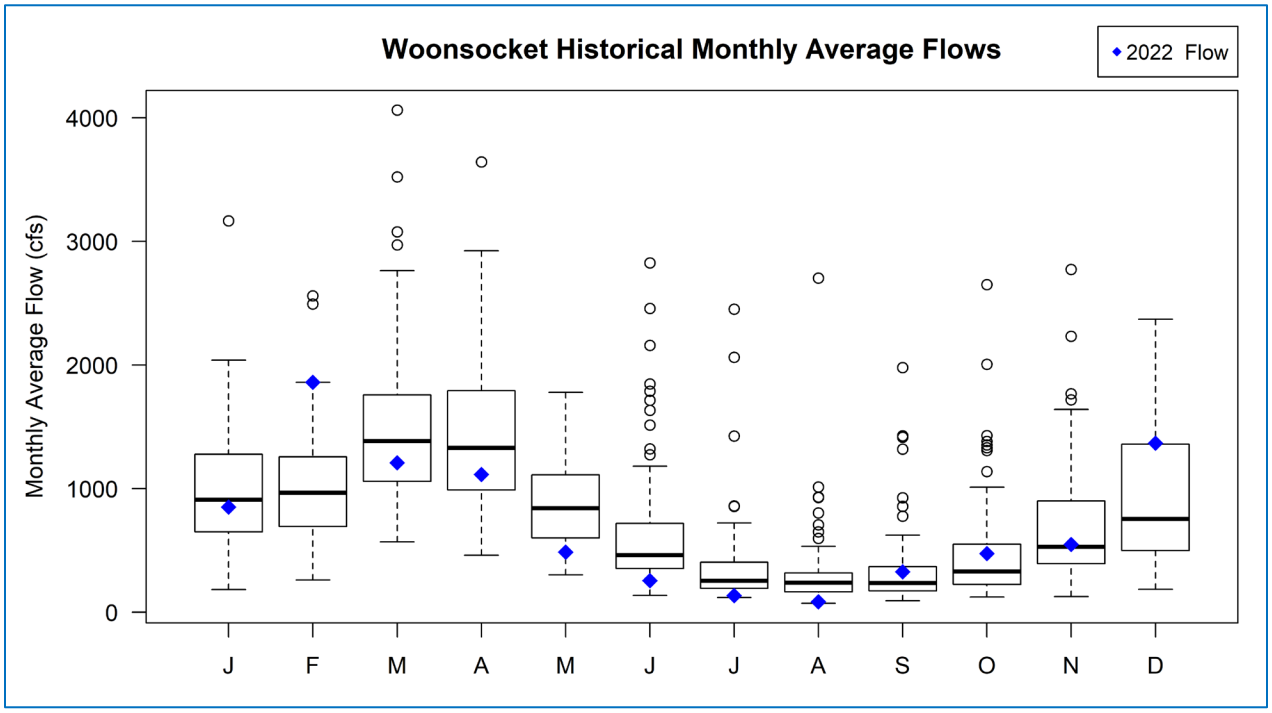
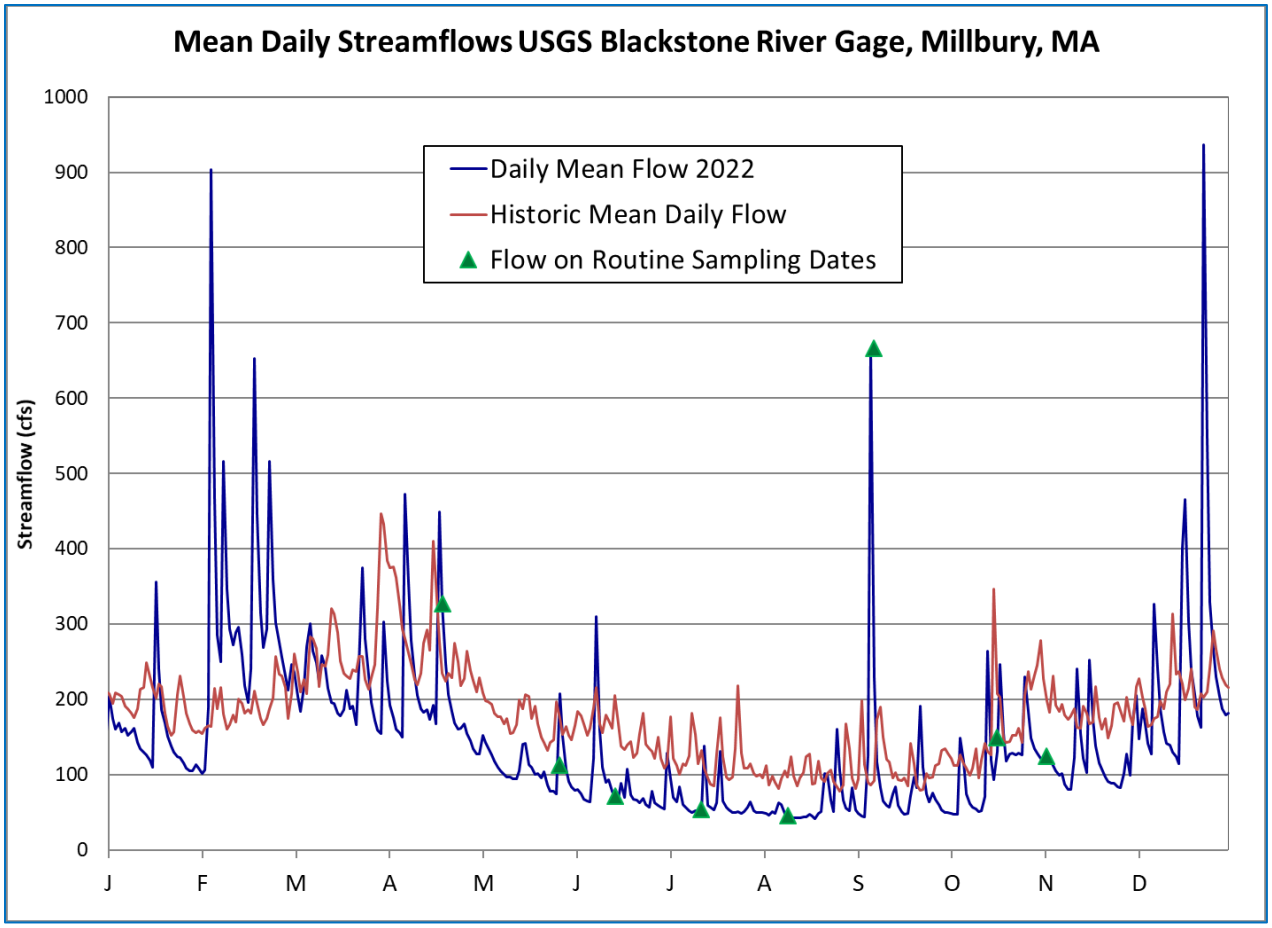


Figure 11: Woonsocket, RI, USGS gaging station (01112500) historical monthly average streamflows, 1930 – 2022

Table 7: Mean monthly streamflows in 2022 compared to median, mean, minimum

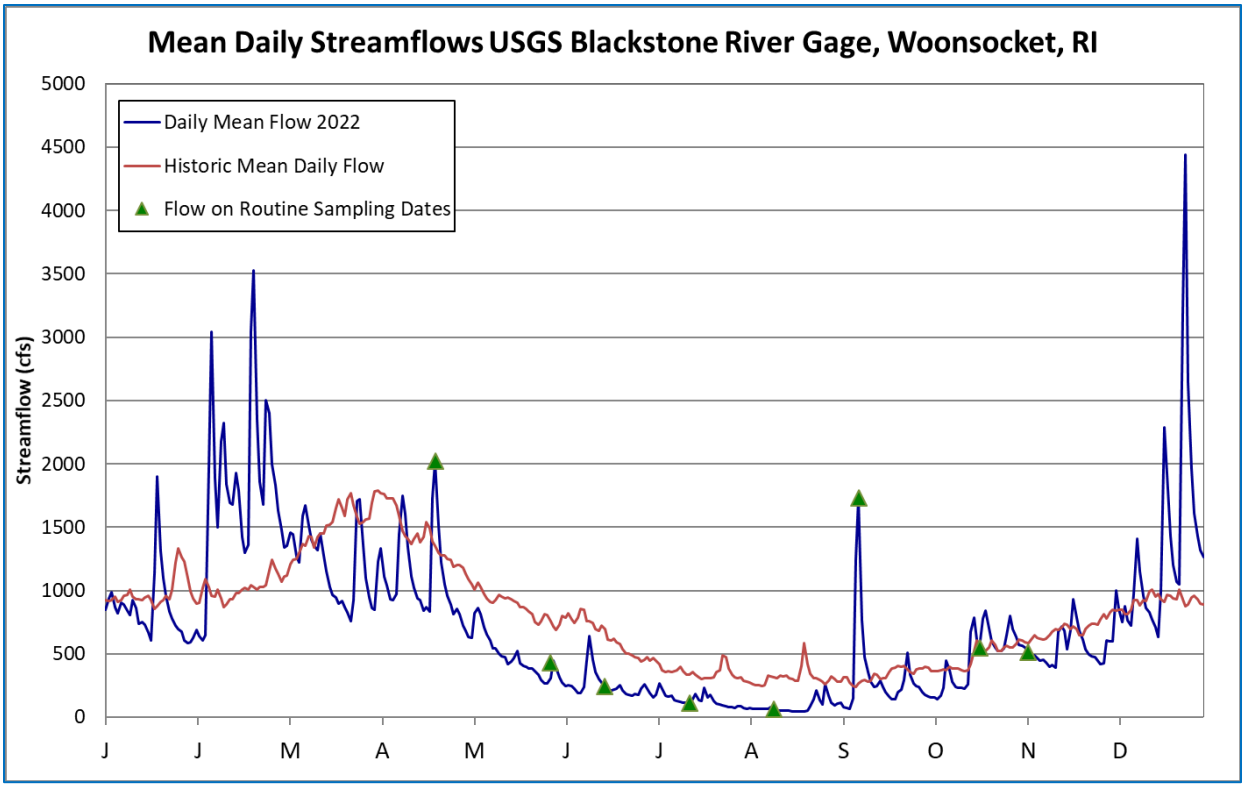
Millbury (cfs)	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov
2022 Monthly Q_{ave}	216.6	113.2	86.2	65	59.4	98.4	243.6	119.7
Median 2003 – 2022	273	171	152	122	101	115	171	178
Average 2003 – 2022	283	166	114	96	78	79	140	150
Minimum 2003 – 2022	95	112	67	49	53	47	75	75
Woonsocket (cfs)	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Sep**	**Oct**	**Nov**
2022 Monthly Q_{ave}	1115	486.9	256	135	85	327	475	548
Median 1930 – 2022	1330	841	462	253	239	236	329	530
Average 1930 – 2022	1431	878	641	358	310	336	481	699
Minimum 1930 – 2022	461	303	137	120	72	93	123	127

Mean daily streamflows measured at Millbury and Woonsocket are compared to historic mean daily streamflows in **Figure 12** and **Figure 13**, respectively**,** for the 2022 sampling season. The solid blue line represents the observed daily mean streamflow for the given year, while the solid red line represents the historic mean daily streamflow. The dates of routine sampling are indicated by green triangles. It has already been noted that monthly streamflows were lower than the historic monthly streamflow throughout most of the sampling season. At both gages, daily mean flow was lower than historic mean flow in May through early September, except for a few isolated storms in the summer. There was a large storm in September that resulted in very high flows, especially at the Millbury gage, and streamflow remained below historical levels through November except, again, during isolated storms.



(Note: Historical Mean Daily streamflow data through 2021)

Figure 12: **2022 mean daily streamflows at USGS Millbury, MA stream gage**



(Note: Historical Mean Daily streamflow data through 2020

Figure 13: **2022 mean daily streamflows at USGS Woonsocket, RI stream gage**

Table 8 provides routine sampling day streamflow data from the figures in tabular format, compared to the mean daily discharge for that day based on the historical record. Note that the historical mean daily discharge is for a specific *day* of the month, rather than the month as a whole. As such, the values reported in **Table 8** may differ from the monthly mean. Except for April and September, mean daily streamflow was always lower than the historical mean daily flow, with lowest flows in June, July and August.

Table 8: Routine sampling day-of streamflow conditions 2022

Sampling Date	Millbury, MA – USGS Station 01109730			Woonsocket, RI –USGS Station 01112500		
	2022 Mean Daily Q (cfs)	[a]Historical Mean Daily Q (cfs)	% of normal	2022 Mean Daily Q (cfs)	[a]Historical Mean Daily Q (cfs)	% of Normal
20 April	327	210	156	2020	1350	150
18 May	113	174	65	429	870	49
15 June	71	168	42	240	697	34
13 July	53	108	49	114	339	34
10 August	46	124	37	61	313	19
7 September	229	173	132	1730	264	655
17 October	131	203	65	547	571	96
2 November	124	183	68	514	586	88

[a] Historical Mean Daily Q (cfs) based on data through 2021

4.3 Environmental Conditions Summary

- Snowfall in the 2021-2022 season was low and snowmelt did not contribute significantly to high spring streamflow.
- Temperatures were higher than average during the entire 2022 sampling season.
- 2022 precipitation was near average most of the year, though summer was characterized by a significant drought, most pronounced in August.
- Streamflow in 2022 was lower than average until September, and also in October-November in Millbury.

The impact of these mixed conditions on stream water quality is discussed in Section 6.

5.0 Upper Blackstone Effluent

Upper Blackstone facility seasonal permit limits[4] for total phosphorus (TP) and total nitrogen (TN) are listed in **Table 9.** Upper Blackstone has been taking steps to comply with the 2008 permit limits in accordance with the 2014 Administrative Order on Consent and a 2016 schedule modification, which include interim effluent limits that are currently in effect. These steps include:

- Implementation of interim measures to further improve plant operation and control, and performance to result in more stable operation and improved effluent quality;
- Facilities Planning to evaluate necessary nutrient removal facility improvements to achieve 2008 permit limits, including development of future flows and loads and an Alternatives Analysis Screening and Evaluation, as well as an analysis of ancillary facilities;

[4] TP 'summer' limits are for April through October; TP 'winter' limits are for November through March. TN 'summer' limits are for May through October; TN 'winter' limits are for November through April.

- WWTF upgrade construction to implement successfully tested interim measures and to modernize facility SCADA and data collection systems;
- Design of phosphorus removal system to meet 2008 permit limits.

Table 9: Upper Blackstone 2008 permit limits

Total Phosphorus (mg/L)[1]	
Apr – Oct (summer)	0.1[2]
Nov – Mar (winter)	1.0
Total Nitrogen (mg/L)	
May – Oct (summer)	5.0
Nov – Apr (winter)	Report

[1] Upper Blackstone effluent limits are typically listed in mg/L. The conversion is 1 mg/L = 1000 ppb.
[2] The 0.1 mg/L total phosphorus limit is a 60-day rolling average limit.

The facility is operated to remove nitrogen and phosphorus year-round, even though it has only a May – October seasonal nitrogen permit limit, and much less stringent wintertime limits for total phosphorus.

Since the facility upgrade and subsequent optimization, WWTF nutrient concentrations and loads have been significantly lower than pre-upgrade conditions and consistently meeting the facility's interim limits. However, in summer 2022, a plant upset occurred which caused exceedances of the interim and final limits for total phosphorus, total nitrogen, and ammonia. Effluent concentrations began to increase in July, exceeded effluent limits in August and September, and returned to normal in October. Upper Blackstone took several steps to evaluate the potential causes of the plant upset and to restore normal WWTF operations. During this evaluation, Upper Blackstone found:

- Elevated wastewater temperatures may have inhibited the organisms responsible for biological phosphorus removal. Upper Blackstone adjusted pH, which resulted in an improvement in biological phosphorus removal.
- Monitoring for nitrification inhibitors and quaternary ammonium compounds (associated with disinfectants) did not find any evidence of these compounds in the influent.
- Microscopic evaluation and DNA analysis found that the wastewater composition within the biological treatment process was atypical and may be contributing to the poor performance. As an interim measure, Upper Blackstone suspended septage receiving.

To recover the biological process faster, Upper Blackstone imported seed sludge from another, nearby WWTF starting in late September. This re-started the biological nutrient removal process, leading to a reduction in effluent concentrations and loads. Upper Blackstone was not able to find a single cause of the upset, but continues to monitor conditions to avoid future upsets.

Figure 14 shows the actual effluent TP and TN annual daily concentrations since 2006, and **Table 10** summarizes TP and TN effluent concentrations by season, corresponding to the permit limits, since 2012. The 2022 effluent nutrient concentrations exceeded both the typical conditions observed post-

upgrade and the facility's interim limits, although the effluent concentrations remained below pre-upgrade concentrations on both a seasonal and annual average basis.

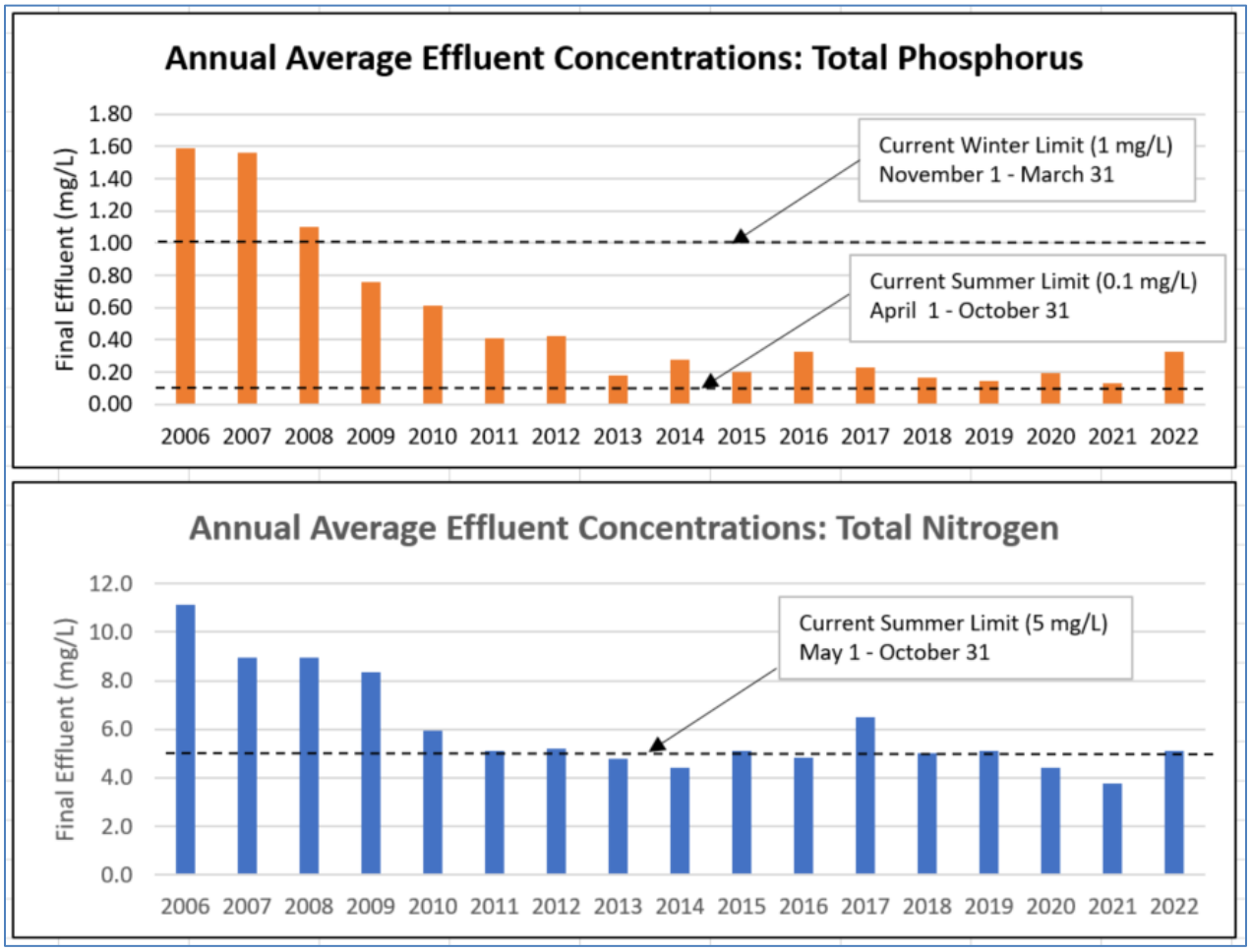


Figure 14: Annual average effluent total phosphorus and total nitrogen concentrations 2006 – 2022

Table 10: Upper Blackstone average permit season TP and TN effluent concentrations*

	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022
Total Phosphorus (mg/L)											
Apr – Oct (Summer)	0.48	0.17	0.35	0.18	0.20	0.17	0.20	0.17	0.24	0.11	0.44
Nov –Mar (winter)	0.43	0.17	0.19	0.18	0.55	0.34	0.12	0.11	0.13	0.15	0.14
Total Nitrogen (mg/L)											
May – Oct (summer)	5.2	4.3	4.5	4.6	3.9	5.0	4.9	5.1	4.4	3.4	5.7
Nov – Apr (winter)	4.0	5.5	4.6	5.3	6.1	9.1	5.1	5.3	4.6	4.0	4.6

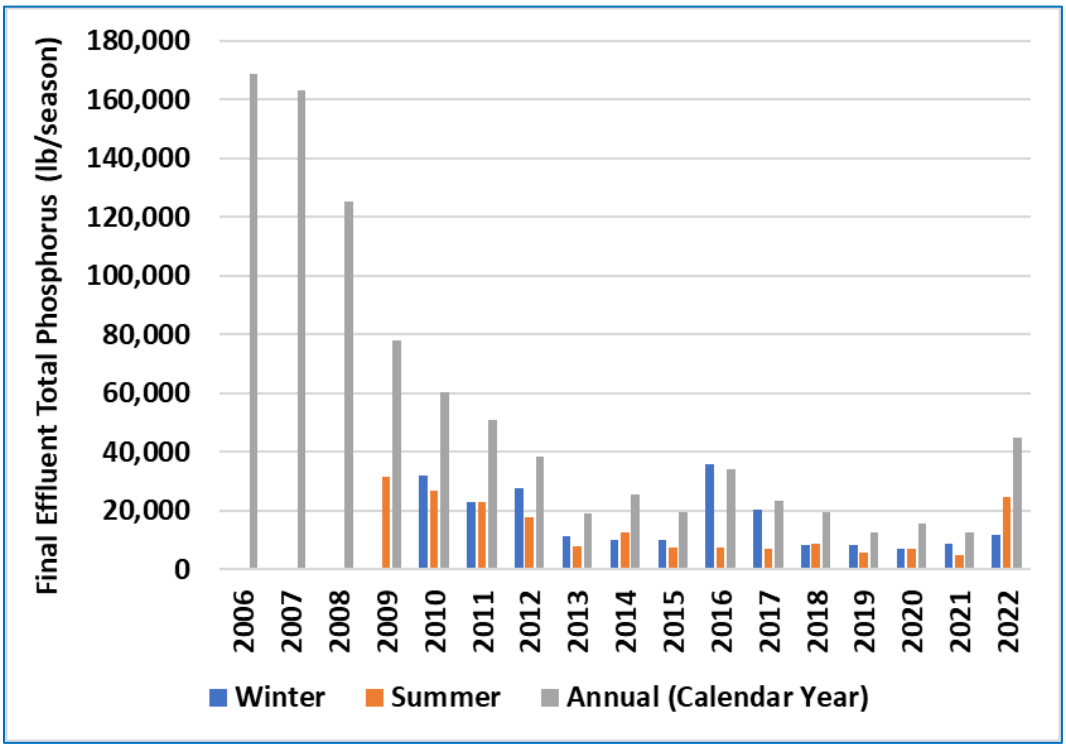
*Summer months are April-October of that year. Winter months are Nov-Dec of the previous year and Jan-Mar of that year

Yearly TP and TN effluent loads prior to plant upgrade (2006-2008) and since 2012 are shown in **Table 11**, along with percent reduction in loads in the effluent since 2006-2008

Table 11: Annual TP and TN Effluent Loads and percent reduction in yearly TN and TP effluent load compared to plant performance 2006-2008

Year	TP (lb/yr)	TP % Reduction	TN (lb/yr)	TN % Reduction
2006 – 2008	153×10^3	--	1045×10^3	--
2012	38.3×10^3	75%	458×10^3	56%
2013	18.9×10^3	88%	452×10^3	57%
2014	25.6×10^3	83%	428×10^3	59%
2015	19.6×10^3	87%	499×10^3	52%
2016	33.9×10^3	78%	485×10^3	54%
2017	23.3×10^3	85%	690×10^3	34%
2018	19.6×10^3	87%	597×10^3	43%
2019	12.8×10^3	92%	495×10^3	53%
2020	15.7×10^3	90%	408×10^3	61%
2021	12.8×10^3	92%	381×10^3	64%
2022	44.7×10^3	71%	456×10^3	56%

Figure 15 shows the effluent TN and TP annual total loads since 2006, and seasonal loads for summer and winter for 2010-2022.



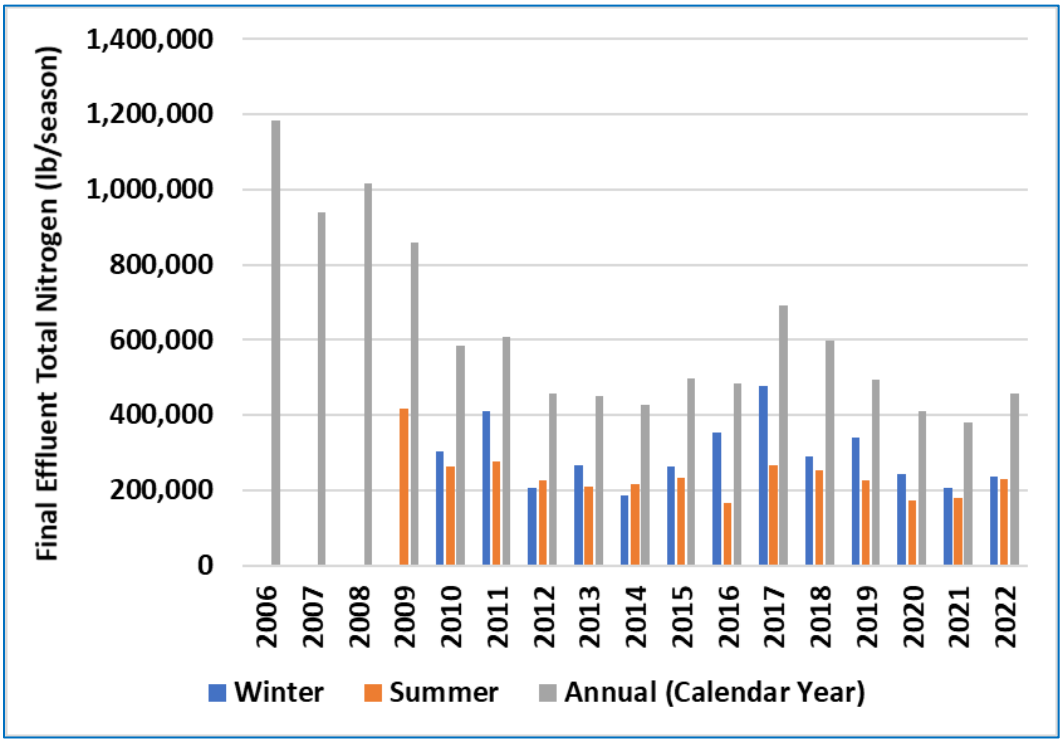


Figure 15: Total annual, winter permit*, and summer permit total nitrogen and total phosphorus loads to the Blackstone River 2006 – 2022

*Summer months are April-October of that year. Winter months are Nov-Dec of the previous year and Jan-Mar of that year

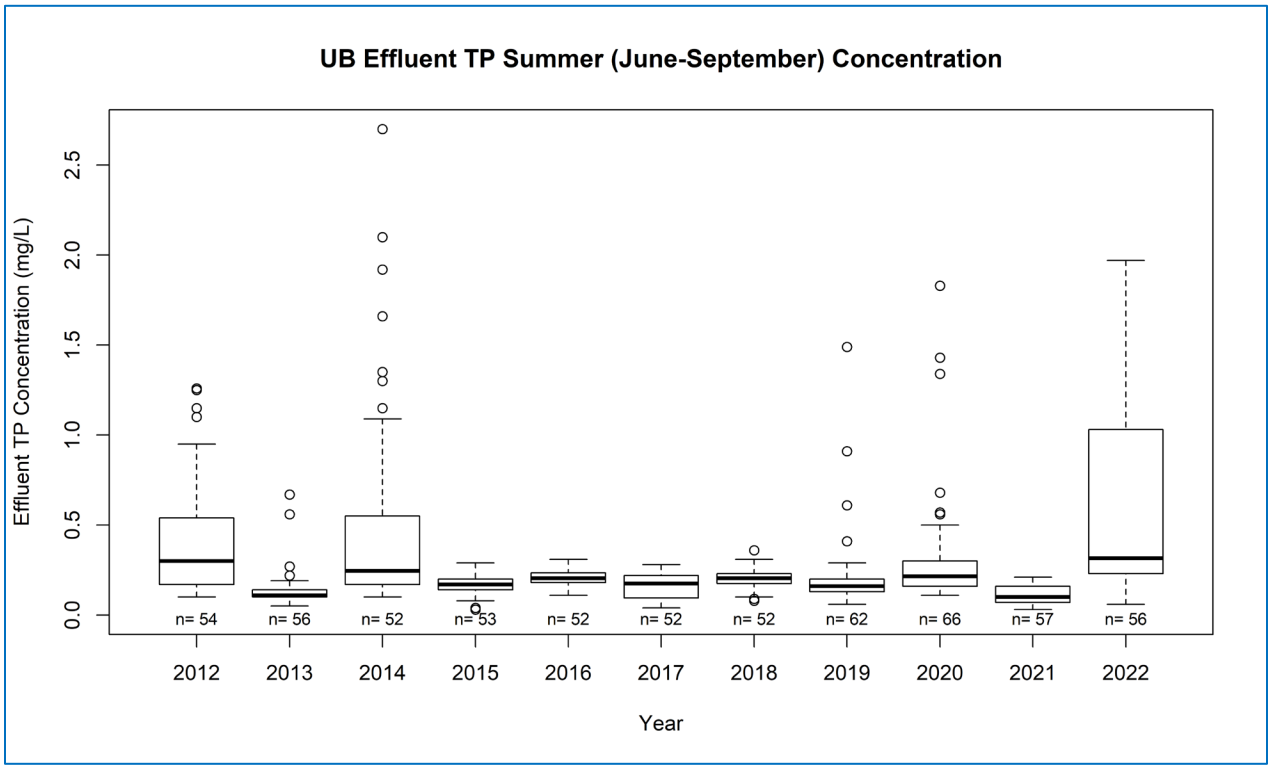
The highest biological activity in the river typically occurs during the warmest months of the year, from June through September. It is thus also useful to identify year-to-year differences in effluent nutrient characteristics for this summer growing period which may provide insight into river conditions captured by the monitoring program.

Effluent nutrient and flow data during each year from 2006 - 2022 were used to calculate the daily average concentration and load from June through September, **Table 12**.

Table 12: Average of the daily effluent nutrient characteristics during the June - September growing season in 2006 to 2022, and Flow (Q) during this season from 2009 to 2022.

Year	Effluent Flow	Effluent TP		Effluent TN	
	June – September Ave. Mean Daily Q (cf/s)	June – September Ave. Daily Conc. (mg/L)	June – September Ave. Daily Load (lb/d)	June – September Ave. Daily Conc. (mg/L)	June – September Ave. Daily Load (lb/d)
2006	n/a	1.7	403	NA	NA
2007	n/a	2.1	424	8.3	1,687
2008	n/a	1.5	421	8.0	2,178
2009	54.9	0.89	238	7.8	2,089
2010	35.7	1.0	237	6.1	1,346
2011	53.6	0.45	151	4.2	1,411
2012	39.9	0.40	99	4.6	1,094
2013	48.3	0.14	45	3.8	1,065
2014	38.2	0.50	114	4.8	1,104
2015	43.2	0.17	44	4.5	1,167
2016	33.1	0.21	43	3.8	782
2017	38.3	0.17	36	4.4	1,729
2018	41.3	0.20	53	4.8	1,280
2019	38.0	0.21	43	5.1	1,066
2020	34.3	0.31	33	3.2	986
2021	56.4	0.11	33	3.2	984
2022	39.4	0.44	163	5.7	1,263

A box plot of the daily data from June through September each year is shown on **Figure 16** for concentrations and **Figure 17** for loads from 2012 – 2022. The box plots provide an indication of the effluent variability during the June – September growing period each year of the monitoring program.



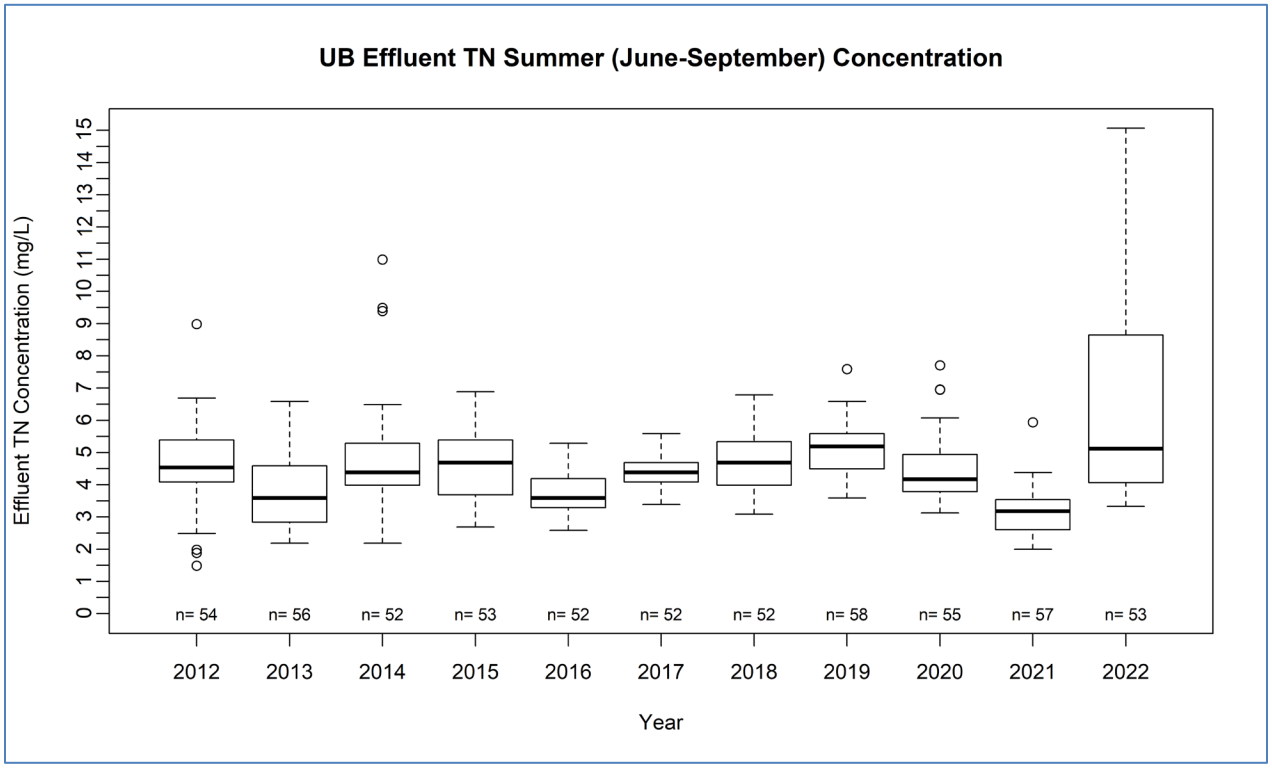


Figure 16: Upper Blackstone daily effluent TN and TP concentrations by year from June - September

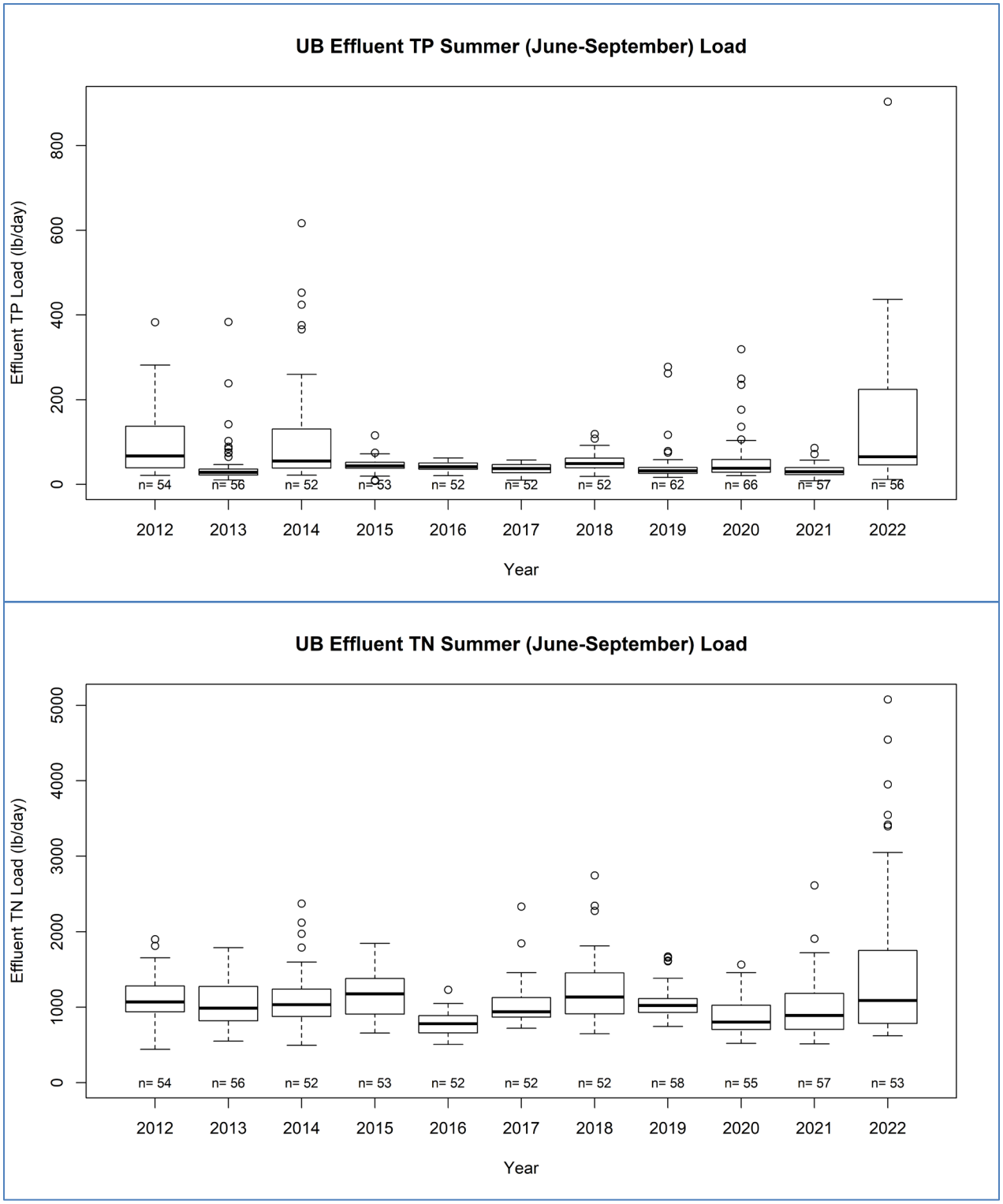


Figure 17: Upper Blackstone daily effluent TN and TP loads to the river by year from June - September

TP effluent concentrations and loads during the summer growing season showed lower variability from 2015 through 2021, as indicated by a small interquartile range in 2015-2021, but larger variability in 2012 and 2014, when Upper Blackstone refined its biological nutrient removal process through plant optimization. In 2022, the median TP concentration and load were higher than in the past few years with significant variability, mostly attributed to the summer plant upset.

Effluent TN concentrations between June and September been relatively consistent during the past ten years, averaging between 3.2 and 5.1 mg/L in 2013-2021, but again, was higher in 2022 due to the plant upset. Similarly, daily growing season TN loads in 2022 were higher and more variable than in the past ten years. Time series plots of effluent TP and TN characteristics, as well as effluent flow, are included in Appendix B.

Upper Blackstone's effluent discharge can account for a significant percentage of the flow in the Blackstone River. Since 2009, the average daily Upper Blackstone effluent flow contributions to summer flows (June through September) at Millbury have varied between 33% and 77%. In 2022, Upper Blackstone flow contributed between 3% (minimum) and 56% (maximum) of the daily streamflow at Millbury between April 20 and November 2, averaging 35% from July through September.

This contribution can be examined on a daily basis, and **Table 13** lists calculated estimates of the relative contribution of Upper Blackstone effluent flow to the streamflow measured at the Millbury gage on each of the 2021 sampling days. On six of the sampling days, this calculated value was below 40%, and it never exceeded 46%.

Table 13: **Relative contributions by volume on sampling days 2022**

Sampling Date	Upper Blackstone % of Millbury streamflow
4/20/2022	11%
5/28/2022	20%
6/15/2022	32%
7/13/2022	56%
8/10/2022	45%
9/7/2022	3%
10/17/2022	26%
11/2/2022	19%

6.0 Sampling Season Data for 2022

Routine monitoring (grab samples) was conducted monthly from April to November for nutrients, chlorophyll-a, dissolved oxygen, temperature, conductivity, and pH at nine in-stream locations. Sampling was conducted monthly, regardless of streamflow conditions.

Four continuous data loggers monitoring water temperature and dissolved oxygen were deployed and calibrated in July 2022: one near the Waters Street bridge (W1258), one immediately upstream of Riverlin Street bridge, one at the former Millbury Wastewater Treatment Plant (WWTP), and one near the Depot Street bridge (**Figure 2**). These sites represent two new sites in addition to the historical sites

(W1258 and Depot Street), and were selected in consultation with MassDEP, and were deployed to better understand water quality dynamics between W1258 and Depot Street observed in previous years' events. All four logger sites are located in MassDEP Assessment Unit MA51-03. The loggers were removed in November 2022.

6.1 Routine Monitoring Data

In order to provide a more focused look at the impact of Upper Blackstone effluent quality improvements on river water quality, the routine monitoring data are presented in terms of both concentration and load. Observed sampling day streamflow at Millbury, MA (USGS 01109730) and Woonsocket, RI (USGS 01112500) were used to estimate streamflow for load calculations at each sampling location. The streamflow at each location for each sampling date was estimated by comparing and extracting representative streamflow values from the simulation results from the HSPF model developed for the Blackstone River (UMass and CDM Smith, 2008).

In this section, streamflow conditions on routine sampling days are first described. River water quality conditions are then summarized by presenting the TP, TN, chlorophyll-a, and field measurement results. In-stream data are reported as ppb in this report. To compare with effluent data from the previous sections, note that 1 mg/L = 1000 ppb = 1000 µg/L.

Sampling data results for TP, TN, chlorophyll-a, and field measurements are summarized in Sections 6.1.1, 6.1.2, 6.1.3, and 6.1.5, respectively, using a consistent series of plots and analyses. Sufficient data are available to conduct a robust trend analysis based on streamflow-weighted concentration data. Streamflow-weighted concentration trend analyses are presented for TP, TN, and chlorophyll-a in Section 6.1.4. Additional information on nitrogen and phosphorus subspecies, as well as laboratory QAQC data, is available upon request.

6.1.1. Total Phosphorus

Available TP concentration data for the Blackstone River since 1996 are summarized in **Figure 18** using box plots. Data for all sampling locations are grouped by year. While, in general, the same sample locations were surveyed 2012 through 2022, the concentrations from 1996 – 2008 represent results of multiple individual sampling programs carried by Upper Blackstone and others and in many cases at different sampling locations. As explained previously, the median of the data for each year is shown by the dark bar in each box, the lower and upper quartile (± 25% around median) of the observed data are shown by the body of the box, the whiskers identify 1.5 times the interquartile range above the upper quartile and below the lower quartile of the data, and the small black circles above and below the whiskers represent observed data that are statistically considered "outliers." **Figure 19** shows the same data with the Y-axis truncated at 400 ppb to help see details in the more recent years when concentrations are much lower than before 2012. The graph illustrates how variable TP concentrations were in 2022, and that the median for all sites and sampling dates is higher than last year (a very wet year) but similar to that of 2020.River TP concentrations since Upper Blackstone upgrades came online in 2009 are less variable and are lower than historical concentrations. Upgrades to the plant have translated into improved river conditions. The total phosphorus concentrations observed in the Blackstone River during routine sampling in 2022 were affected by the plant process upset described in Section 5.0, and were consequently higher than in recent years in the late summer. Late summer was also unusually hot and dry, conditions which would tend to favor higher concentrations of nutrients in the river, which likely contributed to the elevated concentrations in addition to the impacts of the plant upset.

The mean summer (June – September) TP concentration at each sampling location in the Blackstone River is shown on **Figure 20** for sampling data collected since 2012. Data are grouped by sampling site, plotted from the upstream W0680 site (left) to the downstream RMSD site (right). Each year is shown as a different color, with 2022 in red. While the summer average TP concentration at the upstream-most site (W0680) was comparable to that of previous years, all of the downstream sites had higher TP concentrations than in the past few years, likely due to the plant upset in July 2022, with only the 2014 concentrations exceeding the 2022 concentrations.

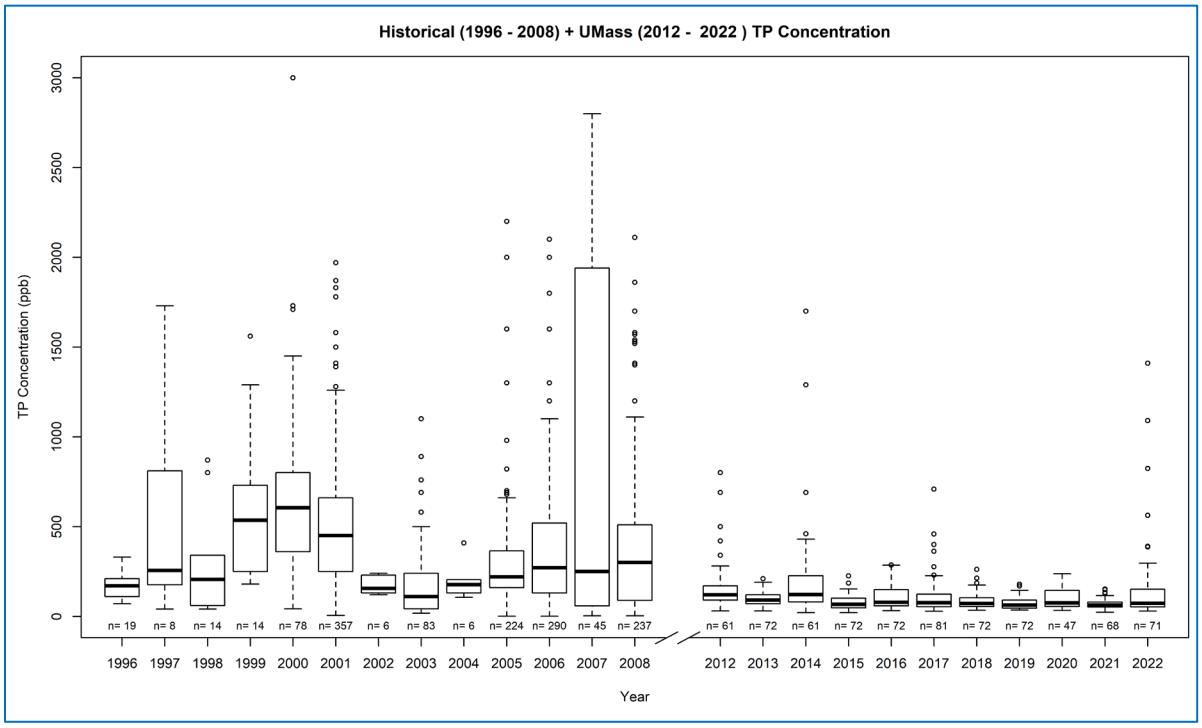
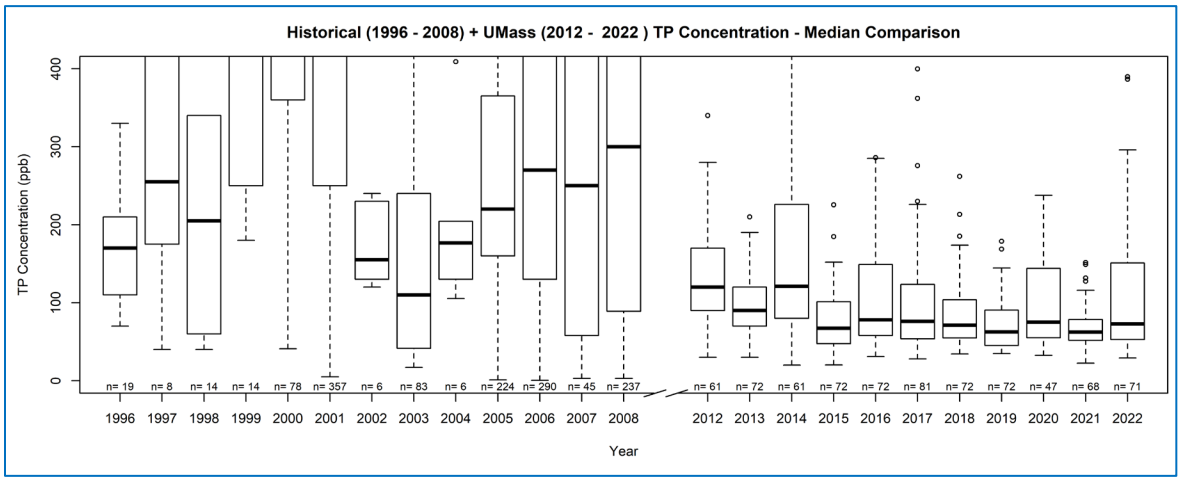


Figure 18: TP concentrations observed in the river 1996 – 2008 and 2012 – 2022



(Y-axis truncated at 400 ppb to highlight post-upgrade conditions)

Figure 19: **TP concentrations observed in the river 1996 – 2008 and 2012 – 2022**

The outliers in 2022 are too numerous to flag on the graph, here is a list TP concentration outliers:

8/10/22		**9/7/2022**	
UBWPAD2:	1090.7 ppb	UBWPAD2	386.5 ppb
W1258:	1409.6 ppb	W1779	293.25 ppb
W1242:	824 ppb	RMSL	212.35 ppb
W0767:	562.8 ppb	R116	159.15 ppb
W1779:	389.9 ppb	RMSD	232.95 ppb

TP (ppb)	W0680	UBWPAD2	W1258	W1242	W0767	W1779	RMSL	R116	RMSD
2012	77	143	157	157	157	220	185	140	87
2013	50	83	83	80	NA	137	77	70	60
2014	100	707	453	403	246	264	215	173	98
2015	71	130	115	81	106	137	86	76	82
2016	60	231	23	161	215	221	76	71	129
2017	55	152	131	112	157	166	83	74	91
2018	60	156	94	97	126	154	136	99	87
2019	50	134	108	90	70	123	57	52	61
2020	55	200	137	156	132	174	62	85	51
2021	54	93	72	53	70	96	65	58	57
2022	50	462	452	298	244	240	100	75	110

[a] These means include June 1 data

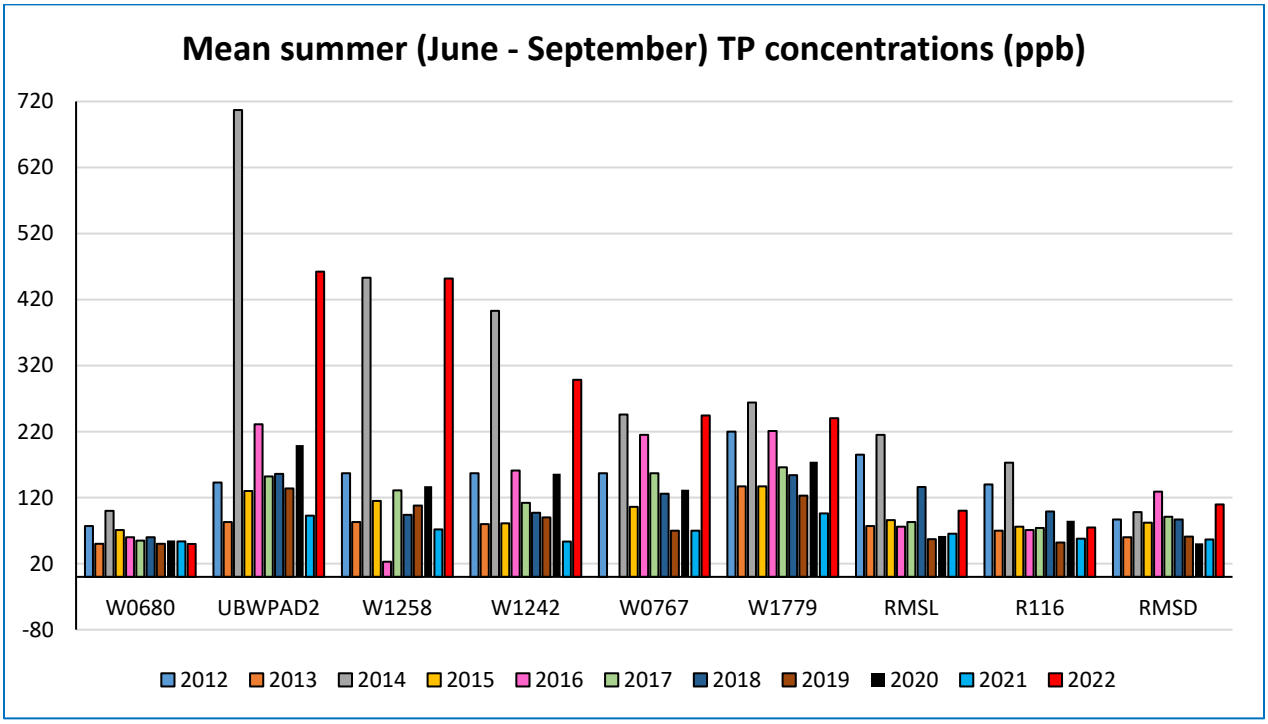


Figure 20: Mean summer (June – September) TP concentrations observed by site 2012-2022

The full range of TP concentrations observed at each site since 2012 is summarized in **Figure 21** with sites plotted from the upstream W0680 site (left) to downstream RMSD site (right) as before. The average concentrations in 2022 are indicated by blue diamonds. It should be noted that data collection at the UBWPAD site occurred from 2012 – 2013, when the site was moved to a better-mixed location downstream, UBWPAD2, where data collection started in 2013 and continues to this day. While average 2022 TP concentrations were close to the historical median at the Rhode Island sites, they were much higher downstream of the UB effluent confluence, decreasing progressively downstream, corresponding to additional dilution from tributary inflows.

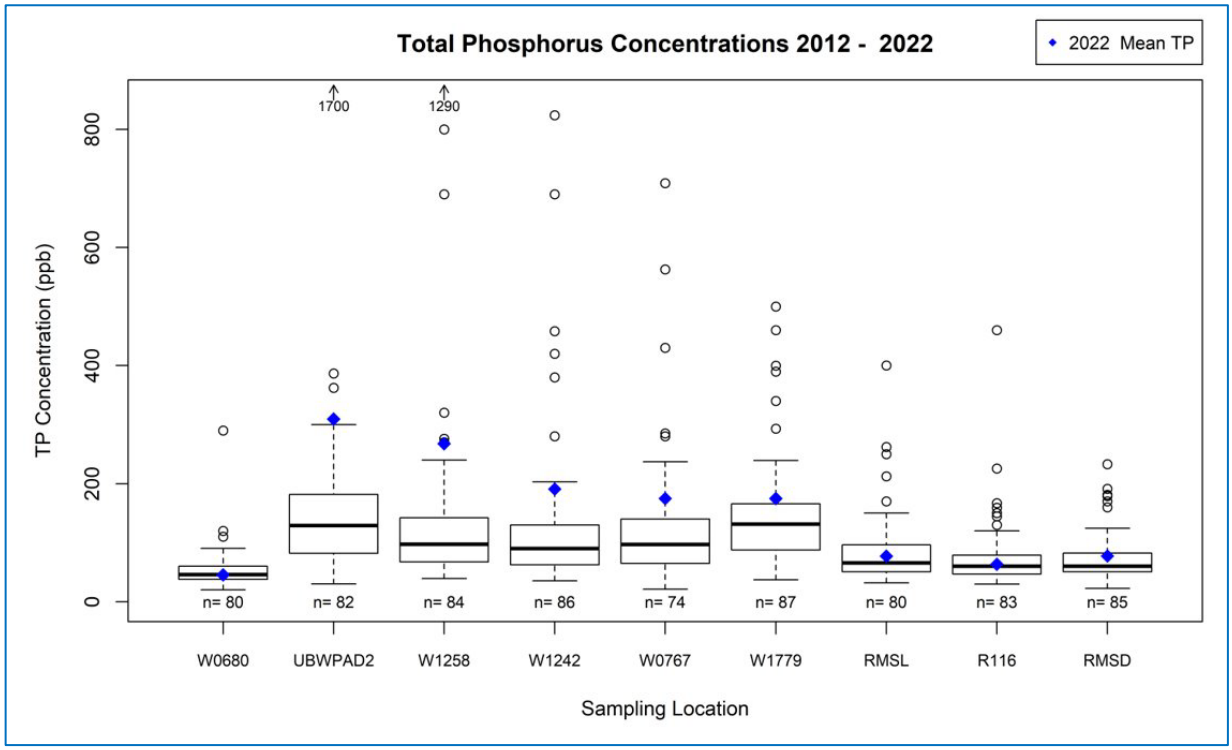
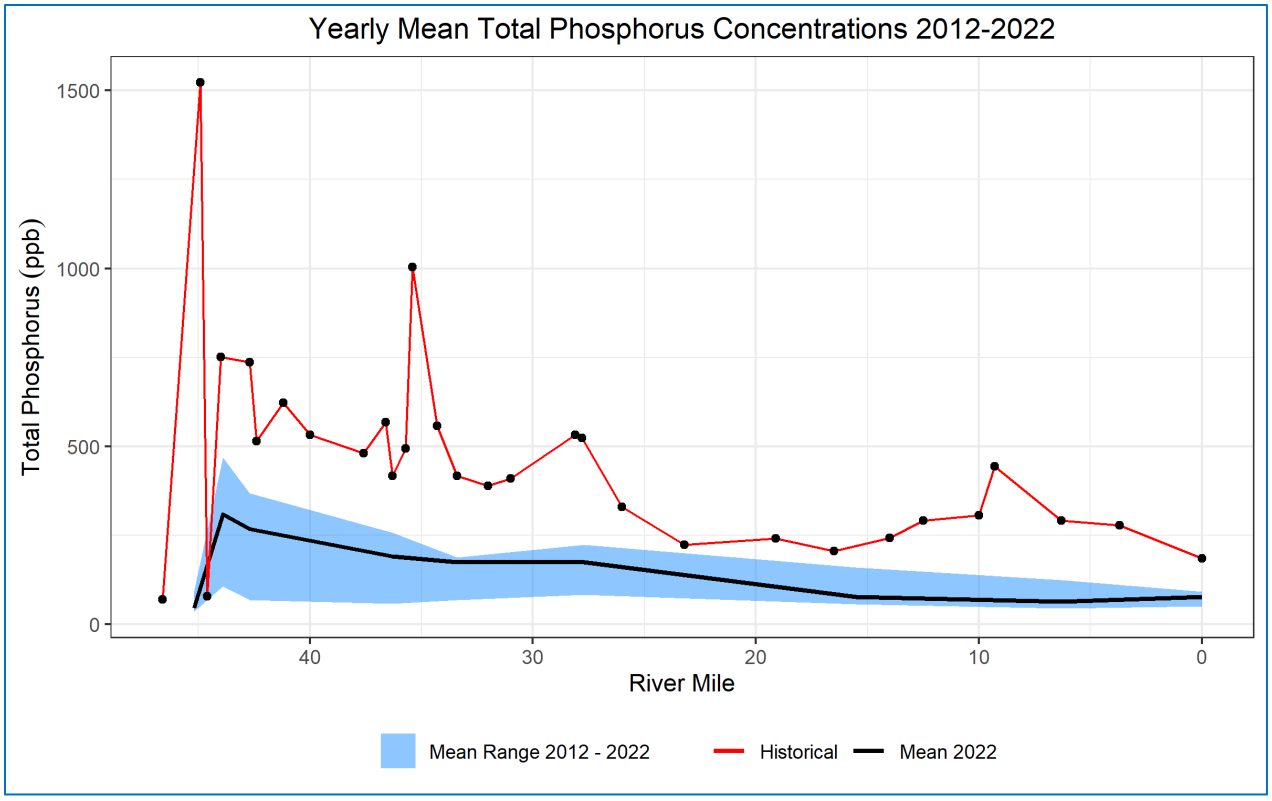


Figure 21: TP concentrations by site from 2012 - 2022

Average TP concentrations in 2012 – 2022 are compared to historical concentrations in **Figure 22**, plotted against river mile with upstream W0680 site on the left (river mile 50) and the downstream RMSD site on the right (river mile 0), analogous to the earlier plots where site name is indicated instead of river mile. While TP concentrations were above average compared to the 10-year records in the upper reach of the river, they decreased to near minimum means at about mile 15 of the river.



Note that historical data are means for sites with >8 data points

Figure 22: Along stream TP concentrations

Massachusetts uses narrative nutrient criteria which are interpreted in the Consolidated Assessment and Listing Methodology (CALM) manual using a weight of evidence approach that integrates nutrient concentrations, dissolved oxygen, periphyton, phytoplankton, benthic macroinvertebrates, and other indicators of aquatic health to evaluate whether a waterbody is impaired. One element of the weight of evidence approach is a TP threshold of 100 ppb; exceeding the TP threshold alone does not necessarily indicate impairment. Rhode Island does not specify a numeric criteria or threshold for phosphorus in flowing rivers; for this report the total phosphorus concentrations at the three Rhode Island monitoring locations (RMSL, R116, and RMSD) are compared against the MassDEP screening threshold.

In 2022, TP concentrations in the Blackstone River were below the MassDEP 2018 CALM screening threshold of 100 ppb 39% of the time May through September, compared to 87% in 2021, but 35% in 2020 (**Figure 23)**. Exceedance of the CALM screening threshold occurred mostly at UBWPAD2 (every month except April) but also at all the other sites in Massachusetts in May and July through September, and even at the Rhode Island sites in September.

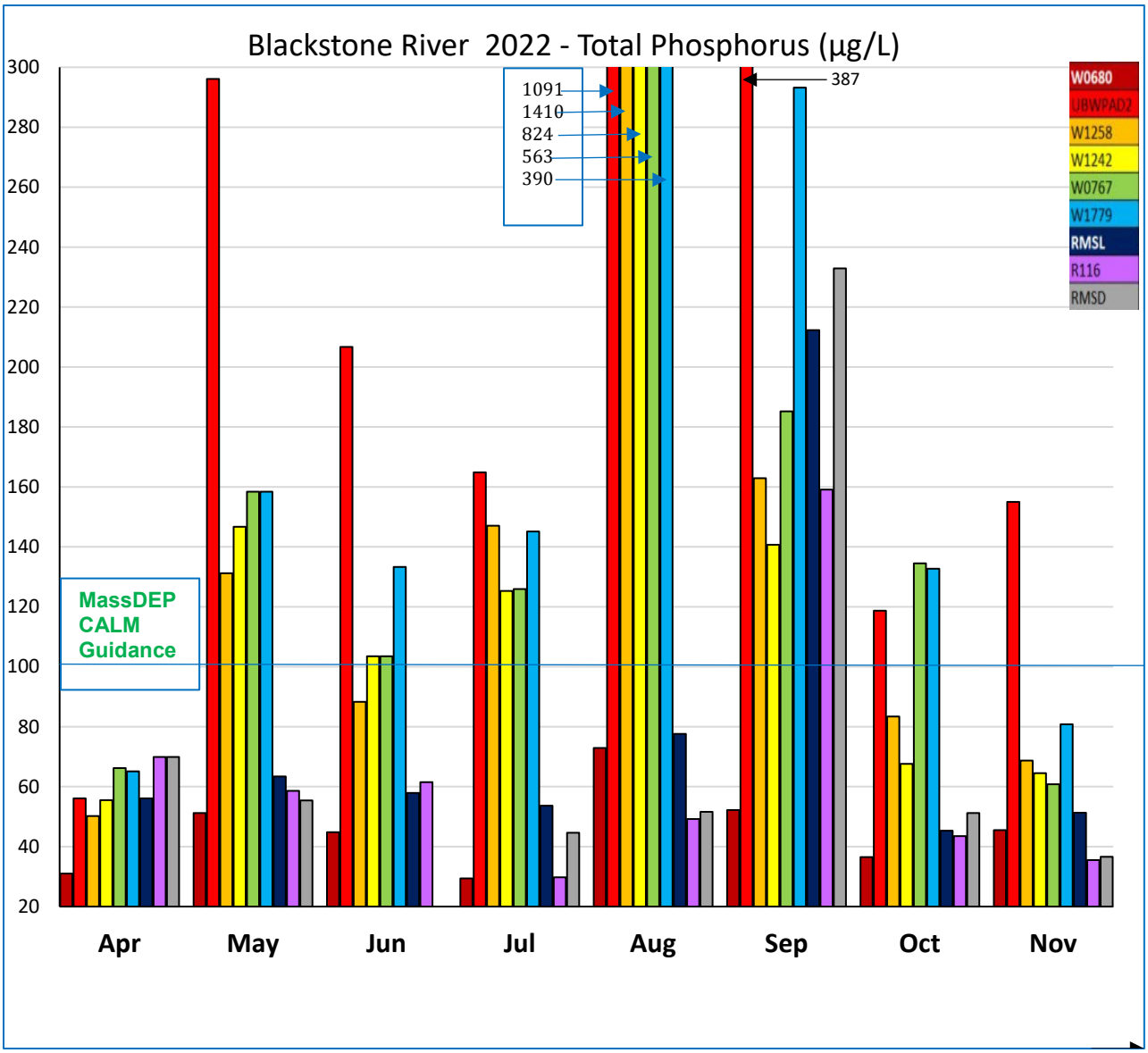
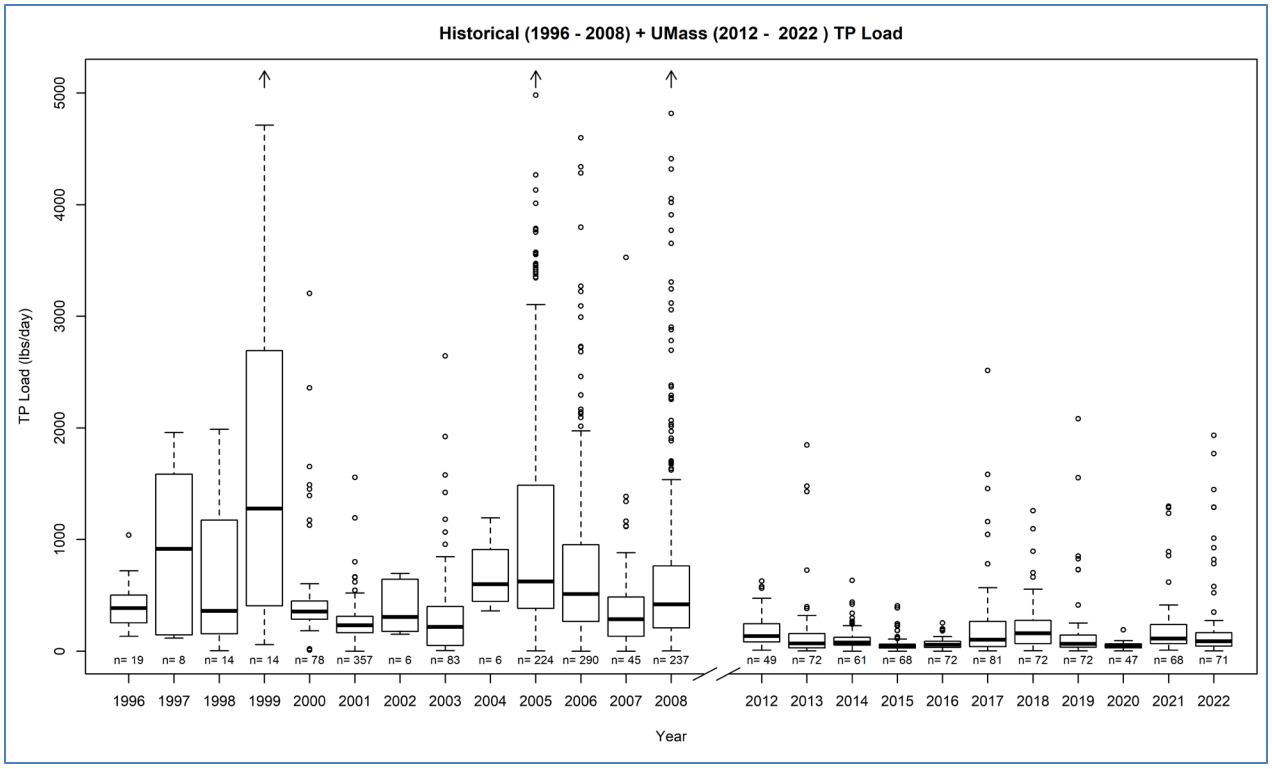


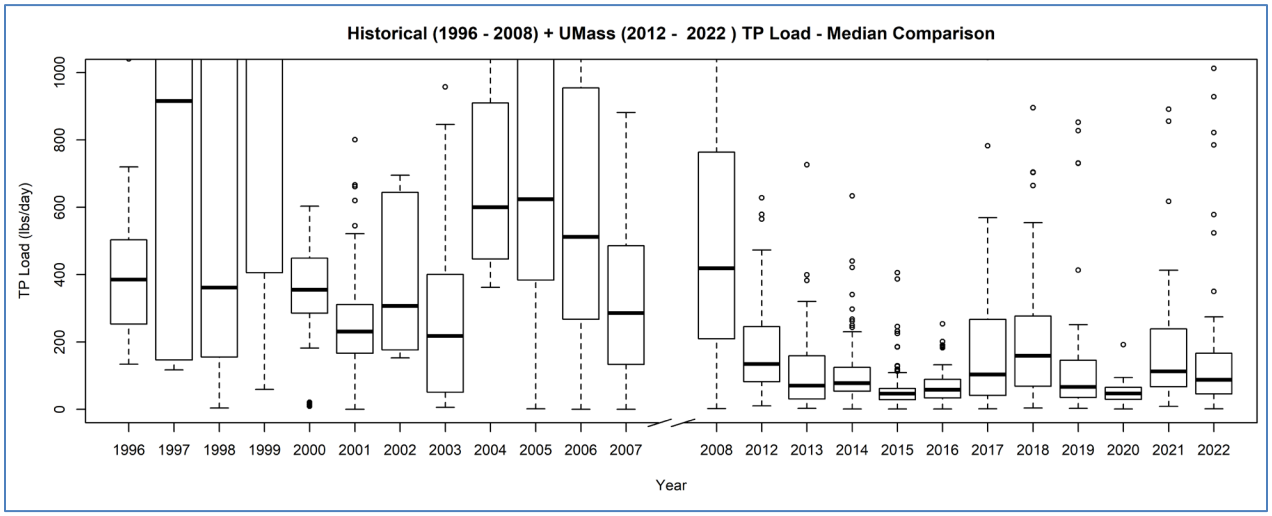
Figure 23: 2022 TP concentrations compared with MassDEP CALM guidance

Estimates of mass flux (or load) based on the observed concentrations and flow estimates provide information on the benefits of the plant upgrades for downstream receiving waters, such as Narragansett Bay. Estimates of TP load since 1996 in the Blackstone River are summarized in **Figure 24** (shown zoomed in on lower graph).

Data for all sampling locations along the river are grouped by year. TP loads in the river remain much lower than they were before Upper Blackstone upgrades came online in 2009. Average riverine loads since routine sampling started in 2012 are less variable and overall lower; 2022 data show a median load that is lower and less variable than last year, and mid-range compared to the 10 year period of this study.



(note, additional extreme outliers not shown, as indicated by arrows)



(Y-Axis truncated at 1000 lb/day to clarify differences in later years)

Figure 24: Summary of calculated TP loads based on streamflow estimates and reported concentrations for sampling days, 1996 – 2008 and 2012 – 2022

TP load outliers:

8/10/2022	UBWPAD2	274.67
8/10/2022	W1258	350.43
8/10/2022	W1242	219.69
8/10/2022	W0767	154.85
8/10/2022	W1779	108.91
9/7/2022	UBWPAD2	1291.18
9/7/2022	W1779	1288.58
9/7/2022	RMSL	1770.98
9/7/2022	R116	1448.92
9/7/2022	RMSD	1934.13

Along-stream average TP loads, **Figure 25** and **Figure 26**, illustrate the impact of streamflow conditions on load estimates. As streamflow increases downstream, typically so do loads, and in 2022 this was the case again. Mean 2022 TP loads were higher than the 10-year median at all sites, despites flows being low this year.

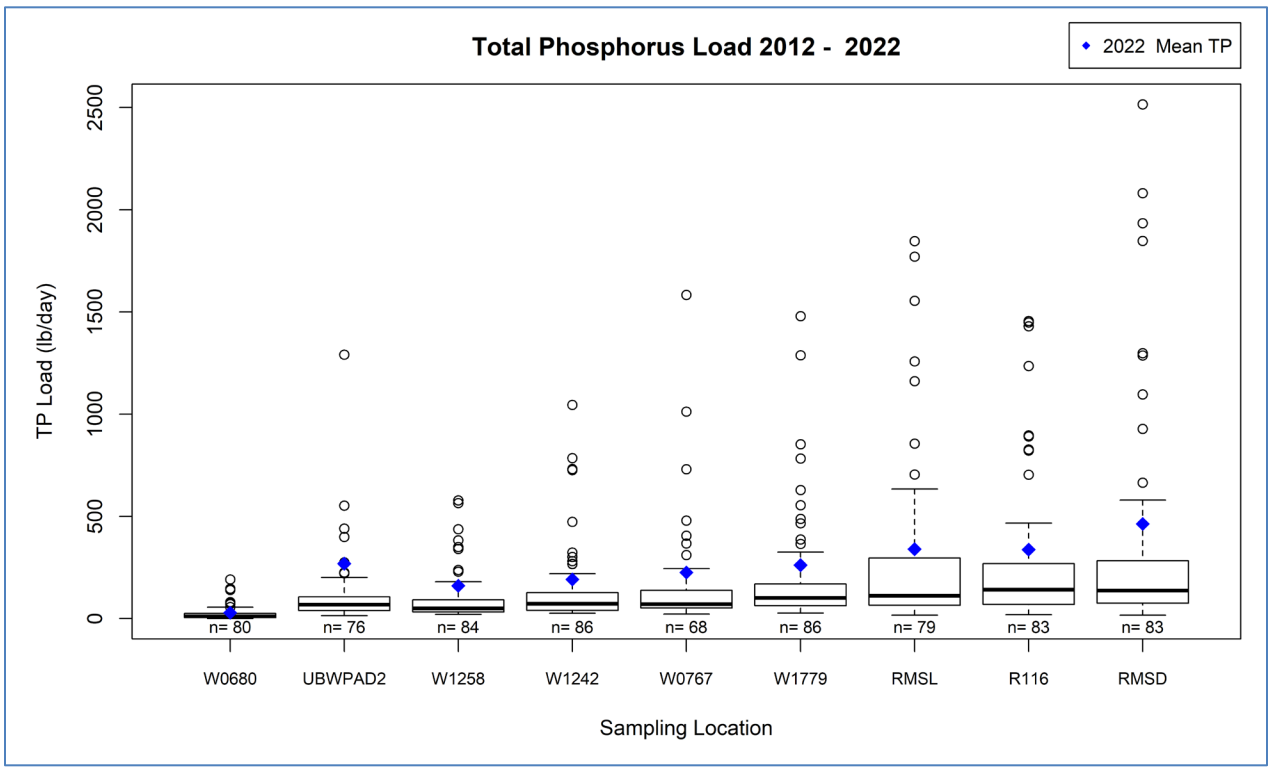


Figure 25: TP load data by site from 2012 – 2022

Figure 26 illustrates how mean summer TP loads were in general higher in 2022, except at W0680 and R116, but most notably at UWBPAD2. The high calculated loads are due to a combination of elevated effluent loads due to the plant upset and the high streamflow in September.

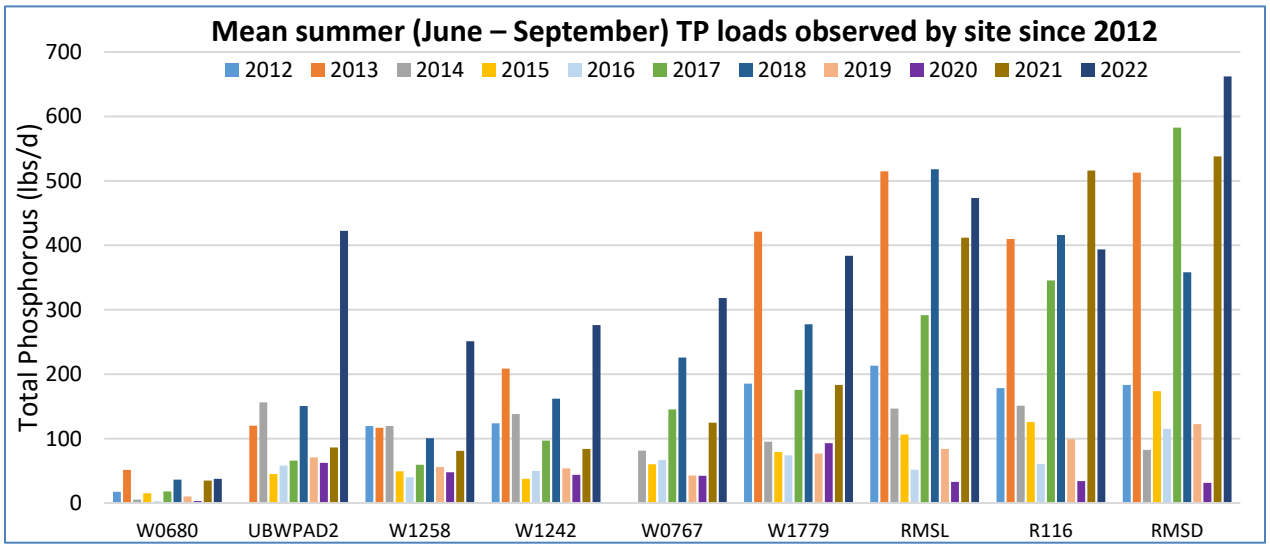


Figure 26: Mean summer TP loads 2012-2022

Figure 27 shows that 2022 (black line) estimated yearly mean TP loads were in the upper range at all sites, particularly W0680 to W1242. They are still much lower than historically (red line is average load from 1996 through 2008).

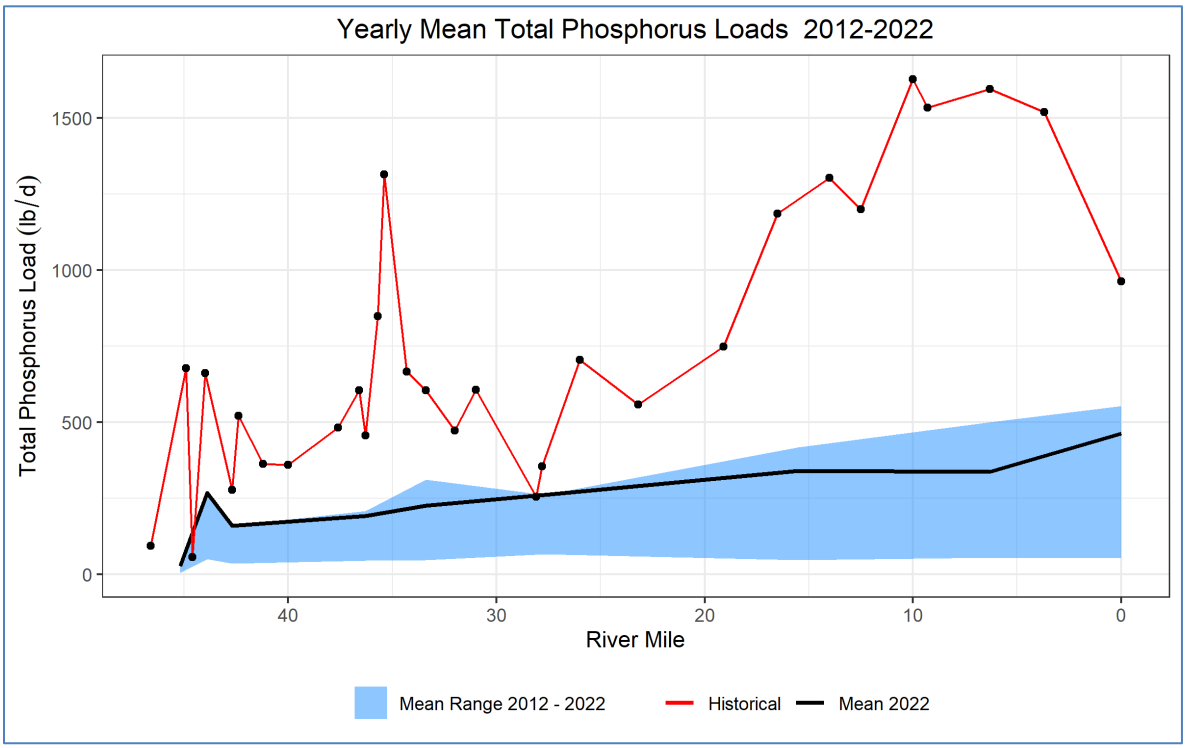


Figure 27: Mean TP Loads on 2022 Sampling Dates

6.1.2. Total Nitrogen

Available TN concentration data for the Blackstone River since 1998 are summarized in **Figure 28**. In 2022, TN concentrations in the Blackstone River were higher and more variable than last year during summer months, but the 2022 median for all dates and sites combined is comparable to previous years. The impact of the new limits and associated plant upgrades which came online in 2009 is evident. Since 2014, there has been a steady reduction in both the span and magnitude of the interquartile range of TN concentrations observed in the river, and the increase this year is attributed primarily to the summer plant upset. The trends in TN are discussed further below.

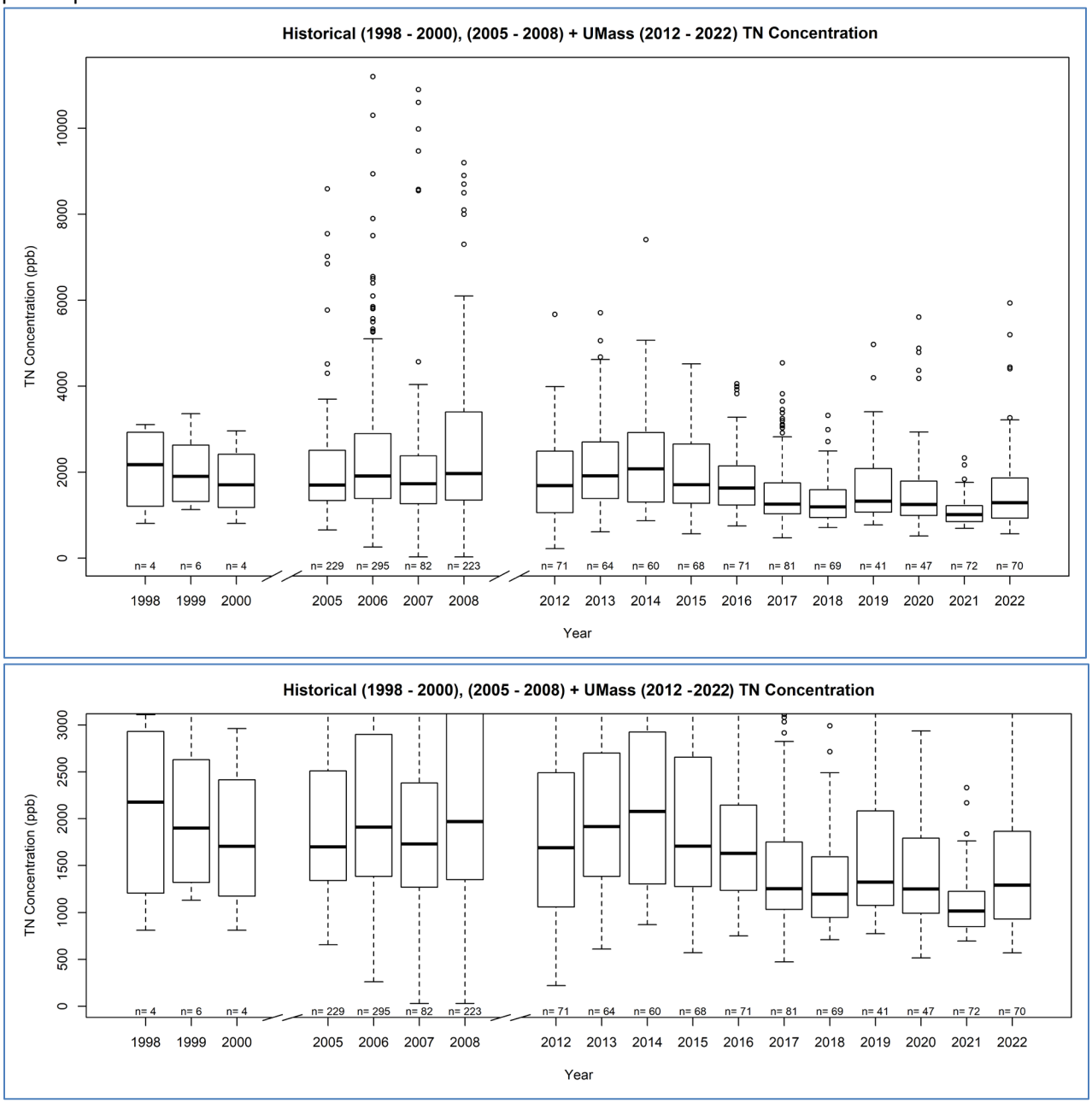


Figure 28: Summary of TN concentrations observed in the river, 1998 – 2000, 2005 – 2008, and 2012 – 2022 (Lower figure is cut off at 3000 ppb)

The mean summer (June – September) TN concentration at each sampling location in the Blackstone River is shown on **Figure 29** for sampling data collected since 2012. Data are clustered by sampling site, plotted from the upstream site W0680 (left) to the downstream site RMSD (right). Each year is shown as a different color, with 2022 in black. It should be noted that the apparent increase in mean summer TN concentrations at sampling site UBWPAD2, downstream of the confluence with Upper Blackstone's Outfall Channel, from 2012 to 2013 is an artifact of relocation of the site farther downstream to a more well-mixed location in 2013. In addition, site W0767 was not sampled in 2013. Mean summer TN concentrations observed in 2022 downstream of the effluent confluence were higher than last year and near the highest since the start of the study in 2012 just below the confluence, decreasing downstream.

TN (ppb)	*W0680*	*UBWPAD2*	*W1258*	*W1242*	*W0767*	*W1779*	*RMSL*	*R116*	*RMSD*
2012	983	1128	2976	2366	2366	2184	1368	1432	1264
2013	1103	2440	2820	2225	NA	2193	1440	1498	1508
2014	1433	3590	3293	2764	3041	2400	1990	1801	1474
2015	1069	2993	2792	2084	2467	2018	1353	1654	1384
2016	1088	3120	2925	2420	2743	2333	1428	1408	1500
2017	1079	2920	2629	2153	2201	1830	1154	1127	1134
2018	820	2290	1706	1298	951	1674	1508	1371	1143
2019	977	4125	3176	2336	2454	1988	1220	1342	1226
2020	915	2647	2787	2976	2704	2208	1345	1229	1143
2021	795	1590	1292	1061	1088	1188	886	862	826
2022	950	3870	2912	2626	2250	2097	1354	1237	1237

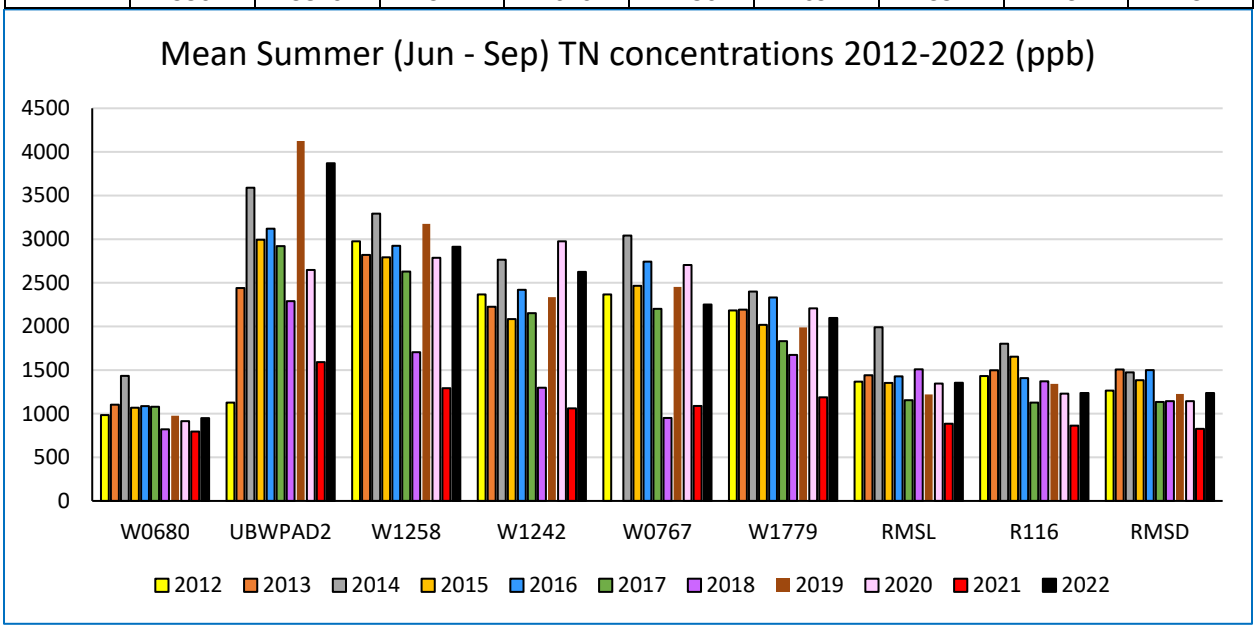


Figure 29: Mean summer (June – September) TN concentrations observed by site since 2012

The full range of TN concentrations observed at each site since 2012 is summarized in **Figure 30**, with sites plotted from the headwaters (left) to outlet (right) as above.

Data for both the original UBWPAD site (2012) and new site, UBWPAD2 (where data collection started in 2013 and continues) are included. Average TN concentrations in 2022 (depicted with blue diamonds) were above the ten-year median at the three sites immediately downstream from the effluent

confluence (UBWPAD2, W1258, W1242). Farther downstream, average TN concentrations were equal to the period's median or slightly lower in the case of Rhode Island sites.

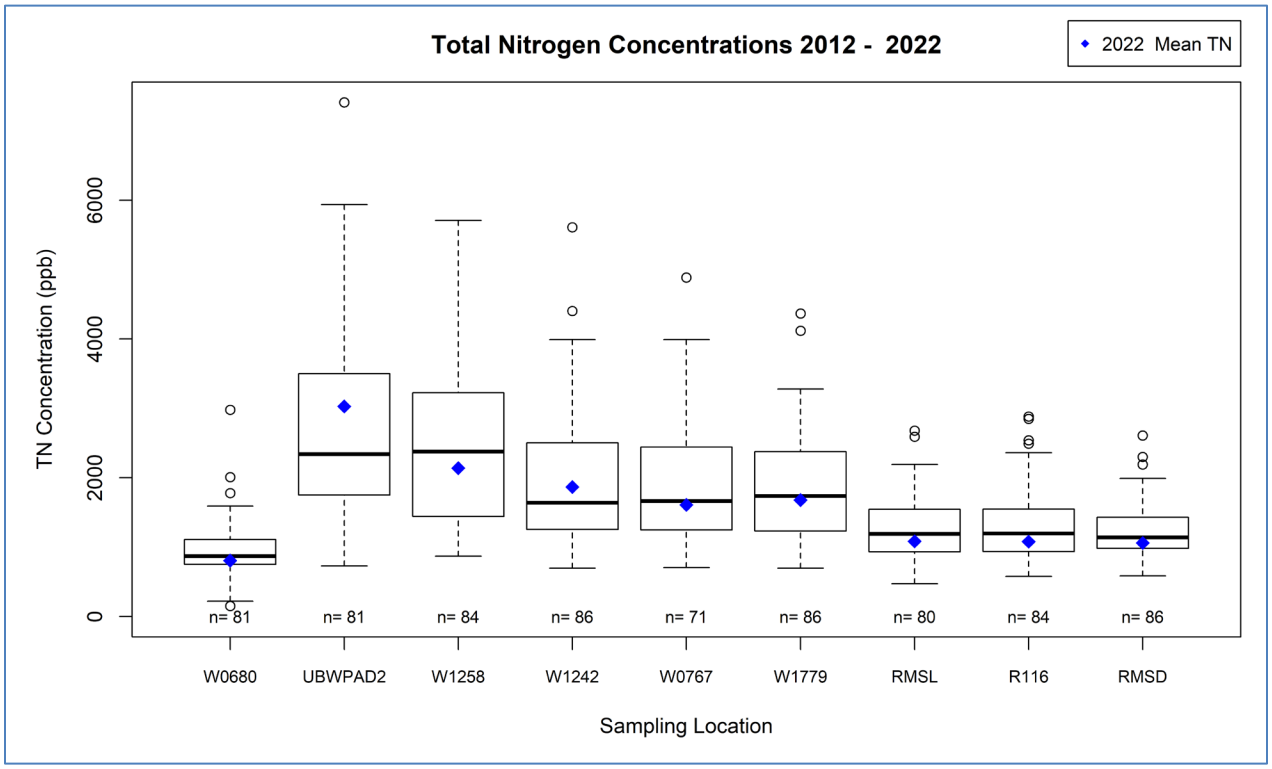


Figure 30: TN Concentrations by sampling location 2012 -2022

Average TN concentrations in 2012 – 2022 are compared to historical concentrations in **Figure 31**, plotted against river mile with headwater locations on the left (river mile 50) and the outlet on the right (river mile 0) (red line is average load from 1998 through 2000).

Mean TN concentrations in 2022 were in the middle of the range of concentrations observed since 2012 at all sites upstream of Rhode Island, where the mean concentrations tended toward the minimum observations. All means were still much lower than historical means.

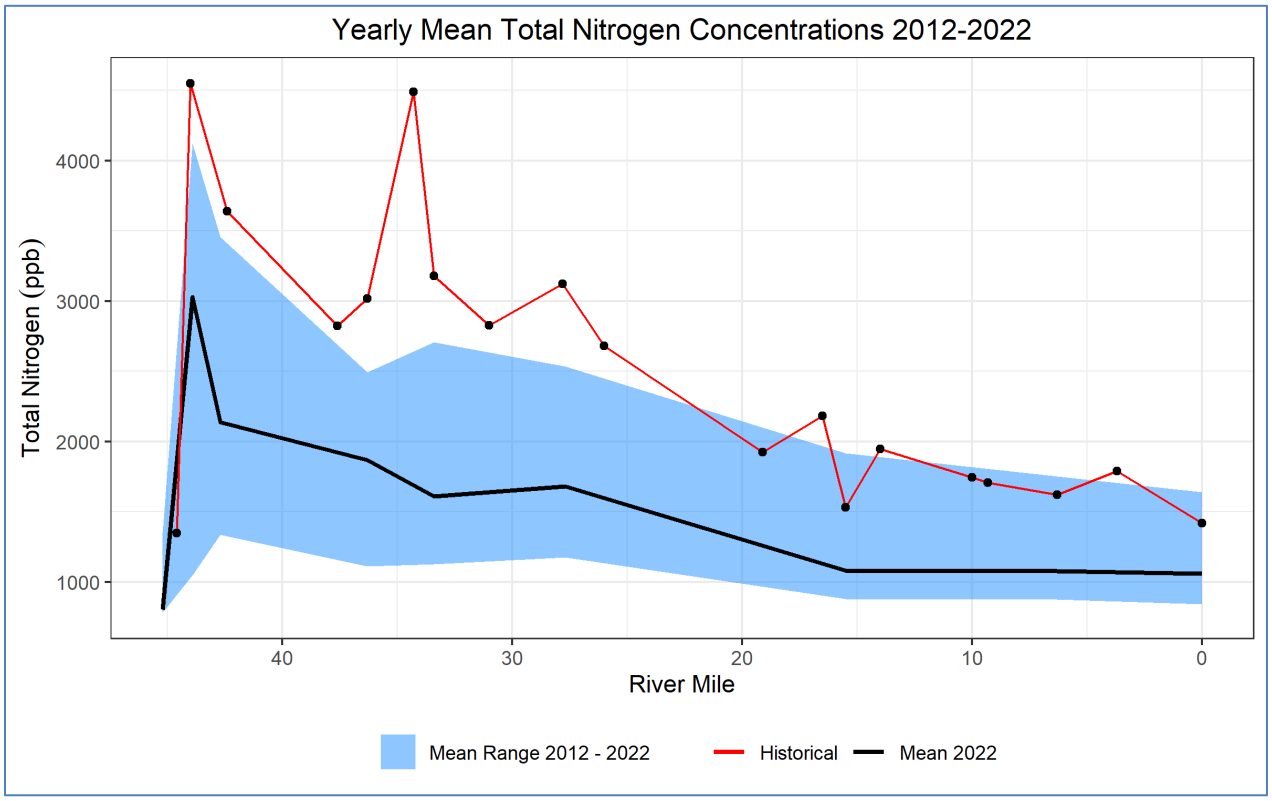


Figure 31: Along stream TN concentration, 2012 -2022

Estimates of mean summer TN loads since 2012 in the Blackstone River are summarized in **Figure 32**. Data for all sampling locations along the river are grouped by site. 2022 TN loads were the highest in 11 years at the Massachusetts sites starting with UBWPAD2, and second or third the highest observed loads at the Rhode Island sites. This is most likely caused by the summer plant upset.

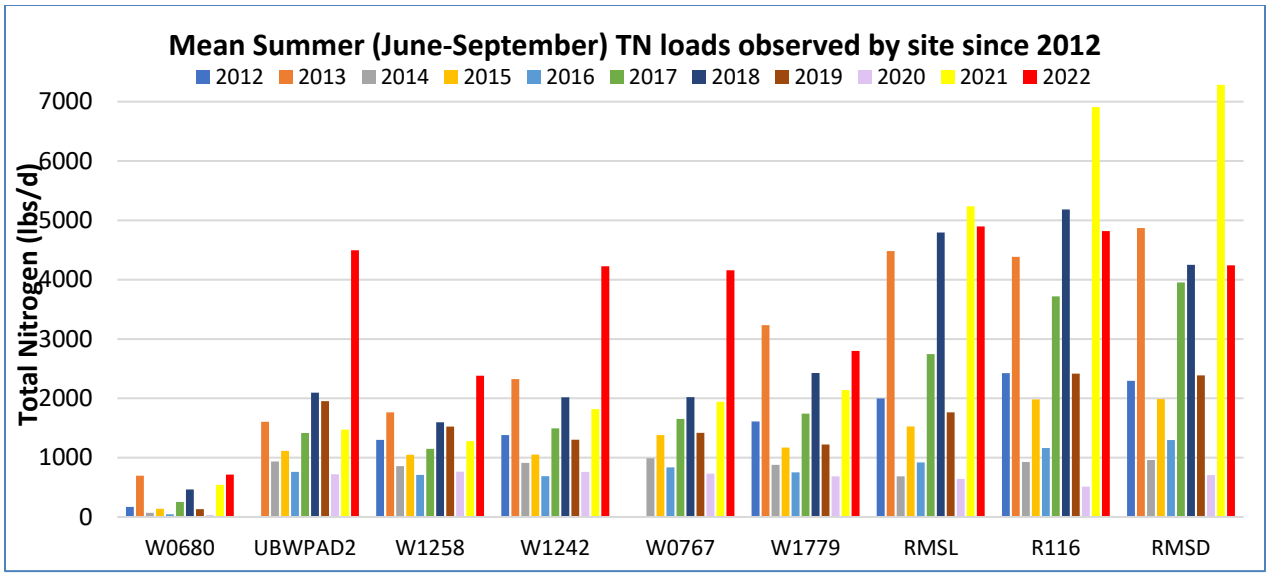


Figure 32: Mean Summer TN Loads for each site, 2012-2022

TN load data statistics are shown in **Figure 33** and zoomed in **Figure 34.** TN loads transported by the river in 2022 were lower and less variable than in 2021. The median TN load was among the lowest observed since 2012, while the interquartile range of the TN load were definitely influenced by the summer plant upset, as the upper quartile was high compared to the overall distribution of loads over all sites and sampling dates.

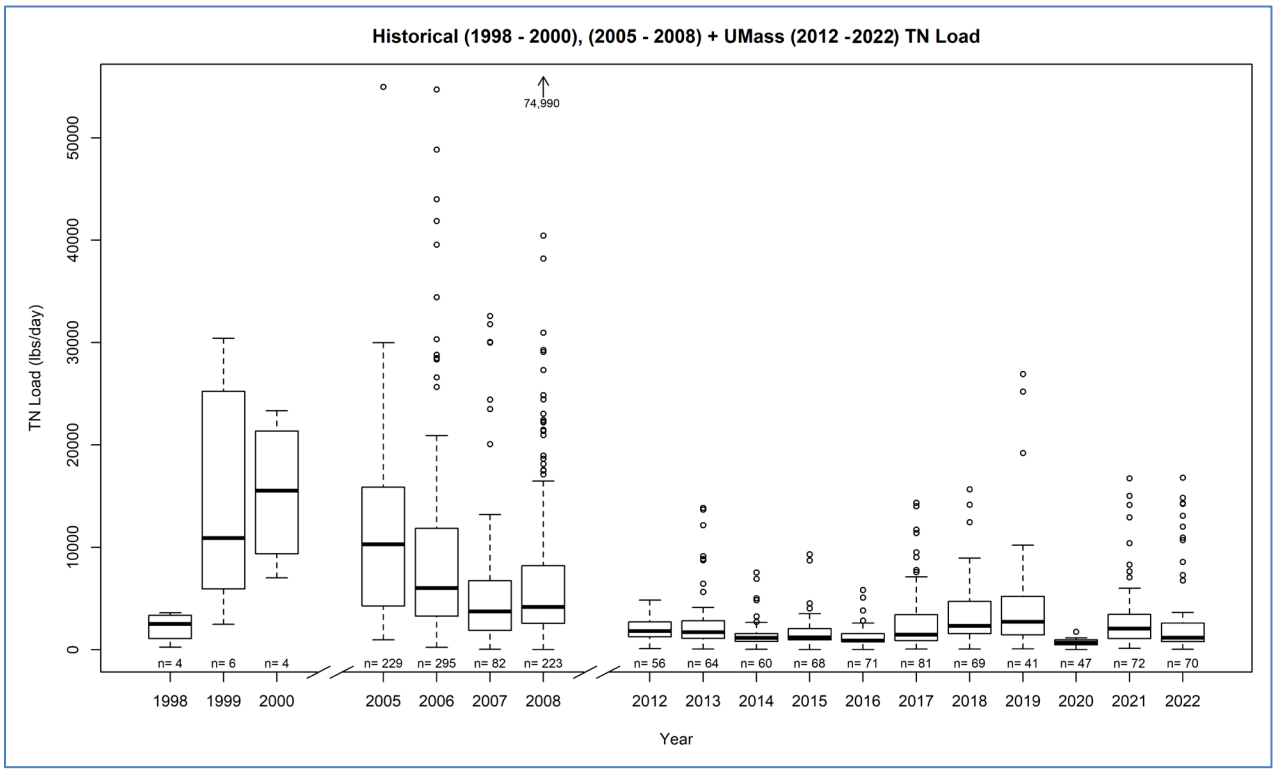


Figure 33: TN loads observed in the river 1998 – 2000, 2005 – 2008, and 2012 – 2022

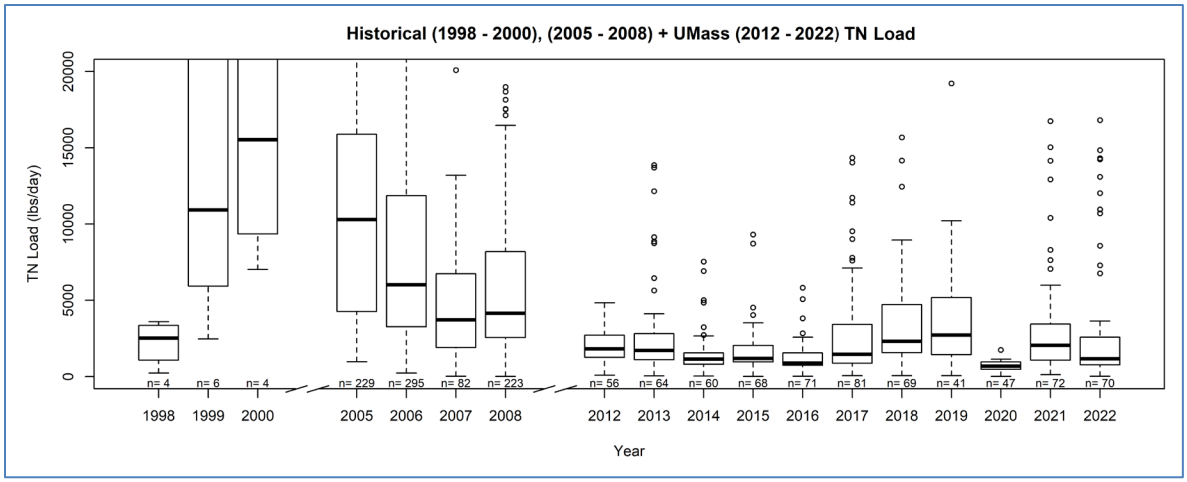


Figure 34: TN loads observed in the river 1998 – 2000, 2005 – 2008, and 2012 – 2022 (zoomed in)

Along stream average TN loads, as summarized by year and site on **Figure 35** and **Figure 36**, show 2022 estimated loads to be on the higher end of the range calculated for 2012-2022, especially at UWBPAD2 where it reaches the upper whisker. This is also seen on **Figure 36**, which shows 2022 TN loads at or above the middle of the mean range in the eleven-year period for all sites, and at the top of the range at the four upstream-most sites.

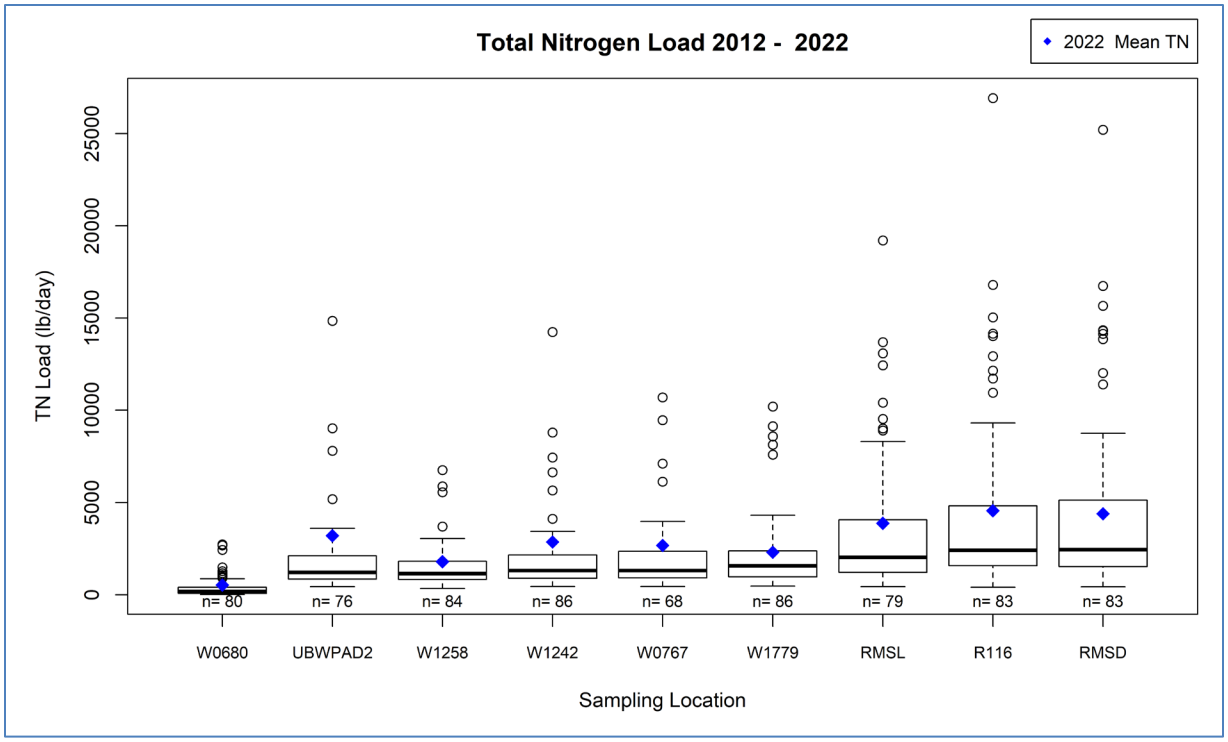


Figure 36: TN load data by sampling location 2012 – 2022

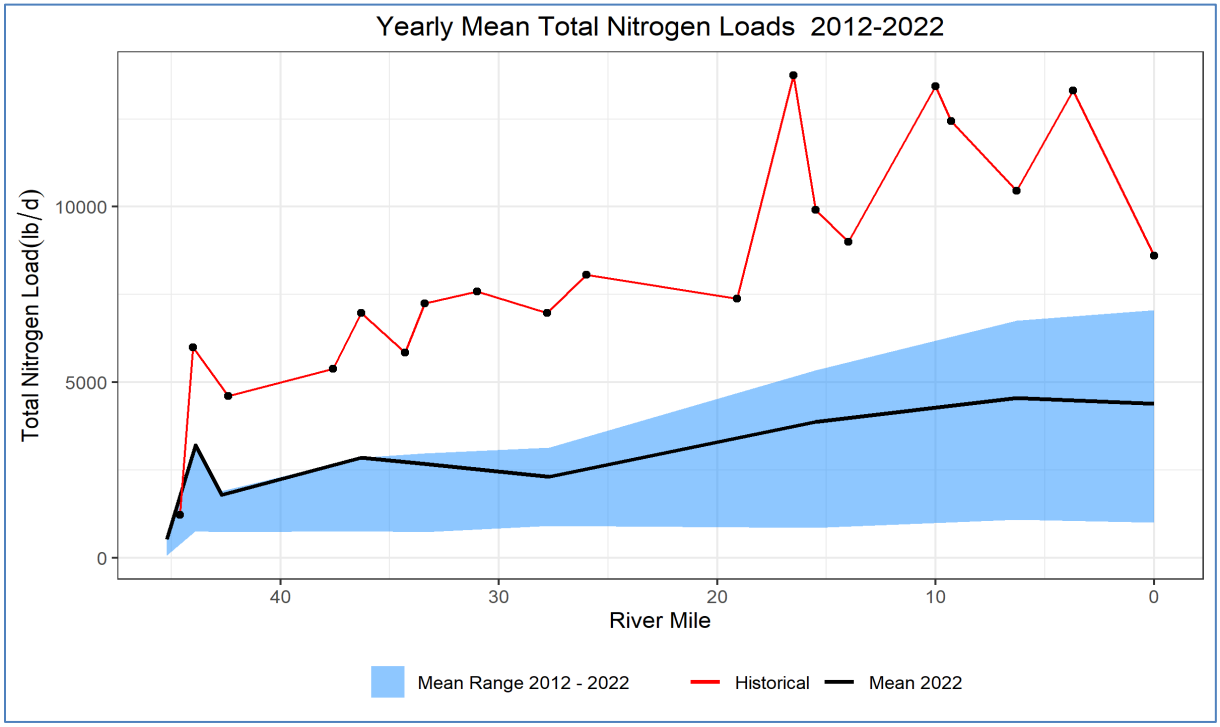


Figure 35: Along stream TN loads

6.1.3. Chlorophyll-a

Nutrients in the river from both point and nonpoint sources can contribute to increased algal growth, measured with chlorophyll-a. Massachusetts does not have a numeric criterion for chlorophyll-a, but has a guidance value in the CALM of 16 µg/L that is used as a screening level to indicate the potential for nutrient-related impairments to the aquatic life designated use. MassDEP typically considers a river to be at risk of impairment if the mean summer (May through September) chlorophyll-a concentration exceeds 16 µg/L. As with the total phosphorus screening level, MassDEP uses a combination of indicators to assess whether a river is impaired. Summer mean chlorophyll-a concentrations exceeding the 16 µg/L threshold are one indicator used in the weight of evidence approach to determine whether an aquatic life use impairment is warranted. Rhode Island does not have a comparable numeric criterion or guidance value but uses a narrative criterion that uses excess algal growth as one indicator of an exceedance of its narrative water quality criteria. Therefore, for the analysis presented in this report the MassDEP 16 µg/L screening value will be applied to data collected at the Rhode Island sites.

Chlorophyll-a concentrations observed during the summer months (June – September) since 2012 are summarized by year in **Figure 37**. Overall, summertime chlorophyll-a levels in 2022 displayed an average interquartile compared to other years in the study period. The 2022 chlorophyll-a concentrations were higher than in 2021, but again, close to average compared to previous years. In drier years like 2022, when streamflow is lower and water temperature higher than in wetter years, conditions are favorable for algae growth. However, the chlorophyll-a concentrations remained below the MassDEP 16 µg/L guidance value across all samples collected during the 2022 monitoring program.

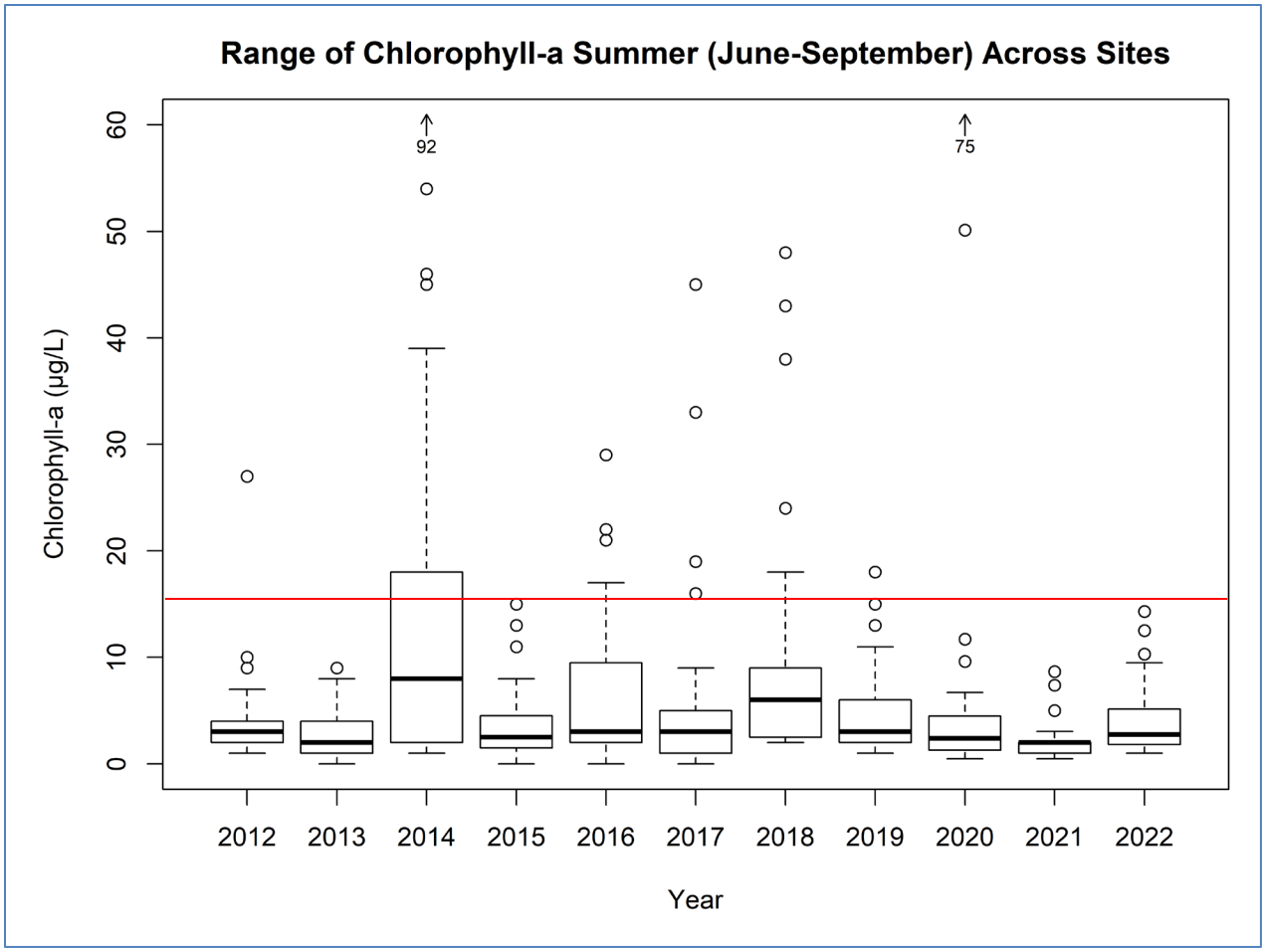


Figure 37: Chlorophyll-a concentrations observed during June, July, August, and September since 2012, summarized by year

The same data are summarized by site in **Figure 38** for just the months of June – September, plotted from the headwaters (left) to the outlet (right). At individual sampling locations, mean summer concentrations in 2022 (blue diamonds) are at or above than the median for all years at all sites (except at W1779 where it is slightly lower), and interquartile spread is largest at the five downstream sites (W0767 to RMSL).

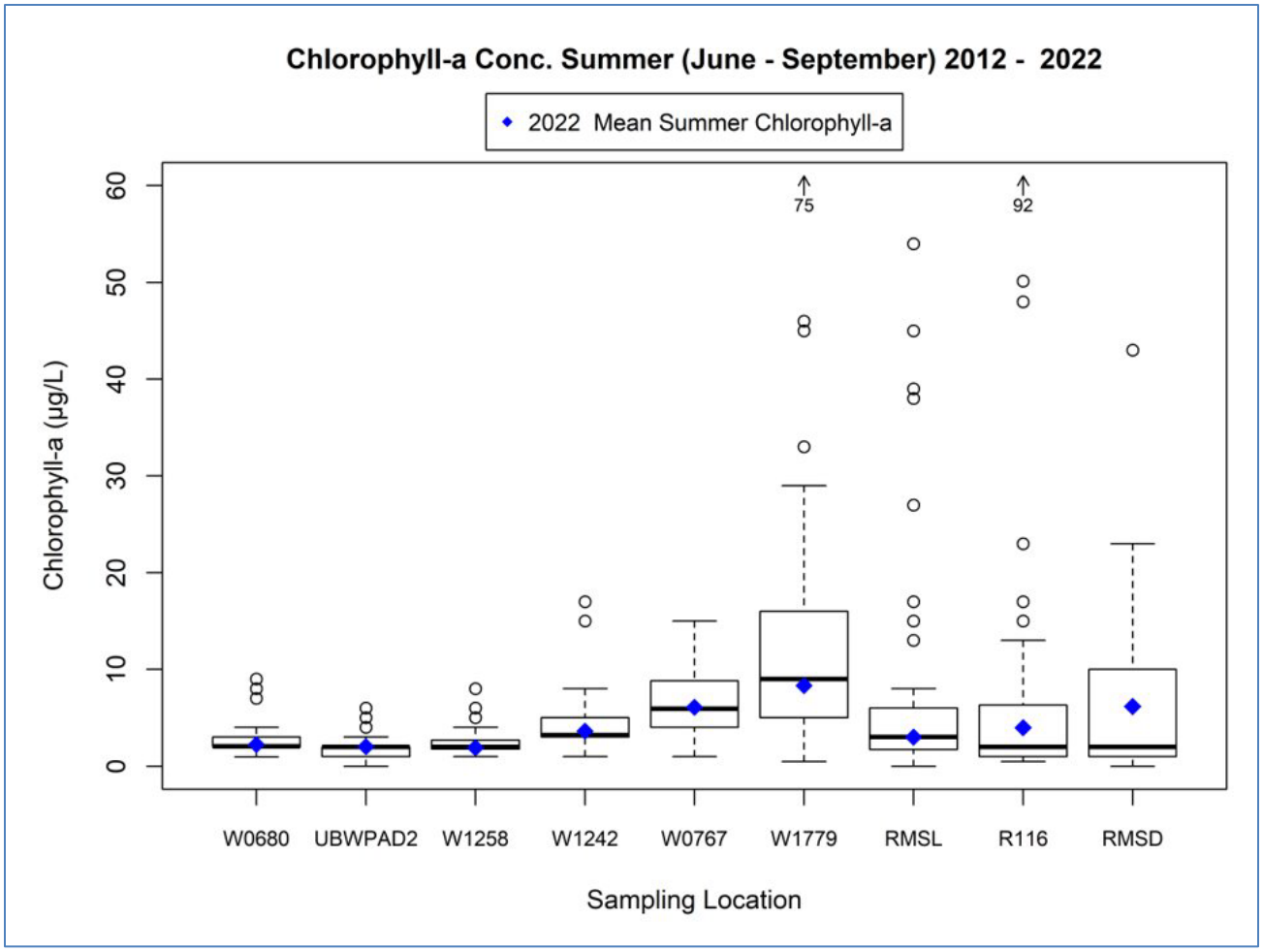


Figure 38: Chlorophyll-a concentrations observed during June, July, August, and September since 2012, summarized by sampling location

The mean summer (June – September) chlorophyll-a concentrations for each year and sampling location on the Blackstone River are also summarized on **Figure 39**. Data are clustered by sampling site, again plotted from the headwaters (left) to the outlet (right). In 2022, summertime chlorophyll-a levels were slightly lower than historical data at the upstream (W0680) site, but higher at all the other sites. The highest summer means were observed at W0767 and W1779 and RMSD, but remained much below the 16 µg/L MassDEP guidance value.

Mean summer (June – September) chlorophyll-a concentrations by site since 2012:

	W0680	*UBWPAD2*	*W1258*	*W1242*	*W0767*	*W1779*	*RMSL*	*R116*	*RMSD*
2012	2.0	NA	1.3	3.5	1.3	7.8	7.5	7.5	9.3
2013	3.3	2.2	3.0	3.0	NA	3.3	3.0	3.3	4.0
2014	1.0	1.3	2.0	8.8	8.0	28.8	26.8	33.5	18.0
2015	2.0	1.3	2.0	3.3	4.5	7.8	7.0	2.5	3.0
2016	4.0	2.3	2.5	6.0	10.3	22.0	2.3	5.0	7.5
2017	3.6	1.6	2.0	4.6	7.8	17.8	10.4	1.4	1.2
2018	5.8	3.8	3.5	5.0	6.5	11.0	15.8	16.8	16.3
2019	2.5	1.3	1.8	2.5	4.5	8.5	4.3	3.8	5.5
2020	2.2	1.6	2.6	3.6	7.3	22.9	2.8	17.8	0.9
2021	2.3	1.4	1.5	2.3	3.7	4.3	1.6	1.1	0.9
2022	2.3	2.0	1.9	3.6	6.1	8.3	3.0	4.0	6.2

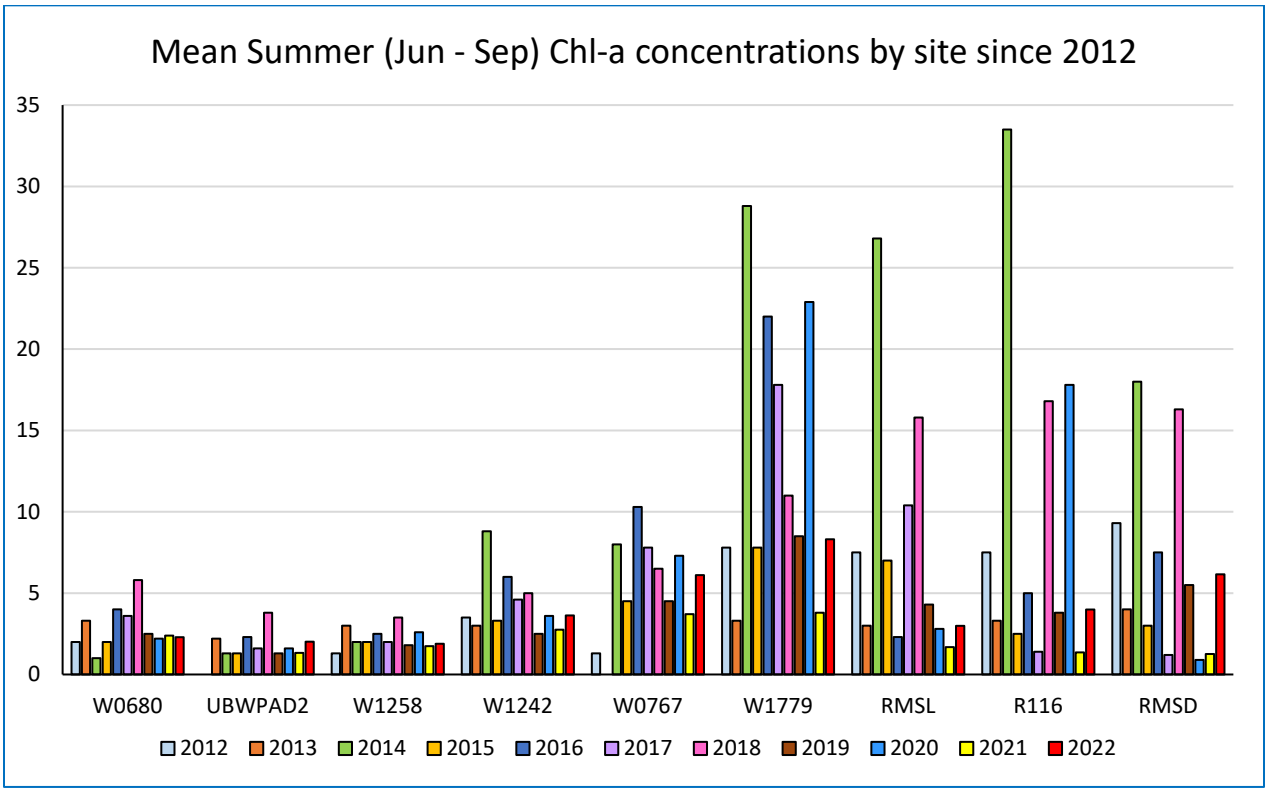


Figure 39: Mean summer (June – September) chlorophyll-a concentrations by site since 2012

The annual average chlorophyll-a concentration data for 2021, **Figure 40**, was below MassDEP screening guidelines at all locations, and in the middle to lower range of the past 11 years (red line is average concentration from 2000-2001 and 2005-2006**)**.

Annual average chlorophyll-a concentration 2012-2022 *(RM= river mile)*:

Ave Chl-a	W0680	UBWPAD2	W1258	W1242	W0767	W1779	RMSL	R116	RMSD
(µg/L)	*RM 45.2*	*RM 44.6*	*RM 42.7*	*RM 36.3*	*RM 33.4*	*RM 27.8*	*RM 15.5*	*RM 6.3*	*RM 0*
2012	1.6	3.2	1.8	3	1.8	5.5	7.7	7.7	6.1
2013	3.6	2.2	2.6	2.25	NA	3.8	3.9	5.3	4.0
2014	3.3	2.3	2.9	6.375	5.6	16.4	16.7	19.8	10.9
2015	2.0	1.4	1.8	2.75	4.3	5.9	5.3	2.6	4.9
2016	4.2	2.5	2.8	5.7	7.7	16.5	1.8	3.3	5.3
2017	4.2	1.9	2.4	4.9	7.6	13.4	7.3	1.8	2.6
2018	5.6	3.3	3.0	4.6	5.3	8.3	9.8	10.3	12.0
2019	3.5	1.7	2.8	4.9	4.7	6.4	3.0	4.8	5.1
2020	2.6	1.5	2.3	3.3	5.7	16.7	2.1	10.9	0.9
2021	2.4	1.3	1.7	2.8	3.7	3.8	1.7	1.4	1.3
2022	2.3	2.0	1.9	3.6	6.1	8.3	3.0	4.0	6.2

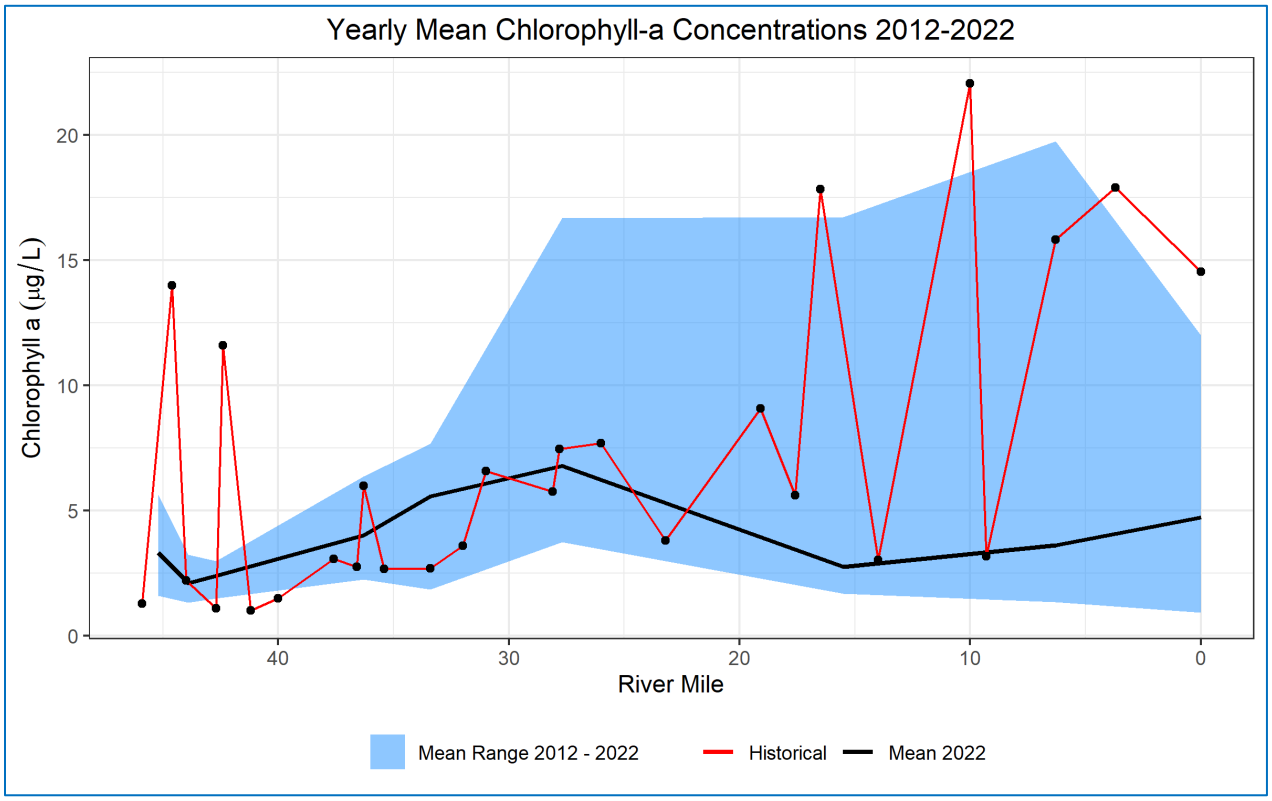


Figure 40: Along stream average chlorophyll-a concentrations

In 2022, chlorophyll-a concentrations in the Blackstone River were below the MassDEP 2016 CALM screening threshold of 16 µg/L at all sites each month (**Figure 41**).

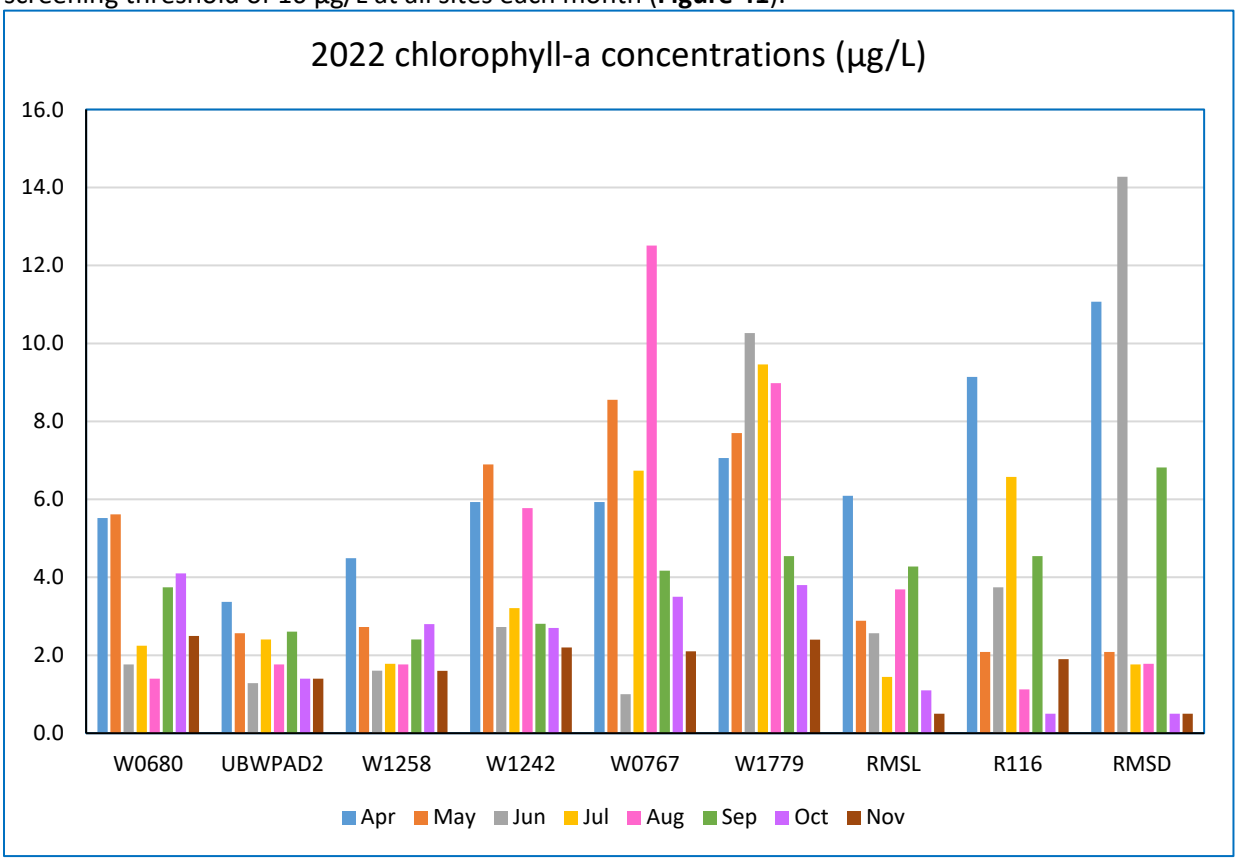


Figure 41: 2022 chlorophyll-a concentrations

6.1.4. Flow-weighted concentration trend analysis

Correlations between streamflow and concentration make it difficult to identify trends in water quality without a more robust statistical analysis. However, streamflow-weighted concentrations, which account for differences in streamflow conditions, can be used to evaluate trends and to additionally account for the influence of location, season, or month on water quality.

Flow-weighted concentration was calculated based on a locally weighted scatterplot smooth regression (LOWESS) between concentration and streamflow. Streamflow-weighted concentrations are the residuals (e.g., the absolute value of the difference between the observed concentration and the LOWESS smooth). Trends in water quality were then evaluated using a seasonal Mann-Kendall test (Helsel, 2006) computed on the streamflow-weighted concentration data collected since 2012. The trend analysis was conducted for each site individually by season. While the data set is limited due to the length of record, sufficient data were available to complete the analysis at all sampling locations, **Tables 14-16**. The Mann-Kendall analysis becomes more robust as more data become available. The analysis was completed on the full dataset and found:

- When all sites are considered together, there is a statistically significant decreasing trend at the 99% significance level in TP streamflow-weighted concentrations when the data are analyzed accounting for

month and also for season. There is no significant decreasing trend for TP when the data are analyzed accounting for month, nor for season.

- Four sites also exhibit statistically significant decreasing trends in streamflow-weighted TP concentration individually when accounting for month: RMSD, R116, RMSL, and W1779. The three Rhode Island sites (RMSD, R116, and RMSL) also exhibit statistically significant decreasing trends in streamflow-weighted TP concentration when accounting for season.
- TP concentrations at W0680, W1258, W1242, and W0767 do not show a statistically significant trend, either when grouped by month or season;W1779 does not show a significant trend either when grouped by season.
- Streamflow-weighted TP concentration shows a 90% significant increasing trend at UBWPAD2, both when analyzed accounting for month and season (**Table 14**).
- Significant decreasing trends in TN streamflow-weighted concentration are observed at nearly all sites, when considered individually at both the monthly or seasonal groupings. Exceptions to this trend are at UBWPAD2, which does not show a statistically significant trend when considering either month or season, and at W0767 when accounting for season (**Table 15**).
- For chlorophyll-a, however, RMSD is still the only site showing a decreasing trend, at the 90% significance level. When all sites are grouped together, no trend is statistically significant (**Table 16**).
- Comparing this year's analysis to last year's, we note that for all three parameters, the trend is decreasing for fewer sites this year than last year. It will be interesting to see if next year continues to show fewer decreasing trends even if there is no plant upset .

Table 14: Streamflow-weighted seasonal trend analysis results for TP, 2012-2022

Site	Point	Block	Significance	Trend
All Sites	Flow-weighted TP	Site+Month	>99%	Decreasing
RMSD	Flow-weighted TP	Month	>99%	Decreasing
R116	Flow-weighted TP	Month	>99%	Decreasing
RMSL	Flow-weighted TP	Month	>99%	Decreasing
W1779	Flow-weighted TP	Month	>95%	Decreasing
W0767	Flow-weighted TP	Month		
W1242	Flow-weighted TP	Month		
W1258	Flow-weighted TP	Month		
UBWPAD2	Flow-weighted TP	Month	>90%	Increasing
W0680	Flow-weighted TP	Month		
All Sites	Flow-weighted TP	Site+Season	>99%	Decreasing
RMSD	Flow-weighted TP	Season	>99%	Decreasing
R116	Flow-weighted TP	Season	>99%	Decreasing
RMSL	Flow-weighted TP	Season	>99%	Decreasing
W1779	Flow-weighted TP	Season		
W0767	Flow-weighted TP	Season		
W1242	Flow-weighted TP	Season		
W1258	Flow-weighted TP	Season		
UBWPAD2	Flow-weighted TP	Season	>90%	Increasing
W0680	Flow-weighted TP	Season		

Table 15: Streamflow-weighted seasonal trend analysis results for TN

Site	Point	Block	Significance	Trend
All Sites	Flow-weighted TN	Site+Month		
RMSD	Flow-weighted TN	Month	>99%	Decreasing
R116	Flow-weighted TN	Month	>99%	Decreasing
RMSL	Flow-weighted TN	Month	>99%	Decreasing
W1779	Flow-weighted TN	Month	>99%	Decreasing
W0767	Flow-weighted TN	Month	>90%	Decreasing
W1242	Flow-weighted TN	Month	>99%	Decreasing
W1258	Flow-weighted TN	Month	>99%	Decreasing
UBWPAD2	Flow-weighted TN	Month		
W0680	Flow-weighted TN	Month	>99%	Decreasing
All Sites	Flow-weighted TN	Site+Season		
RMSD	Flow-weighted TN	Season	>99%	Decreasing
R116	Flow-weighted TN	Season	>99%	Decreasing
RMSL	Flow-weighted TN	Season	>99%	Decreasing
W1779	Flow-weighted TN	Season	>99%	Decreasing
W0767	Flow-weighted TN	Season		
W1242	Flow-weighted TN	Season	>95%	Decreasing
W1258	Flow-weighted TN	Season	>99%	Decreasing
UBWPAD2	Flow-weighted TN	Season		
W0680	Flow-weighted TN	Season	>99%	Decreasing

Table 16: Streamflow-weighted seasonal trend analysis results for chlorophyll-a, 2022

Site	Point	Block	Significance	Trend
All Sites	Flow-weighted Chlorophyll-a	Month		
RMSD	Flow-weighted Chlorophyll-a	Month		
R116	Flow-weighted Chlorophyll-a	Month		
RMSL	Flow-weighted Chlorophyll-a	Month		
W1779	Flow-weighted Chlorophyll-a	Month		
W0767	Flow-weighted Chlorophyll-a	Month		
W1242	Flow-weighted Chlorophyll-a	Month		
W1258	Flow-weighted Chlorophyll-a	Month		
UBWPAD2	Flow-weighted Chlorophyll-a	Month		
W0680	Flow-weighted Chlorophyll-a	Month		
All Sites	Flow-weighted Chlorophyll-a	Site+Season		
RMSD	Flow-weighted Chlorophyll-a	Season	>90%	Decreasing
R116	Flow-weighted Chlorophyll-a	Season		
RMSL	Flow-weighted Chlorophyll-a	Season		
W1779	Flow-weighted Chlorophyll-a	Season		
W0767	Flow-weighted Chlorophyll-a	Season		
W1242	Flow-weighted Chlorophyll-a	Season		
W1258	Flow-weighted Chlorophyll-a	Season		
UBWPAD2	Flow-weighted Chlorophyll-a	Season		
W0680	Flow-weighted Chlorophyll-a	Season		

6.1.5. Field Water Quality Measurements

Water temperature, dissolved oxygen, and pH were measured in situ at each site with hand-held Hach HQ 40 D multimeters. Measurements were taken directly in the river, or if the meter cables were not long enough to reach the stream (because sampling was done from a very high bridge), a sampling container on a rope was lowered into the river, and measurements were taken from the container back on the bridge.

Water temperature at all sites throughout the sampling season is shown in **Figure 42.** Temperature was below 28°C all season at all sites, with the warmest temperatures observed in August. Sampling begins around 8 AM in the upper loop (starting at W0767 and moving upstream to W0680) or 8:30 AM in the lower loop (starting at RMSD and moving upstream to W1779) and continues to about 12PM, but the difference in temperature between sites on a given day is probably not caused by the time of measurement. The temperature difference is probably due to water depth, whether the site is immediately downstream of a reservoir, or flowing through a shaded area. Water temperatures were never observed above the Massachusetts water quality criterion of 28.5°C or the 28.3°C criterion in Rhode Island).

The temperature difference between the nine sites ranges from 1.3°C and 4.5°C. No one site always has the highest temperature.

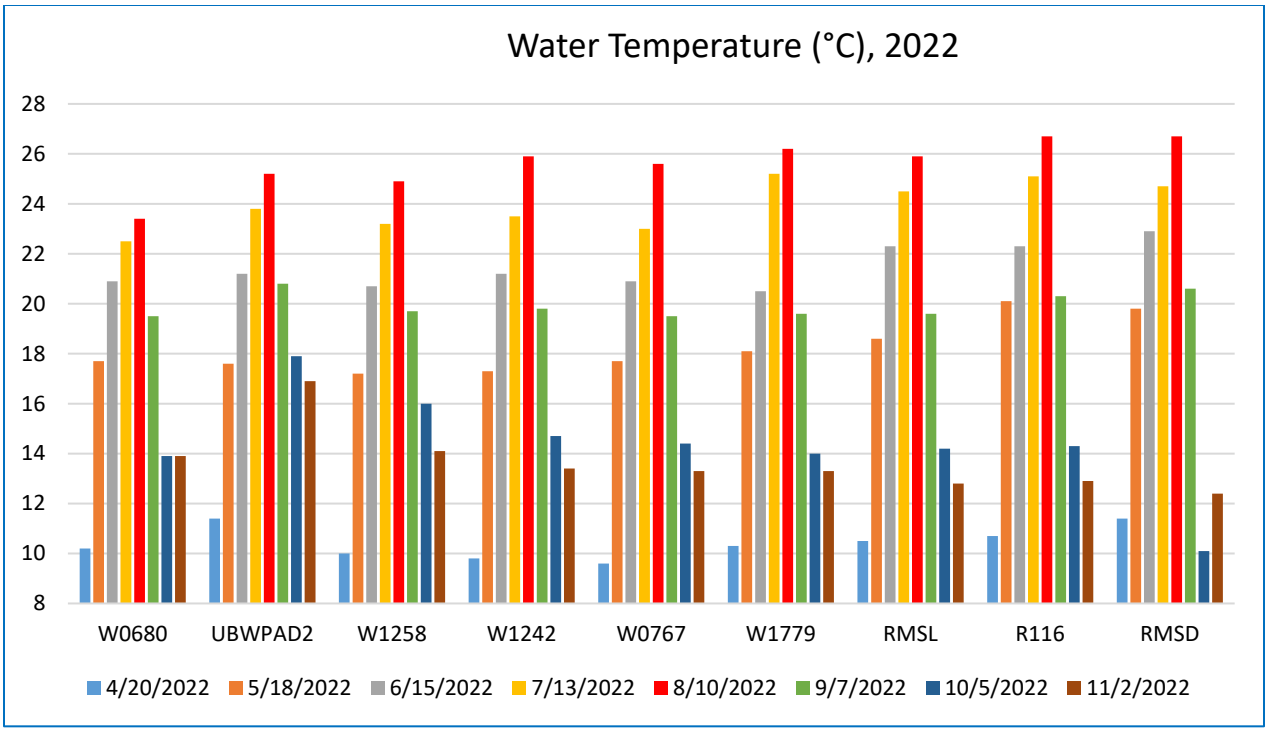


Figure 42: Water temperature at each site and each sampling event

pH at each site for each date can be seen in **Figure 43**. pH was within the Massachusetts Surface Water Quality Standards for class B waters (between 6.5 and 8.3) and the Rhode Island criterion (between 6.5 and 9.0) during the entire sampling season.

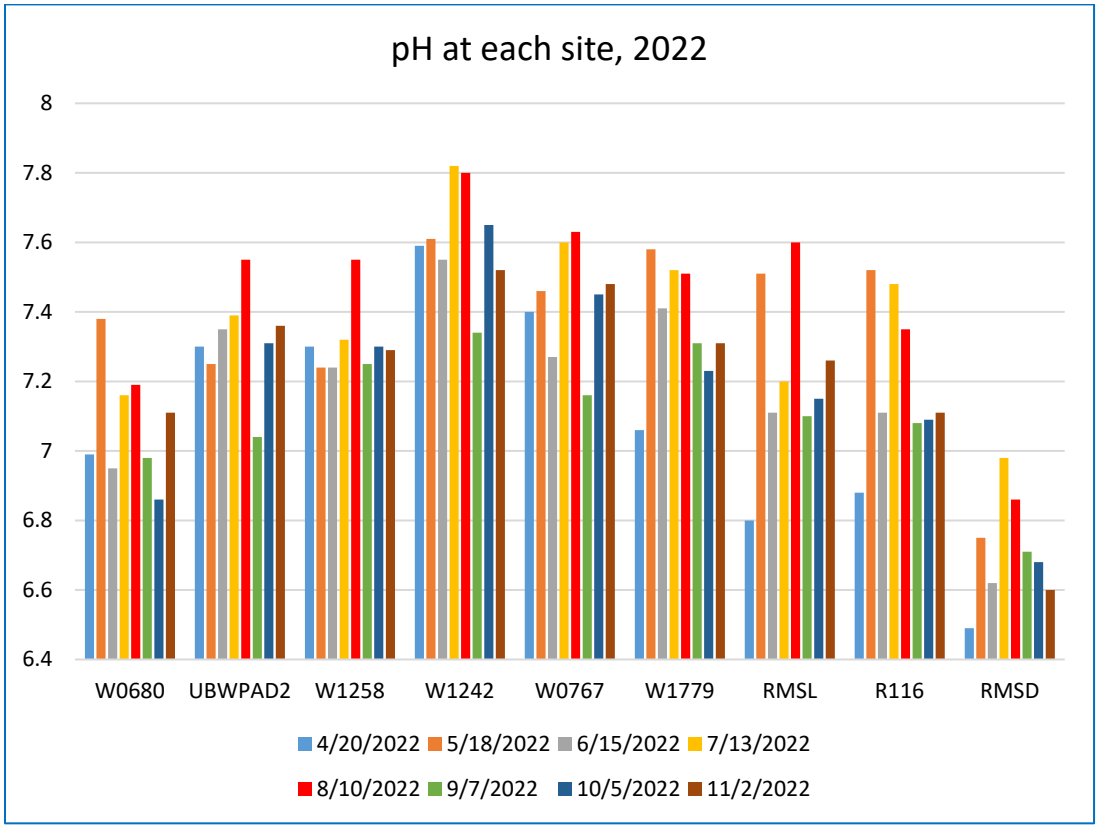


Figure 43: 2022 pH at each site

Dissolved oxygen was also measured between the hours of 8 AM and 12 PM. No measurements fell below the Massachusetts water quality criterion of 5 mg/L (class B waters) at any site (**Figure 44**). Percent saturation exceeded 80% at each site each sampling day. It exceeded 90% saturation 81% of the time (**Figure 45**). Site W1258 had the lowest percent saturation almost all of the time, particularly in August.

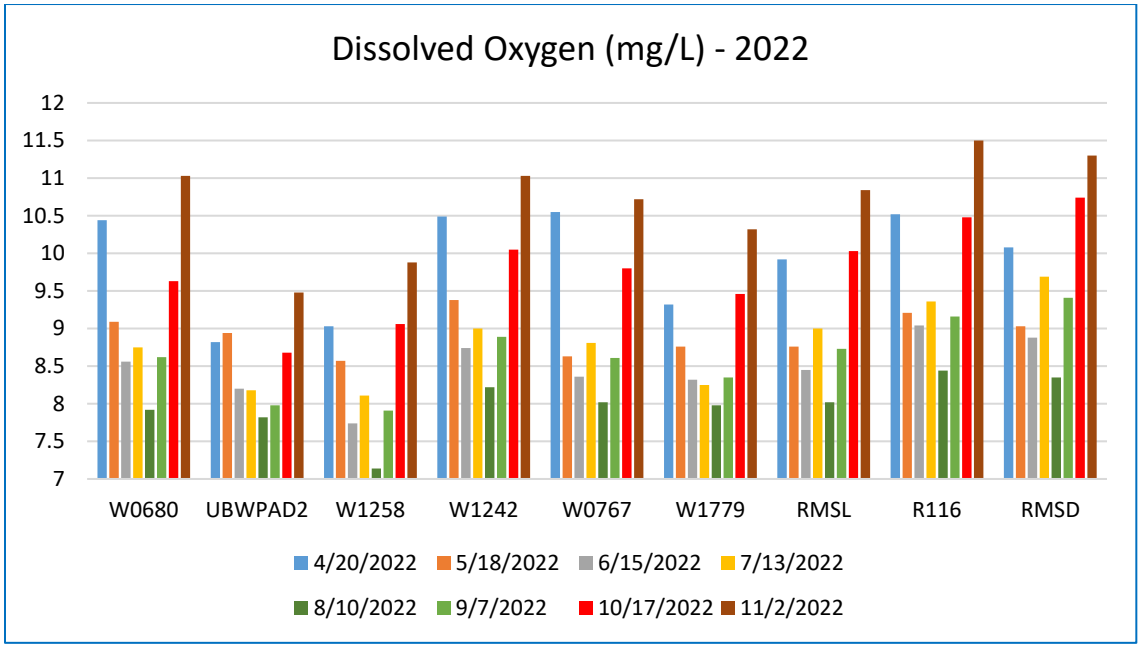


Figure 44: 2022 dissolved oxygen in mg/L at each site

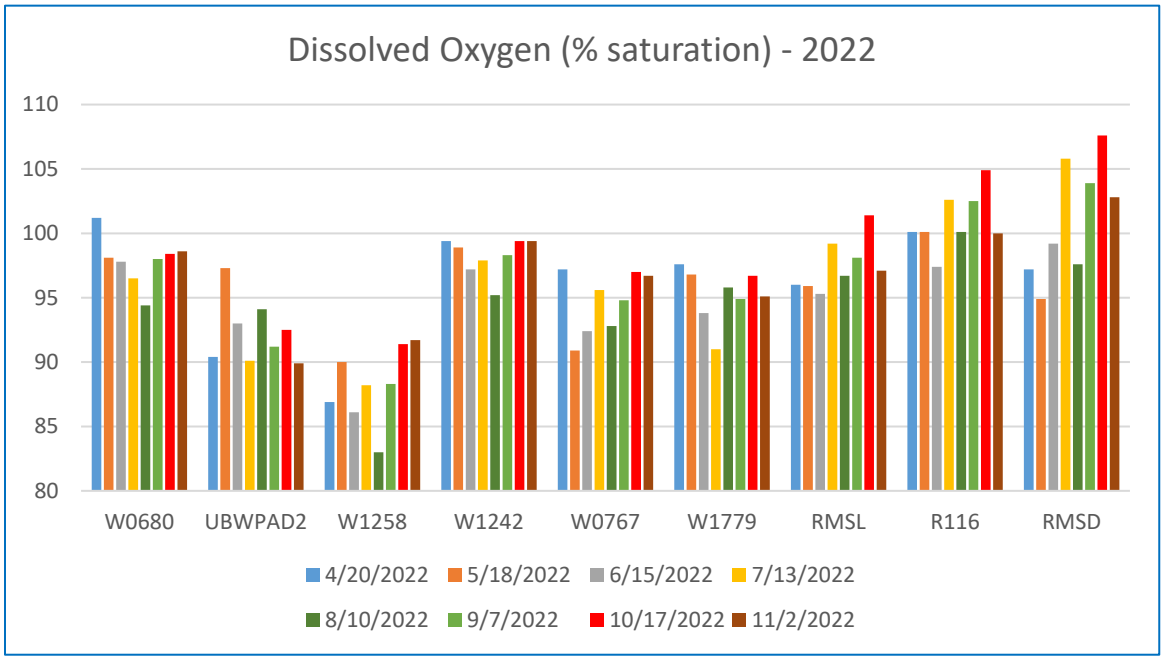


Figure 45: 2022 dissolved oxygen percent saturation at each site

Conductivity

Hand-held meters were used to measure conductivity (specific conductance) in the UB lab. Results are shown in **Figure 46.** Conductivity is highest every month at the site just downstream of the Upper Blackstone effluent confluence (UBWPAD2). At each site, conductivity was highest in August, followed by July and June. The trend follows that of most years, with highest conductivity at UBWPAD2 and decreasing progressively downstream, though once the river enters Rhode Island, conductivity does not vary much between RMSL and RMSD.

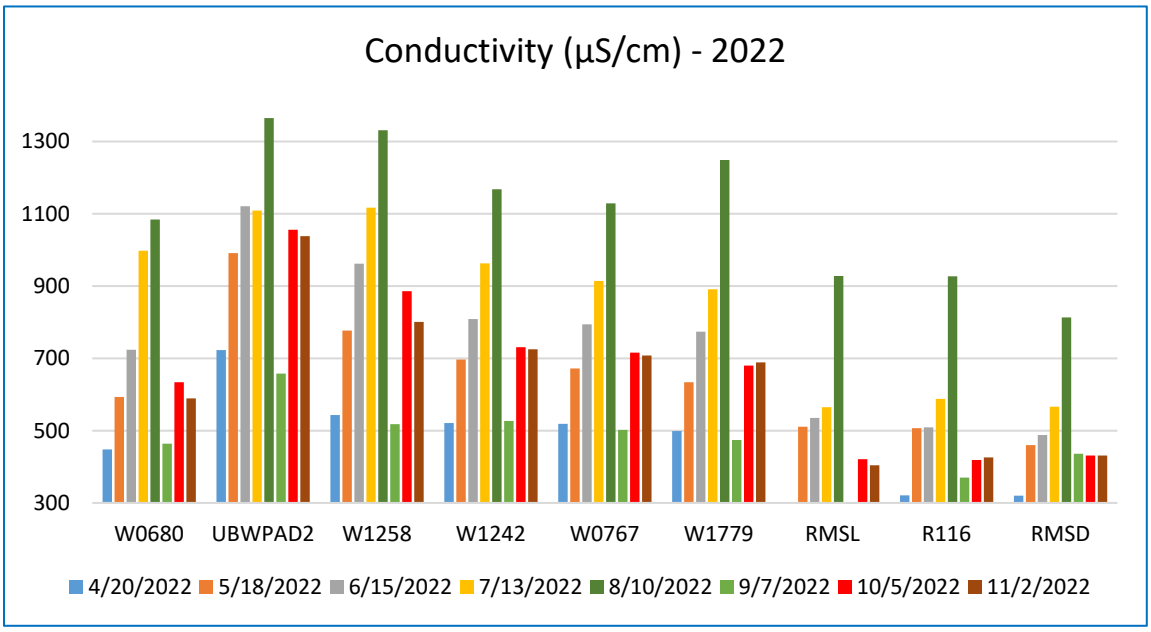


Figure 46: Conductivity at each site on sampling dates, 2022

6.2 Continuous Water Quality Monitoring

Data collected during the regular monthly sampling program provide important information on the Blackstone River's health. However, these data do not provide any information about water quality between sampling events. To help fill this gap, Upper Blackstone deploys and manages four Onset HOBO U26-001 continuous temperature (T) and dissolved oxygen (DO) probes at four locations in the Blackstone River between July and October. Based on results from deployments in previous years, two loggers were relocated to new sites in consultation with MassDEP to investigate changes in water quality between Central Cemetery (W1258), which has historically exhibited exceedances of water quality guidance and standards, and Depot Street, which has historically met guidance and standards. The two new loggers were located at Riverlin Street and the Former Millbury WWTP, between the upstream Central Cemetery and downstream Depot Street. All four of the Blackstone River meters were deployed in MassDEP Assessment Unit MA51-03 (**Figure 2**).

Upper Blackstone staff used a calibrated hand-held T/DO probe to collect grab measurements every one-to-two weeks throughout the deployment period. The measurements were collected next to and at

the same depth as the continuous meter at each site, and were later used to review and correct the meter data. The continuous probes were cleaned during field visits between grab DO measurements. However, during the 2022 monitoring season, all four data loggers malfunctioned and had to be removed for service. This resulted in approximately one month of lost data (late-August to late-September), in addition to greater-than-typical sensor drift that resulted in additional lost DO data due to the measurements falling outside of the guidance for correction.

CDM Smith reviewed the data from the 2022 continuous metering program, corrected the T and DO data at each site using United States Geological Survey (USGS) guidance (Wagner et al., 2006) based on the periodic in situ measurements taken with a handheld probe by Upper Blackstone staff. The corrected data were compared against Massachusetts' surface water quality criteria and guidance for dissolved oxygen at each site (see corrected DO and T data, **Figure 47** and **Figure 48**). Massachusetts Surface Water Quality Standards and guidance for dissolved oxygen Massachusetts water quality standards require a minimum DO concentration of 5 mg/L in the Blackstone River. In addition, the CALM has a guidance value for diel (daily) DO variations, where a diel change in DO greater than 3 mg/L is a potential indicator of nutrient enrichment. This discussion provides a brief summary of the results of the continuous monitoring program; a complete discussion and graphs showing the raw and corrected DO and T concentration values at each of the four sampling locations are presented in Appendix C.

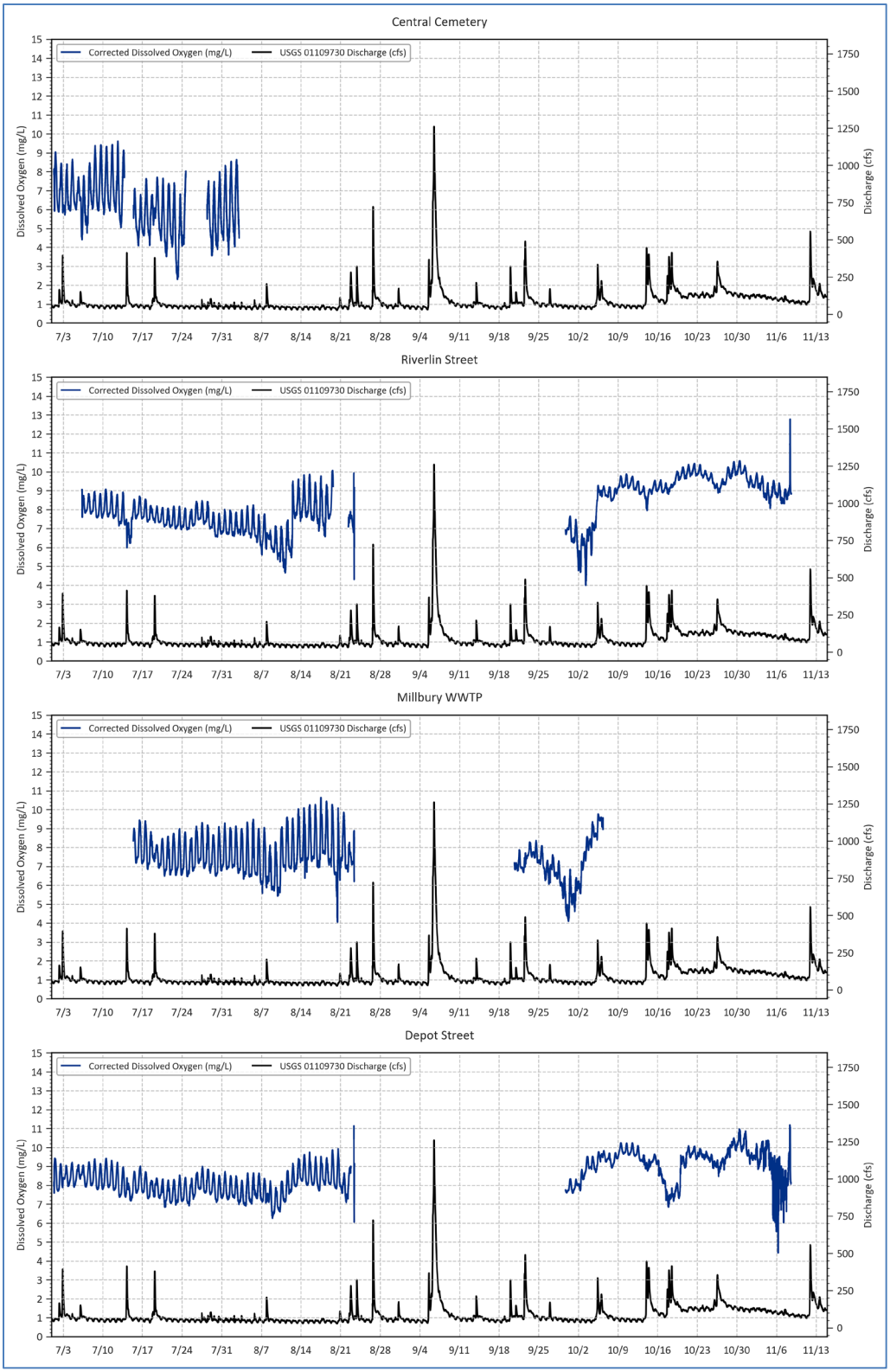


Figure 47: Corrected dissolved oxygen from continuous data loggers at each site, 2022

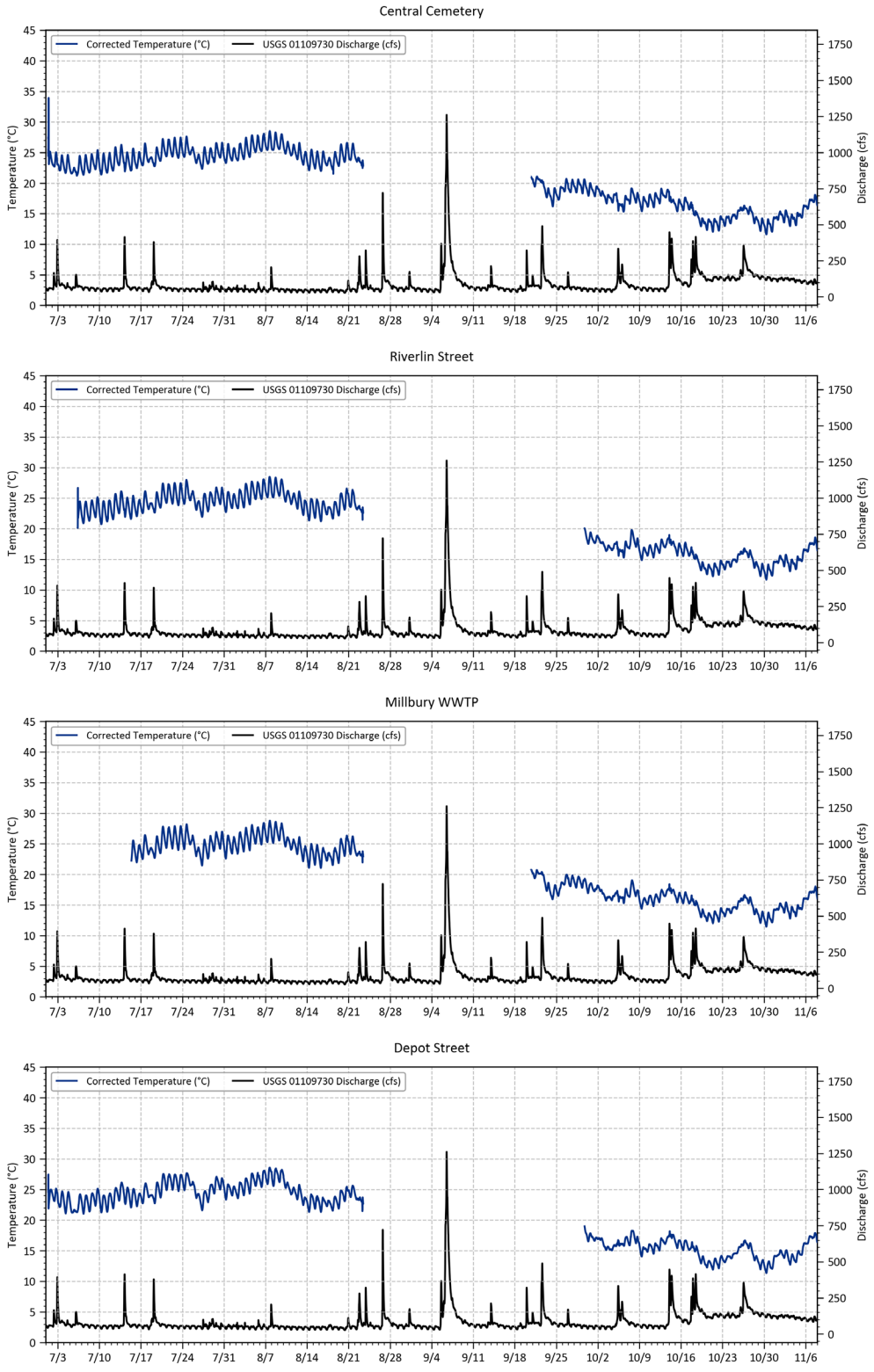


Figure 48: Corrected temperature from continuous data logger at each site, 2022

Data from each of the meters in the Blackstone River showed that compliance with the Massachusetts minimum DO criterion of 5 mg/L ranged from 79% to 100% during the monitoring period (**Table 17**). DO at the Riverlin Street, Millbury WWTP, and Depot Street stations was consistently at levels that support Aquatic Life Use based on the Massachusetts water quality standards and guidance in MassDEP's 2022 CALM. Nearly all of the exceedances of the 5 mg/L criterion occurred at Central Cemetery (79 percent of the measurements were 5 mg/L or higher).

Overall, DO improved between Central Cemetery and Depot Street, as has been observed in previous years. Compliance with the DO criterion of 5 mg/L and aquatic life use guidance significantly improved between Central Cemetery the next downstream Riverlin Street location, suggesting a steep gradient in water quality between these locations. There is a slight decline in quality between Riverlin Street and Millbury WWTP – primarily indicated by the slight increase in the percentage of time where the diel DO exceeds 3 mg/L – before ultimately improving at Depot Street. Precipitation in 2022 was generally lower than average, except for September, leading to generally lower streamflow throughout the summer. These lower-than-average flows, which could result in lower velocity and reaeration during dry weather, likely contributed to lower DO concentrations at Central Cemetery when compared with monitoring in previous drier years. Note that these results do not include the period where the WWTF was experiencing a plant upset due to the equipment malfunction that took the meters out of service during the highest nutrient loads caused by the plant upset in August and September.

Table 17: Summary of continuous corrected dissolved oxygen data against Massachusetts surface water quality standards and guidance

Metric	Central Cemetery (W1252)	Riverlin Street	Millbury WWTP	Depot Street
Days of corrected data	27	85	55	92
Days where diel ΔDO < 3.0 mg/L	7	82	46	87
% of days where diel ΔDO < 3.0 mg/L	26	96	84	95
% of the time DO > 5.0 mg/L	79	100	99	100
Days where % Saturation > 125%	100	100	100	100

6.2.1. Data Quality Objectives

All data collected during the 2022 monitoring program were evaluated against the Data Quality Objectives (DQOs) in the QAPP to determine whether the data quality was adequate for analysis. See Appendix E for the 2020-2022 QAPP.

Several field or lab blanks from the UMD lab did not pass the DQO for TDN and PON, and therefore a subset of the TN data is flagged for failed quality control in 2022. The data was not censored, however, even the one month when TN data was not five times larger than the largest blank value, because we performed a statistical correlation analysis in 2019 to evaluate whether a statistically significant difference exists between the full dataset (with flagged values) and the censored dataset (with flagged

values removed). The result of this analysis indicated that there is no statistically significant difference between the censored and uncensored dataset. Therefore, all data were included in the analysis and discussion presented in this report (See Hatte et al., 2020).

The field split for TP failed data quality objectives in May; however, this sample lost volume during digestion and therefore is not considered to be a representative QC sample. Since the blanks and the field duplicate all passed DQOs that month, no data were censored.

Both hand held meters failed the UMass blind pH QC sample in April, June, and November, and one meter also failed the pH QC sample in May and August. Except in November when the meters read a pH lower than acceptable, they always read pH higher than expected. The meters, however, always passed the QC sample provided by USEOA. Because the field data on the months when UMass PH QC sample was failed were all reasonable (never unexpectedly high), we used all the data for this report's graphs.

7.0 Summary and Discussion

The Upper Blackstone river water quality monitoring program was initiated in 2012 to monitor and assess the impact of WWTF upgrades. Since the 2008 upgrades were completed and brought online in 2009, Upper Blackstone has continued to refine its treatment process to minimize nutrient loads to the river. The WWTF has generally maintained the significant improvement in the water quality of its effluent since the upgrades were brought online. However, in the summer of 2022, a plant process upset occurred and normal operations did not return to normal until October, and as a result, phosphorus and nitrogen were higher than typical post-upgrade concentrations.

The higher nutrient loads in the effluent between July and September 2022 contributed to higher concentrations of TP and TN in the Blackstone River, especially at the Massachusetts monitoring locations. However, river nutrient concentrations were still much lower than those measured prior to the plant upgrade in 2008. In Rhode Island, where the streamflow is much larger and the relative influence of the Upper Blackstone WWTF much lower, river concentrations were only slightly higher than the 2012-2022 median. The nutrient loads were also larger than in most recent years, despite the drought experienced in the region this summer, especially for phosphorus. The highest calculated load levels occurred immediately downstream of the effluent confluence in Massachusetts, but were also observed at the Rhode Island State Line site as well as the most downstream site, presumably because the streamflow was higher at those locations.

Reduced nutrient loads from the WWTF correlate with reduced river nutrient and chlorophyll-a levels, and likewise increased effluent loads result in increased nutrient loads. Mean summer chlorophyll concentrations were higher than the 10-year median in the river's most downstream sites (W0767 through RMSD).The 2022 sampling season was characterized by warmer temperatures and a very dry summer. Streamflow was lower than average in the summer as well. A combination of factors, including temperature, exposure to sunlight, streamflow, nutrient availability on the days preceding routine sampling, and along-stream transport dynamics likely contribute to the observed year-to-year differences in water column nutrient and chlorophyll-a levels.

When taking streamflow into account, decreasing trends in phosphorus are still not statistically significant at the 99% confidence level when all sites are grouped by month or by season. A significant decreasing trend is also seen in nitrogen at most sites. For chlorophyll, a decreasing trend was observed at the 90% confidence level when grouped by site, at RMSD only.

Field measurements of water temperature, pH, and dissolved oxygen, in addition to conductivity measured in the laboratory, documented that the Blackstone River meets state water quality standards on most of the dates and times visited by this project's crews.

Continuous dissolved oxygen levels followed a consistent pattern in the stretch of the Blackstone River that was monitored in 2022. Data from each of the meters in the Blackstone River showed that compliance with the Massachusetts minimum DO criterion of 5 mg/L ranged from 78% to 100% during the monitoring period, with most of the exceedances of the water quality criteria and guidance occurring at Central Cemetery, a typical pattern observed in previous years of monitoring at this location. DO conditions improved significantly at the next downstream site (Riverlin Street), suggesting a steep gradient in water quality between these two locations. DO conditions consistently met Massachusetts water quality standards and guidance at all three downstream sites (Riverlin Street, Millbury WWTP, and Depot Street).

The Upper Blackstone water quality monitoring program has documented significant improvements relative to nutrient and chlorophyll-a concentrations in the Blackstone River since the WWTF upgrade was completed. Despite an unforeseen plant upset in the summer of 2022, nutrient discharges from the plant effluent to the main stem of the Blackstone river are still much lower than they were in prior to the 2008 upgrade.

Continued optimization efforts have resulted in reductions in nutrients and chlorophyll-a concentrations. These trends are promising, and water quality is expected to improve even more as Upper Blackstone continues its work to improve its effluent water quality in accordance with its NPDES permit and Administrative Order on Consent.

8.0 Future Work

Upper Blackstone plans to continue water quality monitoring in the Blackstone River in 2023 to track the impacts of reduced nutrient concentrations in Upper Blackstone plant effluent. Blackstone River data collected in 2022 will be added to the National Water Quality Monitoring Council's Water Quality Portal. The 2022 data will be submitted to MassDEP's Watershed Planning Program to supplement data submitted for the past eight years.

In 2023 the monitoring of nutrients and river chemistry at the 9 sampling sites will be continued, as well as measurement of continuous dissolved oxygen at 4 river sites.

9.0 References

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Blackstone River Water Quality Monitoring Program

2022 Sampling Season Report

APPENDIX

Appendix A: Additional Tables

Table A1: Summary of 2022 precipitation in relation to NWS 30-year average monthly data

Monthly Precipitation (inches)			
Worcester, MA			
(NWS station KORH)			
	2022	**Average Month Total[a]**	**% of normal**
Jan	3.12	3.52	88.6
Feb	5.33	3.26	163.5
Mar	3.46	4.19	82.6
Apr	3.91	4.11	95.8
May	2.43	3.56	68.3
Jun	3.16	4.21	74.9
Jul	3.54	3.93	90.1
Aug	2.91	4.14	70.3
Sep	6.14	4.24	144.8
Oct	4.43	4.84	91.5
Nov	3.83	4	95.8
Dec	6.07	4.28	141.8

Notes: [a] Based on data from 1991 – 2020, NWS Normal Monthly Data, available online: https://www.weather.gov/wrh/climate?wfo=box

Table A2: Summary of 2022 monthly flow conditions

	Monthly Mean Discharge (cfs)					
	Woonsocket, RI – USGS Station 01112500			Millbury, MA – USGS Station 01109730		
	2022	Ave 1930 – 2021	% normal	2022	Ave 2003 – 2021[a]	% normal
Jan	182	982	86.7	151	197	76.8
Feb	1861	1012	184.0	327	189	172.4
Mar	1209	1485	81.4	220	262	84.2
Apr	1115	1434	77.7	217	276	78.4
May	487	882	55.2	113	174	64.9
Jun	256	645	39.7	86	156	55.4
Jul	135	360	37.5	65	121	53.6
Aug	85	312	27.1	59	101	59.0
Sep	327	337	97.2	98	113	86.8
Oct	475	481	98.8	244	164	149.0
Nov	548	700	78.2	120	180	66.5
Dec	1369	922	148.5	116	214	54.1

Notes: [a] Long-term average in January – December based on data from 2002 – 2021.

** October-December 2022 data for Millbury and June-December 2022 data for Woonsocket not available as of 9/7/2023, calculated from MDV

Table A3: Summer 2022 monthly mean streamflows (cfs)

Monthly Mean Streamflow (cfs) at Millbury, MA – USGS Station 01109730													
	2008	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**	**2019**	**2020**	**2021**	**2022**
Jun	114	202	136	434	80	164	67	177	89	102	79	114	86
Jul	151	93	68	105	77	96	49	89	105	106	59	408	65
Aug	143	273	105	86	68	60	59	59	156	81	71	172	59
Sep	228	340	88	82	70	72	48	58	201	65	56	288	98

Appendix B: Additional Figures

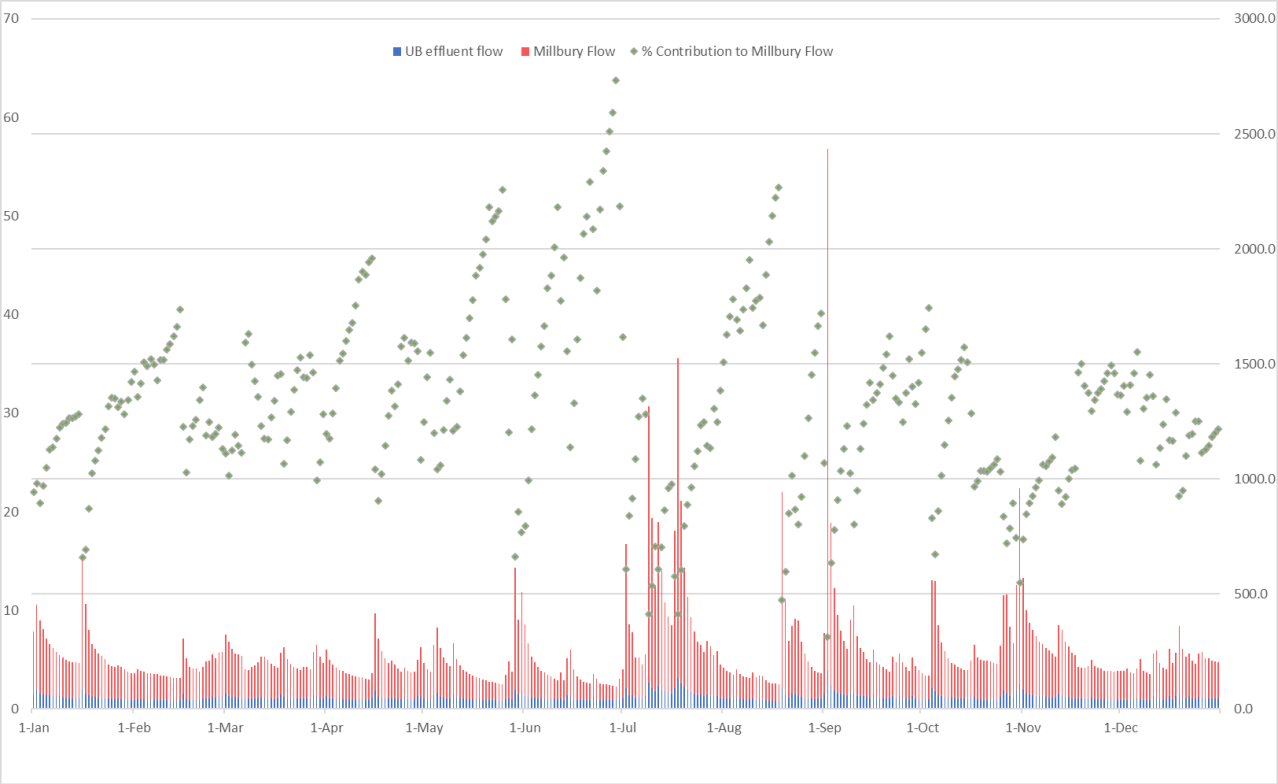
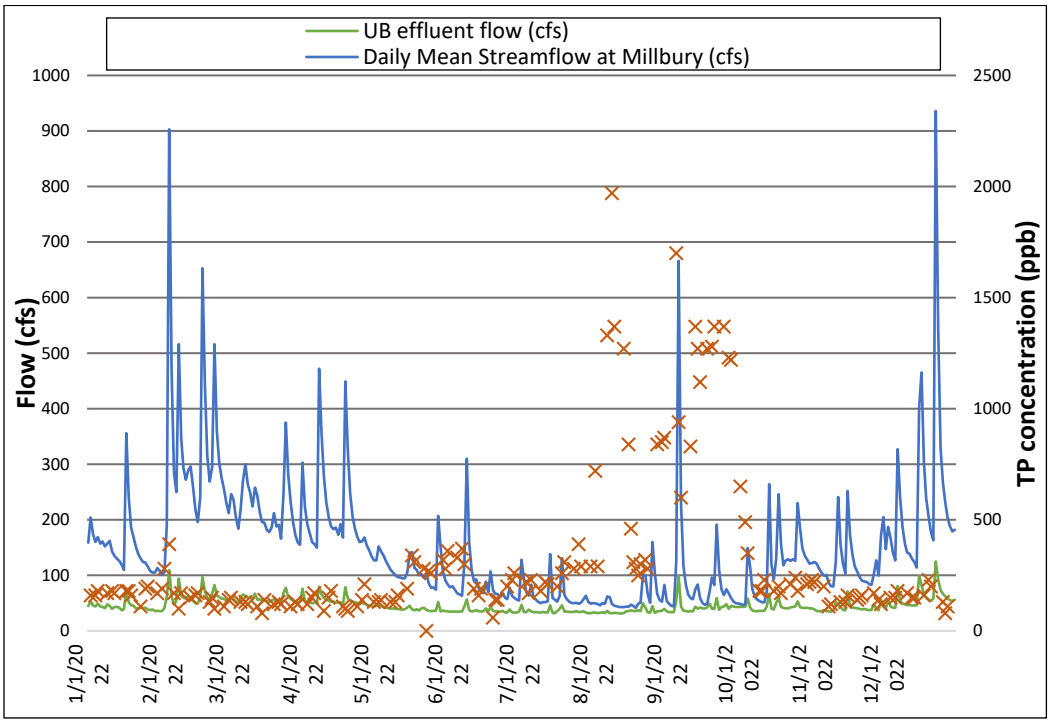


Figure B1: Effluent flow contributions at Millbury, 2022



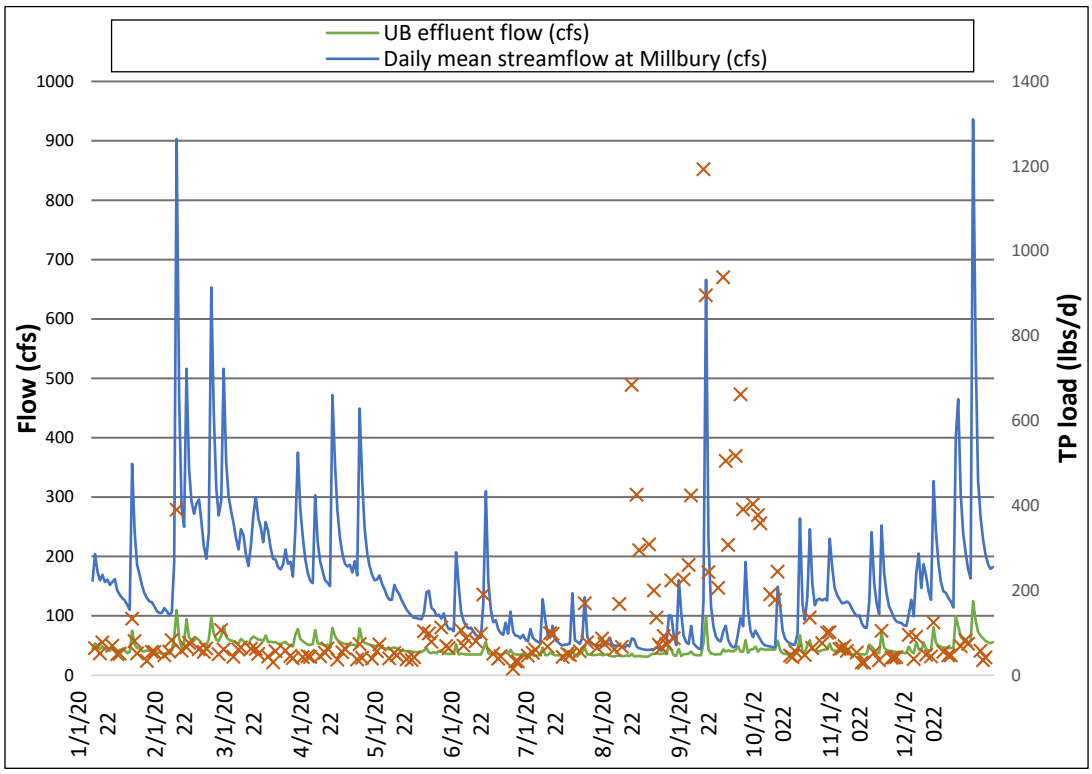
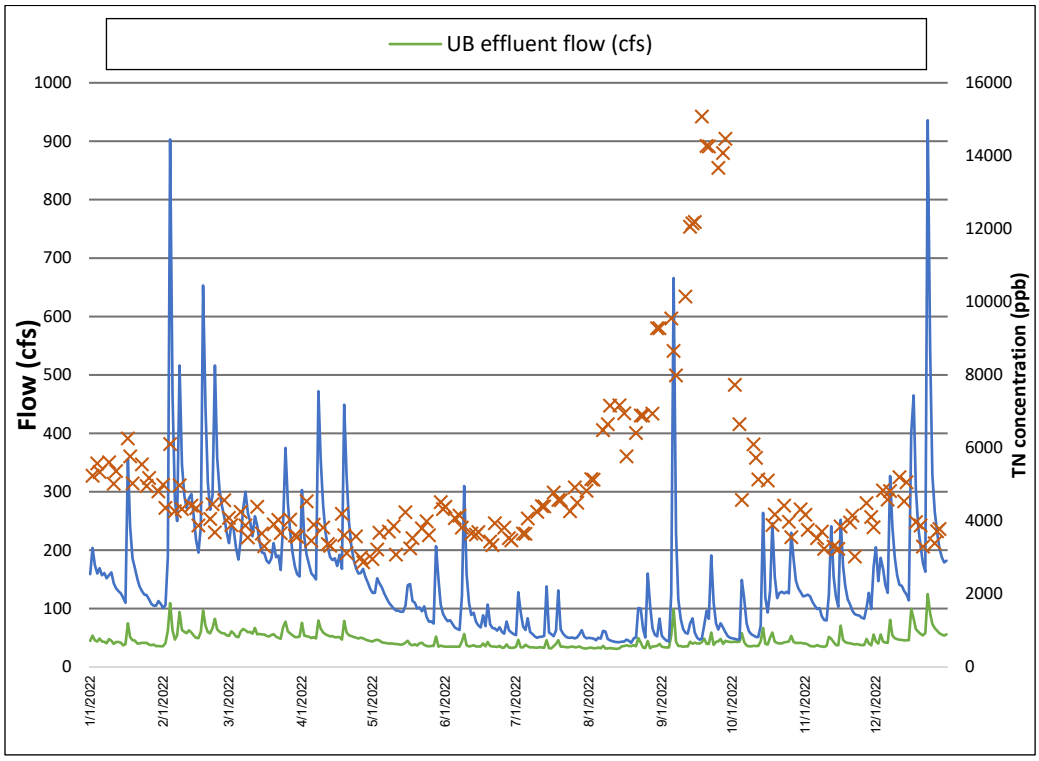


Figure B2: Effluent TP characteristics, 2022



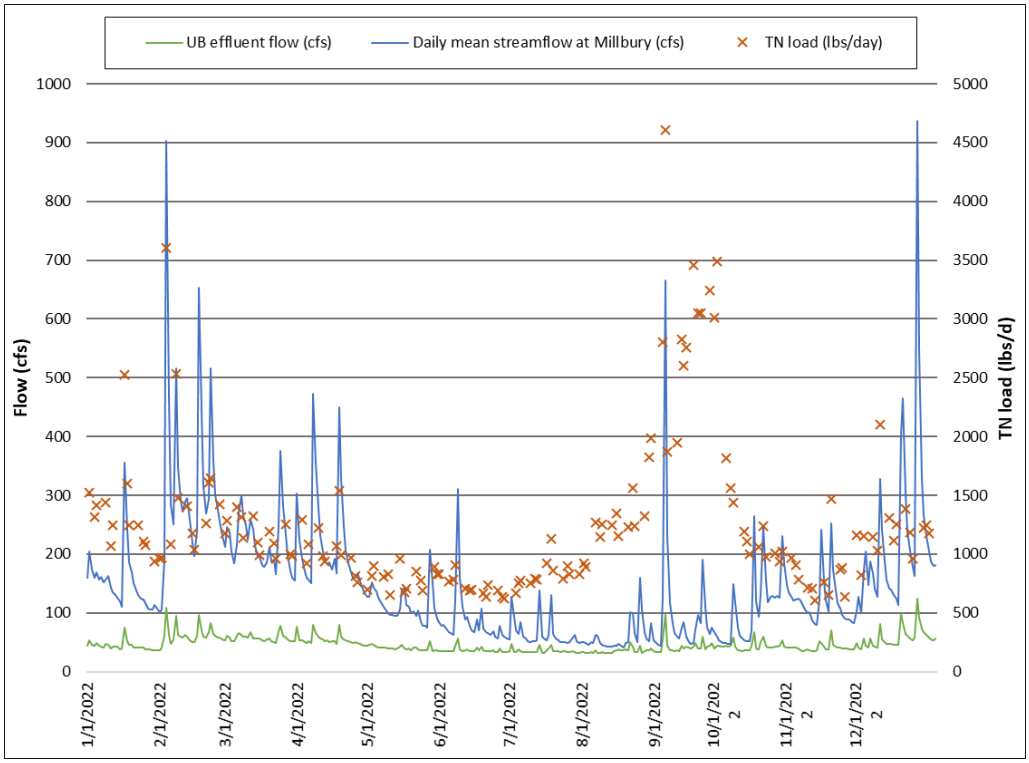


Figure B3: Effluent TN characteristics, 2022

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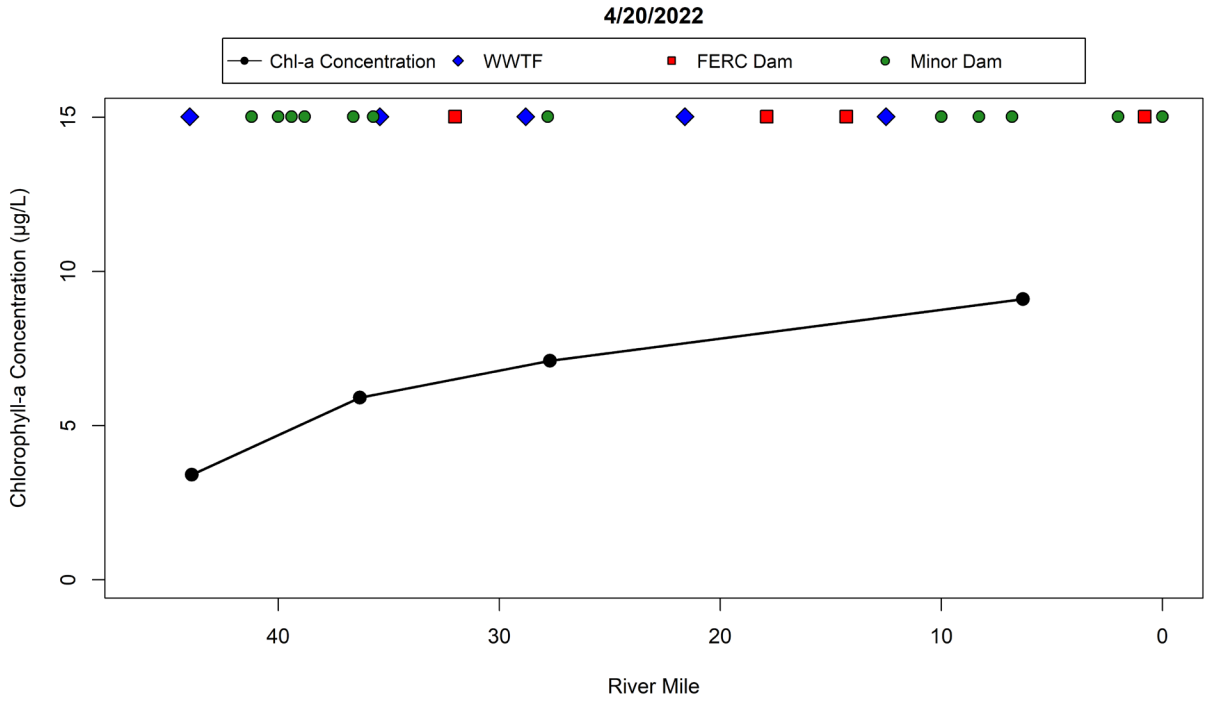
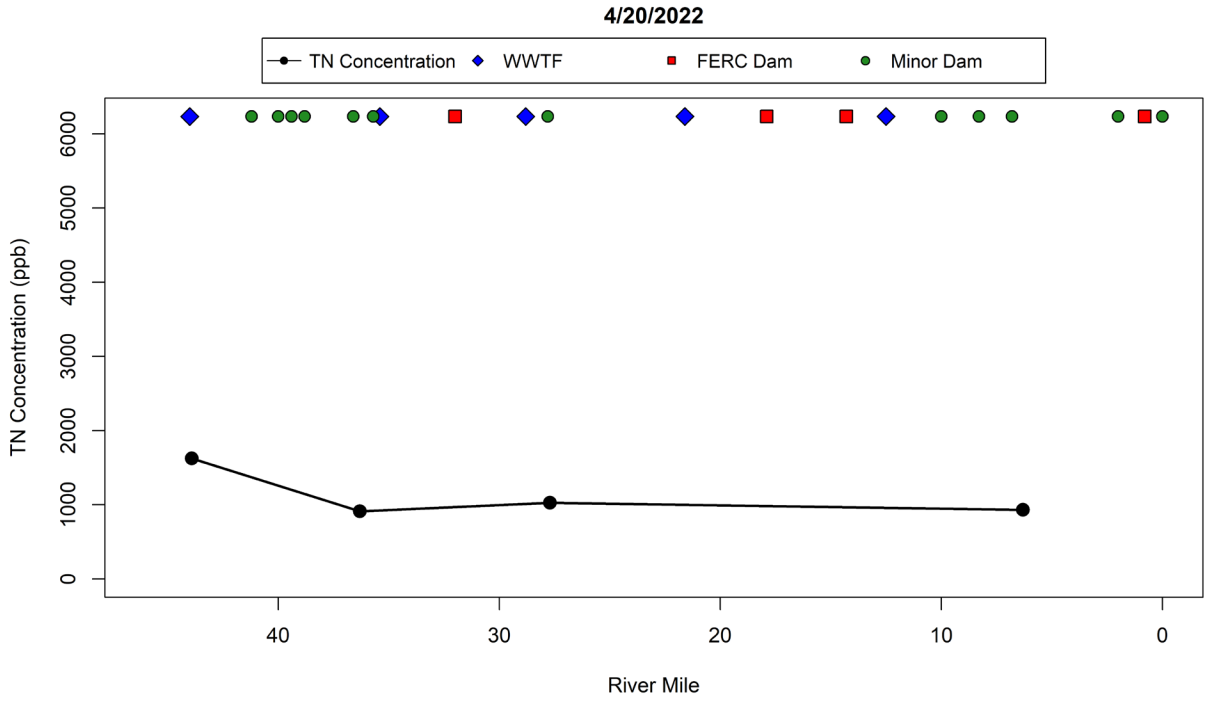




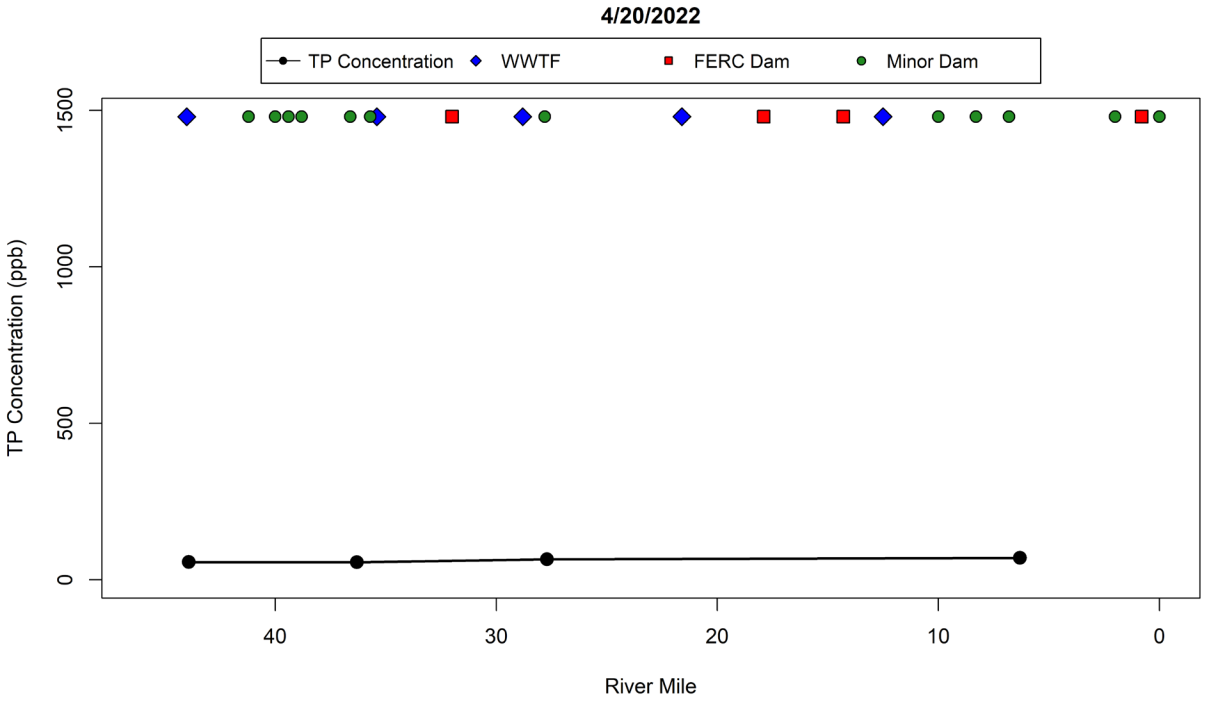
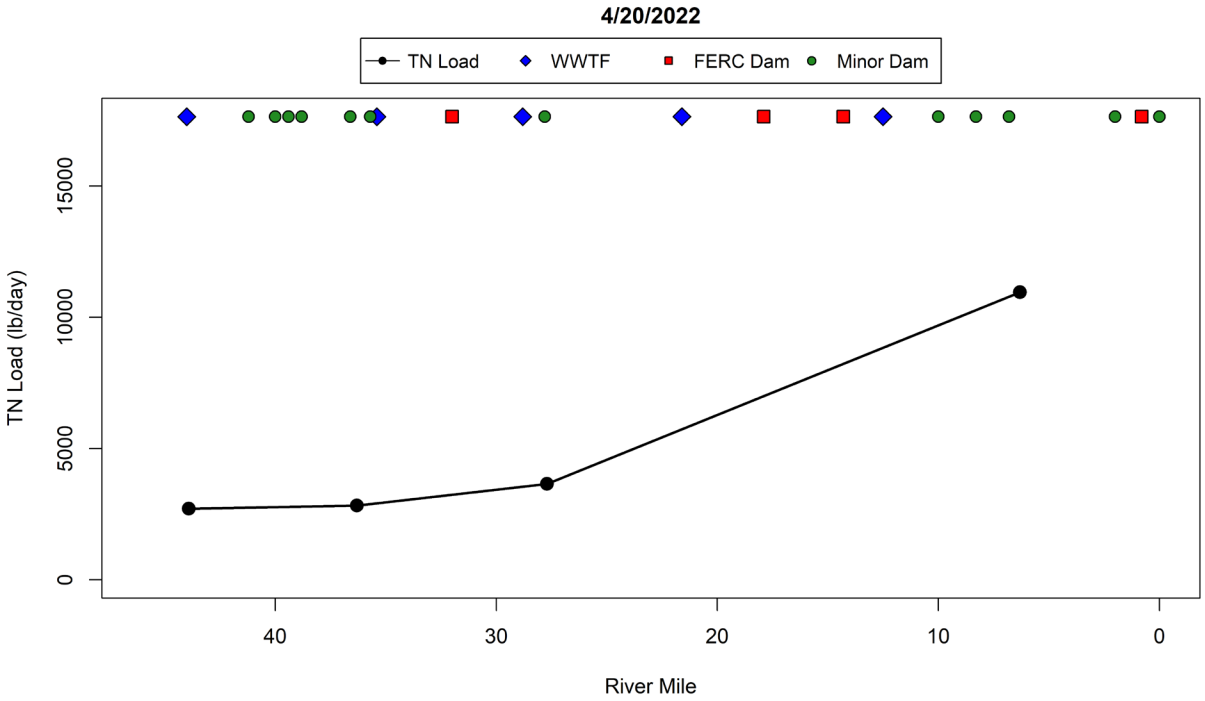


Figure B4: April 2022 along stream concentration (Chl-a, TN, TP, respectively)



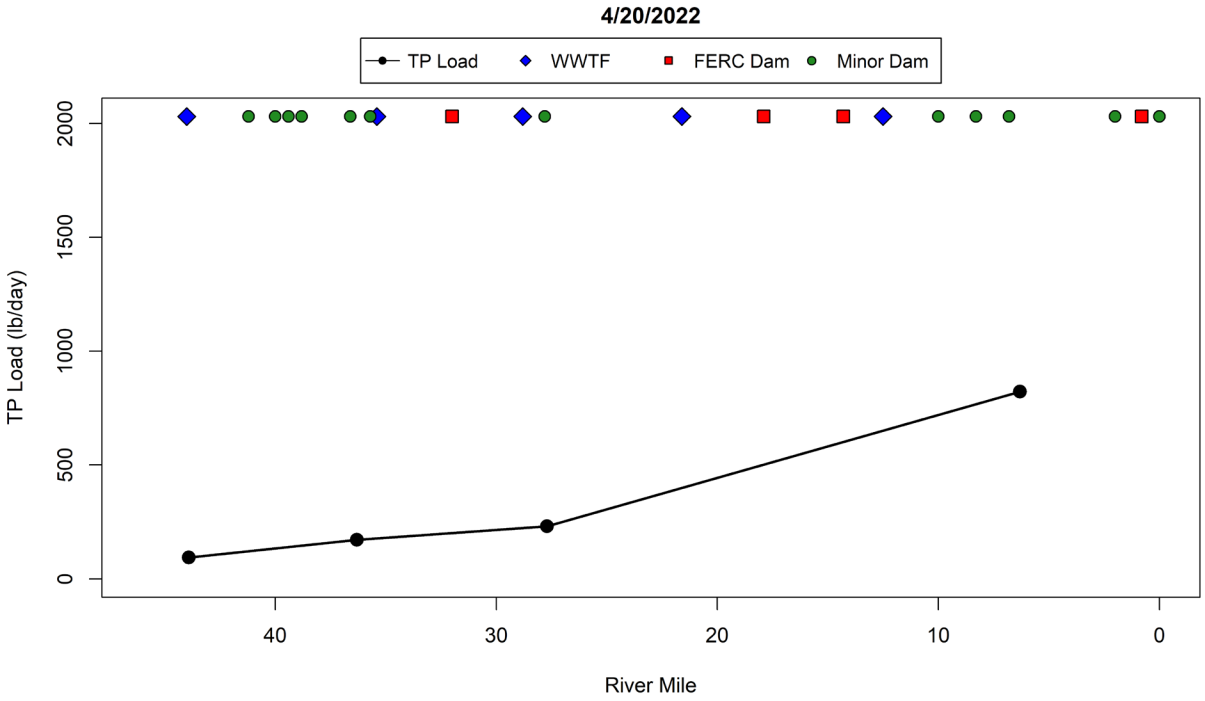


Figure B5: April 2022 along stream load plots (TN, TP)

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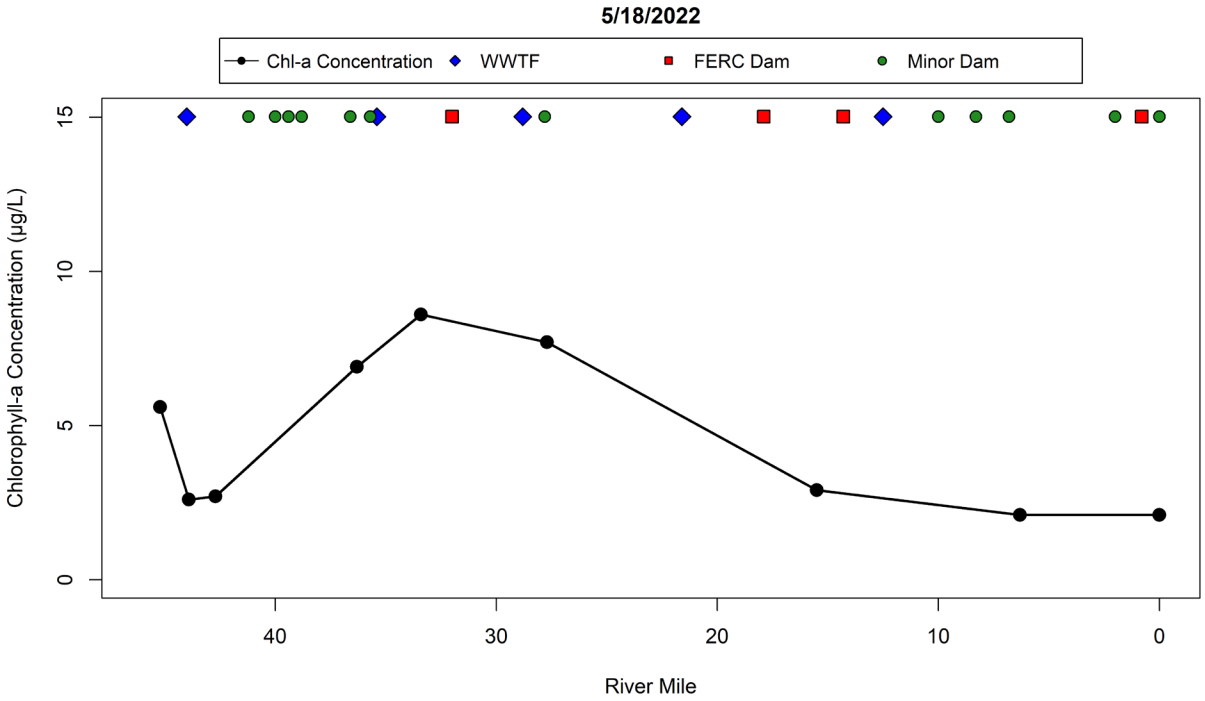

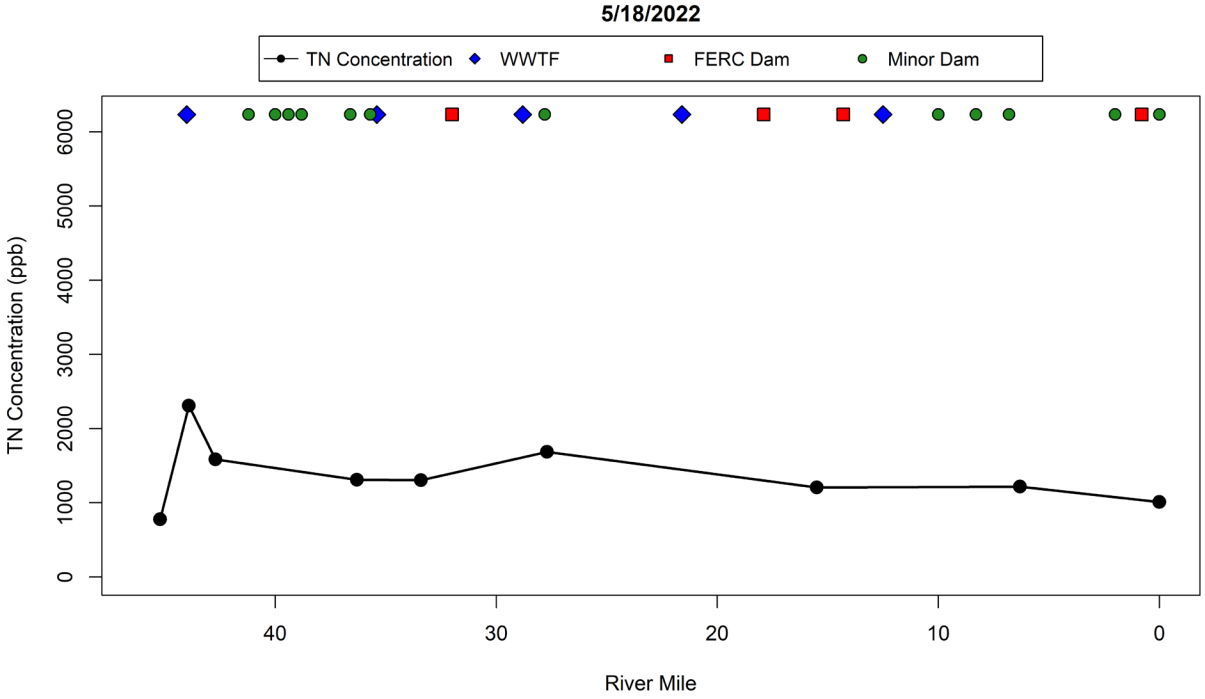

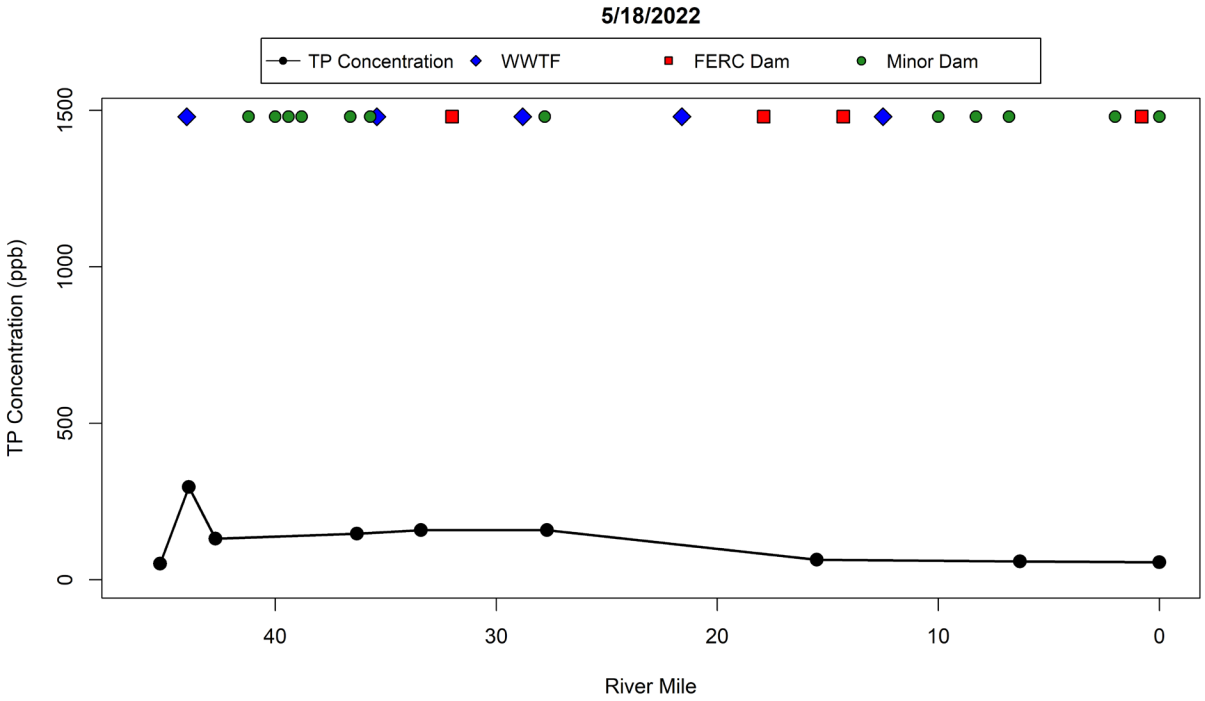

Figure B6: May 2022 along stream concentration (Chl-a, TN, TP, respectively)

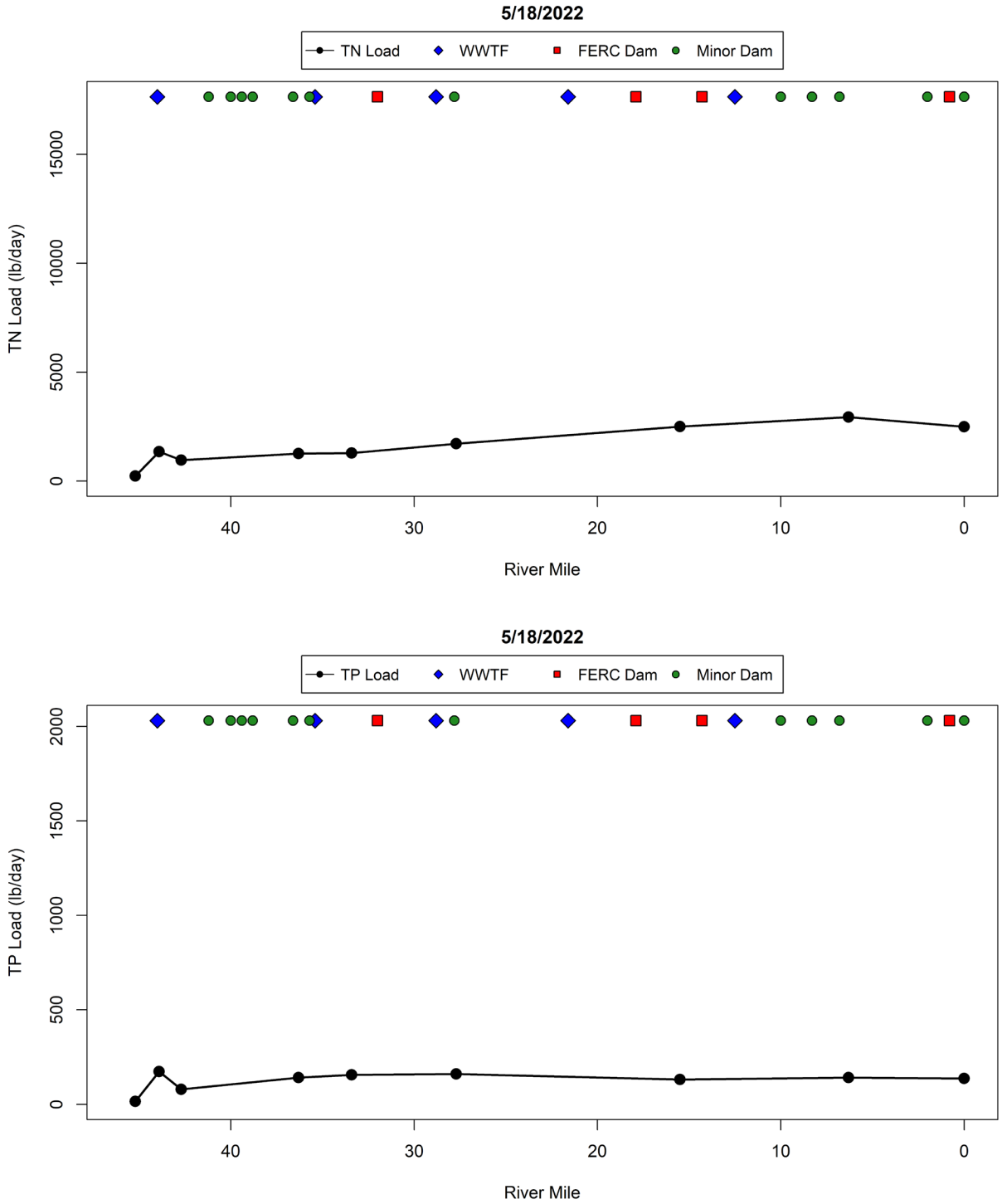

Figure B7: May 2022 along stream load plots (TN, TP)

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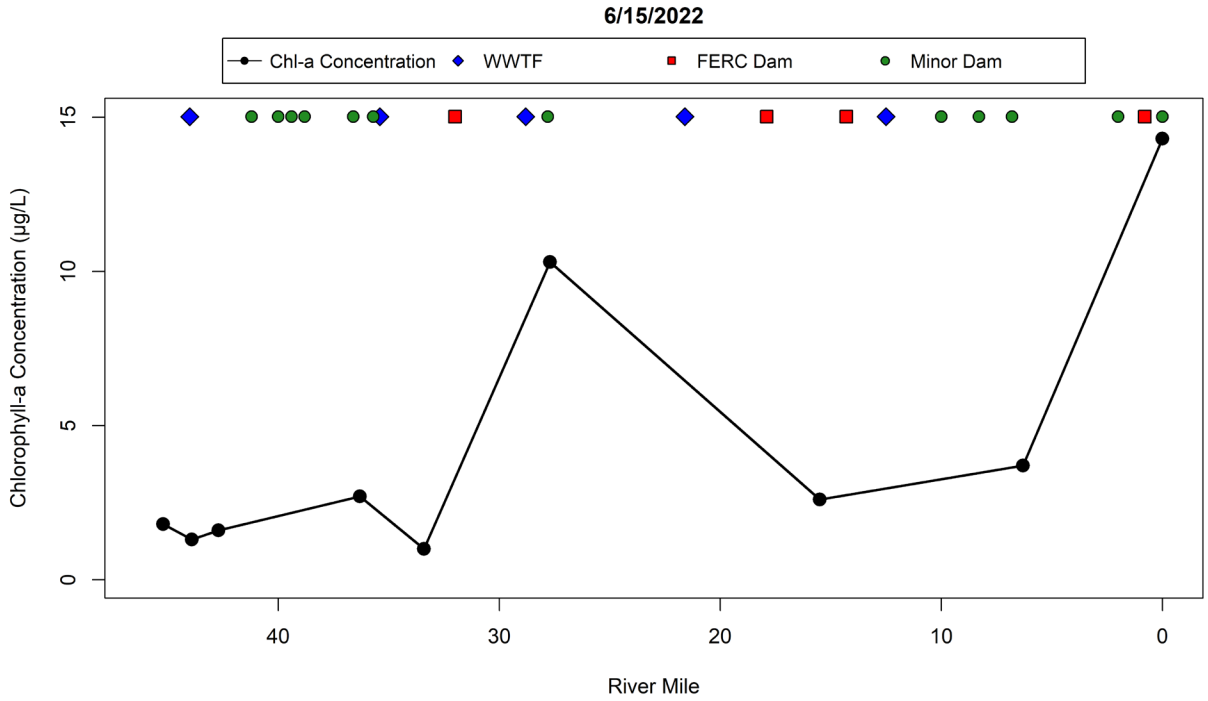
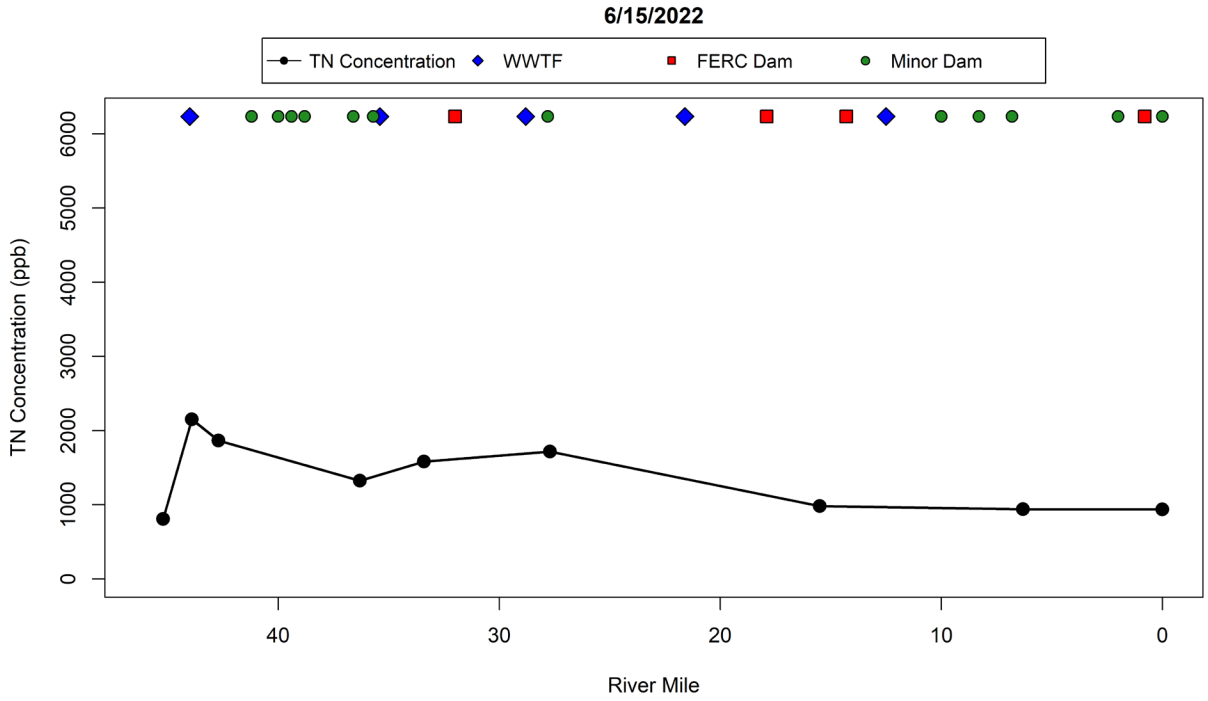




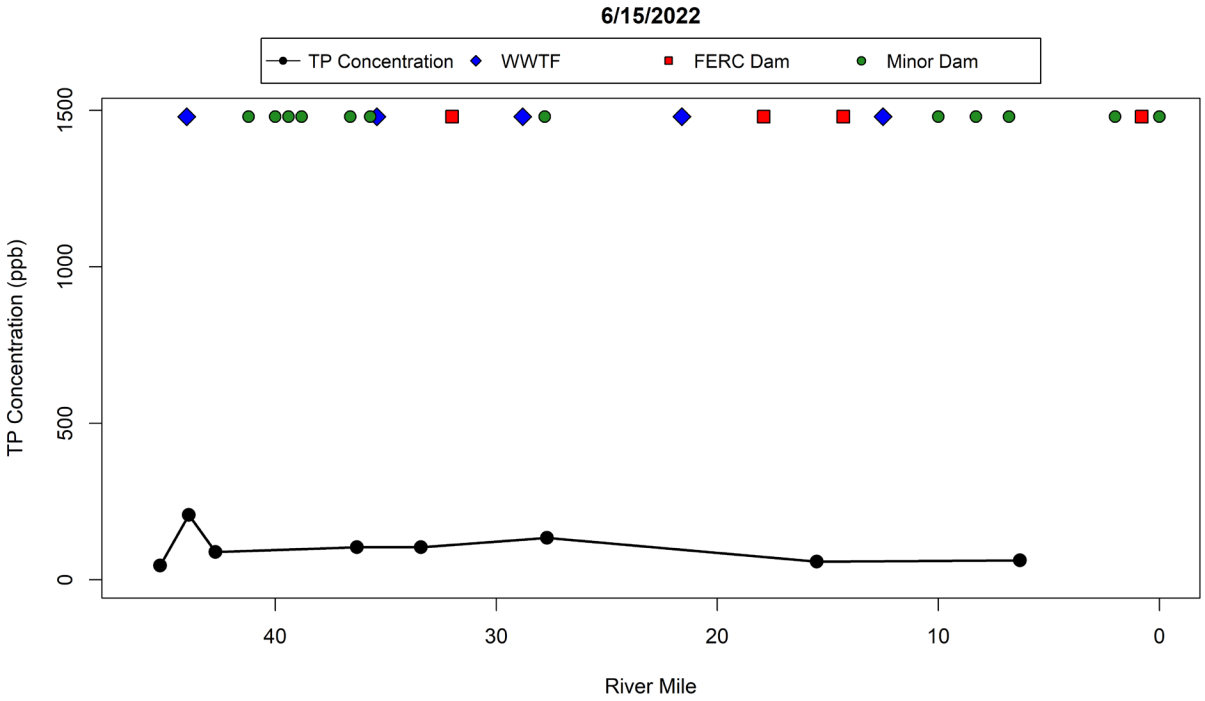
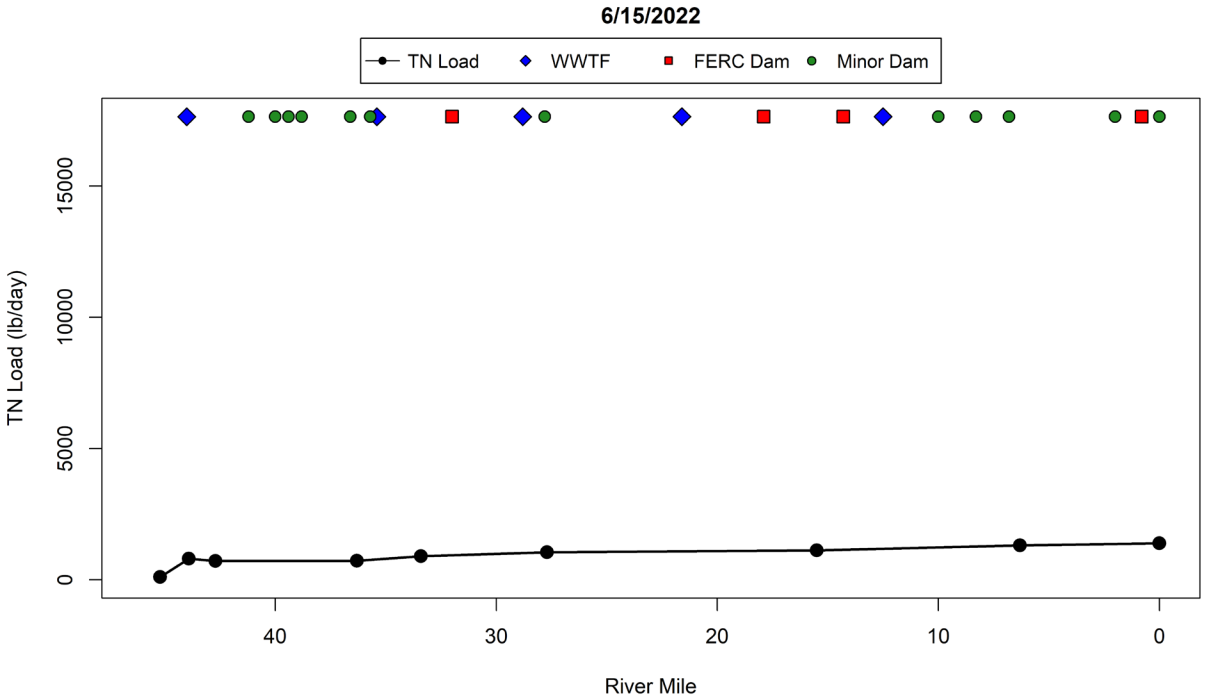


Figure B8: June 2022 along stream concentration (Chl-a, TN, TP, respectively)



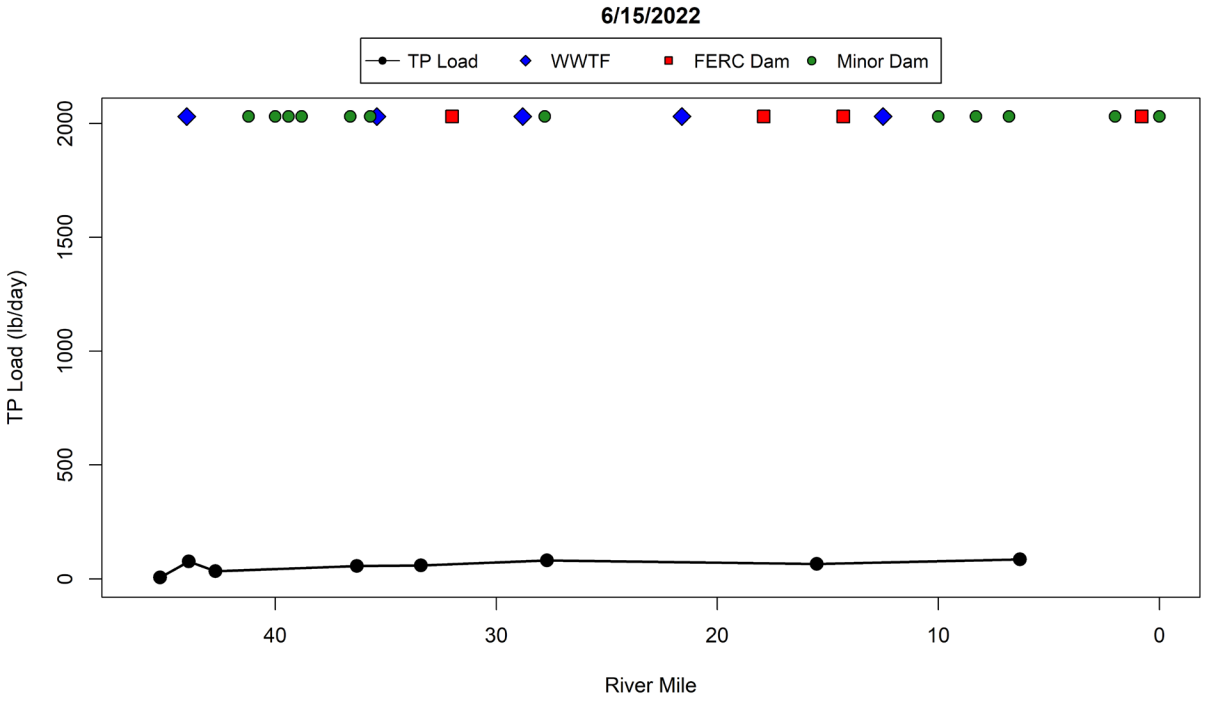


Figure B9: June 2022 along stream load plots (TN, TP)

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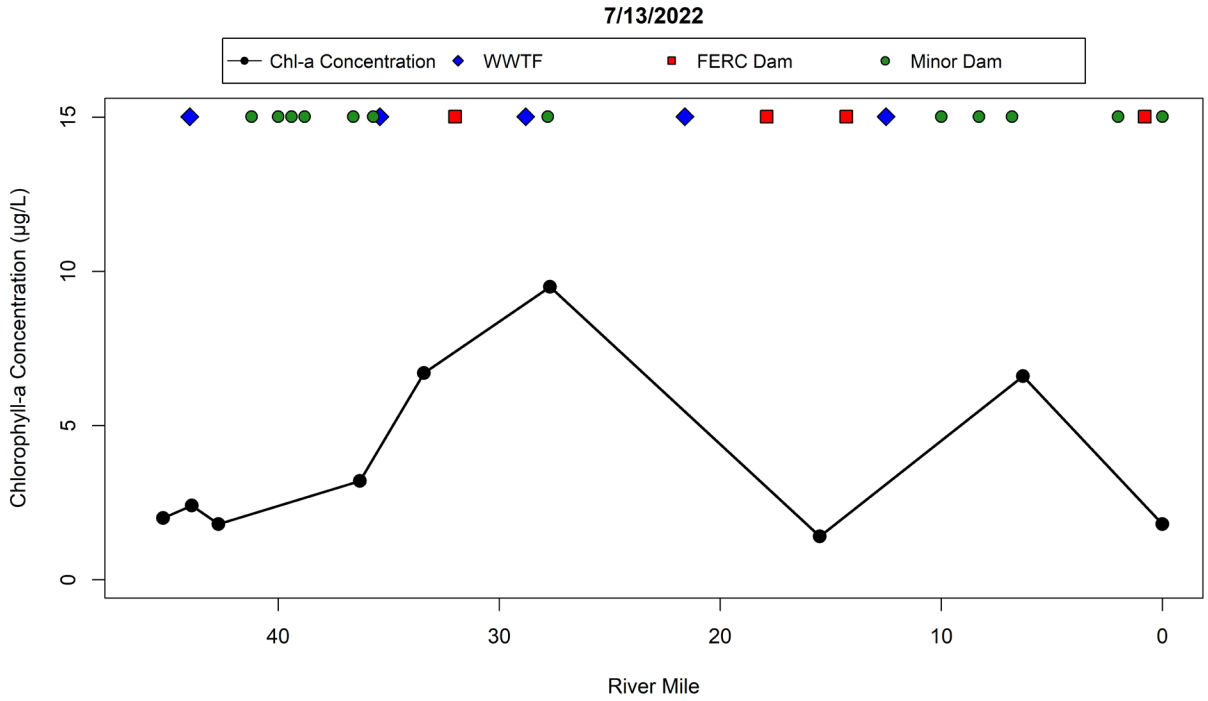
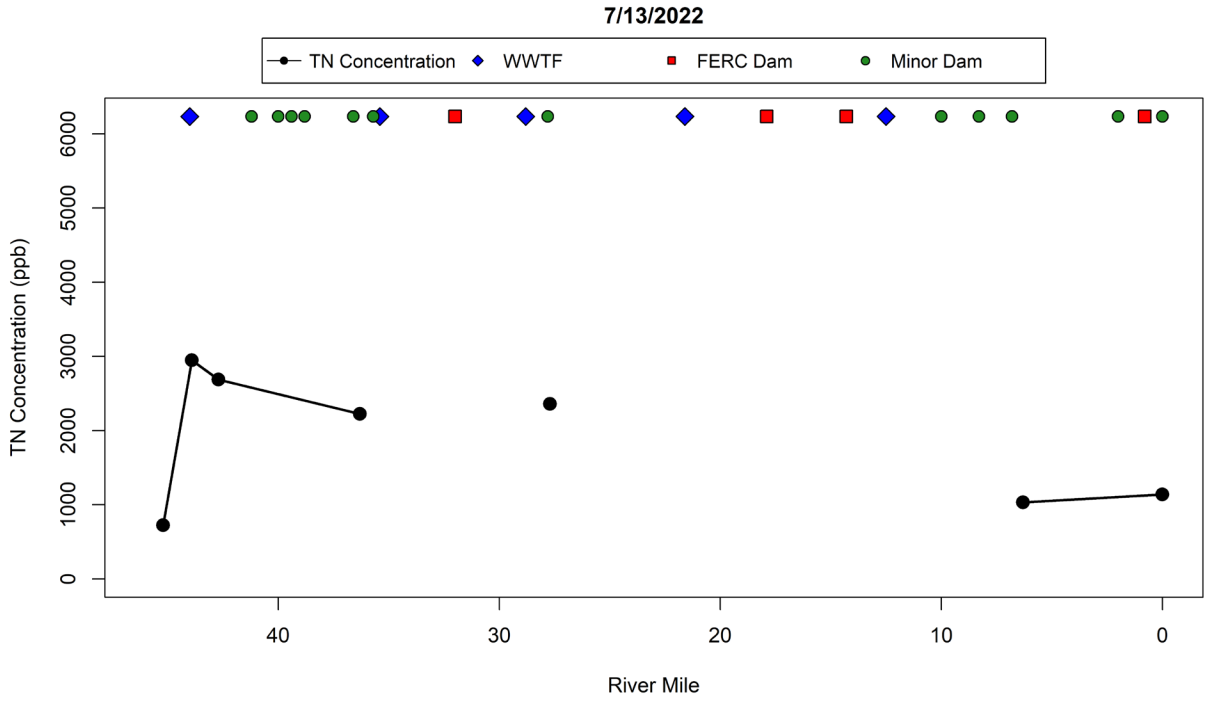




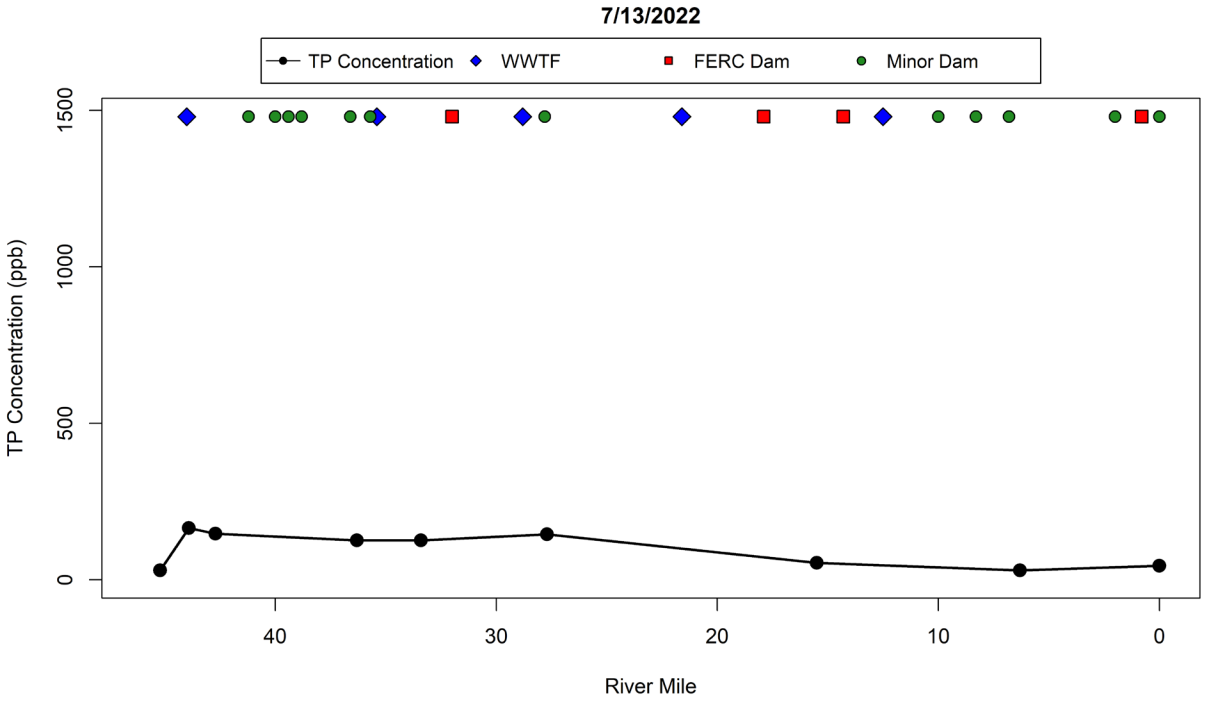
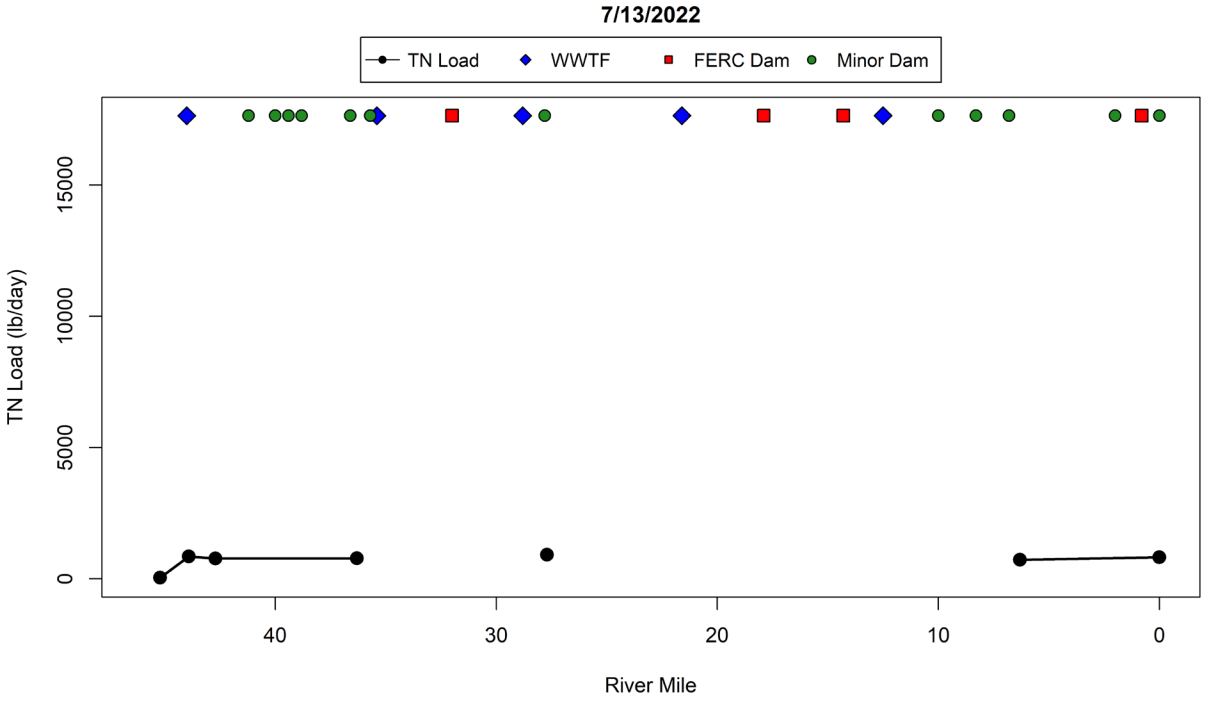


Figure B10: July 2022 along stream concentration (Chl-a, TN, TP, respectively)



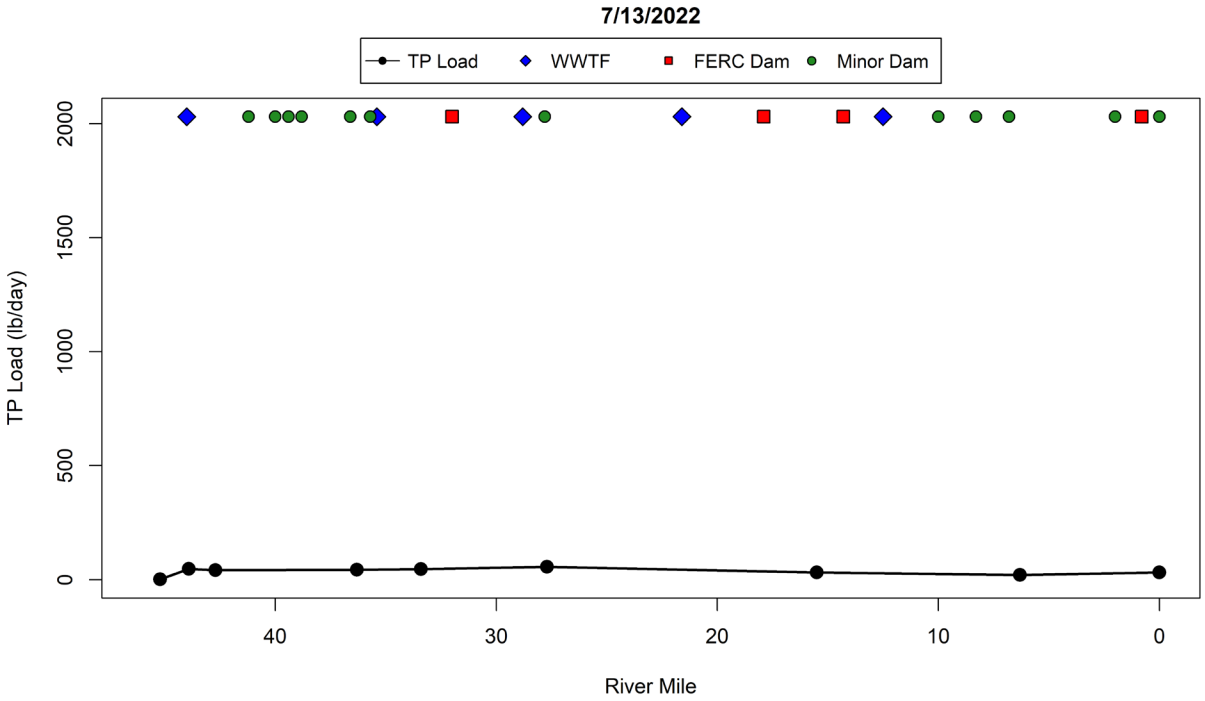


Figure B11: July 2022 along stream load plots (TN, TP)

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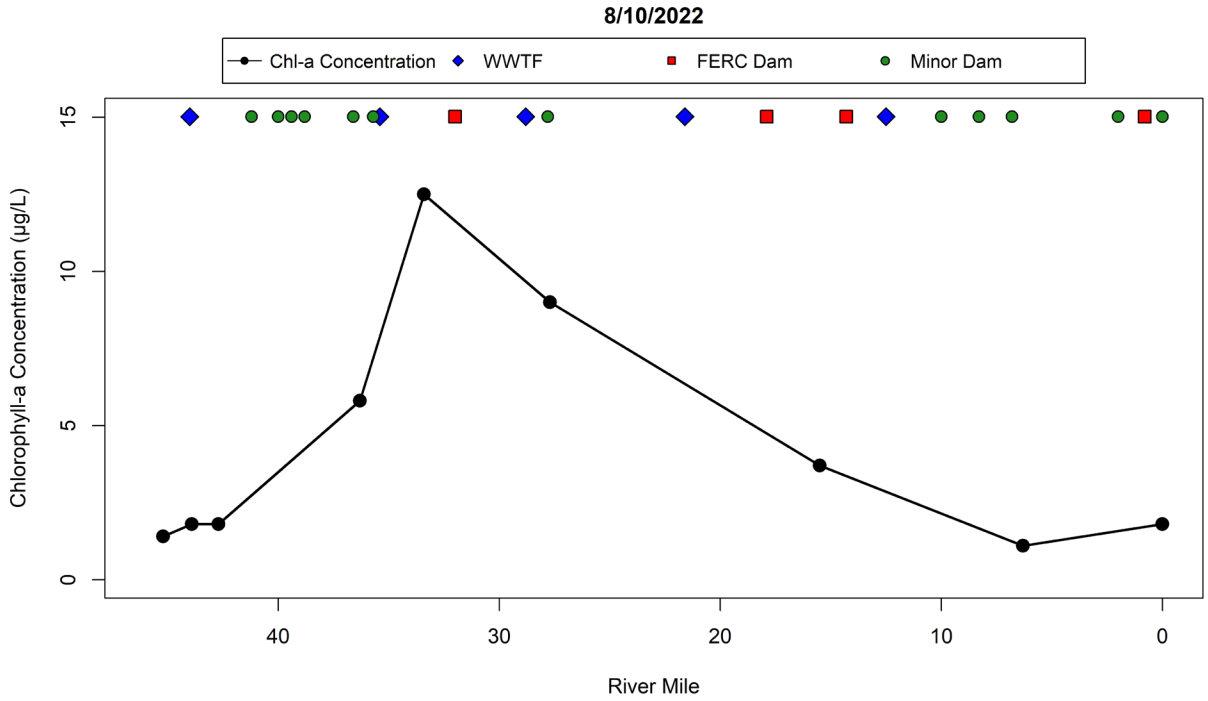
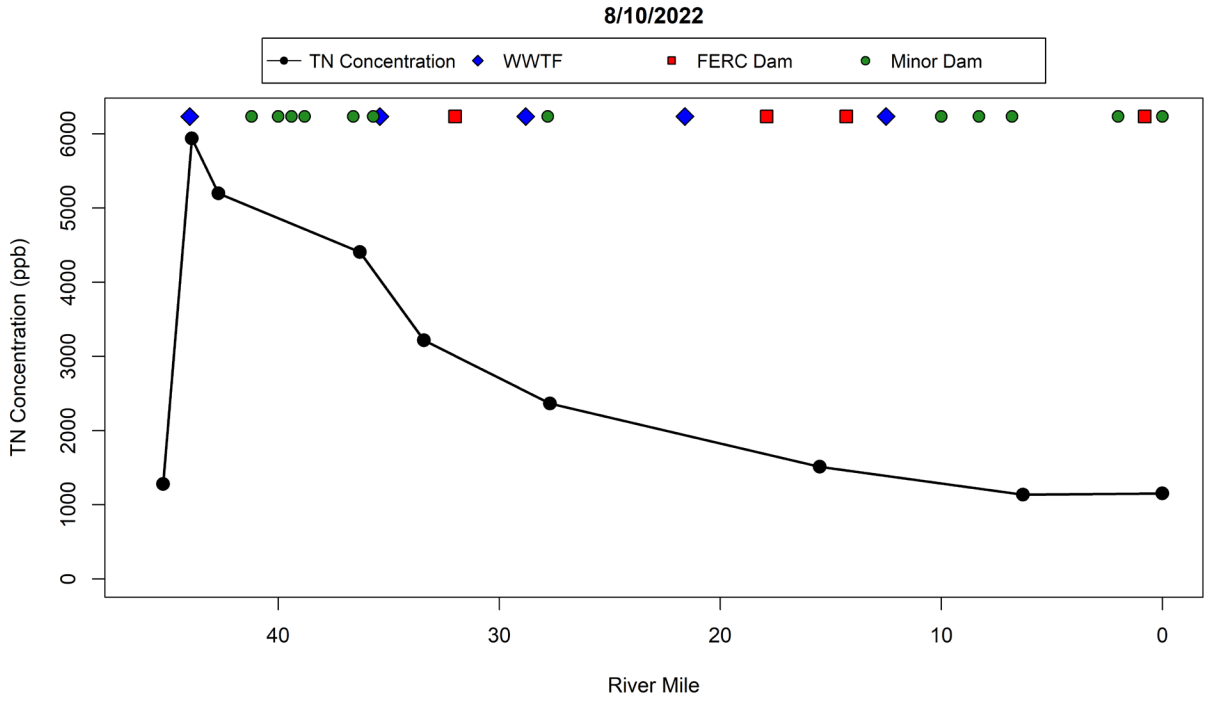




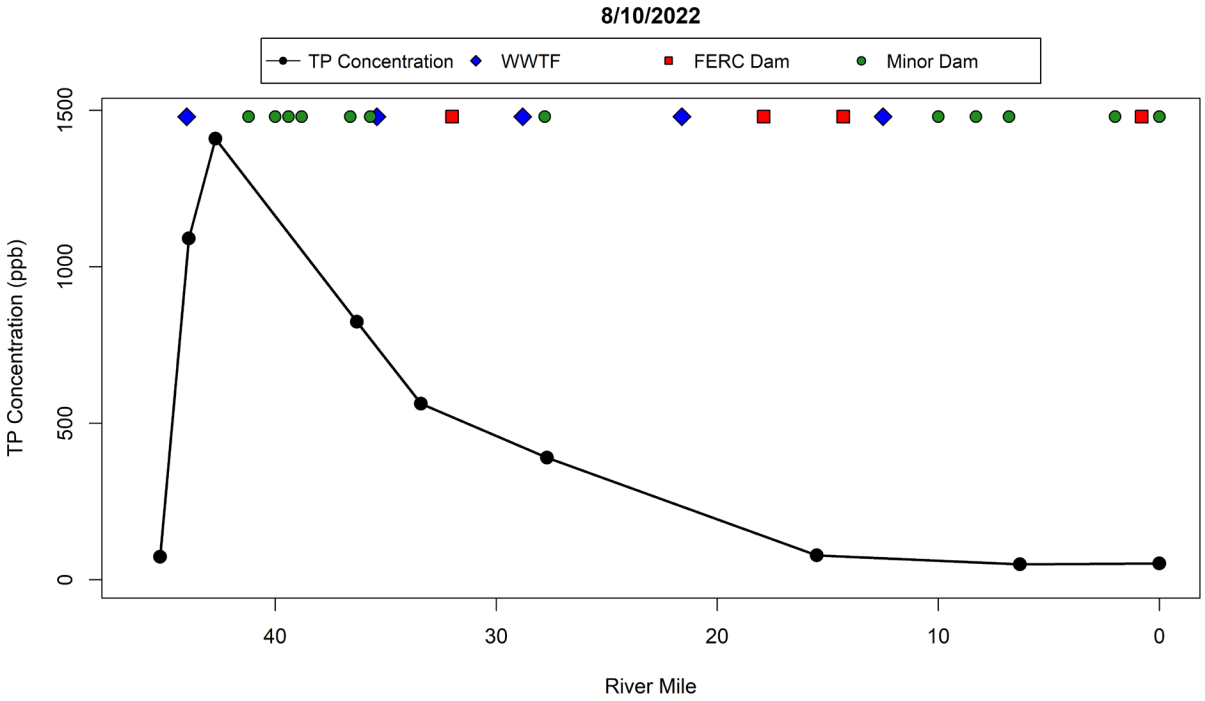
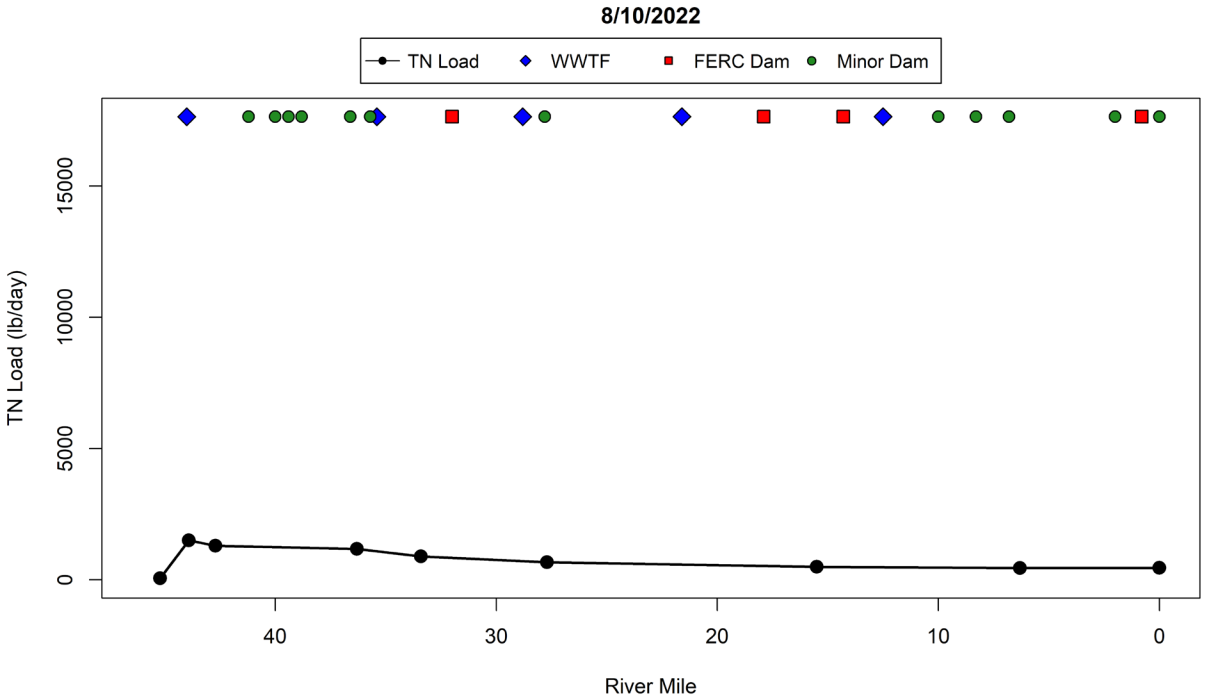


Figure B12: August 2022 along stream concentration (Chl-a, TN, TP, respectively)



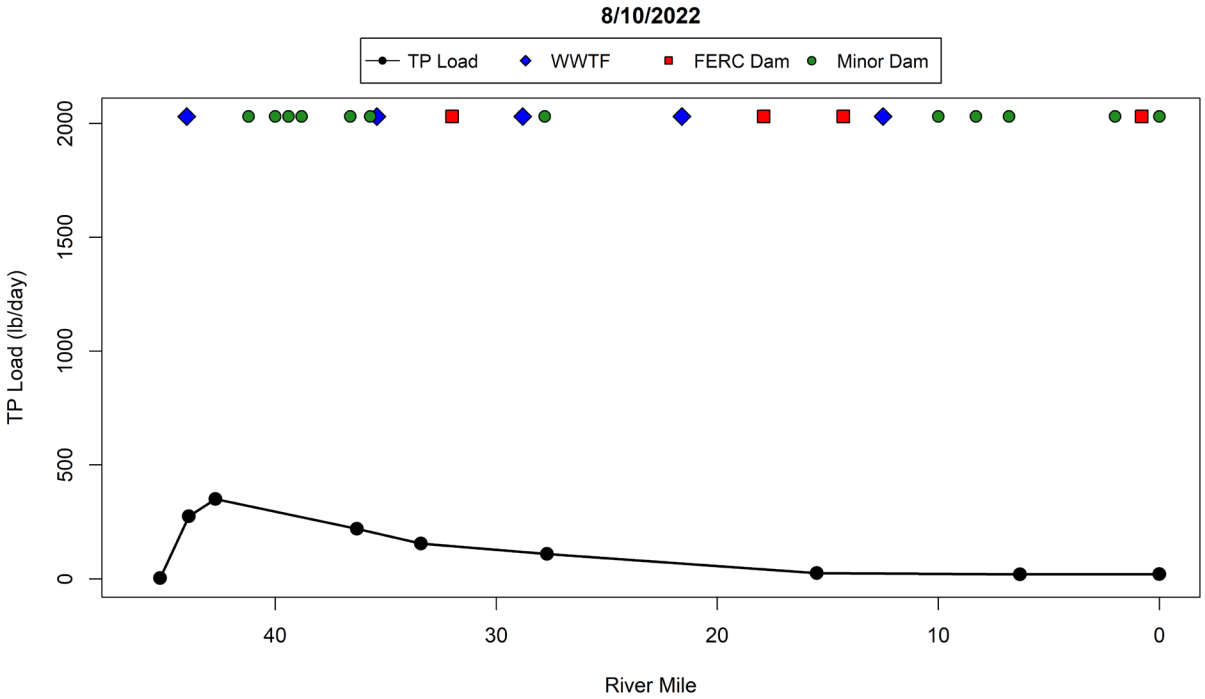


Figure B13: August 2022 along stream load plots (TN, TP)

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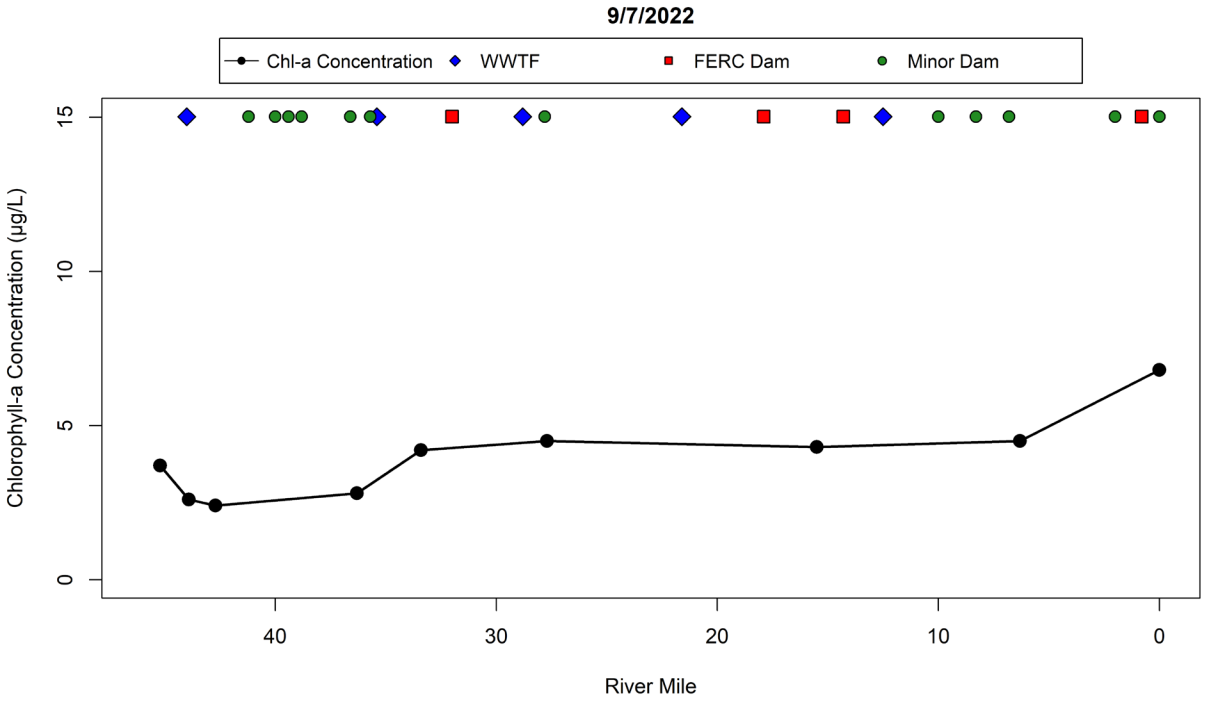
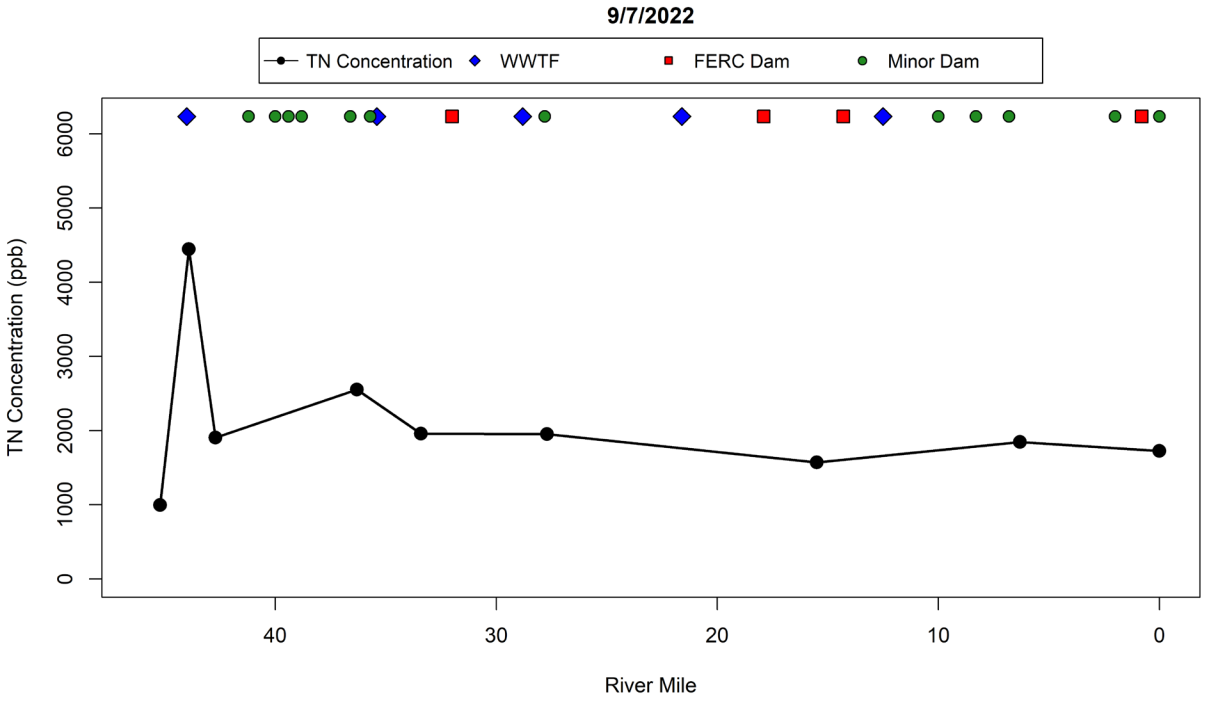




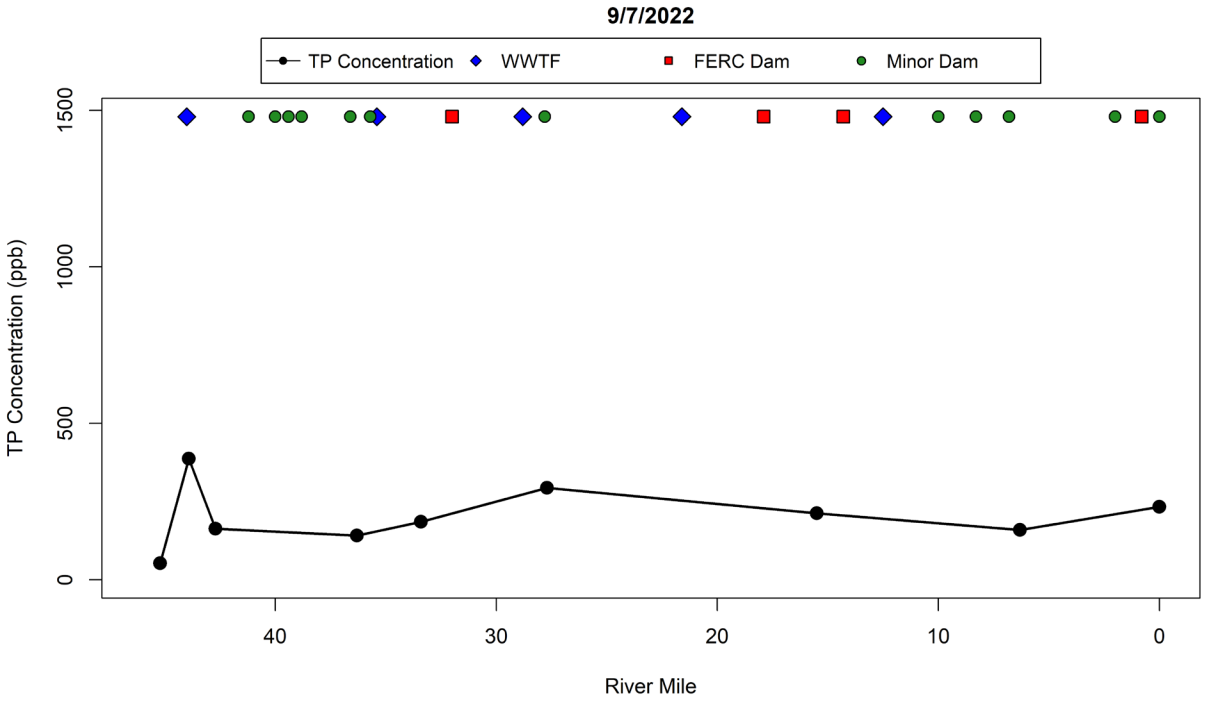
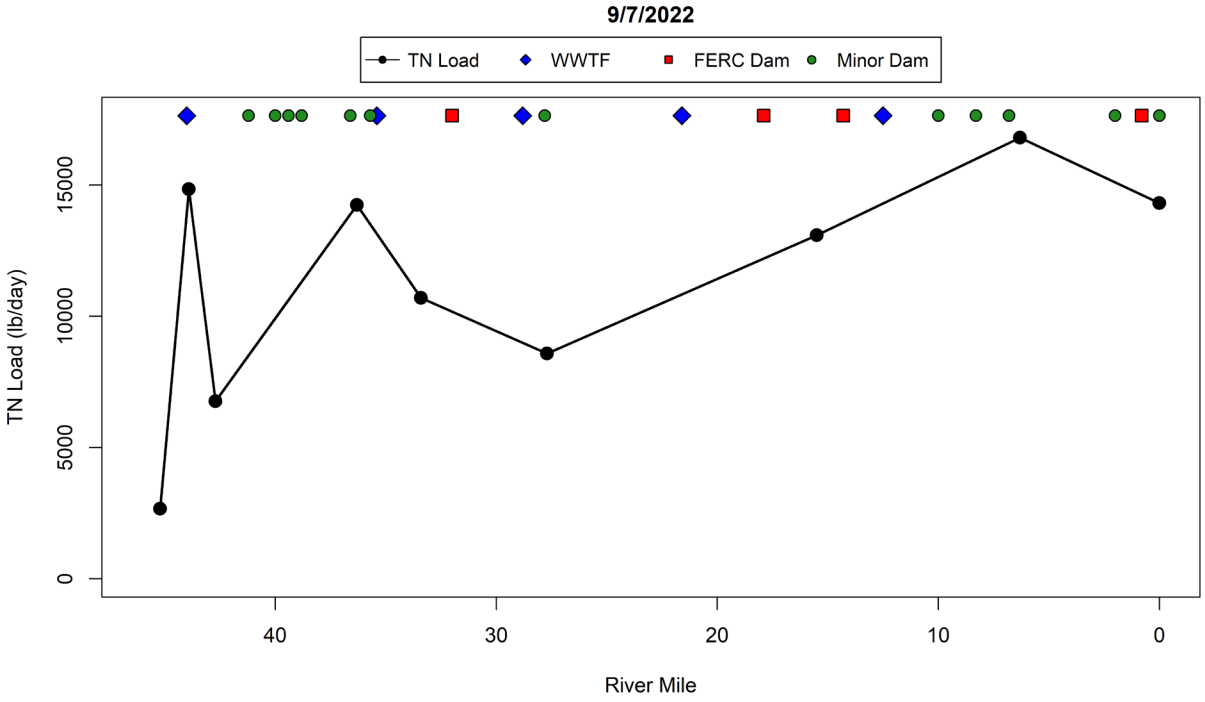


Figure B14: September 2022 along stream concentration (Chl-a, TN, TP, respectively)



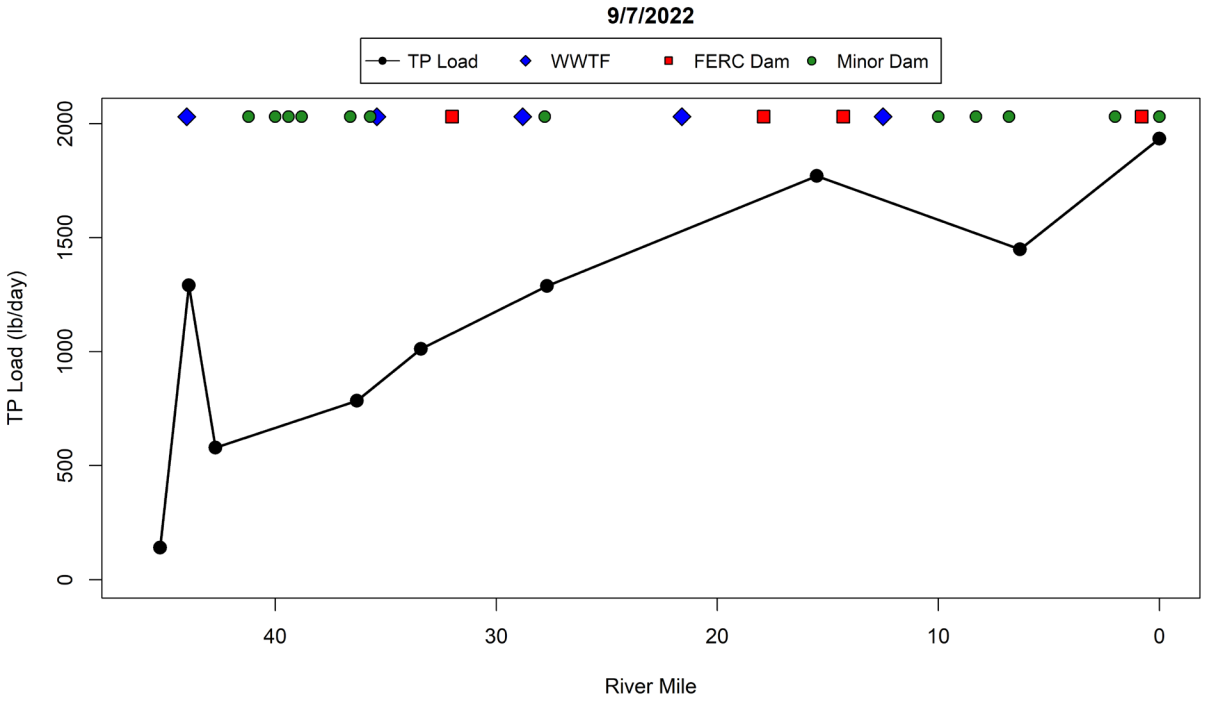
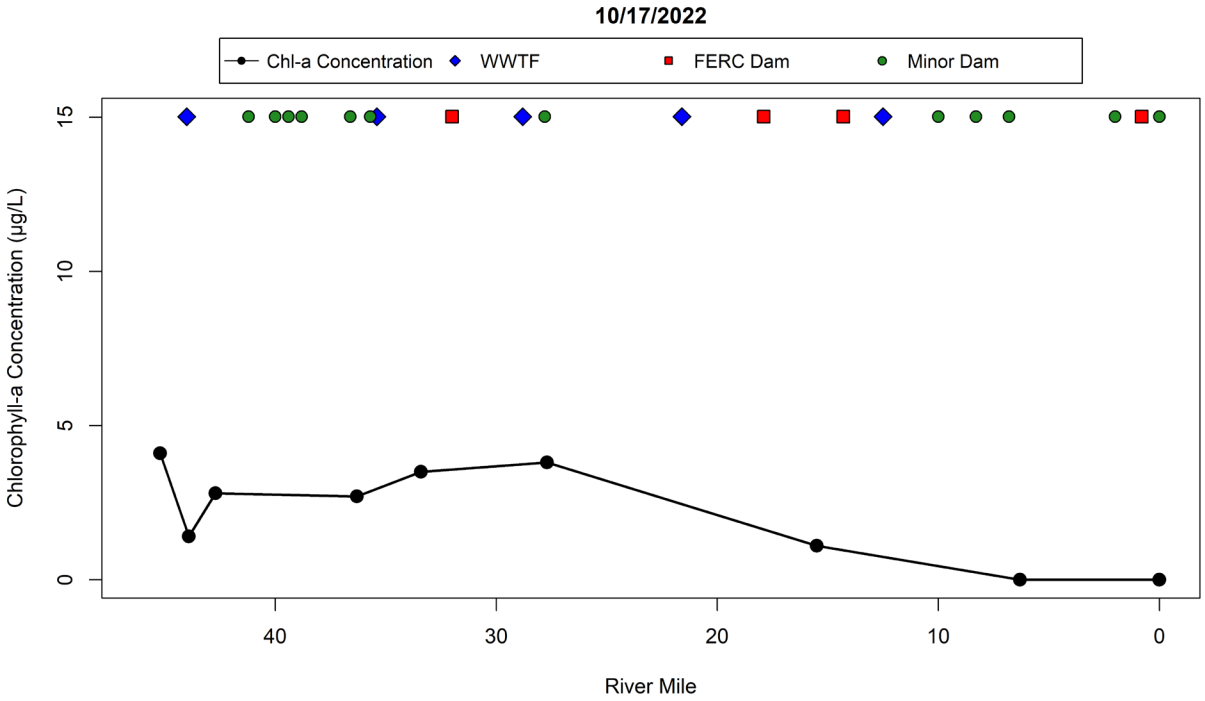


Figure B15: September 2022 along stream load plots (TN, TP)



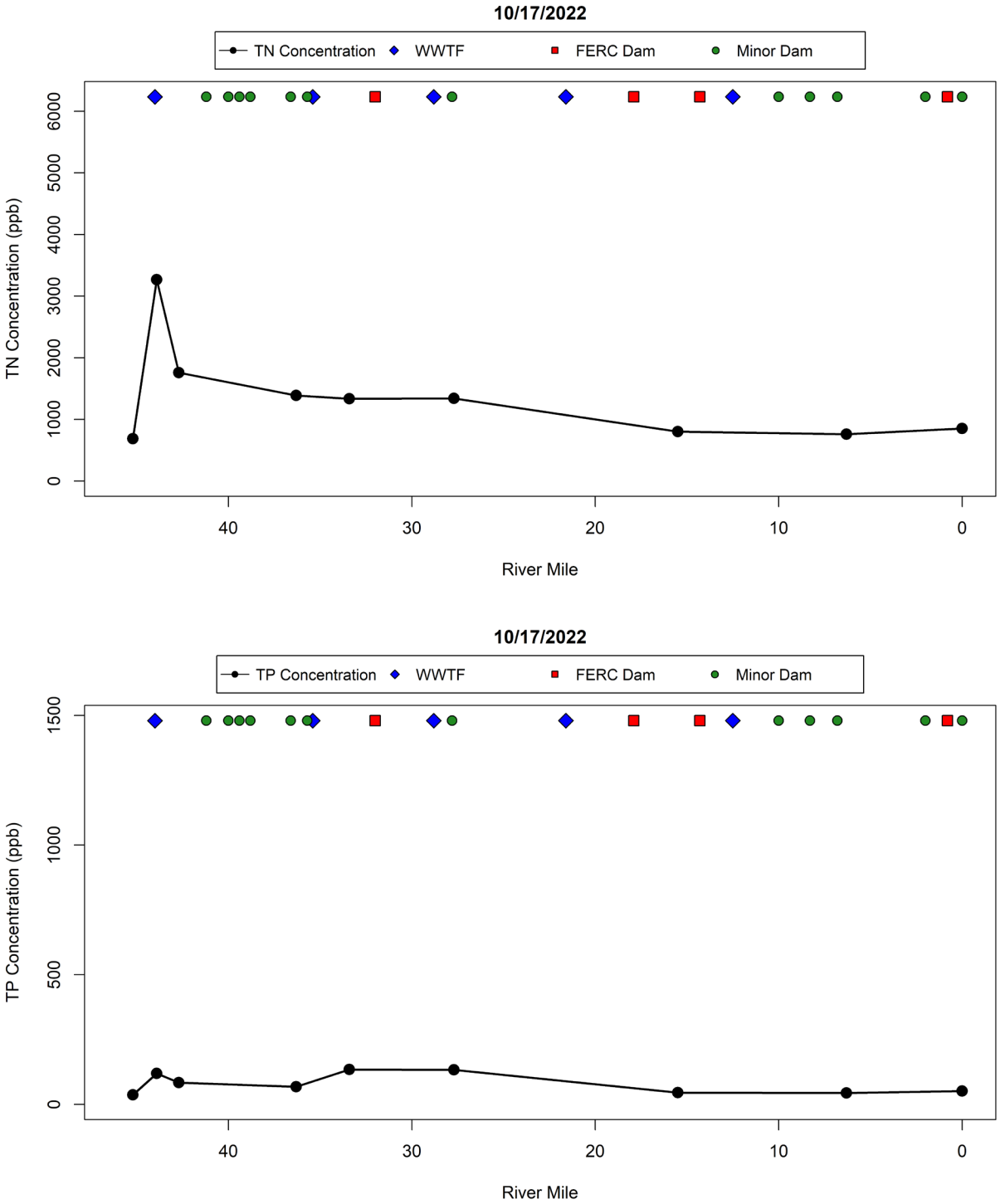
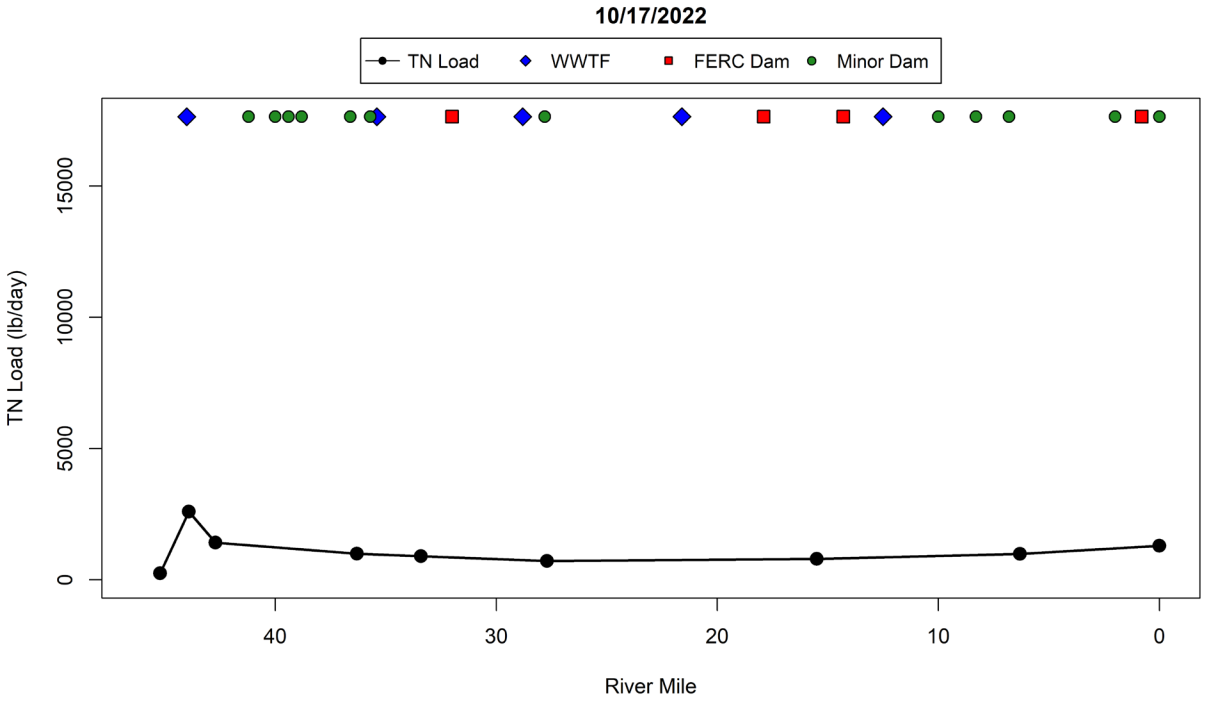


Figure B16: October 2022 along stream concentration (Chl-a, TN, TP, respectively)



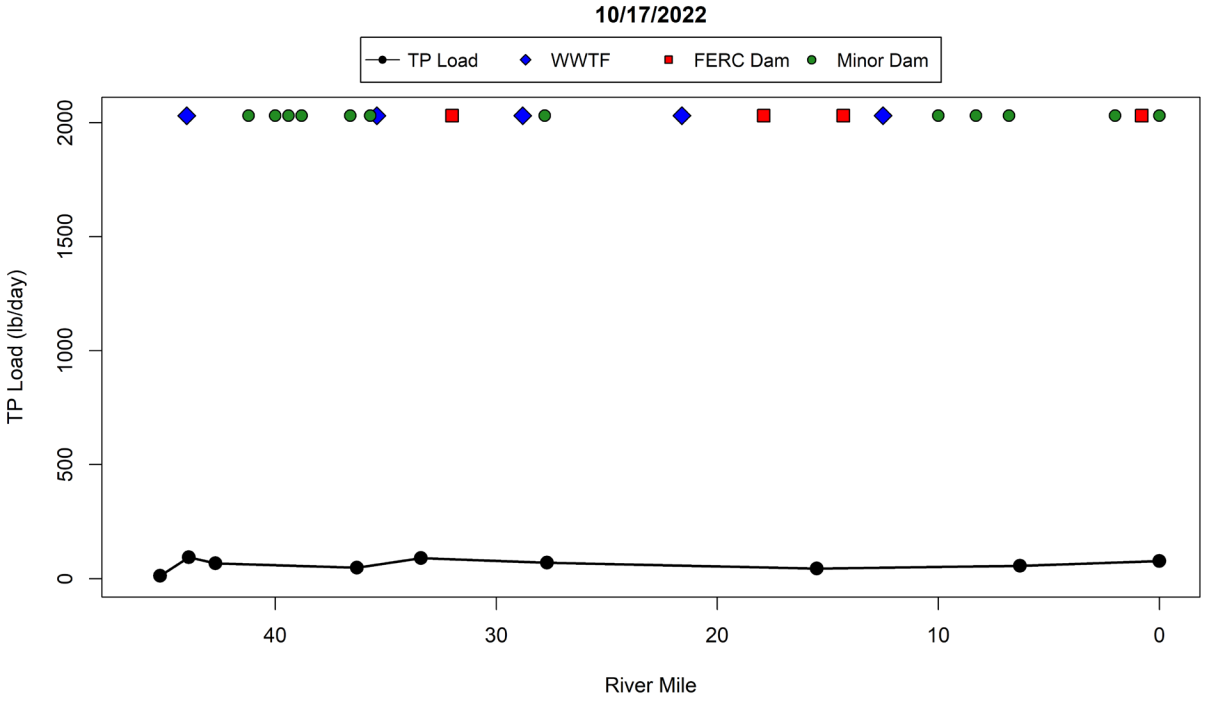


Figure B17: October 2022 along stream load plots (TN, TP)

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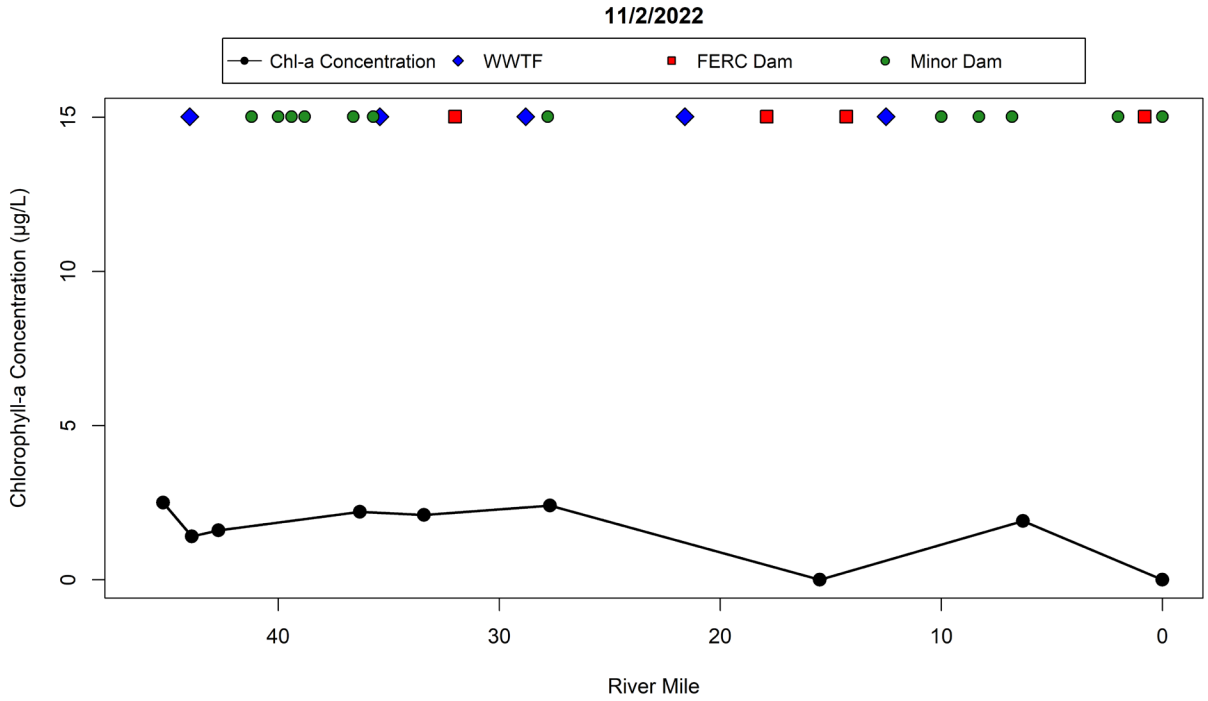
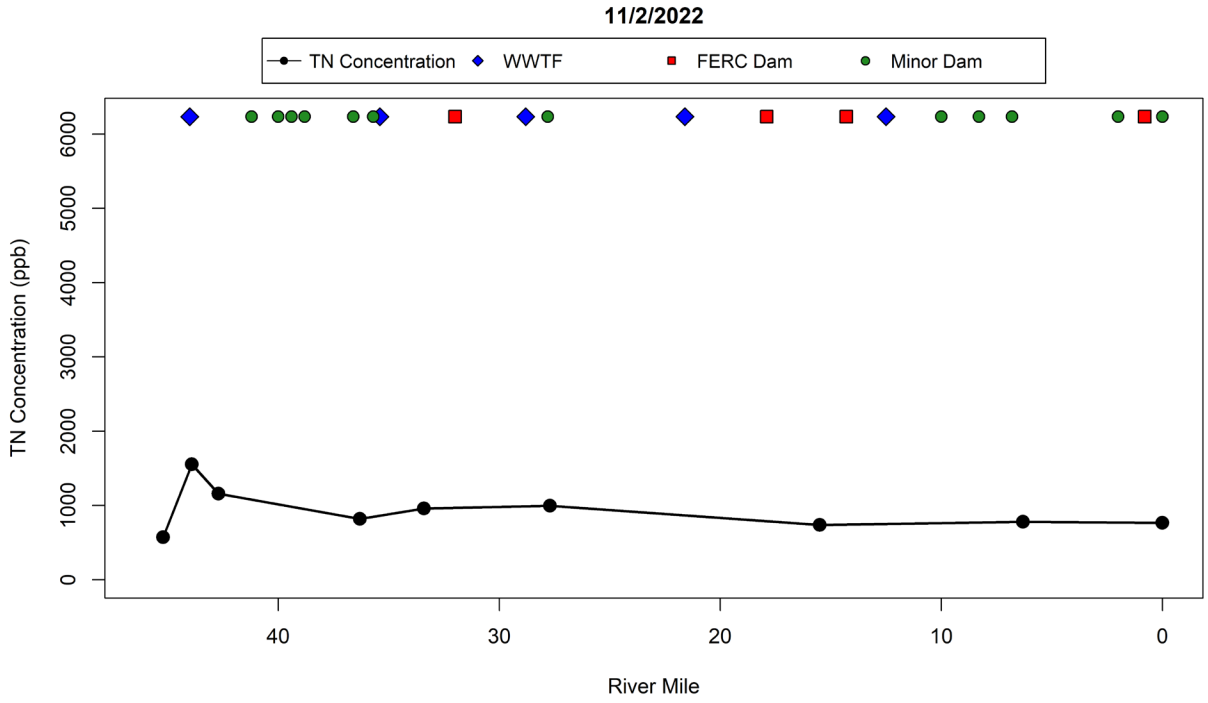




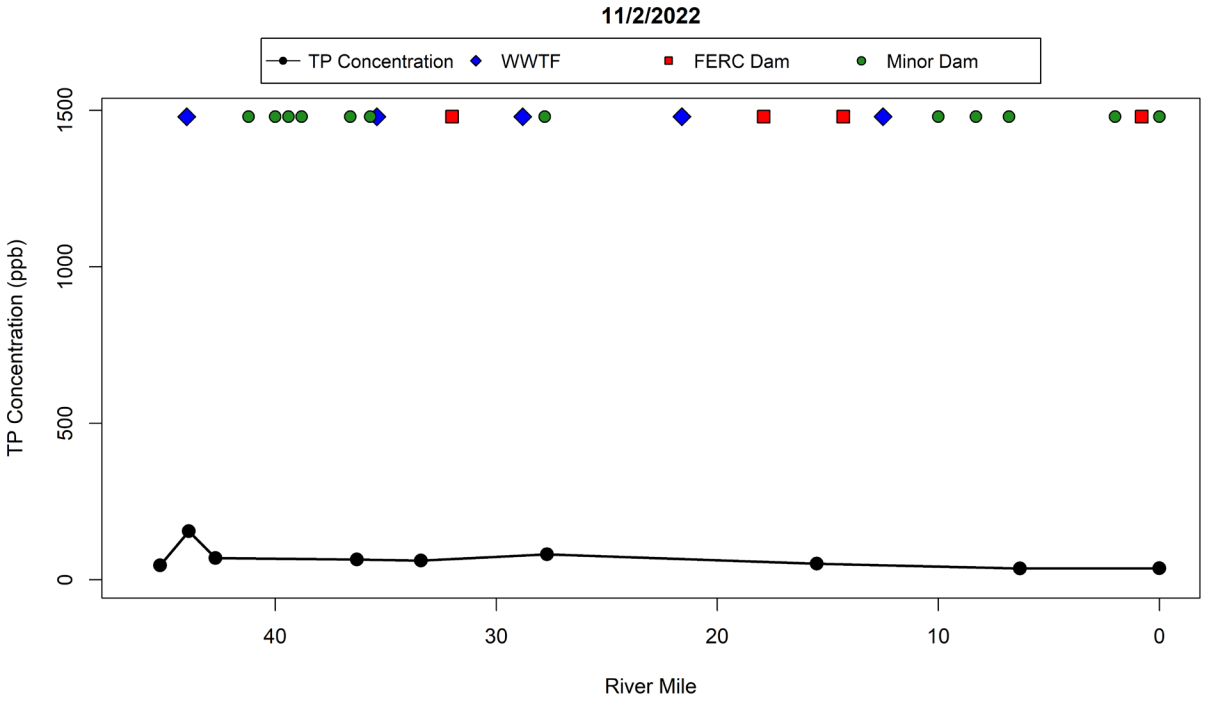
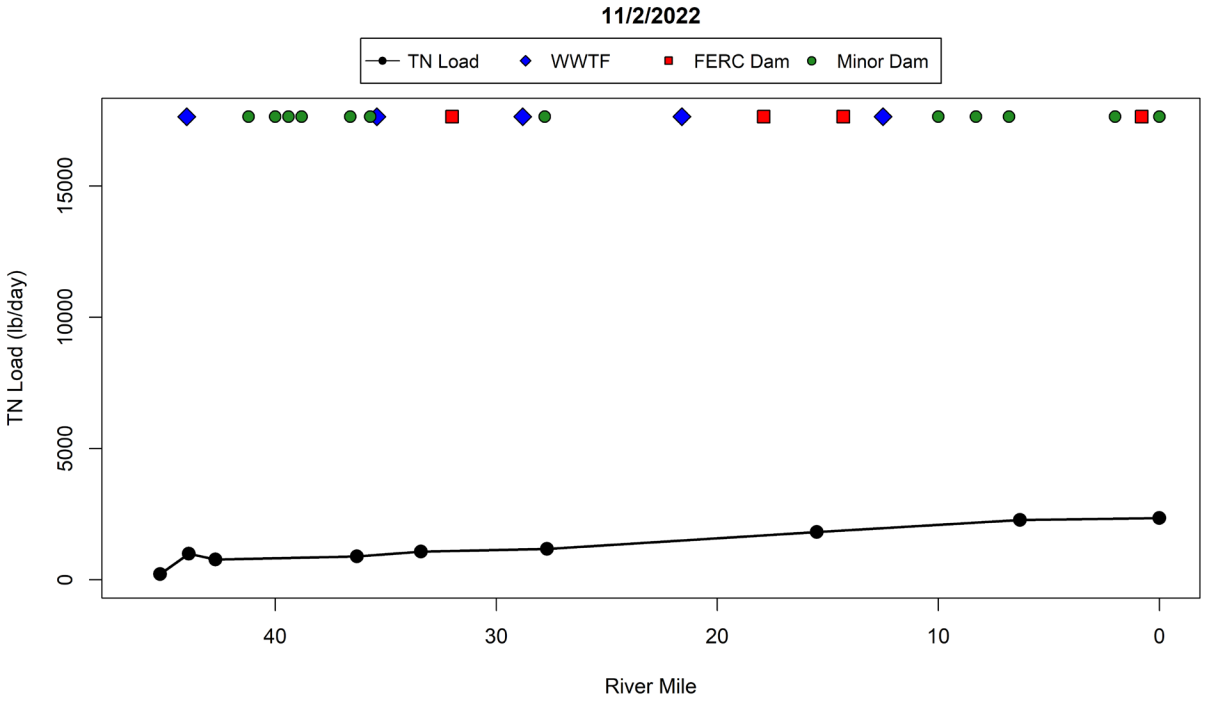


Figure B18: November 2022 along stream concentration (Chl-a TN, TP, respectively)



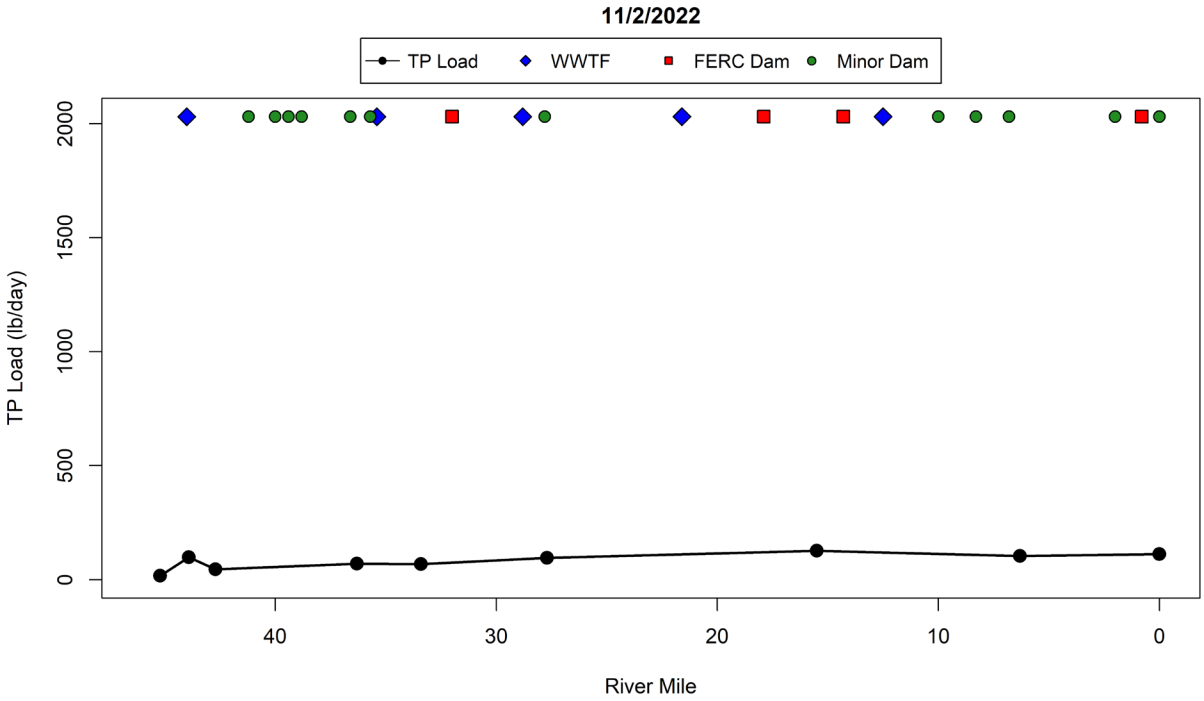


Figure B19: November 2022 along stream load plots (TN, TP)

Appendix C: In-Situ Temperature and Dissolved Oxygen Monitoring: Blackstone River, July – November 2022

In Situ Temperature and Dissolved Oxygen Monitoring: Blackstone River July through November 2022

August 2023

CDM Smith

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In Situ Temperature and Dissolved Oxygen Monitoring: Blackstone River, July – November 2022

1.0 Introduction

Upper Blackstone Clean Water (Upper Blackstone) deployed, managed, and monitored four Onset HOBO U26-001 continuous temperature (T) and dissolved oxygen (DO) data loggers for four months (July through October 2022). In 2022, two new logger sites were selected in consultation with MassDEP to investigate changes in water quality between Central Cemetery (W1258) and Depot Street (MID2). The meters were calibrated and deployed at four locations: one near the Waters Street bridge (Central Cemetery / W1258), one immediately upstream of Riverlin Street bridge, one at the former Millbury Wastewater Treatment Plant (WWTP), and one near the Depot Street bridge (**Figure 1**). The meters were deployed downstream of the Upper Blackstone effluent discharge and were located in MassDEP Assessment Unit MA51-03 (MassDEP establishes river segments, known as Assessment Units (AUs), for Clean Water Act reporting purposes).

Details on the meter locations and 2022 deployment periods are presented in **Table 1**. In the middle of the 2022 program the continuous meters started to malfunction and were pulled from the river in late August for maintenance. Upon consultation with the meter vendor, two of the meters were replaced by the vendor and the meters were redeployed in the river in late September. Thus, the 2022 monitoring program has less DO data than were recorded in previous years.

CDM Smith reviewed the data from the 2022 continuous metering program, corrected the T and DO data using United States Geological Survey (USGS) guidance (Wagner et al., 2006) based on periodic in situ measurements taken with a handheld probe, and compared the corrected data to Massachusetts' surface water quality criteria and guidance for dissolved oxygen.

Table 1: Blackstone River Continuous Logger Locations in 2022

Meter	Location	River Mile[1]	Deployment History[3]
W1258	Central Cemetery, Millbury	42.7	▪ Deployed: 7/1 (ID: 479) ▪ Removed for maintenance: 8/23 ▪ Redeployed: 9/20 (ID: 477)
Riverlin Street	Riverlin Street, Millbury	42.1	▪ Deployed: 7/6 (ID: 480)[2] ▪ Removed for maintenance: 8/23 ▪ Deployed new meter: 9/29 (ID: 852)
Millbury WWTP	Former Millbury WWTP, Millbury	40.8	▪ Deployed: 7/15 (ID: 478) ▪ Removed for maintenance: 8/23 ▪ Redeployed: 9/20 (ID: 480)
Depot	Depot Street, Sutton	38.0	▪ Deployed: 7/16 (ID: 477) ▪ Removed for maintenance: 8/23 ▪ Deployed new meter: 9/29 (ID: 851)

[1]Notes: River Mile 0 is located at the Slater Mill Dam in Pawtucket, Rhode Island.
[2]Housing was moved and flipped over on 7/15
[3]All loggers removed for the season on 11/8

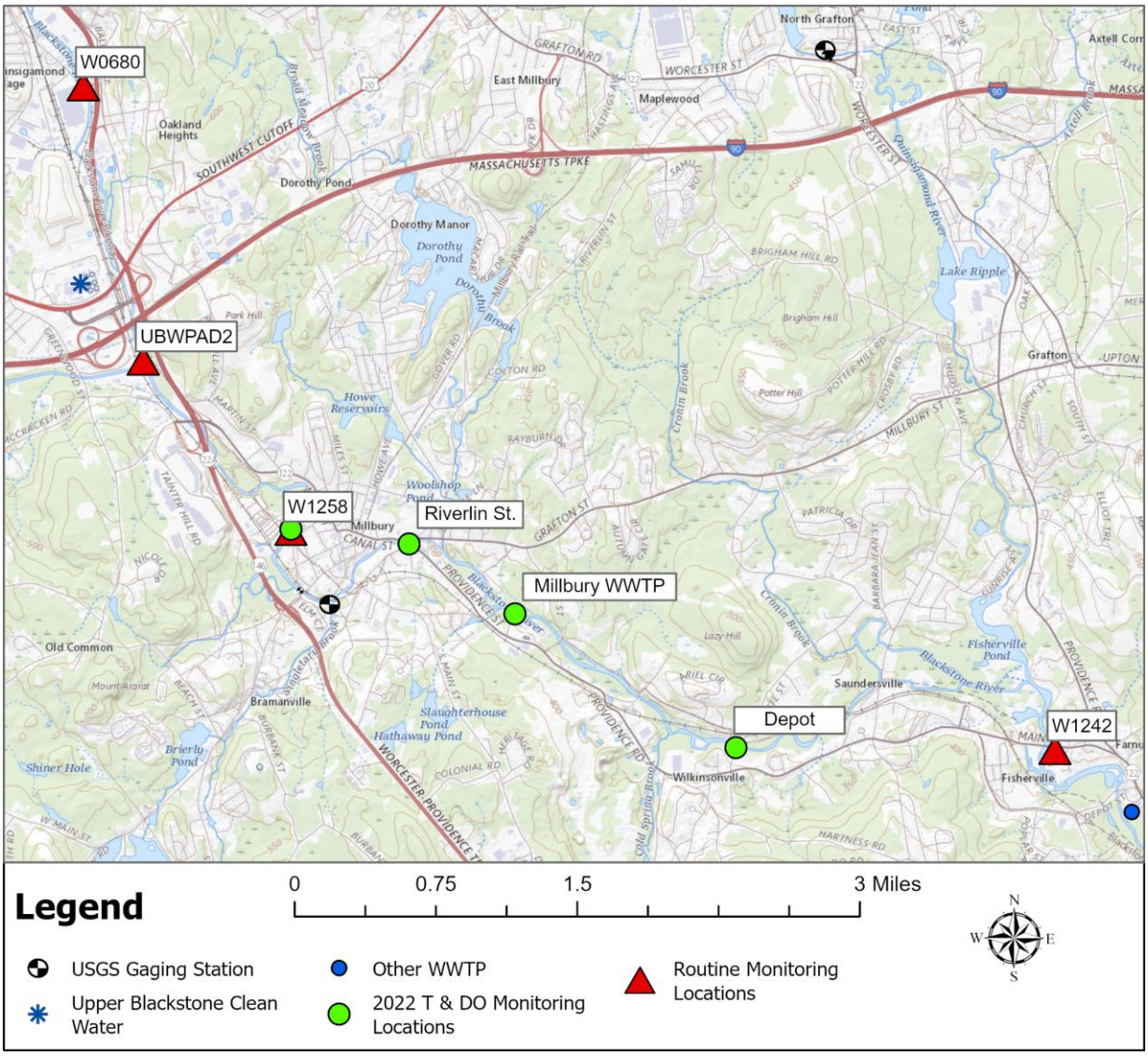


Figure 1: Upper Blackstone Sampling Locations: 2022 Continuous Dissolved Oxygen Meters

2.0 Methodology

The 2022 continuous metering program data collection and analysis were completed following the Data Quality Objectives in the 2020–2022 Quality Assurance Project Plan (QAPP) (Massachusetts Water Resources Research Center, 2020), which references the procedures described in the USGS guidance document *Guidelines and Standard Procedures for Continuous Water-Quality Monitors: Station Operation, Record Computation, and Data Reporting* (Wagner et al., 2006). This section describes the instrumentation, field procedures, and data correction procedures used in this study.

2.1 Instrumentation and Field Maintenance Procedures

Prior to deployment, the four Onset HOBO U26-001 continuous T/DO data loggers were calibrated in the Upper Blackstone water quality laboratory. Each logger was then placed in the river in a PVC pipe housing developed in consultation with MassDEP (**Figure 2**).

Long-term monitoring can be impacted by sensor calibration drift and biofouling (e.g., by growth of algae on the instrument tip). Routine site visits are required to check instrument calibration, clean the sensor tip due to biofouling, and to collect grab T/DO measurements to use to determine if sensor drift has occurred. Grab measurements were collected using a Hach HQ40D portable multiparameter probe. Routine site visit protocols are described in the QAPP, and the visits are targeted to occur at least biweekly during the monitoring season. The following are completed by field staff during each visit.

1. A grab T/DO measurement is collected with a calibrated handheld instrument adjacent to the continuous logger housing.
2. The logger housing is removed from the water and the instrument removed from the housing. The data are downloaded and the logger tip is cleaned.
3. The logger and housing are reassembled and returned to the water. A second grab T/DO measurement is collected with the handheld meter.

Figure 2: Dissolved Oxygen Logger Housing and Cinder Block Anchor

2.2 Data Correction Procedure

The procedure used to correct the DO data collected in this study was performed in two steps following the QAPP and USGS guidance:

- Deployment periods when the logger was malfunctioning physically were removed from the record; these periods are described in **Section 3.**

- The USGS procedures were used to evaluate the remaining data for validity. Data exceeding the maximum limits for correction were removed from the final, corrected dataset, following the procedures in the QAPP.

Valid data were corrected for drift when the deviation between the continuous monitoring data and the calibration points differed by +/- 0.3 mg/L or 5 percent (whichever was greater). Correction was done using a two-point linear algorithm, assuming that the rate of drift is constant between calibration sample points. The percentage error at each calibration point was calculated as follows:

$$\%C_d = 100\left(\frac{V_s - V_c}{V_c}\right)$$

where V_s is the value of the DO calibration measurement using the handheld probe, and V_c is the continuous logger reading at the same time. The percentage error was linearly interpolated between the two grab measurements.

Data accuracy was assessed using the classifications listed in **Table 2**. For DO, a classification is assigned based on the larger of the concentration or percentage differences (on an absolute value basis) comparing the raw and corrected data.

Table 2: Continuous Logger Accuracy Classifications for Dissolved Oxygen and Temperature[1]

Data Type	Measurement Type	Excellent	Good	Fair	Poor	Maximum Allowable Limits for Correction
DO	Conc. or % Diff.	≤ ±0.3 mg/L or ≤ ±5%	±0.3–0.5 mg/L or ±5–10 %	±0.5–0.8 mg/L or ±10–15%	±0.8–2 mg/L or ±15–20%	±2 mg/L or ±20%
Temperature	Degrees	≤ ±0.2°C	±0.2–0.5°C	±0.5–0.8°C	±0.8–2.0°C	>2.0°C

[1] Modified from Table 18 in Wagner et al. (2006).

For this assessment, drift was assumed to occur linearly between calibration points, which means that the accuracy assessment could be evaluated independently for each 10-minute reading throughout the period of record. Periods that exceed the maximum allowable limits for correction and excluded from the final corrected dataset are discussed in **Section 3.2** and presented in **Section 3.3**.

3.0 Data Analysis

The raw T/DO data, handheld T/DO measurements, and streamflow at the USGS gage in Millbury (USGS 01109730) are presented in **Figure 3**. Analysis of the raw data includes consideration of the validation of the data using the USGS procedures as described in **Section 2.2** and evaluation of the influence that precipitation, streamflow and quality of the Upper Blackstone effluent has on the dissolved oxygen levels in the river.

3.1 Influence of Precipitation and Streamflow on Sampling

Environmental conditions during the monitoring program can impact the DO dynamics recorded by the continuous data loggers. Precipitation and streamflow trends are discussed in Section 4 of the Blackstone River Water Quality Monitoring Program 2022 Sampling Season Report (Massachusetts Water Resources Research Center (MaWRRC), 2023). Overall, total snowfall (winter 2021-2022) and precipitation (2022 sampling season) were below average. One exception was total rainfall in September, which exceeded the historical (1991-2022) median September rainfall (MaWRRC, 2023).

Below average snowfall and precipitation contributed to generally lower streamflow in 2022 at the USGS Millbury (01109730) and Woonsocket (01112500) gages when compared to historical (1930-2022) mean monthly streamflow. The average monthly and daily streamflow at both gages were significantly below historical averages during July and August. September's monthly average streamflow was higher than the historical average due to a large storm at the beginning of the month.

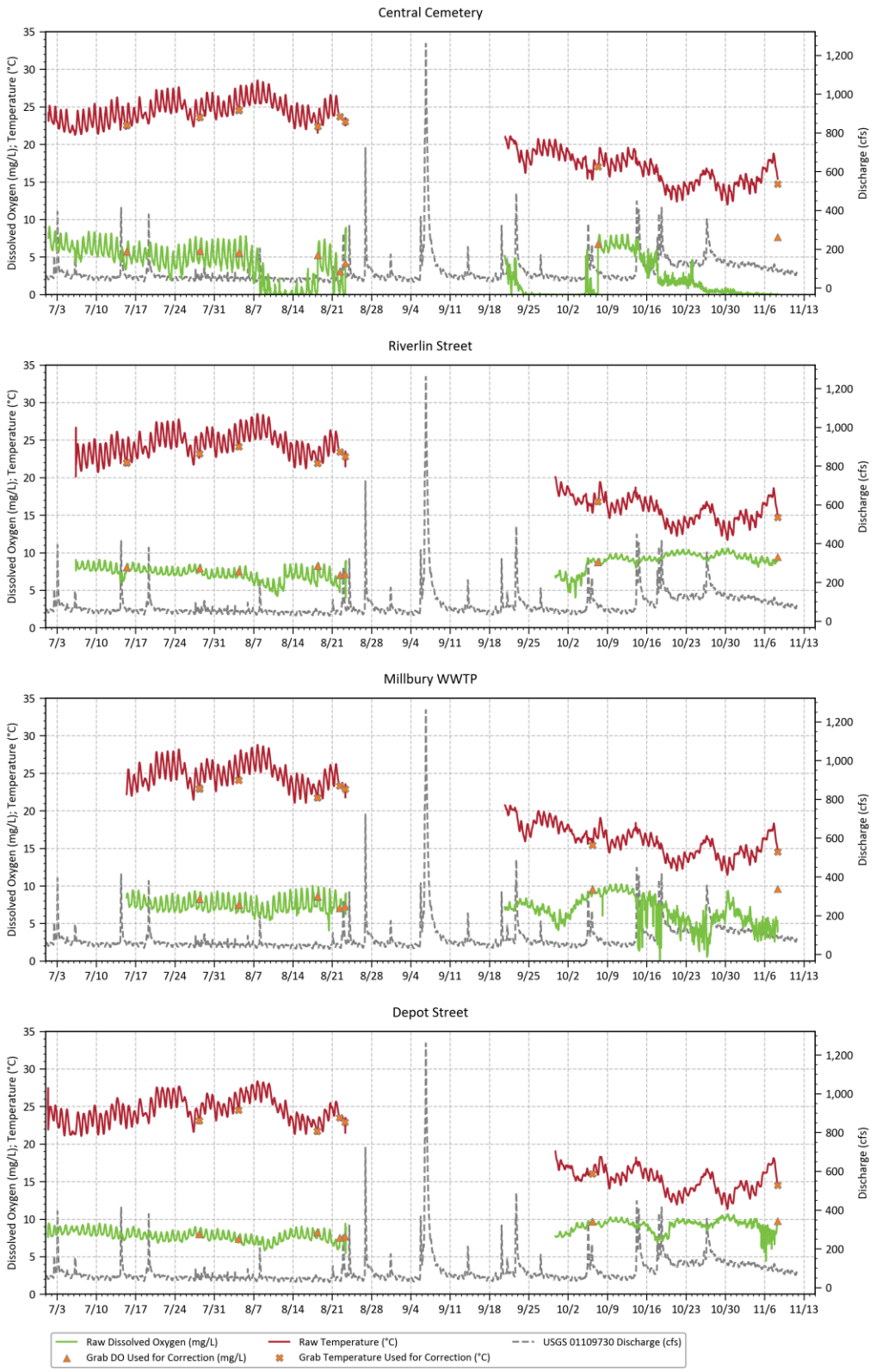


Figure 3: Raw Dissolved Oxygen and Temperature Data (2022 Monitoring)

Since the Blackstone River is effluent dominated during low flows, the effluent diurnal patterns are reflected in the streamflow. This pattern, at times, causes the flow to drop below the 7Q10 flow[1] for a portion of the day. Streamflow at the Millbury gage was frequently recorded below the 7Q10 flow during the monitoring period, particularly in August. The total time by month when Blackstone River flows were below 7Q10 is summarized in **Table 3.** Sub-daily streamflow timeseries for the Millbury gage during the previous five monitoring periods are shown in **Figure 4**; streamflow in 2022 is frequently lower than in 2021, which had four extreme rainfall events over a 3-month period.

Table 3: Blackstone River Time Below 7Q10 at the USGS Millbury Gage (01109730)

Month	Total Time Below 7Q10
July	14 hours
August	4 days and 2 hours
September	1 day and 3 hours
October	14 hours

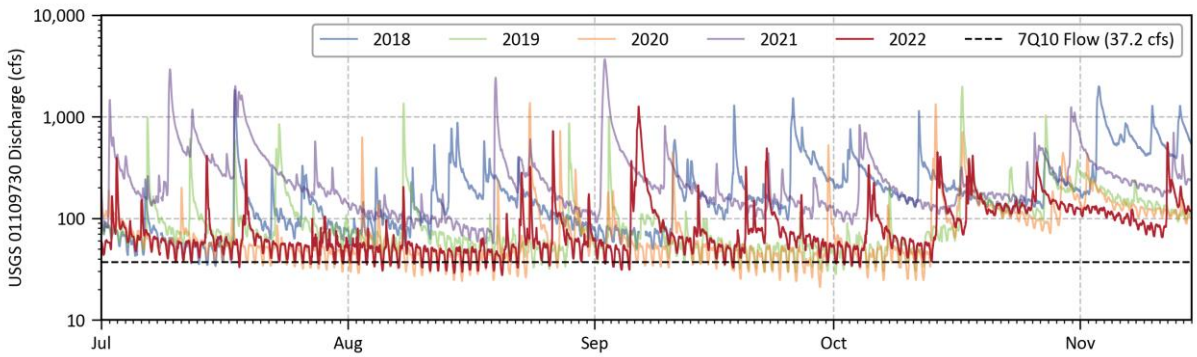


Figure 4: USGS Millbury (01109730) Monitoring Period Streamflow in 2018-2022

In addition to the environmental conditions, Upper Blackstone WWTF plant performance can impact water quality within the Blackstone River, especially in the headwaters where the DO loggers were placed in 2022. In summer 2022, a plant upset occurred that caused exceedances of the interim and final limits for total phosphorus, total nitrogen, and ammonia. Effluent concentrations began to increase in July, exceeded effluent limits in August and September, and returned to normal in October. As described in Section 6 of the 2022 report (MaWRRC, 2023), the low streamflow and the plant upset resulted in observed nutrient concentrations that were high relative to typical conditions observed following the WWTF upgrade. Higher nutrient concentrations can result in more floating or attached algae, which in turn, can influence DO concentrations.

[1] The 7Q10 flow is the 7-day average annual low flow occurring once every 10 years, on average. At the Millbury USGS gage, the 7Q10 flow is 37.2 cfs.

3.2 Data Validation

Upper Blackstone calibrated each of the four meters prior to deployment and assessed calibration drift and fouling periodically throughout the program. If the periodic grab measurements indicated that recalibration was necessary, the instrument was retrieved from the field and recalibrated in the Upper Blackstone lab.

For each continuous meter, **Table 4** compares the synchronous field handheld and continuous logger DO readings taken in the river during field visits and provides the corresponding USGS accuracy classification. If the DO difference exceeds 0.3 mg/L or 5 percent (the maximum allowable difference for a rating of excellent), then some sensor drift has occurred (based on USGS guidelines). However, all continuous data were corrected if the percent error between continuous and field measurements exceed 0. The data in **Table 4** indicate that some DO sensor drift or fouling occurred at least once for each logger (indicated in blue bold text).

In 2022, all four data loggers malfunctioned during the logger deployment which significantly impacted the data validation findings. The Upper Blackstone field team noted that the hand-held DO meter was not matching the measured DO at any of the four locations on 8/18 after cleaning the data logger tips. This pattern was observed again on 8/22, and all four meters were removed from the water on 8/23. The logger tips were replaced, but the loggers were not able to be recalibrated and thus were not returned to the water while Upper Blackstone staff consulted with Onset technical support. Two of the loggers were replaced by the manufacturer, and all four were re-deployed on 9/20. The serial numbers for each logger are documented in **Table 1** for reference. The impact of the malfunctioning meters can be seen in **Table 4**. For instance, for the W1258 meter, the post-cleaning DO measurement was significantly different than the grab sample, with an accuracy rating of only "Good." When Upper Blackstone staff visited 4 days later the logger was already exceeding maximum correction limits, with this pattern repeated the following day prior to the logger being removed from service. This pattern was observed at the other three locations around the same period. This is atypical, and has not been observed in previous years, nor was it observed at the two sites (Riverlin Street and Depot Street) with the replacement meters that were deployed at the end of the 2022 monitoring season.

Table 4: Comparison of Dissolved Oxygen Field Data with Continuous Dissolved Oxygen Data

Station	Grab Reading Date	Continuous DO Logger Reading (mg/L)	Field Handheld DO Reading (mg/L)	Difference in DO Readings (mg/L)	Percent Difference in DO Readings	USGS Accuracy Rating
W1258 Central Cemetery	7/15/2022 10:04	4.65	5.7	1.05	-23%	Exceeds Correction Limits
	7/15/2022 10:24	5.55	5.74	0.19	-3%	Excellent
	7/28/2022 10:04	4.57	5.79	1.22	-27%	Exceeds Correction Limits
	7/28/2022 10:24	5.74	5.83	0.09	-2%	Excellent
	8/4/2022 9:14	4.43	5.5	1.07	-24%	Exceeds Correction Limits
	8/4/2022 9:34	5.51	5.6	0.09	-2%	Excellent
	8/18/2022 9:54	0.99	5.24	4.25	-429%	Exceeds Correction Limits
	8/18/2022 10:14	4.98	5.3	0.32	-6%	Good
	8/22/2022 9:24	0.34	3.15	2.81	-826%	Exceeds Correction Limits
	8/22/2022 9:44	1.04	3.07	2.03	-195%	Exceeds Correction Limits
	8/23/2022 8:04	-0.02	4.21	4.23	21150%	Exceeds Correction Limits
	10/7/2022 7:50	0	6.73	6.73		Exceeds Correction Limits
	10/7/2022 8:10	6.57	6.72	0.15	-2%	Excellent
	11/8/2022 8:30	0.06	7.67	7.61	-12683%	Exceeds Correction Limits
Riverlin Street	7/15/2022 9:26	7.71	8.05	0.34	-4%	Good
	7/15/2022 9:46	8.16	8.09	-0.07	1%	Excellent
	7/28/2022 9:26	7.83	7.96	0.13	-2%	Excellent
	7/28/2022 9:46	7.7	7.93	0.23	-3%	Excellent
	8/4/2022 8:46	7.31	7.51	0.2	-3%	Excellent
	8/4/2022 9:06	7.43	7.53	0.1	-1%	Excellent
	8/18/2022 9:26	6.87	8.23	1.36	-20%	Poor
	8/18/2022 9:46	7.78	8.27	0.49	-6%	Good
	8/22/2022 8:56	4.73	7.03	2.3	-49%	Exceeds Correction Limits
	8/22/2022 9:16	6.33	7.05	0.72	-11%	Fair
	8/23/2022 7:46	6.15	7.14	0.99	-16%	Poor
	10/7/2022 7:13	8.67	8.75	0.08	-1%	Excellent
	10/7/2022 7:33	8.94	8.76	-0.18	2%	Excellent
	11/8/2022 8:13	9.24	9.44	0.2	-2%	Excellent
Millbury WWTP	7/28/2022 8:42	8.03	8.25	0.22	-3%	Excellent
	7/28/2022 9:02	8.21	8.29	0.08	-1%	Excellent
	8/4/2022 8:02	7.16	7.45	0.29	-4%	Excellent
	8/4/2022 8:22	7.28	7.53	0.25	-3%	Excellent
	8/18/2022 8:52	8.06	8.57	0.51	-6%	Fair
	8/18/2022 9:12	8.17	8.64	0.47	-6%	Good
	8/22/2022 8:12	6.76	7.03	0.27	-4%	Excellent
	8/22/2022 8:32	6.89	7.07	0.18	-3%	Excellent

Station	Grab Reading Date	Continuous DO Logger Reading (mg/L)	Field Handheld DO Reading (mg/L)	Difference in DO Readings (mg/L)	Percent Difference in DO Readings	USGS Accuracy Rating
	8/23/2022 7:22	7.23	7.26	0.03	0%	Excellent
	10/6/2022 8:10	**9.03**	**9.56**	**0.53**	**-6%**	**Fair**
	10/6/2022 8:30	**10**	**9.55**	**-0.45**	**4%**	**Good**
	11/8/2022 7:50	**3.89**	**9.61**	**5.72**	**-147%**	**Exceeds Correction Limits**
Depot Street	7/28/2022 8:03	7.88	7.98	0.1	-1%	Excellent
	7/28/2022 8:23	8.25	8.03	-0.22	3%	Excellent
	8/4/2022 7:23	7.1	7.39	0.29	-4%	Excellent
	8/4/2022 7:43	**6.85**	**7.39**	**0.54**	**-8%**	**Fair**
	8/18/2022 8:03	**7.63**	**8.22**	**0.59**	**-8%**	**Fair**
	8/18/2022 8:23	**7.63**	**8.27**	**0.64**	**-8%**	**Fair**
	8/22/2022 7:33	**6.23**	**7.51**	**1.28**	**-21%**	**Exceeds Correction Limits**
	8/22/2022 7:53	**6.71**	**7.51**	**0.8**	**-12%**	**Fair**
	8/23/2022 7:03	**6.03**	**7.7**	**1.67**	**-28%**	**Exceeds Correction Limits**
	10/6/2022 7:47	9.5	9.69	0.19	-2%	Excellent
	10/6/2022 8:07	9.58	9.67	0.09	-1%	Excellent
	11/8/2022 7:27	**9.42**	**9.76**	**0.34**	**-4%**	**Good**

Measurements in blue bold text indicate that sensor drift/fouling occurred.
Measurement shaded in grey are associated with invalid logger data

For each continuous meter, **Table 5** compares the synchronous continuous logger temperature and handheld readings taken in the river during field visits and provides the corresponding USGS accuracy classification. Based on these guidelines, if handheld instrument and continuous logger temperature readings differ by more than 0.2°C (the maximum allowable difference for a rating of excellent), some sensor drift has occurred. While the data in **Table 5** show that each logger exhibited some minor drift at one point during the sampling program, all data were within allowed differences for valid data based on the QAPP.

Table 5: Comparison of Temperature Grab Data with Continuous Temperature Data

Station	Grab Reading Date	Continuous Temp. Logger Reading (°C)	Field Handheld Temp. Reading (°C)	Difference in Temp. Readings (°C)	Percent Difference in Temp. Readings	USGS Accuracy Rating
W1258 Central Cemetery	7/15/2022 10:04	22.4	22.5	0.1	10%	Excellent
	7/15/2022 10:24	22.38	22.57	0.19	19%	Excellent
	7/28/2022 10:04	23.48	23.6	0.12	12%	Excellent
	7/28/2022 10:24	23.98	23.6	-0.38	-38%	Good
	8/4/2022 9:14	24.42	24.5	0.08	8%	Excellent
	8/4/2022 9:34	24.56	24.6	0.04	4%	Excellent
	8/18/2022 9:54	22.32	22.4	0.08	8%	Excellent
	8/18/2022 10:14	22.08	22.4	0.32	32%	Good
	8/22/2022 9:24	23.66	23.67	0.01	1%	Excellent
	8/22/2022 9:44	23.5	23.7	0.2	20%	Excellent
	8/23/2022 8:04	22.8	23	0.2	20%	Excellent
	10/7/2022 7:50	16.92	17	0.08	8%	Excellent
	10/7/2022 8:10	17.34	17	-0.34	-34%	Good
	11/8/2022 8:30	15.28	14.7	-0.58	-58%	Fair
Riverlin Street	7/15/2022 9:26	21.78	21.93	0.15	15%	Excellent
	7/15/2022 9:46	22	22	0	0%	Excellent
	7/28/2022 9:26	22.96	23.2	0.24	24%	Good
	7/28/2022 9:46	23.28	23.2	-0.08	-8%	Excellent
	8/4/2022 8:46	23.88	24.1	0.22	22%	Good
	8/4/2022 9:06	24.1	24.1	0	0%	Excellent
	8/18/2022 9:26	21.74	21.9	0.16	16%	Excellent
	8/18/2022 9:46	21.66	21.9	0.24	24%	Good
	8/22/2022 8:56	23.22	23.4	0.18	18%	Excellent
	8/22/2022 9:16	23.26	23.4	0.14	14%	Excellent
	8/23/2022 7:46	22.62	22.8	0.18	18%	Excellent
	10/7/2022 7:13	16.76	16.8	0.04	4%	Excellent
	10/7/2022 7:33	16.48	16.8	0.32	32%	Good
	11/8/2022 8:13	14.8	14.7	-0.1	-10%	Excellent
Millbury WWTP	7/28/2022 8:42	22.8	22.9	0.1	10%	Excellent
	7/28/2022 9:02	22.84	23	0.16	16%	Excellent
	8/4/2022 8:02	23.88	24.1	0.22	22%	Good
	8/4/2022 8:22	24.04	24.07	0.03	3%	Excellent
	8/18/2022 8:52	21.64	21.77	0.13	13%	Excellent
	8/18/2022 9:12	21.44	21.73	0.29	29%	Good
	8/22/2022 8:12	23.18	23.3	0.12	12%	Excellent
	8/22/2022 8:32	23.16	23.3	0.14	14%	Excellent

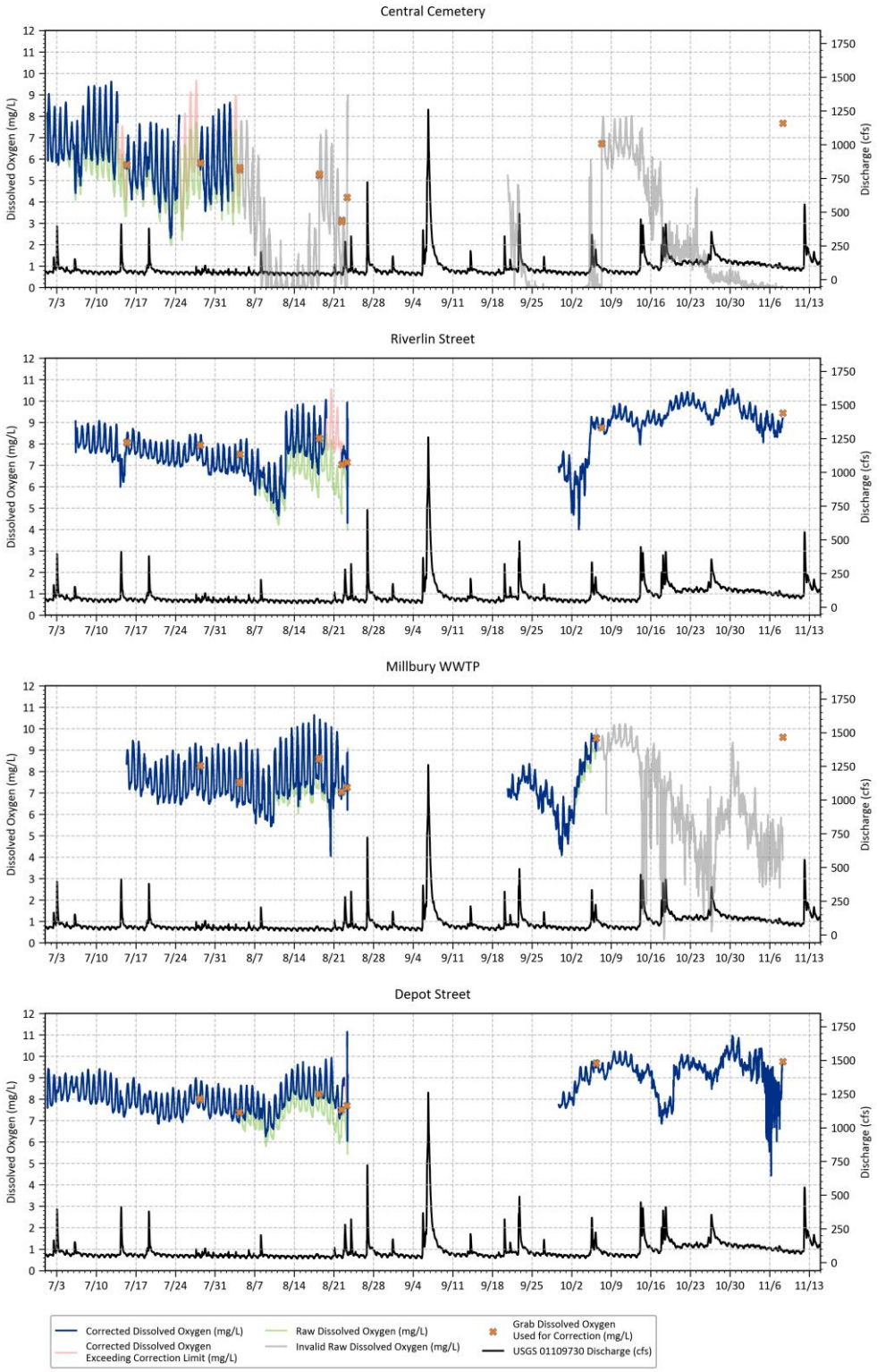
Station	Grab Reading Date	Continuous Temp. Logger Reading (°C)	Field Handheld Temp. Reading (°C)	Difference in Temp. Readings (°C)	Percent Difference in Temp. Readings	USGS Accuracy Rating
	8/23/2022 7:22	**22.68**	**22.9**	**0.22**	**22%**	**Good**
	10/6/2022 8:10	15.34	15.4	0.06	6%	Excellent
	10/6/2022 8:30	15.32	15.4	0.08	8%	Excellent
	11/8/2022 7:50	**14.74**	**14.5**	**-0.24**	**-24%**	**Good**
Depot Street	7/28/2022 8:03	22.92	23.1	0.18	18%	Excellent
	7/28/2022 8:23	**22.74**	**23.1**	**0.36**	**36%**	**Good**
	8/4/2022 7:23	24.42	24.5	0.08	8%	Excellent
	8/4/2022 7:43	24.32	24.5	0.18	18%	Excellent
	8/18/2022 8:03	21.54	21.7	0.16	16%	Excellent
	8/18/2022 8:23	**21.44**	**21.7**	**0.26**	**26%**	**Good**
	8/22/2022 7:33	23.4	23.5	0.1	10%	Excellent
	8/22/2022 7:53	**23.28**	**23.5**	**0.22**	**22%**	**Good**
	8/23/2022 7:03	22.7	22.9	0.2	20%	Excellent
	10/6/2022 7:47	15.96	16	0.04	4%	Excellent
	10/6/2022 8:07	15.9	16	0.1	10%	Excellent
	11/8/2022 7:27	14.68	14.5	-0.18	-18%	Excellent

Measurements in bolded blue indicate that some sensor drift/fouling occurred.

3.3 Final Corrected Data

Figure 5 shows the raw DO concentration values (green), the corrected DO concentration values (blue), the side-by-side calibration sample points (x markers), and the river flow (black) for each of the four sampling locations. The corrected DO data are also shown in **Figure 6** without the raw data and calibration sample points. The Massachusetts minimum DO requirement of 5 mg/L does not apply during flows below 7Q10. The data shown in **Figure 6** include DO measurements above and below 7Q10 conditions.

Figure 7 shows the raw temperature values (red), the corrected temperature values (blue), the side-by-side calibration sample points (x markers), and the river flow (black) for each of the four sampling locations. For each continuous meter, the corrected temperature data are also shown in **Figure 8** without the raw data and calibration sample points.



Pink line represents corrected data that exceed maximum allowable limit for correction.

Figure 5: Raw, Invalid, and Corrected Dissolved Oxygen Data (2022 Monitoring)

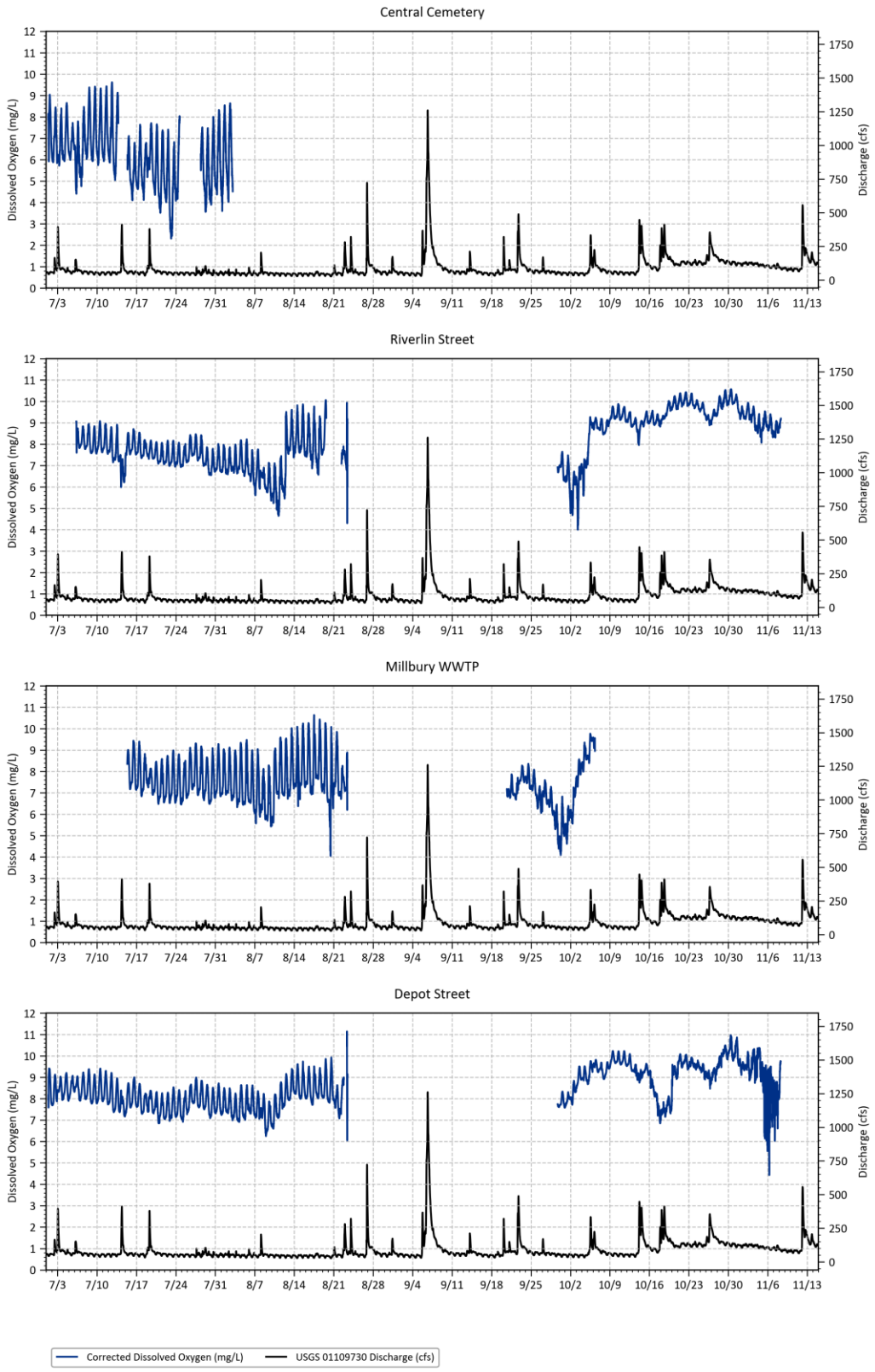


Figure 6: Corrected Dissolved Oxygen Data (2022 Monitoring)

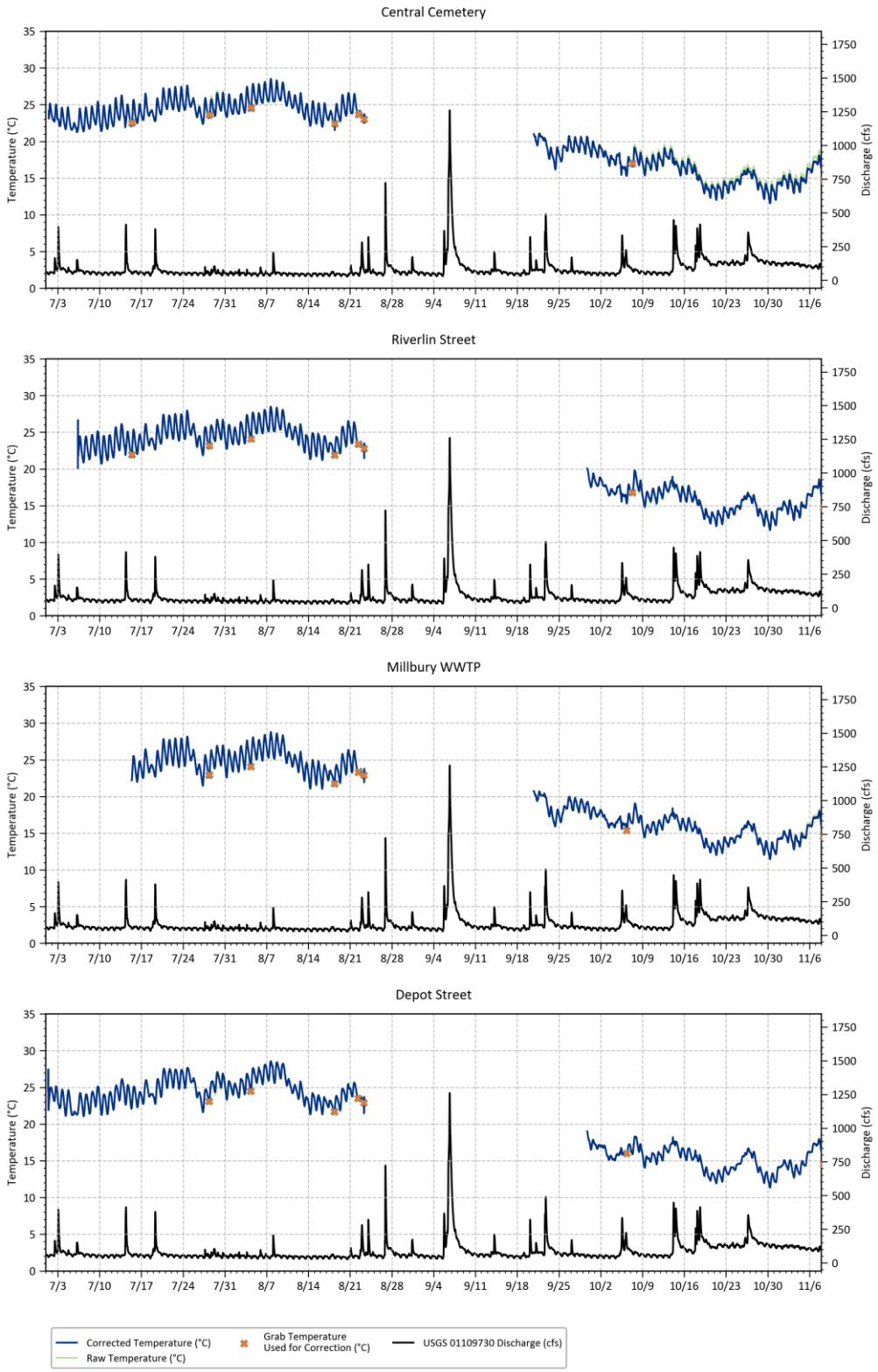


Figure 7: Raw, and Corrected Temperature Data (2022 Monitoring)

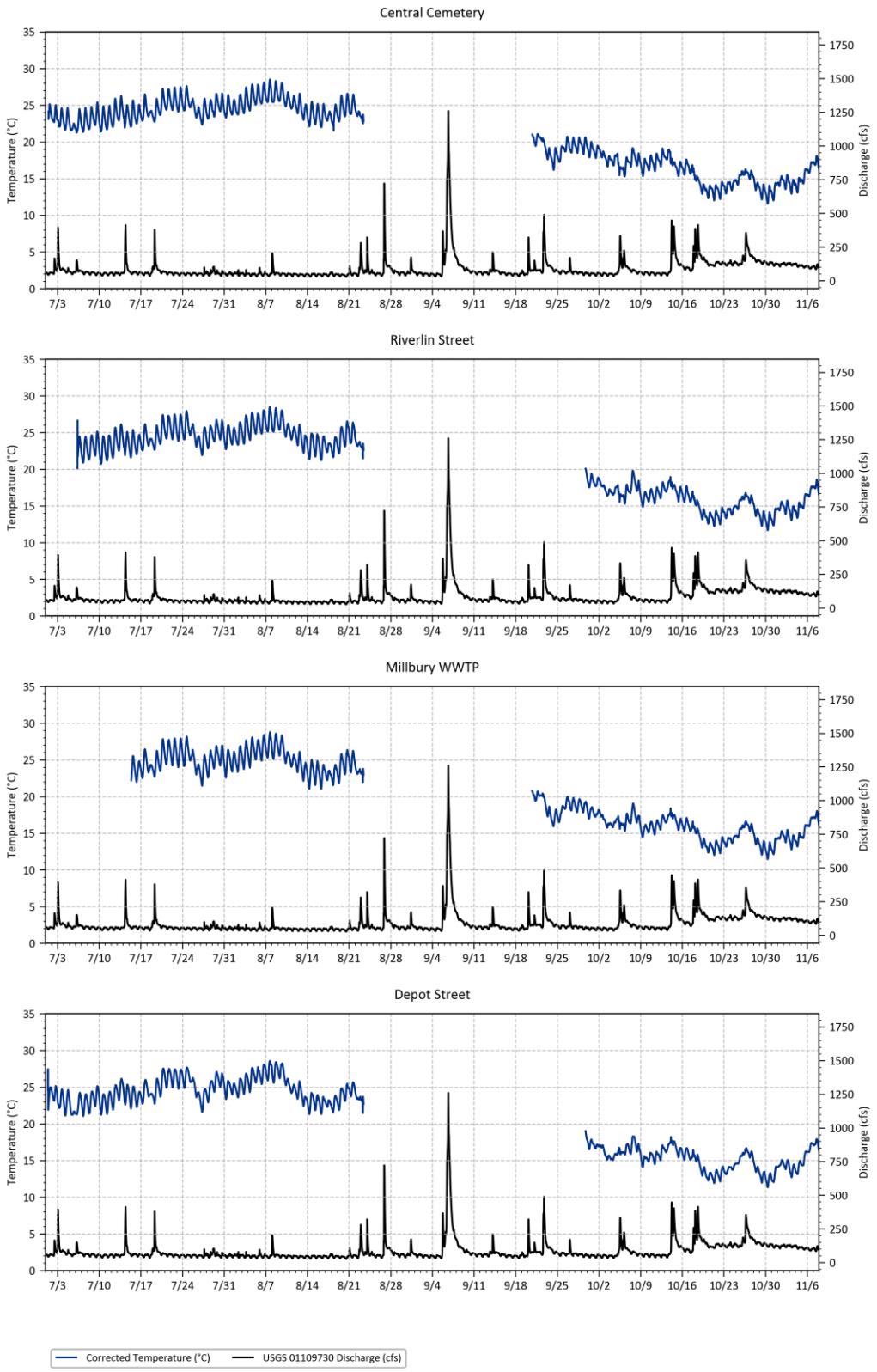


Figure 8: Corrected Temperature Data (2022 Monitoring)

4.0 Discussion – Data Analysis and Interpretation

The corrected DO data were compared to the Massachusetts Surface Water Quality Standards for Class B freshwater as well as the guidance MassDEP uses to define water bodies with DO impairments as described in the 2022 CALM (MassDEP, 2022):

- Minimum DO concentration greater than 5 mg/L (MA Class B Standard)
- Maximum diel DO change less than 3 mg/L (CALM guidance value for the Aquatic Life Use)
- Maximum DO saturation of less than 125 percent (CALM guidance value for the Aquatic Life Use)

The above DO water quality criterion/guidance values for aquatic life use apply when flow is at or above the critical flow (7Q10).

The percentage of time or number of days the data met water quality criteria is provided in **Table 7**; this analysis excludes days when Millbury streamflow was below the 7Q10 flow from all statistical DO calculations. The listed percentages were calculated using only the accepted data as the actual number of hours above 5 mg/L compared to the total number of hours of accepted data. The days when the diel change in DO was greater than 3 mg/L was calculated as the number of days when the difference between the minimum and maximum measurement on that day exceeded 3 mg/L.

Table 6: Summary Days when the Continuous Corrected Dissolved Oxygen Data Met the Massachusetts Surface Water Quality Standards and Guidance[1]

Metric	Central Cemetery (W1258)	Riverlin Street	Millbury WWTP	Depot Street
Days of corrected data	27	85	55	92
Days where diel ΔDO < 3.0 mg/L	7	84	50	87
% of days where diel ΔDO < 3.0 mg/L	26%	99%	91%	95%
% of the time DO > 5.0 mg/L	78%	99%	99%	100%
Days where % Saturation > 125%	100	100	100	100

Note: 1. Only includes periods where the flow at the Millbury USGS gage exceeds 7Q10 (37.2 cfs)

Data logger malfunctions in 2022 resulted in significantly fewer days of corrected data at Central Cemetery (W1258) and Millbury WWTP compared with the other two logger sites (Riverlin Street and Depot Street) and compared with previous years of this study. Corrected continuous data at Central Cemetery are only available between July and early August. Likewise, data at Millbury WWTP are only available from mid-July through late August and for a few weeks in late September to early October. In contrast, the Riverlin Street and Depot Street loggers had longer valid periods after the meters were redeployed, which is attributed to use of new data loggers for the second deployment at those locations. As a result of the continuing issues with the old loggers at Central Cemetery and Millbury WWTP, they were retired at the end of the 2022 season and replacement data loggers have been obtained for the 2023 monitoring season.

The 2022 data showed that compliance with the Massachusetts minimum DO standard of 5 mg/L ranged from 78 to 100 percent. Central Cemetery was the only station with a notable number of DO readings below the DO criterion (22%) compared to the other locations where between 99-100% of the samples met the criterion.

The differences in water quality between the four sites monitored in 2022 are influenced by local conditions within the river. Conditions that can influence water quality in a wadeable stream like the Blackstone River include:

- Depth
- Canopy shading
- Dams
- Bed slope
- Substrate type (e.g., silt, sand, gravel, etc.).

The river at the Central Cemetery and the Millbury WWTP sites is relatively wide and unshaded, allowing for shallower depths and greater light penetration that likely contributes to higher periphyton growth. In contrast, Riverlin Road and Depot Street are characterized by significant tree coverage and slightly deeper water, limiting periphyton growth potential when compared with Central Cemetery and Millbury WWTP. In addition, the Blackstone River is characterized by frequent dams that significantly impact the time of travel and water quality characteristics of the river. Dams in the vicinity of the four 2022 monitoring locations are shown in **Figure 9**. In addition, the river profile is relatively steep between Central Cemetery (W1258) and the next downstream site at Riverlin Street, increasing the velocity and potentially allowing additional reaeration between the Central Cemetery site and the downstream monitoring locations. There is also a dam approximately 300 feet upstream of the Depot Street station, which reaerates the water and produces generally higher DO.

At Central Cemetery, only about 25 percent of days met the CALM's diel fluctuation guidance value of less than 3 mg/L (noting that the only corrected data are from July when diel fluctuations tend to be higher than the rest of the year). Diel fluctuations were also notably high at the Millbury WWTP location, though most fluctuations were close to but met the guidance value. The higher fluctuations at these two sites may be due to the shallower water and more open canopy that would support periphyton growth, which previous periphyton monitoring as shown to be the main contributor to diel fluctuations. In contrast, the diel fluctuations at the two (deeper/shadier) locations nearly always met the CALM guidance value (99% compliance). When compared to Central Cemetery, water quality related to exceedances of the DO criteria and guidance improved at the three downstream sites, with 99 to 100 percent of the data in compliance with the minimum DO criterion and 91 to 99 percent of the data meeting the 3 mg/L diel DO guidance value. DO percent saturation data was always below the 125 percent guidance value at all four monitoring locations.

Given the significant periods of invalid data during the 2022 monitoring period, a second compliance comparison was completed only on periods where valid data were available coincidently across all four monitoring periods to facilitate a direct comparison across each site. This only occurred during a brief period of 18 days in mid-July out of the 130-day monitoring period. The water quality criterion was met at the three downstream locations 100% of the time during this coincident period, suggesting that the impairment to the aquatic life use within this assessment unit is localized to the area at the most upstream 2022 monitoring site (W1258 at Central Cemetery). Diel DO fluctuations were greater at the Millbury WWTP site when compared to the immediate upstream and downstream locations.

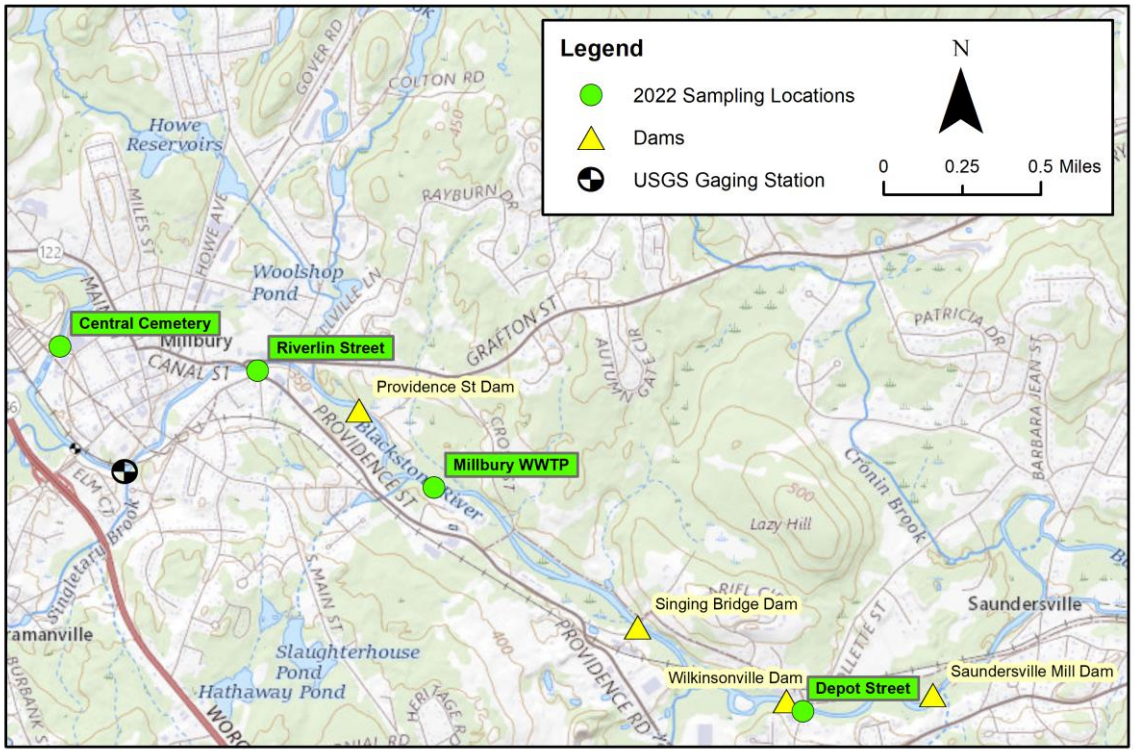


Figure 9: Plan View of 2022 Monitoring Locations and Blackstone River Dams

5.0 Summary

Upper Blackstone, CDM Smith, and the Water Resources Research Center at the University of Massachusetts collaborated to deploy and manage four Onset HOBO U26-001 continuous meters with a temperature (T) and dissolved oxygen (DO) logger on the Blackstone River from July through November 2022. CDM Smith reviewed the data from the 2022 continuous metering program, corrected the T and DO data based on periodic in situ measurements taken with a handheld probe at each site using USGS guidance (Wagner et al., 2006), and compared adjusted data values to Massachusetts Surface Water Quality Standards and guidance for dissolved oxygen.

Based on results from deployments in previous years, two meters were relocated to new sites for the 2022 monitoring period to better understand changes in water quality between Central Cemetery (W1258), which has historically exhibited exceedances of water quality guidance and standards, and Depot Street, which has historically met guidance and standards. The two new meters were located at Riverlin Street and the Former Millbury WWTP, between the upstream Central Cemetery and downstream Depot Street.

Overall, DO improved between Central Cemetery and Depot Street, with a slight decline in quality at the former Millbury WWTP. Precipitation in 2022 was generally lower than average, except for September, leading to generally low-than-average streamflow throughout the summer, and several periods when the river flow was below its 7Q10 flow.

Data from the four meters showed that compliance with the Massachusetts minimum DO criterion of 5 mg/L ranged from 78% to 100% during the monitoring period, noting that the station with 78 percent compliance had a short period where the meter functioned correctly (July) when DO levels have historically been lowest. DO at the Riverlin Street and Depot Street stations was consistently at levels that support Aquatic Life Use based on the Massachusetts water quality standards and guidance in MassDEP's 2022 CALM. DO at the most upstream station (Central Cemetery), had several instances when DO dropped below the 5 mg/L concentration criterion in mid-July and early-August.

6.0 Future Work

Since the primary low flow period in August and September was missed in the 2022 monitoring program, CDM Smith recommends that Upper Blackstone re-deploy the four meters at these locations in 2023 to collect additional data describing water quality gradients between these locations within the MA51-06 Assessment Unit. If additional meters become available, then they could be deployed at the previously monitored locations: UBWPAD2 and W1242.

7.0 References

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Wagner, R.J., R.W. Boulger, Jr., C.J. Oblinger, and B.A. Smith. 2006. "Guidelines and Standard Procedures for Continuous Water-Quality Monitors: Station Operation, Record Computation, and Data Reporting." USGS Techniques and Methods 1-D3. http://pubs.water.usgs.gov/tm1d3.

Appendix D: Blackstone River Water Quality Monitoring program Field 2022 Sampling Plan

BLACKSTONE RIVER WATER QUALITY MONITORING PROGRAM FIELD 2022 SAMPLING PLAN

Presented To:
Karla Sangrey, Director

Upper Blackstone Clean Water
50 Route 20
Millbury, MA 01527-2199

Submitted By:
Marie-Françoise Hatte Massachusetts

Water Resources Research Center
209 Agricultural Engineering Bldg.
250 Natural Resources Way
University of Massachusetts
Amherst, MA 01003

April 15, 2022

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Note that all forms, SOPs, and instructions can be found in the Blackstone River Assessment of Water Quality, Ecological Health, and Ecological Risk through Data Collection and Modeling Quality Assurance Project Plan 2020 – 2022

2022 Sampling Season
Scope of Work
Blackstone River, Massachusetts

1.0 Historical Overview

The Blackstone River Watershed Assessment Study began in 2003 with the goal of conducting a watershed management study of the Blackstone River Basin in Massachusetts and Rhode Island. Objectives included evaluation of trends in river quality as well as flow management opportunities with existing hydraulic structures so that water quality and aquatic habitat can be improved throughout the basin.

In 2004 through 2006, a monitoring program was conducted to collect water quality, streamflow, and sediment data sufficient for the calibration and validation of computer models to simulate pollutant loading, transport, and in-stream fate and distribution along the main stem and tributaries of the Blackstone River. From 2006 – 2012, a water quality model of the Blackstone River was developed, calibrated, and validated using Hydrological Simulation Program – Fortran (HSPF). This model was based on an existing water quantity model of the Blackstone River watershed, which was developed by the United States Geological Survey (USGS) (Barbaro and Zariello, 2006). The HSPF model currently represents conditions through 2011 and has been used to evaluate and model dynamic water quality conditions incorporating daily, monthly, seasonal and inter-annual variability. Both point source (e.g., waste water treatment plants) and non-point source (e.g., stormwater runoff) loads to the river are incorporated explicitly into the modeling analysis.

Upper Blackstone Clean Water (Upper Blackstone or UB) plant upgrades designed to meet the 2001 permit limits have been online since Fall 2009. In late 2009 and early 2010, slight adjustments to the system were made to optimize performance. As of August 2010, the Upper Blackstone Wastewater Treatment Facility 2001 permit upgrades were fully operational. A new monitoring program was initiated in Spring 2011 and expanded in 2012 to help assess response of the river to the reduced nutrient concentrations in the effluent. Water quality monitoring of the main stem river will continue in 2022, as described in this Scope of Work. Sampling in 2022 will continue the program initiated in 2012 and include routine (monthly) sampling for nutrients and chlorophyll-a, measurement of water temperature, dissolved oxygen, pH and conductivity, and deployment of four dissolved oxygen data loggers.

2.0 Objectives for 2022 Monitoring

The Blackstone River is formed by the confluence of the Middle River and Mill Brook in Worcester, Massachusetts. From there, the River flows approximately 48 miles south into Rhode Island where it becomes the Pawtucket River at the Main Street Dam in Pawtucket, Rhode Island. The main stem Blackstone River is joined by many small tributaries, as well as six major rivers: the Quinsigamond River, the Mumford River, the West River, the Mill River, the Peters River, and the Branch River. The

watershed consists of over 1,300 acres of lakes and ponds; the largest is Lake Quinsigamond in Shrewsbury and Grafton.

The scope of the 2022 monitoring program is outlined in this document. The 2022 water quality monitoring program is designed to:

- Build upon work conducted by Upper Blackstone, Massachusetts Department of Environmental Protection (MassDEP), the U.S. Geological Survey (USGS) and others;
- Support future analysis, if needed, of river surface water flow and quality;
- Collect data to assess changes in riverine nutrient and chlorophyll-a concentrations and fluxes through comparison against historical data; and
- Collect data to describe riverine water temperature, dissolved oxygen, pH, and conductivity.

These objectives were used to select sampling locations as well as suitable sampling methods, analytes, measurement techniques, and analytical protocols with the appropriate quality assurance and quality control guidelines. This Scope of Work falls under the Blackstone River 2020 – 2022 Quality Assurance Project Plan (QAPP) and associated Standard Operating Procedures (SOPs), submitted to MassDEP in March, 2020. The 2020 – 2022 QAPP is a revision of the 2017 – 2019 QAPP last approved by MassDEP in December, 2019. The QAPP is designed to cover the range of sampling activities anticipated under the Blackstone River Watershed Assessment Study and serves as an umbrella document for specific Field Sampling Plans, such as this Scope of Work, that will be conducted as part of the study.

3.0 Nutrient Sampling

3.1 Nutrient Sampling Locations & Rationale

The number and location of sampling sites are described in this section. Nutrient sampling will be conducted at 9 main stem run-of-river locations deemed to be the most relevant for understanding potential impacts of the Upper Blackstone's wastewater effluent on downstream water quality. The main stem sampling locations included in the 2022 FSP have been selected in order to provide:

1. Data on changes in concentration and load along the river, particularly downstream of the confluence with the Upper Blackstone effluent and upstream of the confluences with the Mumford and West Rivers,
2. Information on nutrient loads crossing the MA/RI state line, and
3. Information to help understand the impact of the impoundments and nutrients on productivity within RI reaches.

Starting in April 2022, UMass, with the assistance of Upper Blackstone staff, will collect samples for nutrient and chlorophyll-a analysis and collect hand-held meter measurements monthly (e.g., roughly every 4 weeks) at nine locations, including three Rhode Island sites along the main stem of the Blackstone River that will be co-sampled with the Narragansett Bay Commission (NBC). Sampling will continue through November (see **Table 1**). Samples will be collected routinely each month for nutrients,

including phosphorus, nitrogen, and chlorophyll-a, regardless of weather conditions, as described in Section 4.0. Information on sampling frequency, sampling program logistics, schedule, and sampling methods is provided in subsequent subsections.

Table 1: 2022 sampling dates

20 April
18 May
15 June
13 July
10 August
7 September
5 October*
2 November

*Due to illness, the Massachusetts crews sampled on October 17,2022. NBC sampled on oct. 5.

The sampling sites are provided in **Table 2** and are consistent with the sites sampled in since 2019. Detailed text descriptions, driving directions, and maps of the locations are provided in Appendix A. Figure 1 shows the location of the sampling sites relative to each other and the basin.

Table 2: 2022 Sampling Sites (all sites located on the main stem)

Site ID#	Site Name	Lat	Lon	River Mile[2]
RMSD[1]	Slater Mill Dam, Pawtucket, RI	41.876909	-71.381940	0.0
R116[1]	Rte 116 Bikepath Bridge, Pawtucket, RI	41.938066	-71.433769	6.3
RMSL[1]	State Line, RI	42.009974	-71.529313	15.5
W1779	Below Rice City Pond Sluice Gates, Hartford St., Uxbridge, MA	42.097270	-71.62241	27.8
W0767	Sutton St. Bridge, Northbridge, MA	42.153922	-71.652521	33.4
W1242	Route 122A, Grafton, MA	42.177153	-71.687964	36.3
	Millbury WWTP, Millbury, MA			
	Canal Street, Millbury, MA			
W1258	Central Cemetery, Millbury, MA	42.19373	-71.76603	42.7
UBWPAD2	New Confluence site, downstream of effluent canal	42.20702	-71.78154	44.6
W0680[3]	New Millbury St Bridge, Worcester, MA	42.22784	-71.78762	45.9

[1] Locations of co-sampling with NBC
[2] Corresponding river mile
[3] W0680 is located between the Worcester CSO discharge and UBWPAD2. The Worcester CSO enters the river downstream of the confluence of Mill Brook and the Middle River at approximately river mile 46.4.

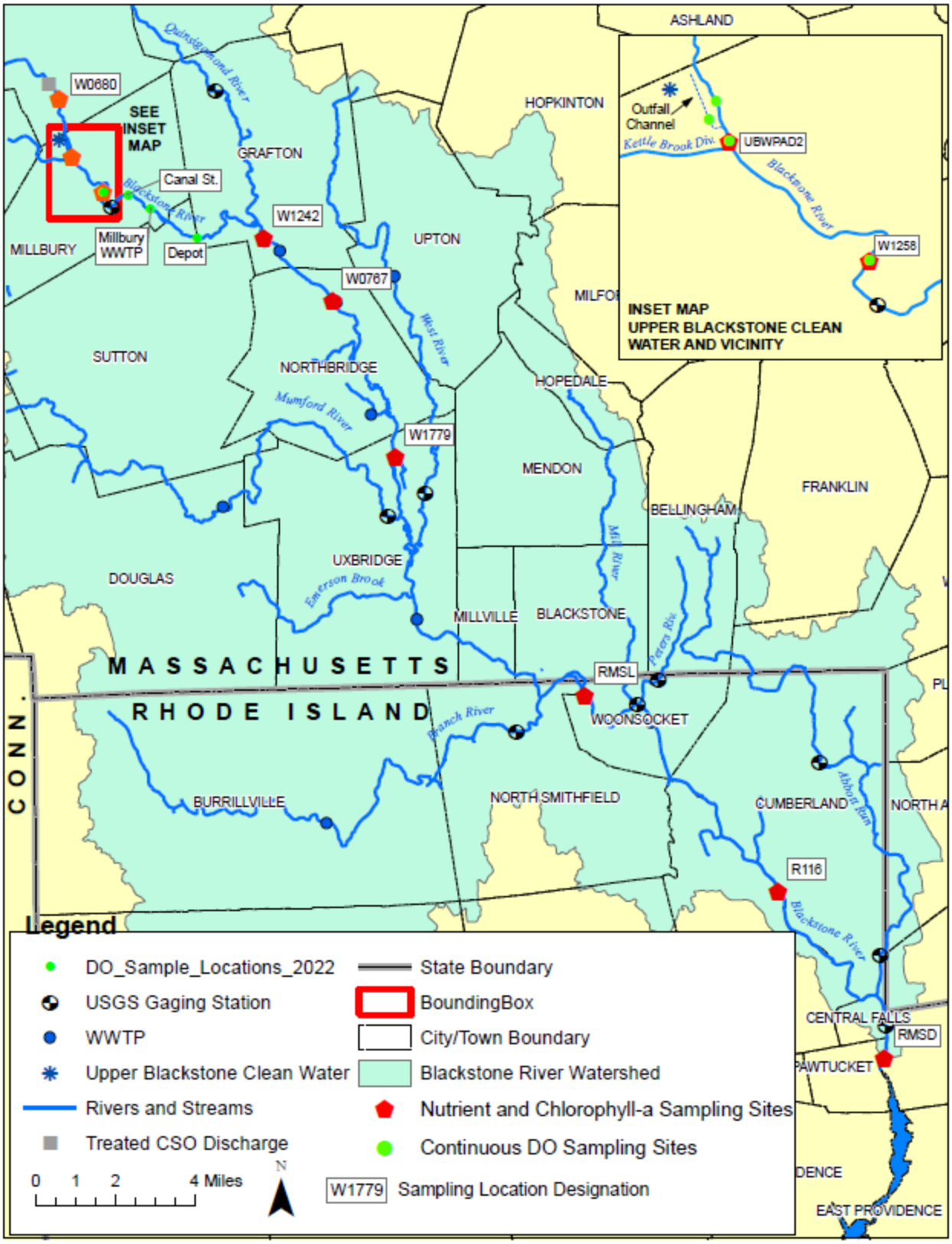

Figure 1: 2022 Blackstone River water quality monitoring locations

3.2 Nutrient Parameters, Methods, and Detection Limits

Aliquots prepared from the surface water grab samples will be analyzed at the Upper Blackstone laboratory, UMass Dartmouth (UMD) laboratory, or the UMass Environmental Analysis Laboratory (EAL), depending on the parameter. Samples collected from the sites co-sampled with NBC will also be analyzed at the NBC laboratory. Laboratory analysis methods and detection limits are summarized in **Table 3**.

Method Detection Limits (MDLs) are the lowest values at which a parameter can be measured using the reference method. The MDL is defined as the constituent concentration that, when processed through the complete method, produces a signal with 99 percent probability that it is different from the blank. Lab specific MDLs are developed for each particular analyte of interest and are established as targets for ensuring that the data quality obtained is adequate for interpreting the data; these MDLs are the minimum to be achieved by the laboratories.

The reporting limit (RL) is defined as the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions and can vary by sampling date. For this project, laboratories will be responsible for calculating the RL for each analysis batch, and will report out values below their RL as "non-detect."

In the database for the project, these data points will be entered at "BRL" (Below Reporting Limit). Half the reporting limit value from **Table 3** will be utilized for calculations. Data uploaded to WQX (EPA water quality portal) will be also entered as half the BRL for BRL results, and in Results Comments the note will say LT for [parameter].

The analyses and responsible laboratories for the 2022 sampling season are as follows:

- Samples will be analyzed at Upper Blackstone for total suspended solids (TSS), conductivity (Specific Conductance or SC), and total orthophosphate (TOP).
- The NBC lab[1] will analyze samples collected at the three Rhode Island sites for dissolved nitrate/nitrite (dNO_{23}), dissolved ammonia (NH3) and ammonium (dNH_4), total dissolved nitrogen (TDN), dissolved orthophosphate (DOP), total nitrogen (TN), dissolved silicate and total suspended solids (TSS). These three sites are co-sampled by UMass and NBC. A single large volume bulk environmental sample is collected, and aliquots for analysis at each lab are then split from this volume.
- Samples will be sent to the UMD laboratory for analysis of total dissolved nitrogen (TDN), dissolved nitrite/nitrate nitrogen (dNO_{23}), and dissolved ammonium (dNH_4). These samples will be filtered in the field utilizing a 0.22-micron filter.
- UMD will also analyze samples for particulate organic nitrogen (PON) and calculate total nitrogen (TN) for each sampling location/date based on the results of these analyses, Table 3.
- Samples will be analyzed for chlorophyll-a (chl-a) and total phosphorus (TP) at EAL.

Table 3 provides a summary of the data calculated by each lab.

[1] SOPs and the QAPP for the NBC were not included under cover of the QAPP for this project, as these data are part of their sampling program and considered external to the UMass sampling program. Details of their analysis methods, however, are provided herein.

Table 3: 2022 Analyses, Laboratories, Methods, and Limits

Upper Blackstone Clean Water		
Parameter	Method	Minimum Detection Limit
TOP	Hach 8048	20 ppb[4]
TSS	USGS I-3765-85	2 ppm
Conductivity	STD Method 2510B	0.0 µS/cm
UMass EAL		
Parameter	Method	Minimum Detection Limit/Minimum Reporting Limit
TP	STD Method 20th ed., 4500P	2 ppb/8 ppb
Chl-a[1c]	STD Method 20th ed., 10200 H	1 ppb
UMass Dartmouth		
Parameter	Method	Minimum Detection Limit/Minimum Reporting Limit
dNH_4[1d]	STD Method 20th ed, 4500-NH3-F	1.4 ppb/2.8 ppb
dNO_{23}[1d]	STD Method 19th ed, 4500-NO3-F	7 ppb/14 ppb
TDN[1d]	STD Method 19h ed, 4500-Norg	14 ppb/28 ppb
PON	EPA 440.0	14 ppb/28 ppb

[1] Filtration for dissolved nutrients varies by lab as detailed below.

[a] Starting in 2015, NBC moved to lab filtration for their dissolved constituents utilizing 0.45 micron filters.

[c] Filtered in the lab within 4-hours of sample collection with Whatman GF/F 47 mm, 0.70 micron filter.

[d] Field filtered utilizing Millipore (SLGP033RS), Millex-GP Syringe 0.22-micron filter units.

[3] Laboratories will be responsible for calculating the RL for each analysis batch, and will report out values below their RL as "BRL.". In the database for the project, these data points will be flagged with the code "LT" (less than) and the detection limit value listed as the result. This value will be use in plotting; half of the MDL will be utilized for calculations.

[4] The Upper Blackstone lab has worked to achieve the lowest detection limit possible with their existing equipment and methodologies, however the labs primary focus is analysis of WWTF effluent. It is acknowledged that these DLs are high for riverine analysis.

Table 4: Parameters Calculated Based on Lab Results

Lab	Parameter	Calculation[1]
NBC	Dissolved Inorganic Nitrogen	DIN = dNO_{23} + dNH4
	Dissolved Organic Nitrogen	dON = TDN - DIN
	Dissolved Kjeldahl Nitrogen	dTKN = TDN - dNO_{23}
UMD	Total Nitrogen	TN = TDN + PON

Note: [1] Half the MRL limit will be utilized in the calculation when laboratories report results for constituent parameters below the reporting limit.

3.3 Sampling Collection Details

This section describes the procedures for collecting and analyzing samples. It identifies the sampling equipment, performance requirements, and decontamination procedures utilized. The procedures for identifying sampling or measurement system failures and for implementing corrective actions are also summarized.

General Sample Collection

The field program will be conducted based on the Standard Operating Procedures (SOPs) on file as part of the 2020-2022 Quality Assurance Project Plan (QAPP) prepared for the Blackstone River Watershed Assessment Study. The QAPP is designed to serve as an umbrella document for any field sampling conducted as part of the project. Utilizing standard procedures and sampling techniques helps ensure the collection of accurate, precise, and representative samples, as well as helping to ensure data comparability and usability.

The SOPs on file that will be utilized during this field monitoring program were submitted as part of the QAPP prepared for the project and are listed in **Table 5**.

Table 5: Summary of SOPs for Sample Collection of Nutrients and Field Measurements

Document Name	Title
SOP-FLD-001	Collection and Handling of Water Samples for Water Quality Analyses
SOP-FLD-009	Calibration and Maintenance of Measuring and Test Equipment
SOP-FLD-010	Field Sampling of Chlorophyll-a
SOP-FLD-013	Field Measurement of Temperature, Dissolved Oxygen, and pH
SOP-FLD-014-2	Data Logger Measurement of Temperature and Dissolved Oxygen

Samples collected during the 2022 sampling season will be surface water samples collected from locations believed to be generally representative of net water quality within the river. Routine monthly samples will be collected regardless of precipitation and antecedent conditions.
Field data sheets will be used to document daily site activities and sample collection. Any variations from established procedure will be documented on the project Field Change Request and submitted to the Project Manager for review and archival.

Prior to collecting samples, the sampling location will be visually inspected and a Rivers and Streams Field Sheet completed. Any sampling issues will be noted either on an Equipment Problem Report Sheet or a Field Change Request Form. At each sampling location, the collection date, time, and additional collection details will be noted on the Bulk Sample Collection Data Sheet for the sampling event. Sampling data sheets will be transferred to UMass and retained as part of the monitoring record. Project field sheets and checklists are provided in Appendix B. Any observation that is not appropriate to note on individual field sheets will be recorded in the sampling crew's Field Notes Log Book.

Sample collection and bulk storage bottles will be cleaned with non-phosphate containing detergent between each sampling event as per the project SOPs, summarized in **Table 6**. The bottles will be filled with DI water after washing and the conductivity tested after 24-hours. Bottles with conductivity results above 2 microsiemens/centimeter will be rejected. Bottles that pass will be emptied, allowed to air dry, then capped and stored for the next event. All aliquot bottles, with the exception of those received from

UMD, will be similarly washed, tested, and dried. At least two spare bottles will be available each sampling trip in case of mishap.

Table 6: Sampling Container Decontamination Procedures

Sample type	Container	Decontamination	Staff
Sampling container	4 L, plastic	Phosphate-free soap, DI rinse	UMass
Bulk sample container	4 L and 6 L, plastic	Phosphate-free soap, DI rinse	UMass
Chl-a	500 mL and 1 L, amber plastic	Phosphate-free soap and acid wash, DI rinse	UMass
TP	125 mL, amber plastic	Phosphate-free soap and acid wash, DI rinse	UMass
TOP	237 mL, plastic	New, DI rinse	UMass
TSS, SC	1 L, plastic	New, DI rinse	UMass
dNH_4, dNO_{23}, TDN	60 mL, plastic	Acid wash, DI rinse	UMD
PON	1 L, plastic	Acid wash, DI rinse	UMD

Nitrile gloves will be worn by all sampling personnel, and will be changed between sampling sites.

Bulk water samples for nutrient analysis will typically be collected from either a bridge, utilizing a Nalgene 4-L wide-mouth HDPE bottle attached to a rope and reel or a peristaltic pump, or from the stream bank directly using the bulk sampling bottle attached to a sampling pole. The sampling rope and reel are technically considered to be non-dedicated sampling apparatus, as they contact surface water samples from more than one monitoring location. However, because they come into contact with the outside of the bottle only, this will not cause cross-contamination. The associated sampling container, however, is also utilized at more than one location. To minimize potential cross-contamination, the sampling container will be rinsed three times with river water prior to collecting the final sample. The sampling container is filled twice after rinsing with river water. The first time, the water is poured from the sampling container to the chlorophyll sample bottle to rinse it three times, then to fill it. The second fill is transferred into a clean 4-L wide-mouth HDPE bottle (the bulk collection bottle), which will also be rinsed three times with the sample water previous to final sample collection. An equipment blank will be collected at one site from the sampling container at the start of the sampling season, mid-season, and at the end of the season.

To collect samples from the stream bank, the sample bottle will be attached to the sampling pole. At W1779, the sample bottle used is the 4-L bulk sample bottle. At W0680 and UBWPAD2, the sample bottle used is the 1-L brown Nalgene bottle. The sample bottle is uncapped and dipped upside down in the water, rinsed and emptied downstream three times. The sample bottle is then dipped upside down in the water until fully submerged. The bottle is then turned right-side up and held in place until no more air bubbles come out and brought back to the stream bank. This bottle is used to rinse the other bottle three times at the stream bank (where the other bottle is a 1-L brown Nalgene bottle or a 4-L bulk sample bottle), and is refilled as many times as necessary to fill the other sample bottle at the stream bank. It is then filled and capped.

At the RI sites, a 6-L Nalgene carboy bottle with spigot will be utilized as the collection bottle to enable collection of a bulk sample large enough to provide splits for both NBC and UMass. At these three

locations, the sample will be collected utilizing NBC's peristaltic pump. This pump is designed to have minimal effect on water quality. Cross-contamination will be minimized by fully flushing the pump tubing prior to rinsing the collection bottles and caps three times with river water. Rinse water will be emptied away from the sampling location.

The bulk sample bottles will be labeled and put into a cooler packed with ice until they can be transferred to the lab for splitting into sub-sample bottles and preserved for subsequent laboratory analysis. Labels for the bulk sample bottles will be printed prior to the event (see Appendix C).

Chlorophyll-a Sample Collection

As per the chlorophyll-a SOP, samples for chl-a analysis are collected in amber containers, protected from sunlight, and filtered as soon as possible through a 47 mm diameter Whatman GF/F 0.7-micron pore size glass microfiber filter. Amber bottles will be put into a cooler packed with ice until they can be transferred to the Upper Blackstone lab where they will be filtered. Filtering will typically occur within four hours of sample collection.

Field Filtering for Dissolved Nutrients

NBC analyzes samples collected at their three Blackstone River sampling locations for dissolved nutrients. NBC filters samples in the field with a 0.45 µm filter. UMass began field filtration in 2015 per MassDEP guidance, both with a 45 µm filter and with a 0.22µm filter. UMass now filters only with 0.22 µm filter for analysis of dissolved nutrients at UMD as part of the project. **Table 7** provides an overview of the preparation of filtered samples.

Table 7: Summary of Sample Filtration

Parameter	Filter	Sites	Filtering location	Staff filtering
dNO_{23}	0.22 µm	All	Field	UMass (5 sites), Upper Blackstone (4 sites)
dNH_4	0.22 µm	All	Field	UMass (5 sites), Upper Blackstone (4 sites)
TDN	0.22 µm	All	Field	UMass (5 sites), Upper Blackstone (4 sites)
Chl-a[1]	0.7 µm	All	Upper Blackstone Lab	UMass

[1] Sample analyzed is filter residue, not the filtrate.

At all sites, aliquots for dissolved analysis will be field filtered with Millipore (SLGP033RS) 0.22-micron filter units attached to a Millex-GP syringe for analysis of the nitrogen series at UMD. A new syringe and filter unit will be utilized at each site. The syringe will be rinsed three times with water from the bulk collection bottle by removing the plunger, pouring into the barrel, and then replacing the plunger to shake and then dispose of the rinse water. After the final rinse, the Millipore filter unit will be attached, and the syringe filled with water from the bulk collection bottle. Next, 20 mL of sample will be filtered through the disposable 0.22-micron filter housing and discarded. Then, 20 mL of sample will be filtered

into the sample bottle to rinse and discard. The remaining 20 mL water in the syringe will be filtered into the 60 mL sample bottle. After removing the plunger, the filter will be removed from the syringe and discarded, then a new 0.22-micron filter will be attached. The syringe will be refilled with sample water, 20 mL wasted through the filter, and the remaining 40 mL of sample in the syringe then utilized to fill the 60 mL bottle containing 20 mL of sample from the first 0.22-micron filter. It should be noted that aliquot bottles provided by UMD will not be washed at UMass.

Field Blanks

Field blanks will consist of water that is transferred from one bulk collection bottle that was filled with DI water from the EAL lab the day before sampling, to a "field blank" collection bottle at the sampling site. A field blank will be collected for all parameters at a frequency of at least ten percent, or one field blank per ten samples. Sampling crews will be given specific instructions as to the sampling location where field blanks should be processed, transferring the DI water from the lab bottle to the bulk sample bottle. Processing of the field blank to aliquots, including the field filtration step, will occur in the same manner as for regular grab samples. Field blanks will provide an indication of whether atmospheric conditions or field procedures have the potential to lead to sample contamination.

Equipment Blanks

To ensure that samples collected with the 4-L sampling container are not contaminated from water collected at previous sites, an equipment blank will be collected the first sampling day in 2022 at a randomly selected bridge site. Two one-gallon jugs of Upper Blackstone DI will be transported to the field and used to rinse the sampling container three times and fill the sampling container. A bulk sample bottle labeled 'Equipment Blank' will then be filled from the sampling container. Processing of the equipment blank to aliquots, including the field filtration step, will occur in the same manner as for regular grab samples. An equipment blank will be also run mid-season and at the end of the season at another bridge site.

Field Duplicates

Field duplicates will consist of a second bulk sample collected at approximately the same time. Field duplicates will be collected for all parameters at a frequency of at least ten percent, or one duplicate per ten samples. Processing of the field duplicates, including the field filtration step, will occur in the same manner as for regular grab samples. Field duplicates will provide an indication of the inherent variability of nutrients in the water column over short spatial and temporal differences.

Field Splits

Field splits will consist of a second set of aliquots processed from the bulk collection bottle. Field splits will be collected for all parameters at a frequency of at least ten percent, or one split per ten samples. Field splits will provide an indication of the inherent variability within a sample, independent of replicates run by the laboratories. Enough water will be collected to allow splitting into all the aliquots at the UB lab. An extra 2-L bottle will be given to the crew collecting the field split in order to have enough sample water for 2 TSS/SC samples.

Performance Tests

A performance test (PT) will be provided to each laboratory per sampling event for dissolved phosphorus, dissolved orthophosphate, dissolved nitrite-nitrate, and dissolved ammonia, depending on the parameters analyzed for in their laboratory. The PT aliquots will be prepared each day before sampling by EAL staff from standards of a known concentration.

Sample Processing

The remainder, after field filtration, of the bulk samples will be transported back to the Upper Blackstone Alden building, where they will be split into smaller volume bottles for subsequent analysis. Labels for the aliquot splits will be printed prior to the event (see Appendix C). In general, when the coolers are brought inside for sample processing, the amber bottles for Chl-a analysis will be separated so that one crew member can begin filtering. The second crew member will begin to process the aliquots from the bulk samples.

All lab personnel will wear nitrile gloves, and will change gloves when switching to processing a new site. Working from downstream to upstream, the order in which sites were sampled, the bulk sample for each site will be found in the cooler and processed. Sets of bottles (a 1-L jug, a 243 mL squat bottle, etc.) will be set out for the given sampling location. Based on a sampling QAQC table provided to the sampling crew identifying sites where field splits are to be analyzed, additional bottles will be added to the site sets. Labels for the bulk and aliquot bottles will be compared; the sample collection time will be added to the aliquot bottle labels. After loosening the aliquot bottle caps, the bulk sample bottle will be fully mixed by inverting 10 times and the aliquot bottles rinsed three times. The bulk sample bottle will then again be fully mixed and the aliquot bottles filled with sample. Both the aliquot and bulk sample bottles will be re-capped as soon as possible and the bulk sample returned to its cooler. After completing the appropriate line on the chain of custody forms for the aliquots, the aliquots will be placed in separate coolers, one for each bottle type. If called for, bulk sample field blanks and duplicates will be processed after the bulk grab sample for the same site is processed.

At least one split duplicate (e.g., two aliquots taken from the same bulk sample bottle) and one field duplicate (a second bulk sample co-collected in the field) will be collected, processed, and analyzed for each parameter and sampling event to meet our QAQC objectives.

Table 8 summarizes the container, handling and preservation, and hold time for each analyte. At least two spare bottles for each aliquot type and blank labels will be available in case of mishap. Step-by-step directions utilized by the aliquot splitter have been developed and are available upon request.

Table 8: Sample Container Codes, Types, Volumes, Preparation, Special Handling, Preservation, Holding Times

Analysis	Cont. Code	Container	Handling & Preservation	Holding Time
TOP	A - Upper Blackstone	237 mL, plastic	Store ≤6°C	48 hours
TSS, SC	C - Upper Blackstone	1 L, plastic	Store <=6°C	7 days
Chl-a[1, 2]	D – EAL (filter retained only[1])	1 L, amber plastic	0.7-micron pore size glass microfiber filter, dry filter and freeze, store in dark, discard filtrate	21 days
TP	E - EAL	125 mL, amber plastic acid washed	Freeze	1 year
PON[1]	H – UMass Dartmouth	1 L, Plastic	Store 4±2°C. Transport to UMD (lab filtered by UMD; filter analyzed, filtrate discarded)	48 hours
dNH_4, dNO_{23}, TDN	I – UMass Dartmouth	60 mL, Plastic	0.22 µm filter[3]. Store filtrate 4±2°C. Transport to UMD.	48 hours

Notes:

[1] Sample analyzed is filter residue, not the filtrate

[2] Filtration occurs within 4 hours of sample collection.

[3] Filters are analyzed within 21 days according to the EAL QAPP

Preparation of Lab Blanks

The day prior to sampling, lab blanks will be prepared by filling aliquot bottles directly from the EAL source of DI water. The lab blank aliquot bottles will travel with the samplers from site-to-site and then be added to the appropriate cooler based on analyte type and lab at the end of the day. Lab blanks will provide an indication of whether DI source water, transportation steps, or laboratory analysis procedures have the potential to lead to sample contamination. In the event that positive blanks or duplicates are outside the acceptable precision range, additional blanks and/or duplicates will be added in subsequent sampling events to try and determine the source of contamination if it is not readily identifiable from existing data and documentation.

Sample Preservation

Once all aliquots are split, the 243 mL (TOP), 1 L (TSS/SC) for analysis at the Upper Blackstone will be moved from coolers to the walk-in refrigerator, unpreserved. Samples for delivery to UMD will be placed in a dedicated cooler with fresh ice and shipped via FedEx overnight. Samples for delivery to EAL will be moved from the Upper Blackstone freezer to a cooler, transported, and immediately placed in the EAL freezer.

Filtering for Chlorophyll-a

Following SOP protocols, water samples collected in amber bottles for chlorophyll-a analysis will be filtered in the Upper Blackstone lab through a 47 mm diameter Whatman GF/F 0.7-micron pore size

glass microfiber filter as soon as possible but no later than within 4 hours. Prior to filtering, all filtering equipment and containers will be rinsed three times with deionized (DI) water and then once with sample water. The filtering process will be set up with vacuum flask, filter holder, glass fiber filter, and filling funnel. After placing the filter rough side up on the filter holder, an exact sample volume will be measured out using a graduated cylinder, filtered, and the volume filtered recorded. Each sample will be filtered until the filter is visibly green or greenish brown. This coloration indicates enough chlorophyll has been collected for the chlorophyll-a analysis. For the Blackstone River, 250 mL of water will be typically filtered during the growing season, but during early spring and late fall, when productivity in the river is less, larger volumes will likely be filtered. During July and August, peak seasons for growth, smaller volumes may be filtered. When the entire measured sample has been filtered, the filling funnel will be removed and the filter carefully transferred from the filter holder with forceps, folded in half (green side in), and placed in an air-drying box. When all samples have been filtered, the drying box will be plugged in and the sample filters completely air-dried for approximately 25 minutes. The filters will then be removed with forceps, placed in aluminum foil, and labeled with the site name, date, time of sampling, and volume of water filtered. Filters will be frozen as soon as possible for preservation prior to chlorophyll-a analysis.

Chain of Custody

Chain of custody will be maintained in accordance with standard procedures. Chains of custody will be pre-filled out with the expected samples and analyses, including a line for each aliquot. At the time bulk samples are split into aliquots for preservation and subsequent analysis, chain of custody forms will be checked against the aliquot bottles and the collection times will be added. One chain of custody form will be prepared for each lab (Upper Blackstone, EAL, UMD), plus one for the NBC lab to accompany the PT sample given to the NBC sampling crew. Copies of the chain of custody forms are provided in Appendix D. Once the chain of custody forms are checked and signed by UMass staff, they will be transferred to the respective laboratories for their staff to sign.

Sample ID Nomenclature

Sample IDs will follow a set nomenclature consisting in general of four parts: sampling site ID, sample type, filtration code, and date. Unique sampling site identifications for each site are listed in the first column of Table 1. Sample types include both the sample itself, designated as a grab sample, as well as the quality assurance quality control (QAQC) samples such as splits, duplicates, blanks, and performance evaluation samples, **Table 9**. Each sample ID will also include a filtration code, as indicated in Table 9. The last field will be the sample collection date as MMDDYY.

Table 9: Sample Type Codes

Code	Description
G	Grab sample
FS	Field split
FD	Field duplicate
LB	EAL DI water lab blank
FB	EAL DI water field blank
EB	UB DI water equipment blank
P	Performance evaluation sample
TC	Temperature Check bottle

Table 10: Filtration Codes

Code	Description
UF	Unfiltered
FF22	22-micron field filtered
NA	Not applicable (e.g., for lab blanks)
FR	Filter residue (e.g., analysis done on a filter, such as for PON)

4.0 Field Water Quality Measurements

In 2022, field water quality measurements (water temperature, dissolved oxygen [DO], and pH will be collected at all sites. Field parameters will be collected with a hand-held Hach HQ 40 D multimeter equipped with two probes. Temperature, DO, and pH will be measured in situ by each field crew.

Each meter will be calibrated by UB staff at the UB lab on the morning of each sampling day, prior to sampling. Both DO and pH probes will be attached to the meter. Calibration forms are found in Appendix E, along with measurement instructions from the meter manual.

At the sampling site, measurements will be taken with the meter before or at the same time as the collection of river samples. The probe comes with a 25-foot cable. If the river surface cannot be reached, measurements will be taken from a sampling container. At each site:

1. Rinse the probes with DI water, then lower the probes into the river where water chemistry samples are collected, just below the water surface.
2. Press the READ key. When the screen shows that the measurements have stabilized, record the readings for water temperature (°C), DO saturation (%), DO concentration in mg/L, and pH on the field sheet.
3. Rinse the probes with DI water, and place the probes in their respective sleeves/flasks. Place the meter and probes in the travel bucket.

An SOP was created in 2019 and submitted as an addendum to the QAPP: SOP-FLD-013: Handheld Multimeter Field Measurements (see SOP-013 in Appendix F).

At the RI sites, the field parameters recorded by NBC should also be recorded on the field sheet.

Upon return to the UB lab, the pH probe will be placed in each of the buffers and readings recorded on the calibration form. The DO probe will be placed in the air-saturated water flask and the reading will be recorded on the calibration form. A photocopy of the calibration form for the sampling day will be given to the UMass team.

Conductivity will be measured with the Hach meter and a conductivity probe in the UB lab from the same samples used for TSS analysis. The lab SOP for conductivity measurement is included in Appendix F.

Upper Blackstone will install four continuous temperature and dissolved oxygen probes in the Blackstone River (see **Figure 1** for locations). The data loggers will be installed in late spring or early summer, depending on river streamflow, and will be removed in late October or early November. SOPs governing the deployment of the data loggers are described in Appendix F.

5.0 Schedule

The nutrient sampling program will follow the sampling schedule NBC has in place for their Blackstone River sampling. Because NBC sometimes needs to adjust their schedule, sampling dates will be confirmed with NBC and the labs one-week prior to each planned event. Samples will be collected routinely for nutrients once every 4th Wednesday, regardless of weather conditions, starting in April. See **Table 1** for sampling dates in 2022.

6.0 Quality Assurance

Prior to the first sampling event, sampling staff from UMass and Upper Blackstone will read through the Field Sampling Plan, sampling SOPs, and review field data sheets. UMass and Upper Blackstone sampling staff will then participate in a conference call or meeting which will act as a refresher on sampling protocols and will also enable staff to discuss any questions or concerns related to sampling. To ensure sampling procedures are followed and QAQC objectives are being met, Zachary Eichenwald will conduct a field audit during the May sampling event to observe sampling crews and document any deviations from the sampling SOPs. Field audit results will be made available to all sampling staff and any issues will be corrected.

Measurement performance criteria, including the precision, accuracy, completeness, comparability, and representativeness of the data will be used to assess the quality of all environmental measurements in relation to the objectives of this Scope of Work. The criteria for this project are presented in Appendix E. To meet these objectives, field duplicates, laboratory replicates, and blanks will be run. QAQC samples will at a minimum consist of 1 field duplicate (rate of 1:9) and one blank each sampling run (rate of 1:9). Additional blanks and duplicates will be added if positive blanks or duplicates outside of the acceptable precision range are noted.

In addition, one Performance Test (PT) sample will be used each month as a double-blind evaluation on the respective laboratory's performances for the following parameters: total dissolved phosphorus (TDP), dissolved orthophosphate (DOP), dissolved nitrate/nitrite (dNO_{23}), and dissolved total ammonia (dNH_4). The PT samples will be purchased from an outside PT manufacturer, diluted to concentrations representative of riverine conditions, and will be provided with a known quantity of analyte. Typically, one set of PT samples will be incorporated within the batch of river samples and submitted blindly to the laboratories. The laboratory's analytical results will be compared to the known analyte concentrations provided based on the PT manufacturer and known dilutions.

To ensure proper temperature storage of samples on sampling day, a 500 mL bottle filled with tap water will be added to each cooler before setting out to sample. The temperature of the water in this bottle will be measured when the cooler arrives at the UB laboratory.

7.0 Team Organization and Contact Information

Key team members participating on the Blackstone River Watershed Assessment Study include the following:

- Upper Blackstone Clean Water (Upper Blackstone)
- University of Massachusetts at Amherst (UMass)
- University of Massachusetts at Dartmouth (UMD)
- CDM Smith
- Narragansett Bay Commission (NBC)

The following section provides a brief discussion of the team member roles and responsibilities. Table 10 provides contact information for these team members and others that will assist with the sample collection.

Program Management and Technical Oversight. Ms. Karla Sangrey, P.E., Upper Blackstone Director, shall serve as the primary point of contact for the UB on the river sampling. Ms. Kristina Masterson, P.E., CDM Smith, will serve as the primary point of contact for CDM Smith on the river sampling. They will provide program management guidance and technical oversight, including review of the proposed Scope of Work and data reporting.

Upper Blackstone Laboratory Coordinator. Mr. Timothy Loftus will be the primary contact for the UB laboratory. He will coordinate with UMass to ensure UB can assist with sampling and analysis on sampling week, reserve the Upper Blackstone vehicle, and coordinate with the Upper Blackstone staff in terms of meeting times and duties. In addition, he will assist UMass to ensure the sample volumes and plans for filtering/preserving meet the UB needs.

EAL Laboratory Coordinator. Mr. Cameron Richards will be the primary contact for the EAL laboratory. He will ensure that all necessary supplies are available. He will also run Chl-a and TP samples sent to EAL.

NBC Laboratory Coordinator. Ms. Karen Cortes will be the primary contact for NBC. She will assist in coordinating sampling dates and co-sampling timing.

UMD Laboratory Coordinator. Ms. Sara Sampieri Horvet will be the primary contact for UMD. She will assist with coordinating aliquot bottle and filter delivery to UMass prior to each sampling event, and be the interface for data delivery and questions.

Principal Investigator. UMass will be responsible for field sampling and associated activities performed under this Scope of Work under the direction of Ms. Marie-Françoise Hatte, who will serve as principal investigator. Ms. Hatte will ensure that the work completed by the Project Team meets the prescribed scope of work; she will be the primary point of contact between UMass and the Upper Blackstone. Ms. Hatte will work closely with the Upper Blackstone, CDM Smith and NBC to make any necessary adjustments to the sampling plan and solicit feedback regarding the effort. Ms. Hatte and staff will also be responsible for coordinating the specific details of the data collection and review efforts, including:

- Oversight/assistance of the field program
- Oversight of identifying and resolving problems at the field team level
- Identifying, implementing, and documenting corrective action
- Oversight of documentation
- Data review and reporting.

Field Program Coordinator. Mr. Cameron Richards will serve as the Field Program Coordinator. He will be responsible for mobilizing, coordinating and managing sampling events, as well as, gathering and analyzing data in the field. Ms. Hatte will provide assistance where necessary.

Document and Data Custodian. Mr. Cameron Richards will serve as the document custodian, assisted by Ms. Hatte and Sara Molla, UMass Amherst undergraduate student. The Document Custodian will be responsible for maintaining project files and filing project documents, project correspondence, sample integrity data sheets, chain of custody forms, field report forms, field and equipment notebooks, generated data and other associated and pertinent project information. The Document Custodian will:

- Review documents for quality control when submitted, ensuring that data recording procedures have been carried out as per this SOP
- Maintain hardcopy and electronic records, converted paper files to an electronic database as needed
- Maintain and backup the master database for the project
- Assist in data analysis and visualization
- Assist in the interface between the monitoring and modeling portions of the project
- Be responsible for transferring data to Project PI
- Complete the required QAQC calculations based on duplicate and blank sample data returned from the labs
- Perform data review, verification, and validation, as described in Section 4

QAQC Officer. Ms. Hatte will serve as the QAQC Officer. She will review the QAQC data and suggest modifications to the sampling plan to address any concerns.

External QAQC Officer. Zachary Eichenwald of CDM Smith will serve as external QAQC Officer. He will conduct a field sampling audit on May 18, 2022.

Table 11: Team Contact Information

Name/Organization	Role	Contact
UMass: Marie-Françoise Hatte Cameron Richards	Principal Investigator Field Sampling Assistance QAQC Review EAL Lab Coordinator Field Program Coordinator Document & Data Custodian Primary Field Sampler	mfhatte@umass.edu 413.545.5531 (w) 413.768.8402 (c) cameronr@umass.edu 413.545.5979 (w) 978.732.4007 (c)
CDM Smith: Zach Eichenwald	Program Management & Technical Oversight "	eichenwaldzt@cdmsmith 508.654.2866 (c)
Upper Blackstone: Timothy Loftus Ornela Piluri Sharon Lawson Denise Prouty Patty Burke Sophia Kostoulas Amanda Coffuire Shawn Seely	 Upper Blackstone Lab Manager Upper Blackstone Sampling and Lab Assistance " " " " " " "	TLoftus@ubcleanwater.org (774.312.3956) opiluri@ubcleanwater.org (508.981.5540 Ornela) slawson@ubcleanwater.org (774.696.8423 Sharon) dprouty@ubcleanwater.org (508.523.9538 Denise) pburke@ubcleanwater.org (774-708-0146 Patty) skostoulas@ubcleanwater.org (617-291-5210 Sophia) acoffuire@ubcleanwater.org (774-571-1137 Amanda) SSeeley@UBClenawater.org (774-239-4811 Shawn)
UMD: Sara Sampieri Horvet Dr. David Schlezinger Brian Howes	 UMD Lab Coordinator UMD Lab Director UMD Lab QA Officer	508.910.6325 ssampieri@umassd.edu dschlezinger@umassd.edu bhowes@umassd.edu
NBC: Karen Cortes Eliza Moore John Motta Luis Cruz Molly Welsh Sara Nadeau Tyler Bissonnette Jeff Tortorella	 Asst Mgr, Environmental Monitoring Sr. Environmental Scientist Manager, Environmental Monitoring Environmental Scientist Environmental Scientist Field Supervisor Field Supervisor Field Supervisor	 Karen.cortes@narrabay.com 401.461.8848 ext. 274 eliza.moore@narrabay.com 401.461-8848, ext. 267 401.641.3216 401.461-8848, ext. 486 401.461-8848, ext. 389 401.461.3274 401.461.2709 401.461.1635

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APPENDIX

A: Site Directions and Maps

B: Field Sheets and Check Lists

C: Labels

D: Chains of Custody

E: Calibration Forms and Meter Manual

F: Field SOPs

Appendix E: Blackstone River Water Quality Monitoring Quality Assurance Project Plan 2020-2022

Blackstone River

Assessment of Water Quality, Ecological Health, and Ecological Risk through Data Collection and Modeling

Quality Assurance Project Plan

2020 – 2022

Version 3 (Amendment 2)

Prepared for:

Upper Blackstone Clean Water

Prepared by:

The University of Massachusetts Amherst

CDM Smith

April 16, 2021

QUALITY ASSURANCE PROJECT PLAN

for

Blackstone River Watershed Assessment Study

PREPARED BY: Massachusetts Water Resources Research Center
University of Massachusetts at Amherst
250 Natural Resources Rd, Ag Engineering Room 209
University of Massachusetts
Amherst, MA 01003

APPROVED BY:

Upper Blackstone Engineer-Director/Treasurer:

_____ Date:_____

Karla Sangrey, P.E., Upper Blackstone Engineer-Director/Treasurer
UB Clean Water, 50 Route 20, Millbury, MA 01527
Tel: 508-755-1286, Fax: 508-755-1289
Email: ksangrey@ubcleanwater.org

Project Manager:

_____ Date:_____

Kristina Masterson, P.E., CDM Smith
75 State Street
Suite 701
Boston, MA 02109
Tel: 617-452-6284, Fax: 617-452-8284
Email: mastersonkk@cdmsmith.com

Monitoring Program Coordinator & Field Program Coordinator:

_____ Date:_____

Marie-Françoise Hatte UMass
Massachusetts Water Resources Research Center
250 Natural Resources Road, Ag Engineering Room 201, University of Massachusetts Amherst
Amherst, MA 01003
Tel: 413-545-5531
Email: mfhatte@umass.edu

Program Quality Assurance Officer, Document & Data Custodian, and Lab Program Coordinator:

_____ Date:_____

Cameron Richards, Massachusetts Water Resources Research Center

Massachusetts Water Resources Research Center
250 Natural Resources Road, Ag Engineering Room 203, University of Massachusetts at Amherst
Amherst, MA 01003
Tel: (413) 545-5579
Email: cameronr@umass.edu

External Quality Assurance Manager:

_____ Date:_____

Zach Eichenwald, P.E. CDM Smith

75 State Street
Suite 701
Boston, MA 02109
Tel: 617-452-6283, Fax: 617-452-8284
Email: eichenwaldzt@cdmsmith.com

Upper Blackstone Lab Project Quality Assurance Officer and Technical Manager:

_____ Date:_____

Timothy Loftus, Upper Blackstone

UB Clean Water, 50 Route 20, Millbury, MA 01527
Tel: 508-755-1286, Fax: 508-755-1289
Email: TLoftus@ubcleanwater.org

UMass Dartmouth Coastal Systems Program Lab Technical Manager:

_____ Date:_____

Sara Sampieri Horvet, UMD Coastal Systems Program Lab

Coastal Systems Program, 706 South Rodney French Blvd, New Bedford, MA 02744
Tel: (508) 910-6325
Email: ssampieri@umassd.edu

UMass Dartmouth Coastal Systems Program Lab Quality Assurance Officer:

_____ Date:_____

Brian Howes

Coastal Systems Program, 706 South Rodney French Blvd, New Bedford, MA 02744

Tel: (508) 910-6365
Email: bhowes@umassd.edu

Environmental Analysis Laboratory Quality Assurance Officer and Technical Manager:

_____ Date:_____

Cameron Richards, Massachusetts Water Resources Research Center

Massachusetts Water Resources Research Center

250 Natural Resources Road, Ag Engineering Room 203, University of Massachusetts at Amherst

Amherst, MA 01003

Tel: (413) 545-5579
Email: cameronr@umass.edu

REVIEWED BY:
Massachusetts Department of Environmental Protection (MassDEP)

_____ Date:_____

Suzanne Flint, QA Officer
MassDEP, 8 New Bond Street, Worcester, MA 01606
Suzanne.flint@mass.gov
508-767-2789

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3 - UMD Coastal Systems Lab Chain of Custody Form

Appendix G **Lab QAPPs and Standard Operating Procedures for Laboratory Analyses**

1 - EAL QAPP 2019 (includes SOPs)
2 - UMD Coastal Systems Program Lab QA Plan 2020(includes SOPs)
3 - Upper Blackstone Laboratory SOPs

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Acronyms and Abbreviations

%R	Percent Recovery
µg/L	Micrograms per Liter (0.000001 L)
AOC	Administrative Order on Consent
ASTM	American Society of Testing and Materials
BRL	Below Reporting Limit
Chl-a	Chlorophyll-a
CMR	Code of Massachusetts Regulations
COC	Chain of Custody
DO	Dissolved Oxygen
dNO23	Dissolved Nitrite-Nitrate Nitrogen
DQO	Data Quality Objective
EPA	United States Environmental Protection Agency
EAL	Environmental Analysis Laboratory
FSP	Field Sampling Plan
HSPF	Hydrologic Simulation Program – Fortran
L	Liter
LCS	Laboratory Control Sample
LCSD	Laboratory Control Sample Duplicate
MassDEP	Massachusetts Department of Environmental Protection
MassDPH	Massachusetts Department of Public Health
MaWRRC	Massachusetts Water Resources Research Center
MDL	Method Detection Limits

mL	Milliliter (0.001 L)
NBC	Narragansett Bay Commission
NCEI	National Centers for Environmental Information
NO23	Total Nitrite-Nitrate
NPDES	National Pollutant Discharge Elimination System
NWS	National Weather Service
PE	Performance Evaluation
P.E.	Professional Engineer
PON	Particulate Organic Nitrogen
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Project Plan
RIDEM	Rhode Island Department of Environmental Management
RL	Reporting limit
RPD	Relative Percent Difference
SC	Specific Conductance (also called Conductivity)
SOP	Standard Operating Procedures
TAC	Technical Advisory Committee
TMDL	Total Maximum Daily Load
TDN	Total Dissolved Nitrogen
TN	Total Nitrogen
TP	Total Phosphorus
TOP	Total Orthophosphate
TSS	Total Suspended Solids
UB	Upper Blackstone Clean Water

UMD	UMass Dartmouth
Upper Blackstone	Upper Blackstone Clean Water
UMass	University of Massachusetts Amherst
USGS	United States Geological Survey
WPP	Watershed Planning Program (at MassDEP)
WWTF	Wastewater Treatment Facility

3. QAPP Distribution List

The following individuals shall receive copies of the approved QAPP and any subsequent revisions:

Karla Sangrey, P.E.
Engineer-Director/Treasurer
Upper Blackstone
50 Route 20
Millbury, MA 01527

Kristina Masterson, P.E.
Project Manager
CDM Smith
75 State Street
Suite 701
Boston, MA 02109

Marie Françoise Hatte
Monitoring Program Coordinator
MaWRRC, UMass
250 Natural Resources Road
Amherst, MA 01003

Timothy Loftus
Laboratory Director and Quality Control Officer
Upper Blackstone
50 Route 20
Millbury, MA 01527

Zach Eichenwald, P.E.
External Quality Assurance
CDM Smith
75 State Street
Suite 701
Boston, MA 02109

Cameron Richards
Lab Program Coordinator
Program Quality Assurance
Document & Data Custodian
EAL Lab Manager
MaWRRC, UMass
250 Natural Resources Road
Amherst, MA 01003

Sara Sampieri Horvet
Lab Technical Manager
Coastal Systems Program
UMass Dartmouth
706 South Rodney French Blvd
New Bedford, MA 02744

Brian Howes
Lab Quality Assurance Officer
Coastal Systems Program
UMass Dartmouth
706 South Rodney French Blvd
New Bedford, MA 02744

Richard Chase
Technical Reviewer
MassDEP
8 New Bond Street
Worcester, MA 01606

Suzanne Flint, QA Officer
MassDEP, 8 New Bond Street,
Worcester, MA 01606

4. Project / Task Organization

4.1 Study Authority

The Blackstone River Watershed Assessment Study was initiated by Upper Blackstone Clean Water (Upper Blackstone) in 2003, and over the years has included data collection and analysis as well as numerical modeling of Blackstone River flow and water quality.

Wastewater treatment plant upgrades at Upper Blackstone designed to meet the 2001 NPDES permit limits were completed in fall 2009. Since that time, Upper Blackstone has continued a river monitoring program to collect data to assess the response of the river to reduced nutrient concentrations in the Upper Blackstone wastewater treatment plant effluent.

This Quality Assurance Project Plan (QAPP) was developed to cover routine river monitoring conducted by Upper Blackstone from 2020 – 2022. This document is based on the United States Environmental Protection Agency's (EPA) *QA/R-5: EPA Requirements for Quality Assurance Project Plans* (March 2001), the Massachusetts Inland Volunteer Monitoring General Quality Assurance Project Plan (December 2008), and the 2017 - 2019 QAPP approved by the Massachusetts Department of Environmental Protection (MassDEP). This submittal is comprised of the following four components:

- QAPP: Provides a summary of the project scope and objectives, defines the project quality objectives, methods for water quality measurements and provides an overview of the field, analytical, and quality assurance/ quality control (QA/QC) activities;
- 2020 Field Sampling Plan (FSP): Describes the specific sampling criteria, locations, and frequency for water quality measurements and other river monitoring activities conducted in 2020;
- Standard Operating Procedure (SOP) Compendium: Compilation of SOPs detailing the specific sampling and laboratory procedures; and
- Associated laboratory QAPPs and SOPs.

FSPs for each year will be provided when available.

The QAPP is designed to cover the range of sampling activities anticipated under the Blackstone River Watershed Assessment Study and serves as an umbrella document for sampling season specific FSPs. Sampling locations, the number of samples per sampling location, and parameters analyzed will be specified in each annual FSP. Amendments will be made to this QAPP as necessary to encompass new sampling activities or the measurement of additional environmental parameters.

Copies of this QAPP are provided to the Massachusetts Department of Environmental Protection (MassDEP) for review, comment, and acceptance so that data collected by Upper Blackstone may be submitted to the MassDEP Watershed Planning Program (WPP) for use in decision making regarding surface water quality assessments required by Sections 305(b) and 303(d) of the Clean Water Act.

4.2 Team Organization

Key team members participating on the Blackstone River Watershed Assessment Study include the following:

- Upper Blackstone Clean Water (Upper Blackstone)
- University of Massachusetts Amherst (UMass)
- CDM Smith
- UMass Dartmouth Coastal Systems Program Lab (UMD)

A project organizational chart is shown in Figure 1.

The following section provides a general discussion of the team member roles and responsibilities.

Upper Blackstone Engineer-Director/Treasurer. Ms. Karla Sangrey, P.E., Upper Blackstone Engineer-Director/Treasurer, shall serve as the primary point of contact for Upper Blackstone on the Blackstone River Watershed Assessment Study. In her role, Ms. Sangrey will provide direction regarding the scope and focus of the program including sampling locations and the proposed parameters to be measured. She, with the assistance of UMass and CDM Smith, will present annual field sampling program plans to the Upper Blackstone Board of Directors for approval.

Monitoring Program Coordinator. All field sampling and associated activities performed under this QAPP, and the preparation of associated yearly Field Sampling Plans, will be completed by the UMass Massachusetts Water Resources Research Center under the direction of Marie-Françoise Hatte, who will serve as the Monitoring Program Coordinator. Ms. Hatte will ensure that the work completed by the Project Team meets the prescribed scope of work; she will be the primary point of contact between UMass, CDM Smith, and Upper Blackstone. Ms. Hatte will also be responsible for coordinating the specific details of the data collection and review efforts, including:

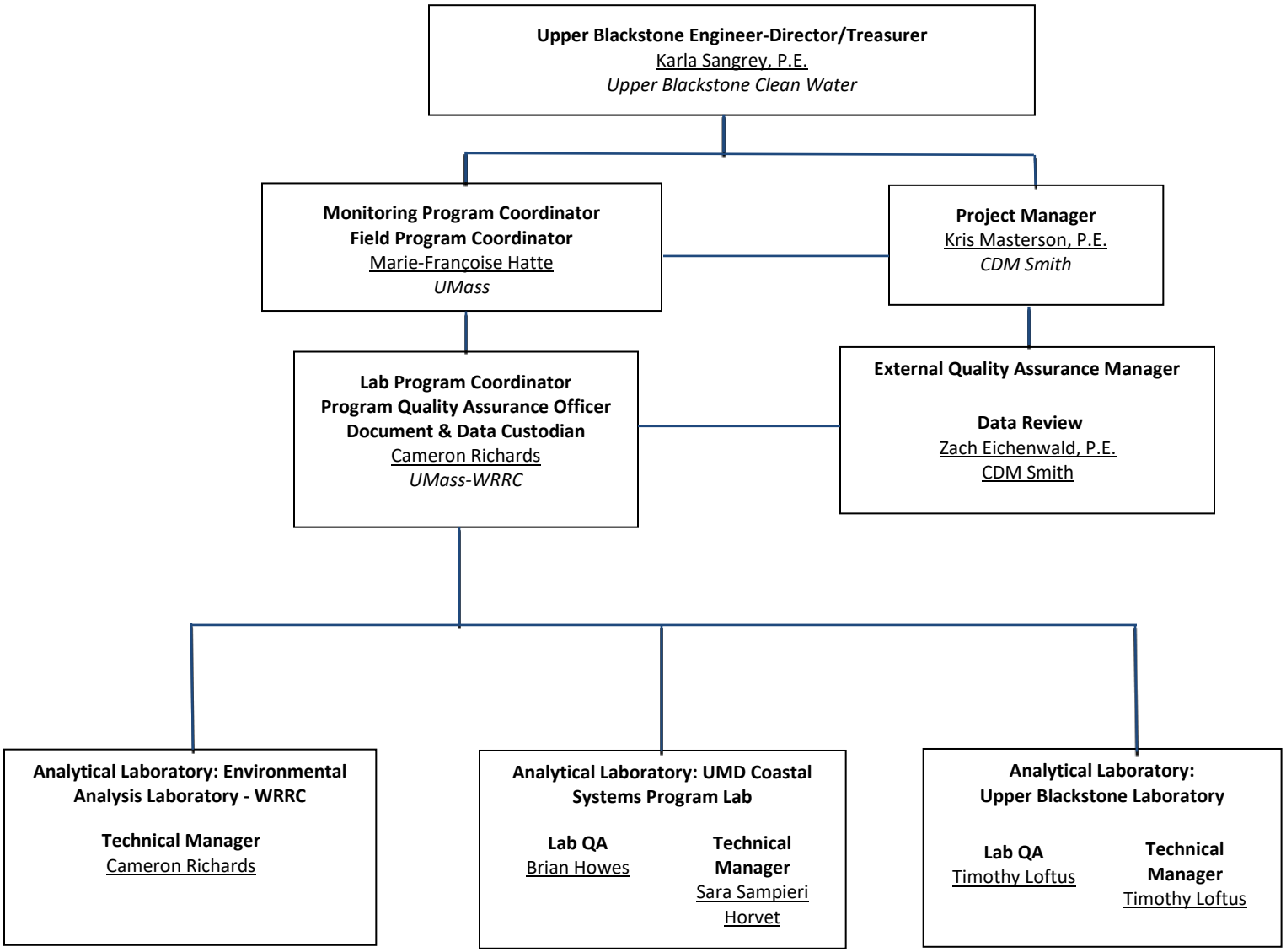

Figure 1: Project Organizational Chart

- Overseeing preparation for sampling events, including bottle and sampling equipment preparation, organization of field crews, and notification of the laboratories;
- Identifying and resolving problems at the field team level;
- Identifying, implementing, and documenting corrective action; and
- Oversight of data review and reporting.

Project Management and Technical Oversight. CDM Smith will provide project management guidance and technical oversight for the Blackstone River Watershed Study. Ms. Kristina Masterson will serve in a project management/coordination role to provide technical guidance for the field program, including technical review of the collected data, review of annual program reports, and assistance with public outreach.

Field Program Coordinator. The Field Program Coordinator will be responsible for mobilizing, coordinating and managing sampling events, as well as gathering and analyzing collected data. Marie-Françoise Hatte, or a designated UMass staff member or student, will serve as the Field Program Coordinator. CDM Smith will provide field program coordination assistance as necessary.

The Field Program Coordinator will be responsible for tracking weather conditions to determine when sampling events dependent on weather conditions will be conducted, however the Monitoring Program Coordinator will make the final go or no-go decisions in collaboration with the lab technical managers, CDM Smith, and Upper Blackstone.

The Field Program Coordinator will also oversee equipment function checks and calibration as detailed in the annual Field Sampling Plan and associated Standard Operating Procedures. He/she will be responsible for ensuring the completion of all appropriate Calibration Sheets, Field Sheets (FS), and/or notebooks documenting completion of these duties. They will also be responsible for transferring raw data, calibration, equipment check and other FS's to the Document and Data Custodian.

The Field Program Coordinator will be assisted in these duties by trained staff and/or student project personnel.

Field Samplers: Collection of samples will be performed by two teams: The Upper Loop or Northern team will consist of the Program Quality Assurance Officer assisted by a trained UMass undergraduate student (or the Field Program Coordinator), and the Lower Loop or Southern team will consist of two Upper Blackstone laboratory staff.

Lab Program Coordinator. The Lab Program Coordinator will be responsible for interface between labs, the Field Program Coordinator, the Monitoring Program Coordinator, the Program Quality Assurance Officer, and the External Quality Assurance Managers. As such, they will complete the required Quality Assurance/Quality Control calculations based on duplicate and blank sample data returned from the labs. In addition, they will coordinate external review of these data and all sampling procedures. Specifically, the Lab Program Coordinator will:

- Organize Field Quality Control Check data into a separate database so that lab performance on duplicates, blanks, and Performance Evaluation (PE) samples may be evaluated;
- Organize Field Analytical Quality Control Check data either into a separate database or integrate with existing field database so that quality can be assessed;
- Perform data review, verification, and validation, as described in Section 4;
- Calculate measurement performance criteria, as described in Section 1.4.2;
- Submit results of internal quality control checks to the Monitoring Program Coordinator, who will review and submit to appropriate delegates for further review;
- Lead data review, analysis and visualization; and
- Assist with project reporting.

Cameron Richards will be the Lab Program Coordinator but may be assisted by trained student project personnel.

Program Quality Assurance Officer. The Program Quality Assurance Officer will also serve as the Document and Data Custodian. WRRC staff member Cameron Richards will serve in these roles. As such, he will be responsible for ensuring the QA/QC objectives of the project, as outlined in this QAPP, are met. In addition, he will be responsible for maintaining project files and filing project documents, project correspondence, sample integrity data sheets, chain of custody forms, field report forms, field and equipment notebooks, generated data and other associated and pertinent project information. In summary, the Program Quality Assurance Officer will:

- Review documents for quality control when submitted, ensuring that data recording procedures have been carried out as per this QAPP;
- Ensure that hardcopy data entries (calibration dates, field checks, etc.) are converted to an electronic database;
- Maintain and backup the master database for the project;
- Review the adherence of the monitoring and laboratory analysis portions of the project to the stated quality objectives;
- Coordinate and respond to the review of External Quality Assurance Managers; and
- Assist in project reporting of these items.

External Quality Assurance Manager. The External Quality Assurance Manager will provide an independent review of the project both in terms of technical procedures and data quality. CDM Smith's Zach Eichenwald will serve in this capacity as both the Technical and Data reviewer. The Quality Assurance Manager will be responsible for assessing the effectiveness of the field sampling program

implementation and associated quality assurance and control activities. The purpose of this assessment is to ensure that the QAPP is implemented as prescribed and that appropriate responses are in place to address any non-conformances and deviations from the QAPP. Specific duties of the Quality Assurance Manager include:

- Conduct Field Audits, as described in Section 20.2;
- Review Laboratory Audits, as described in Section 20.3;
- Ensure that proper corrective actions are taken (Section 20.4);
- Review data validation and usability procedures and documentation, conducted by Program Quality Assurance Officer; and
- Review measurement performance criteria results, produced by Program Quality Assurance Officer, Section 7.2.

The External Quality Assurance Manager, in terms of both technical and data review, will be an independent reviewer.

Analytical Laboratories. The Upper Blackstone Lab, the Environmental Analysis Laboratory (EAL) at UMass Amherst, and the UMass Dartmouth Coastal Systems Program Lab will provide analytical support of water samples collected during this investigation. If additional labs are needed, the QAPP will be amended as necessary. The contacts at the Upper Blackstone Lab, EAL, and UMD labs are Timothy Loftus, Cameron Richards, and Sara Sampieri Horvet, respectively. Each analytical laboratory has identified both a Lab Quality Assurance Officer and a Lab Technical Manager for the project. Their duties will be as described in Section 19. The Program Quality Assurance Officer is responsible for assuring that the Quality Assurance Plans for their respective laboratories is adhered to and that the quality assurance and quality control criteria stipulated in this QAPP is achieved and documented for all analyzed samples. Laboratory technical staff is responsible for sample analysis and identification of corrective action. None of the labs used in this project are state-certified by MassDEP.

5. Problem Identification / Background

5.1 Problem Definition and Background

5.1.1 Study Background

The study was initiated in 2003 with the objective of developing key planning documents necessary for monitoring and modeling in the Upper Blackstone watershed. During this period, the study team developed a framework for evaluating the relative impacts of the following:

- Phosphorus and nitrogen in the effluent from the Upper Blackstone wastewater treatment plant,
- Phosphorus, nitrogen, and bacteria from other point sources and diffuse sources in the Upper Blackstone basin, and

- The likely in-stream effect of various mitigation/abatement plans for these pollutant sources.

From 2004 – 2006, monitoring was conducted as specified in the 2005 Upper Blackstone FSP. In addition to the development and implementation of a watershed-monitoring plan for the Blackstone River, a computer simulation model was refined to enhance understanding of the causal mechanisms and fate of nutrients in the Blackstone River Basin. The modeling effort built on earlier work conducted by the U.S Geological Survey (USGS), and included simulation of river flows and water quality using the Hydrologic Simulation Program - Fortran (HSPF).

During the period between 2007 and 2010, the model calibration was refined per recommendations suggested by the Technical Advisory Committee (TAC). In particular, the calibration and validation incorporated data collected by USGS and MassDEP in 2007 and 2008.

Since 2011, the river has been monitored annually for nutrients and associated indicator parameters such as chlorophyll-a and dissolved oxygen. In 2011, data on dissolved nutrients and chlorophyll-a were collected monthly at 14 mainstem locations from May through November. Mid-month, additional samples were collected at 11 mainstem locations only for chlorophyll-a analysis. In 2012, the focus shifted to total nitrogen and phosphorus, subspecies, and chlorophyll-a, with the sampling sites and sampling schedule remaining the same. Periphyton sampling was incorporated into the monitoring program, occurring at 8 sites in August and September. In 2013, the number of monthly monitoring locations was reduced to 9 and the additional mid-month chlorophyll-a sampling was dropped. Three sites were sampled for periphyton in June, July, August, and September. In 2017 and 2019 continuous temperature and dissolved oxygen data loggers were deployed at four locations during the growing season.

This QAPP was developed to cover the 2020 Sampling Season Scope of Work as well as sampling anticipated in 2021 and 2022. In 2020, monthly routine sampling for nitrogen, phosphorus, and chlorophyll-a as well as hand-held meter measurements (dissolved oxygen, temperature, pH, and conductivity) will continue from April through November at 9 locations. In addition, the continuous temperature and dissolved oxygen data loggers will be deployed from approximately June through October (conditions permitting).

Table 1 summarizes the various phases of the project since it began in 2003. A QAPP was submitted to MassDEP in 2004 outlining sampling and analysis procedures for river samples collected in 2004-2006. A revised QAPP addressing comments provided by MassDEP was submitted in August 2005 (UMass and CDM Smith, 2005). The QAPP covering the period 2014 – 2016 was submitted in April 2015 and subsequently revised based on comments and approved in June 2015. The QAPP covering the 2017-2019 period was revised several times during that period.

Table 1: Summary of Blackstone River Monitoring and Modeling Study

Dates	Phase	Activities
2003 – 2004	I	Project framework development
2004 - 2006	II	▪ HSPF water quality model development, calibration, and validation ▪ **Water quality monitoring 2005** - Parameters o Bacteria (fecal coliform, *E. coli*, enterococci) o Total nutrients (phosphorus[1], orthophosphate[2], nitrogen, nitrate/nitrite, ammonia, total suspended solids, chlorophyll-a) o Total and dissolved heavy metals (cadmium, copper, lead, zinc) o Biochemical oxygen demand (BOD) - Dry weather event o Upper watershed (above confluence with the Quinsigamond River) - 5 upper watershed tributaries - 4 mainstem locations in upper watershed - 1 point source o 5 mainstem locations in Massachusetts o 1 tributary (Quinsigamond River) - Three wet weather events o Same locations as dry weather, plus an addition of 1 point source - Continuous in situ monitoring for physical data at 9 locations, including 5 headwater tributaries and 5 mainstem locations ▪ **Water quality monitoring 2006** - Same parameters as in 2005 - Dry weather event o Upper watershed (above confluence with Quinsigamond River) - 6 upper watershed tributaries - 4 mainstem locations in upper watershed - 1 point source o Massachusetts mainstem (confluence with Quinsigamond River to state line) - 5 mainstem locations - 4 point sources - 3 tributaries o Rhode Island - 3 tributaries - 3 mainstem locations - Two wet weather events o Upper watershed (above confluence with Quinsigamond River) - 3 mainstem locations - 2 point sources - 1 tributary o Massachusetts mainstem (confluence with Quinsigamond River to state line) - 5 mainstem locations - 3 tributaries o Rhode Island - 3 tributaries - 2 mainstem locations - Continuous in situ monitoring for physical data at 9 locations o 1 upper watershed tributary o 2 mainstem locations in the upper watershed above confluence with the Quinsigamond River

		o Quinsigamond River outlet o 4 mainstem locations in Massachusetts between the confluence with Quinsigamond River and the state line o 1 mainstem Rhode Island location
2007 - 2010	III	▪ Data analysis ▪ Work with Technical Advisory Committee (TAC) ▪ Refinement of HSPF model calibration ▪ Incorporation of data collected by USGS and MassDEP in 2007 and 2008
2011	IV	▪ Water quality monitoring - April – November monthly dissolved nutrient and chlorophyll-a data at 14 mainstem locations - "Off" bi-weekly sampling at 11 mainstem locations for chlorophyll-a
2012	V	▪ Water quality monitoring - April – November monthly total nutrient and chlorophyll-a data at 14 mainstem locations - "Off" bi-weekly sampling at 11 mainstem locations for chlorophyll-a - Periphyton sampling in August and September at 8 sites - Collection of in-situ continuous physical data (pH, conductivity, turbidity, and dissolved oxygen) the week of periphyton sampling at 4 locations
2013	VI	▪ Water quality monitoring - April – November monthly total nutrient and chlorophyll-a data at 9 mainstem locations - Periphyton sampling in June, July, August and September at 3 sites - Collection of in situ continuous physical data (pH, conductivity, turbidity, and dissolved oxygen) the week of periphyton sampling at 2 locations
2014	VII	▪ Water quality monitoring - April – November monthly nutrient and chlorophyll-a data at 9 mainstem locations - Periphyton sampling in June, July, August and September at 4 sites - Collection of in-situ continuous physical data (pH, conductivity, turbidity, and dissolved oxygen) the week of periphyton sampling at 2 locations - Macroinvertebrate sampling 5 locations
2015	VIII	▪ Water quality monitoring - April – November monthly nutrient and chlorophyll-a data at 9 mainstem locations - Periphyton sampling in July, August and September at 4 sites - Macroinvertebrate sampling at 5 locations - In situ physical data collected at each site on the day of sampling (pH, conductivity, turbidity, and dissolved oxygen).
2016	IX	▪ Water quality monitoring - April – November monthly nutrient and chlorophyll-a data at 9 mainstem locations - Periphyton sampling in July, August and September at 4 sites
2017	X	▪ Water quality monitoring - April – November monthly nutrient and chlorophyll-a data at 9 mainstem locations - Periphyton sampling in July, August and September at 4 sites - Continuous water temperature and dissolved oxygen monitoring at 4 sites from June through November
2018	XI	▪ Water quality monitoring - April – November monthly nutrient and chlorophyll-a data at 9 mainstem locations

		- Periphyton sampling in July, August and September at 4 sites
2019	XII	▪ Water quality monitoring - April – November monthly nutrient and chlorophyll-a data at 9 mainstem locations - Point data collected at each site on the day of monthly sampling (water temperature, pH, conductivity, and dissolved oxygen) - Continuous data for water temperature and dissolved oxygen at 4 mainstem locations July through October

1 Dry weather events and first wet weather event did not include; both total and dissolved phosphorus were added starting with the 2nd wet weather event. 2 Both total and dissolved orthophosphate was analyzed for during wet weather events

5.1.2 Description of Existing Conditions

The Blackstone River originates at the confluence of the Middle River and Mill Brook in Worcester, Massachusetts. It flows southeast for 48 miles into Rhode Island where it discharges into the Seekonk River. The Seekonk River discharges into the Providence River, which flows into Narragansett Bay. The mainstem of the Blackstone River is joined by six major tributaries: Quinsigamond River, Mumford River, West River, Mill River, Peters River, and Branch River, as well as many smaller tributaries. The Blackstone River watershed, shown on Figure 2, has an area of approximately 480 square miles. The watershed consists of over 1,300 acres of lakes and ponds including the largest, Lake Quinsigamond. Several reservoirs in the northwest portion of the basin are used for the City of Worcester water supply. Several USGS streamflow gaging sites are located in the watershed, and hourly precipitation data are available for several locations in and near the watershed from the National Weather Service (NWS) and the National Centers for Environmental Information (NCEI), also shown on Figure 2.

The Blackstone River Valley of Massachusetts and Rhode Island is the "Birthplace of the American Industrial Revolution." A farming and milling area in colonial days, the Blackstone River Valley was transformed into one of the 19th century's great industrial areas. With a 430-foot drop in elevation from Worcester, MA, to Providence, RI, the river was an excellent place to locate mills in the days before steam or electricity turned machinery. Water powered textile mills proliferated up and down the river. During the transformation from farm to factory economy, the river became polluted and its course was altered by intense industrial activity and settlement along it. The many dams, canals and other human interventions resulted in a river very different from its original free-flowing state. Nineteen of the dams are still in place today, and the presence of these dams influences the flow and quality of the river. In its natural, free flowing condition, water took approximately 5 days to travel from Worcester to Providence during periods of low river flow. Now, because of the impoundments, it could take almost a month for water to travel this same distance during low river flow conditions.

There are nine wastewater treatment facilities (WWTFs) that discharge into the Blackstone River watershed. The largest facility, in terms of average effluent flow volume, is the Upper Blackstone WWTF, which is located near the headwaters of the Blackstone River. The Woonsocket WWTF is the second largest plant in the watershed and is located in Rhode Island. Other WWTFs that discharge to the river include: Grafton, Northbridge, Burrillville, Uxbridge, Hopedale, Douglas, and Upton. In order to meet National Pollutant Discharge Elimination System (NPDES) permits, which are jointly issued by EPA and MassDEP, most WWTFs that discharge to the Blackstone River have incorporated advanced treatment upgrades.

In fall 2009, Upper Blackstone completed upgrades to its wastewater treatment facilities to meet more stringent discharge limits set by EPA and MassDEP in 2001. The 2001 permit established a seasonal (April through October) total phosphorus (TP) limit of 0.75 mg/L. Recognizing that nitrogen removal could be required in the future to control algal problems in Narragansett Bay, Upper Blackstone concurrently upgraded the plant to achieve total nitrogen treatment to 8-10 mg/L, consistent with limits then being imposed on other dischargers.

Upper Blackstone's current NPDES permit was issued in August 2008, with two modifications occurring in April 2009 and July 2010. The permit's nutrient limits became fully effective in May 2014 with an Administrative Order on Consent (AOC) that established interim limits for total phosphorus and total nitrogen as well as a schedule for compliance. The interim limits in the AOC required a total nitrogen level of 5.0 mg/L and a total phosphorus level of 0.1 mg/L for all 'dry' weather flows in each of the summer months by the end of October 2019. In addition, the AOC requires Upper Blackstone to examine options for achieving permit limits during 'wet' weather flows. A number of innovative measures to improve plant performance in the near-term have been piloted since 2014.

Reductions in the total phosphorus and nitrogen loads leaving the Upper Blackstone facility have been reflected in lower river total phosphorus and nitrogen concentrations and loads (Hatte et al., 2019). While exact values vary slightly from year-to-year, phosphorus has been reduced by 80 - 90% compared to previous levels. Nitrogen has been reduced by 57 - 61%.

MassDEP and the Rhode Island Department of Environmental Management (RIDEM) each maintain a list of impaired waters for sections of the river under their jurisdiction (MassDEP, 2019; RIDEM, 2018). The mainstem of the Blackstone River is considered impaired in Massachusetts due to total phosphorus and, in some sections, nutrient/eutrophication biological indicators and will require development of a TMDL, although no timeline for development has been set (Massachusetts Division of Watershed Management Watershed Planning Program, 2015). The Rhode Island mainstem is considered impaired due to total phosphorus. The timeline for completion of a TMDL in RI has been set for 2024, however in their 2014 303d list, RI DEM notes that the need for a TMDL will be determined post WWTF upgrades (RI DEM, 2015). While it is not clear why the two states have addressed TMDL development plans in slightly different ways (e.g., no TMDL schedule for nutrients in MA; TMDL scheduled for TP in RI, but with a qualifier that the need will be reassessed), both states appear to be acknowledging the disconnect between the 303(d) list publication date, ongoing WWTF upgrades, and the timeframe over which data utilized for the assessment is collected. For example, the data collection surveys upon which the 2014 MA assessments are based were conducted prior to the Upper Blackstone upgrades, and as such may not reflect current river conditions. The most recent water quality surveys by MassDEP on the Massachusetts portions of the Blackstone River were conducted in 2008 (MassDEP, 2008).

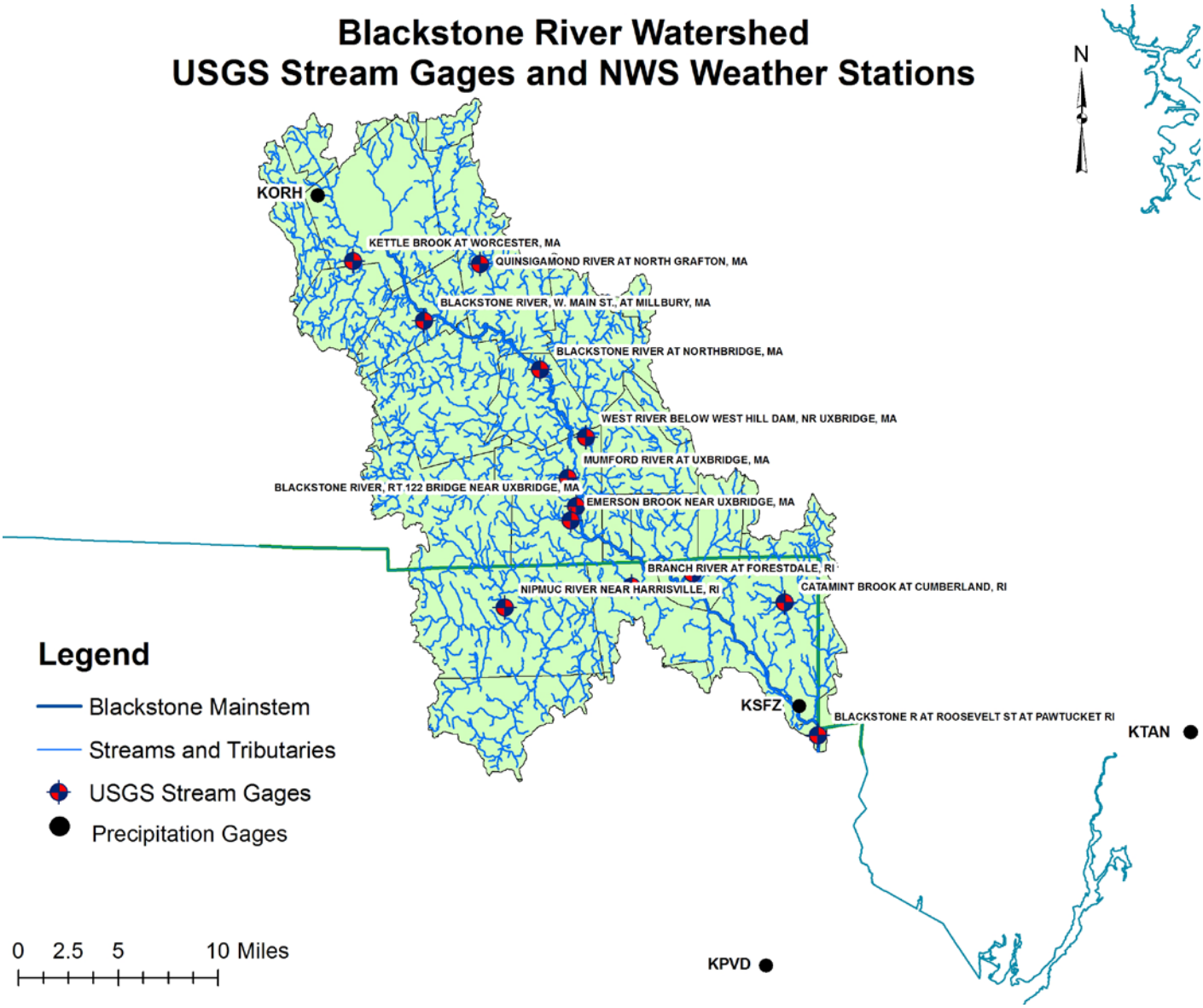

Figure 2 : Blackstone River watershed, USGS streamflow and NCDC precipitation gages

6. Project Purpose/Task Description

6.1 Study Purpose

Specific objectives for the 2020 - 2022 monitoring programs are to:

- Build upon earlier work conducted by Upper Blackstone, MassDEP, USGS and others;
- Support future analysis, if needed, of river water streamflow and water quality;
- Collect data to assess changes in riverine water column nutrient and chlorophyll-a concentrations and nutrient loads as well as some physical and chemical parameters through comparison against historical data; and
- Collect continuous dissolved oxygen data in the vicinity of the Upper Blackstone facility discharge to the river, in order to document the river's status with regard to its stated uses.

These objectives were used to select sampling locations as well as suitable sampling methods, analytes, measurement techniques, and analytical protocols with the appropriate quality assurance and quality control guidelines.

As necessary, additional field monitoring programs in the watershed may be specified in accordance with the procedural and quality-assurance guidelines in this QAPP. If necessary, this QAPP may be amended (following its approval) to include procedural and quality-assurance guidelines for additional water quality constituents or indicators, such as biological indicators, sediment toxicity, etc. Any amendments will be presented for review and approval to the QAPP reviewers listed at the beginning of this document.

6.2 Task Description

The overall goal of the field sampling program is to provide an accurate and representative picture of the current water quality conditions, relative to historical data for similar flow conditions, at specific sampling stations in the Blackstone River watershed. The environmental data collected under this task may be used as input to extend the water quality and hydrologic/hydraulic model of the Blackstone River that was developed, calibrated, and validated earlier in the study. The data may also help inform the development of future 303(d) impaired waters lists and TMDLs.

6.2.1 Study Area

The study area covered by this QAPP and the associated FSP is defined as the roughly 480 square mile watershed area upstream of Slater Mill Dam, located on the Blackstone River near Main Street in Pawtucket, RI. Data collection efforts are focused along the 48-mile mainstem of the river, extending from Slater Mill Dam to Worcester, upstream of the Upper Blackstone effluent channel.

The mainstem Blackstone River is joined by many small tributaries, as well as six major rivers: the Quinsigamond River, the Mumford River, the West River, the Mill River, the Peters River, and the Branch

River. The watershed consists of over 1,300 acres of lakes and ponds; the largest is Lake Quinsigamond in Shrewsbury and Grafton. Monitoring of these water bodies is beyond the scope of this study.

6.2.2 Field Sampling Program

This QAPP is designed to be an overarching document while yearly FSPs will provide the salient details for each sampling season. This QAPP is designed to cover the range of sampling activities anticipated under the Study. However, amendments to this QAPP will be made as necessary to include additional parameters and/or methodologies.

Individual FSPs will be developed for each year of the monitoring program. The FSPs are intended to provide the specifics with respect to the sampling location and frequency, sampling program logistics, schedule, sampling methods, field designation, and health and safety requirements. The sampling locations for 2020 are shown in Figure 3 and **.** In general, the monitoring programs include the following elements:

- Routine in-stream water quality sampling and subsequent analysis for nutrients (detailed below),
- Routine hand-held meter data collection,
- Continuous water quality collection with data loggers, and
- Download of basic hydrologic data (e.g., precipitation and streamflow data) from USGS and NCEI data sources.

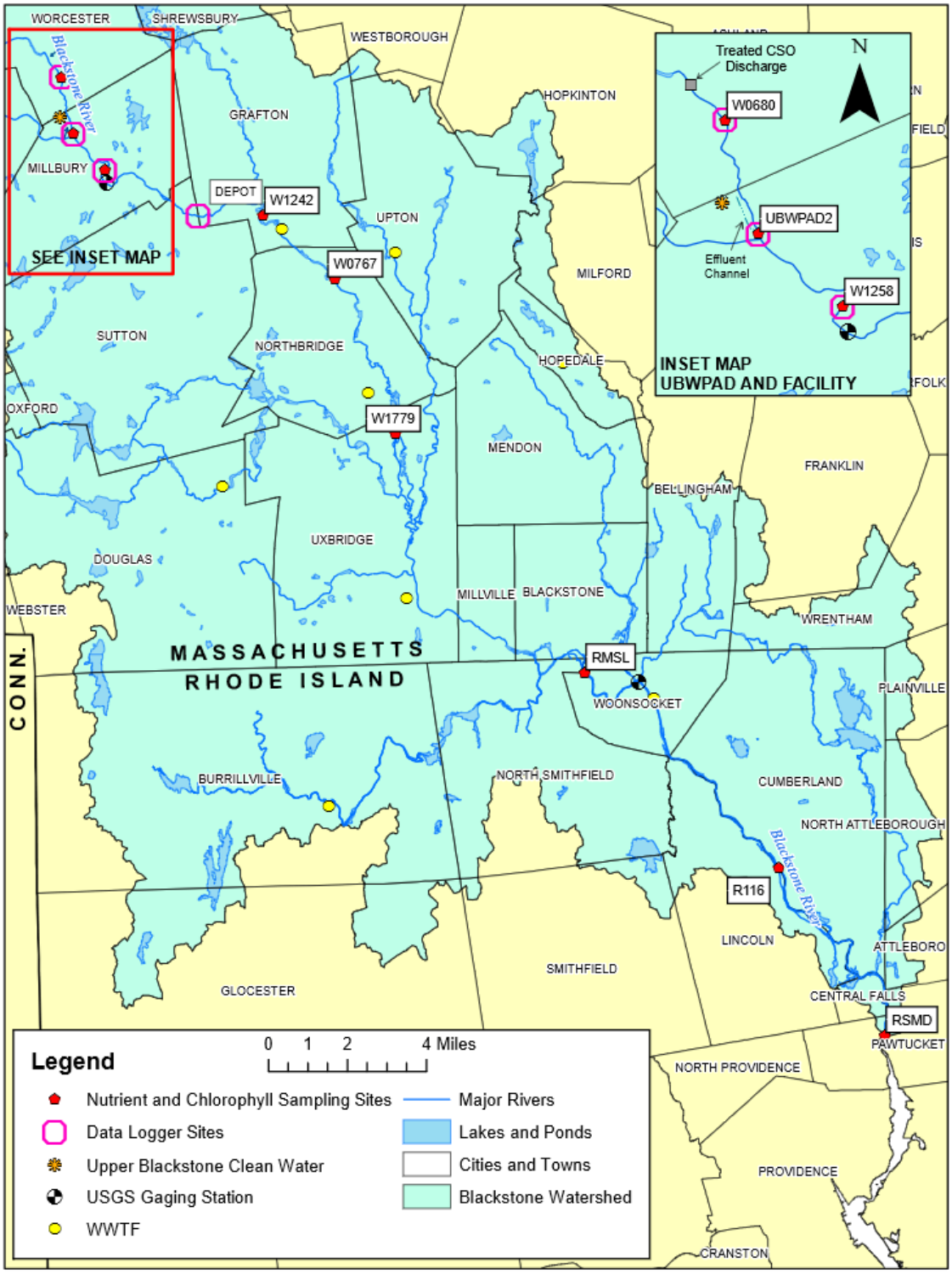

Figure 3: Current Field Sampling Sites

Table 2: 2020 Sampling Sites (all sites located on the main stem)

Site ID#	Site Name	Lat	Lon	River Mile[2]
RMSD-h[1] RMSD-n[1]	Slater Mill Dam, historical site Slater Mill Dam, new site Pawtucket, RI	41.876909[5] 41.879836[6]	-71.381940[5] -71.381556[6]	0.0
R116[1]	Rte 116 Bikepath Bridge, Pawtucket, RI	41.938066	-71.433769	6.3
RMSL[1]	State Line, RI	42.009974	-71.529313	15.5
W1779	Below Rice City Pond Sluice Gates, Hartford St., Uxbridge, MA	42.097270	-71.62241	27.8
W0767	Sutton St. Bridge, Northbridge, MA	42.153922	-71.652521	33.4
W1242	Route 122A, Grafton, MA	42.177153	-71.687964	36.3
DEPOT[4]	Depot St., Sutton, MA	42.177	-71.720	38.0
W1258[4]	Central Cemetery, Millbury, MA	42.19373	-71.76603	42.7
UBWPAD2[4]	New Confluence site, downstream of effluent canal	42.20702	-71.78154	44.6
W0680[3, 4]	New Millbury St Bridge, Worcester, MA	42.22784	-71.78762	45.9

[1] Locations of co-sampling with NBC

[2] Corresponding river mile and model reach in Blackstone River HSPF model: *Blackstone River HSPF Water Quality Model Calibration Report (*CDM Smith and UMass, August 2008) and the *Blackstone River HSPF Water Quality Model Calibration Report Addendum* (CDM Smith and UMass, October 2011)

[3] W0680 is located between the Worcester CSO discharge and UBWPAD2. The Worcester CSO enters the river downstream of the confluence of Mill Brook and the Middle River at approximately river mile 46.4

[4] Location of data logger deployments

[5] Historical RMSD site, will be sampled periodically in 2020 to determine whether the proposed new site is comparable to the historical site

[6] Proposed new site for RMSD starting in 2020

7. Quality Objectives and Criteria

Environmental data and streamflow measurements to be collected by the study team in support of the Blackstone River Watershed Assessment Study will meet the quality objectives outlined in this section. The specific quality assurance objectives and the measurement performance criteria serve as the basis for the annual FSP (Appendix H). This section provides overall guidelines as to the minimum requirements for quality control, whereas the FSP presents detailed information on locations, methods, and frequencies for environmental measurements and sample collection.

7.1 Data Quality Objectives

Data Quality Objectives (DQOs) are qualitative and quantitative statements that specify the characteristics of data required to support defensible decisions relating to specific environmental problems. DQOs are based on the end uses of the data to be collected; as such, different data uses may require different type and level of data quality. The data collection and analysis procedures will therefore be designed to meet the most stringent DQOs.

The following overriding DQOs have been developed for the Blackstone River Watershed Assessment Study:

- Collect water quality data to determine the likelihood that waterbodies in the Blackstone River Watershed meet state water quality standards;
- Collect water column data sufficient for identifying changes in water quality over time;
- Collect data to support assessment of the biological health of the river;
- Collect water quality data necessary to estimate the net daily and seasonal flux of pollutants along select reaches of the river; and
- Collect water quality data sufficient for the calibration and validation of computer models[1] to simulate pollutant loading, transport, and in-stream fate and distribution.

These objectives are used to select sampling locations, as specified in the annual Field Sampling Plan, as well as suitable parameters, sampling methods, measurement techniques, and analytical protocols with the appropriate quality assurance and quality control guidelines.

State Water Quality Standards

Both Massachusetts and Rhode Island categorize waters according to their use class. Each class is associated with a series of designated uses; the ability of a water body to support these uses is assessed based on its ability to meet the applicable water quality standards. In Massachusetts, these uses include fish consumption, aquatic life support, drinking water, shellfishing, primary contact recreation (swimming), and secondary contact recreation (boating). In Rhode Island, these uses include freshwater and seawater uses for fish and wildlife habitat, drinking water (freshwater only), primary and secondary contact recreation, and shellfishing (freshwater only).

Table 3 provides a summary of water quality guidelines as well as available data on background concentrations for constituents included in the monitoring program. It should be noted that neither Massachusetts nor Rhode Island have published numerical nutrient criteria, so the values listed in Table 3 are subject to change. These guidelines will be used to assess the likely compliance/non-compliance status of the waterways in the Blackstone River Watershed per the second DQO. All waterways in the watershed are classified Class A, the most stringent class designated for human consumption and shellfish harvesting, or Class B and Class SB, designated for primary and secondary contact recreational

[1] The HSPF Water Quality Model is calibrated to model total phosphorus (TP), orthophosphate, total nitrogen (TN), total ammonia, total inorganic nitrogen, nitrate-nitrate, chlorophyll-a, (chl-a) and dissolved oxygen. To enable validation of the model if it is extended beyond 2011, collection of additional data for these parameters is necessary. It is typically assumed that routine monitoring will capture the impacts of both dry and wet weather. For further information on the HSPF Water Quality Model, please see the Blackstone River HSPF Water Quality Model Calibration Report (UMass and CDM Smith, 2008), the Blackstone River HSPF Water Quality Model Calibration Report Addendum (UMass and CDM Smith, 2011), and the Blackstone River HSPF Model Validation Report (UMass and CDM Smith, 2011). All are available upon request.

activities in freshwater and saltwater, respectively. All classes include supporting fish and wildlife habitat.

Table 3: Water Quality Guidelines and Nutrient Background Concentrations

Metric	Acceptable Range	Rational for Metric	Source
Seasonal Mean Chlorophyll-a	< 10 µg/L	Target applied in Lower Charles TMDL	US-EPA (2007)
Peak Chlorophyll-a	< 18.9 µg/L	Target applied in Lower Charles TMDL	US-EPA (2007)
Chlorophyll-a Concentrations	< 3 µg/L	N.H. river guidance – "Excellent" conditions	NHDES
	3 – 7 µg/L	N.H. river guidance – "Good" conditions	NHDES
	7 – 15 µg/L	N.H. river guidance – "Less than desirable" conditions	NHDES
	> 15 µg/L	N.H. river guidance – "Nuisance" conditions	NHDES
	< 4.9 µg/L	New England Interstate Water Pollution Control Commission	NEIWPCC (2001)
Total Phosphorus	< 25.0 µg/L	EPA-within lakes or reservoir	US-EPA (1986)
	< 50.0 µg/L	EPA-entering lakes or reservoirs	US-EPA (1986)
	< 100.0 µg/L	EPA-in streams or other flowing waters not discharging directly to lakes or impoundments	US-EPA (1986)
	< 23.75 µg/L	EPA Ecoregion XIV, Subregion 59, 25th percentile guidance, all seasons	US-EPA (2000)
	< 25.0 µg/L	EPA Ecoregion XIV, Subregion 59, 25th percentile guidance, TP summer	US-EPA (2000)
	< 50.0 µg/L	EPA Ecoregion XIV, Subregion 59, 50th percentile guidance, TP summer	US-EPA (2000)
	< 28.0 µg/L	USGS 25th percentile guidance for Ecoregion XIV	Zimmerman & Campo (2007
	< 30.0 µg/L	USGS 25th percentile guidance for MA nutrient Ecoregion "High", which includes Blackstone	Zimmerman & Campo (2007
	< 20.0 µg/L	New England Interstate Water Pollution Control Commission median of four seasonal 25th percentiles, Northeastern Coastal Zone	NEIPCC (2003)
Total Nitrogen	440.0 µg/L	Eutrophication threshold utilized by OARS	OARS (2014)
	< 610.0 µg/L	EPA Ecoregion XIV, Subregion 59, 25th percentile guidance, TN calculated all seasons	US-EPA (2000)
	< 570.0 µg/L	EPA Ecoregion XIV, Subregion 59, 25th percentile guidance, TN reported all seasons	US-EPA (2000)
	< 440.0 µg/L	EPA Ecoregion XIV, Subregion 59, 25th percentile guidance, TN summer	US-EPA (2000)

	< 740.0 µg/L	EPA Ecoregion XIV, Subregion 59, 50th percentile guidance, TN summer	US-EPA (2000)
	< 583.0 µg/L	USGS 25th percentile guidance for Ecoregion XIV	Zimmerman & Campo (2007
	< 642.0 µg/L	USGS 25th percentile guidance for MA nutrient Ecoregion "High", which includes Blackstone	Zimmerman & Campo (2007
	< 560.0 µg/L	New England Interstate Water Pollution Control Commission median of four seasonal 25th percentiles, Northeastern Coastal Zone	NEIPCC (2003)
Conductivity	150-1500 µmhos/cm	EPA summary of studies of stream supporting good mixed fisheries	EPA
Dissolved Oxygen	≥5.0 mg/L ≥6.0 mg/L	Class A: ≥6.0 mg/L unless background conditions are lower Class B: ≥5.0 mg/L unless background conditions are lower	MassDEP Massachusetts Surface Water Quality Standards 314 CMR 4.00 (2013)
pH	6.5 – 8.3	MassDEP Surface Water Quality Standards	Massachusetts Surface Water Quality Standards 314 CMR 4.00 (2013)
Temperature	<20°C <26.7°C <26.7°C <28.3°C	Class A: < 83°F (28.3°C) and Δ1.5°F (0.8°C) for warm water fisheries, <68°F (20°C) cold water fisheries Class SB: <85°F (29.4°C) nor a maximum daily mean of 80°F (26.7°C) and Δ1.5°F (0.8°C) between July through September and Δ4.0°F (2.2°C) between October through June	Massachusetts Surface Water Quality Standards 314 CMR 4.00 (2013)

7.2 Measurement Performance Criteria

Measurement performance criteria, including the precision, accuracy, completeness, comparability, and representativeness of the data, will be used to assess the quality of all environmental measurements in relation to the DQOs. In order to meet the quality assurance objectives, the data must be (1) of known quantitatively measured precision and accuracy; (2) representative of the actual site in terms of physical and chemical conditions; (3) complete to the extent that necessary conclusions may be reached; and (4) comparable to previous and subsequent data collected under this program. Both field and laboratory quality objectives are addressed in each section. The percent frequency for each QC parameter can be found in **Table 4**.

Table 4: Quality Control Percent Frequency

QC Parameter	Frequency	Sample Parameters
Field Blank	10% each collection	TP, chl-a, dNH_4, dNOx, dTN, TSS, TOP, SC
Lab Blank	10% each collection	TP, chl-a, dNH_4, dNOx, dTN, TSS, TOC, SC
Field Duplicate	10% each collection	TP, chl-a, dNH_4, dNOx, dTN, TSS, TOC, SC
Field Split	10% each collection	TP, chl-a, dNH_4, dNOx, dTN, TSS, TOC, SC
Performance Test	10% each collection	TP, TOP, dNOx, dNH_4, pH
Equipment Blank	10% first collection and an additional collection mid-season	TP, chl-a, dNH_4, dNOx, dTN, TSS, TOC, SC
Calibration (accuracy for hand-held meters)	Before and after each collection Before and after sampling season	DO, pH Temp
Meter comparison (precision for hand-held meters)	After each collection	DO, pH, Temp

7.2.1 Precision

The precision of a measurement is the degree to which two or more measurements are in agreement. Precision is quantitative and is most often expressed in terms of Relative Percent Difference (RPD). RPD is calculated for each pair of duplicates as indicated below:

$$RPD = \frac{(S - D) \times 100}{(S + D)/2}$$

where:

S = First sample value (original or matrix spike value)
D = Second sample value (duplicate or matrix spike duplicate value)

Field Precision Objectives

Field precision for measurements taken in the field with hand-held meters will be assessed by measuring a sample of river water at the laboratory with both instruments concurrently, at the end of each sampling day (once every 9 measurement, or 10%). Quality assurance precision objectives for field measurements are listed in Table 5.

For Data Logger measurements, DO and temperature precision will be assessed as follows: During the sampling season (at least biweekly), measurements of water temperature and dissolved oxygen will be taken with a hand-held meter next to the data logger at each site. The data will be downloaded from the logger, and results compared between data logger and hand-held meter. The difference between the hand-held meter and the data logger indicates the cumulative impact of fouling and meter calibration drift and will be used to evaluate meter precision.

Table 5: Quality Assurance Precision and Accuracy Objectives for Field Measurements

Parameter	Precision (RPD)	Accuracy
Water Temperature	≤ 5%	± 5% or 0.3 ˚C
Dissolved Oxygen	≤ 5%	± 5% or 0.3 mg/L
pH	± 0.2	± 0.2

For collected samples, field precision is assessed by analysis of duplicate and split samples. The results of the duplicate and split analyses are used to assess the degree of precision in the field samples. Duplicate samples will be bulk samples collected from the stream in two different bottles, collected at the same time and side-by-side at the sampling location. Split samples will be aliquots split from the same bulk sample bottle and submitted to the laboratory for analysis. Note that field split samples are distinct from lab replicate samples. Field precision for samples analyzed in the laboratories will be assessed at the rate of ten percent, or one duplicate for every 10 samples collected. The RPD will be calculated per the above equation.

Quality assurance precision objectives for field measurements are listed in Table 6.

Table 6: Quality Assurance Precision and Accuracy Objectives for Laboratory Analytical Analyses

Parameter[1]	Field Precision (RPD)[2]	Lab Precision (RPD)[2]	Accuracy (%R)[3]	Field Blank Cleanliness[4]
Water Column				
Total Phosphorus	≤ 30%	≤ 20%	80-120%	< RL
Total Orthophosphate	≤ 30%	≤ 20%	80-120%	< RL
Chlorophyll-a[5]	≤ 30%	≤ 20%	80-120%	< RL
Dissolved Ammonia-N	≤ 30%	≤ 20%	80-120%	< RL
Dissolved Nitrate/Nitrite	≤ 30%	≤ 20%	80-120%	< RL
Total Dissolved Nitrogen	≤ 30%	≤ 20%	80-120%	< RL
Particulate Organic Nitrogen	≤ 30%	≤ 20%	80-120%	< RL
Total Nitrogen[6]	≤ 30%	≤ 20%	80-120%	< RL
Total Suspended Solids	≤ 30%	≤ 20%	80-120%	< RL
Specific Conductance	≤ 30%	≤ 20%	80-120%	< RL

[1] Please refer to Section 10 for further discussion on the analyzed water column parameters and methods utilized for each laboratory;
[2]RPD= Relative Percent Difference
[3]%R= Percent Recovery
[4] RL= Reporting Limit
[5] Precision for chlorophyll shall be ± 2.0 if less than 15 µg/L or 30% RPD if more than 15 µg/L
[6] UMD does not directly measure total nitrogen, but rather calculates it as the sum of TDN and PON

Laboratory Precision Objectives. Precision in the laboratory is determined by the comparison of laboratory-generated replicate samples, where replicates result from an original aliquot sample that has been split for identical purposes. The precision is evaluated by determining the RPD of duplicate (replicate) analyses, as provided in the equation above. Specific laboratory precision requirements are discussed in the applicable analytical SOP and/or laboratory Quality Assurance Plan. Precision goals for each water quality parameter are provided in Table 6. Laboratories will be requested to provide their internal QA/QC data, including lab replicate results. In general, however, release of the data will indicate that the laboratory precision objectives have been met, as certified by the lab quality assurance officer.

7.2.2 Accuracy

Accuracy is defined as the extent of agreement between an observed value (*i.e.* sample result) and the accepted, or true, value of the parameter being measured. Accuracy is quantitative and is usually expressed as the percent recovery (%R) of a sample result as indicated below:

$$\%R = \frac{(A-B)\times 100}{C}$$

where: A = Analyte concentration determined experimentally with known quantity of reference material added
B = Background determined by separate analysis of sample or, in the field, a blank
C = True value of reference or standard added

Field Accuracy Objectives. Accuracy of water quality sample collection activities will be assessed using field blanks and by adherence to all sample handling, preservation, and holding times. Field blanks consisting of distilled, deionized water will be submitted to the analytical laboratories at a rate of ten percent, or one blank per ten samples collected. Field blank cleanliness requirements are provided in Table 6.

An equipment blank is intended to assess the contamination caused by sampling and processing equipment. Equipment blanks will be collected and analyzed under two circumstances: (1) when a cleaning procedure is followed for the first time; and (2) initial equipment blanks will also be run any time new procedures or equipment are used. These pre-sampling equipment blank checks will be conducted in a controlled field or laboratory setting.

Suitable deionized water will be collected and stored in a suitable and appropriately labeled (e.g., “Source Solution Blank” or “Blank”) bottle. An aliquot will be taken from the source solution blank water and adequately preserved as per the analyte. If the Blank Water is purchased, the date and lot number of the blank water will also be recorded and the same lot will be used for the entire procedure.

For equipment blanks, the source solution will then be taken through each phase of the sampling process for the analyte (as needed), saving sequential sample blanks. Initially only the first stage equipment blank will be submitted for analysis. If the data for all of the analytes come back from the laboratory at acceptable levels, then the equipment blank is acceptable and no further work is required. The sequential samples will then be discarded. If all or some of the data come back higher than acceptable levels, the previously collected sequential blanks will be submitted to the laboratory for analysis. The data from these sequential samples will be used to identify the source of contamination detected in the equipment blank, and remedial measures will be taken to eliminate it. The process will

then be repeated. These steps should be evaluated in either field or laboratory conditions, depending on where sample processing will occur for the environmental samples.

Testing of equipment will be carried out for each type of sampler (split method and analyte) once per sampling season. Specific procedures for each sampler type are provided below.

To evaluate grab samples, source water will be poured into the sample bottle at the sampling site, then transported, preserved, and split in the same manner as regular river samples.

Quality assurance accuracy objectives for field measurements are listed in Table 6.

Field accuracy for measurements performed in the field with hand-held meters will be assessed by calibrating probes first thing in the morning on sampling days, and checking the probes against calibration samples or buffers upon return to the lab that day. For pH, a Quality Control sample manufactured at UMass EAL will also be used to assess accuracy. Data quality objectives for field measurements are listed in Table 5.

For Data Logger measurements, DO and temperature accuracy will be established with calibration of the data loggers prior to deployment. In addition, the data loggers will be pulled out of their housing (at least biweekly) and cleaned. To evaluate meter calibration drift, water temperature and dissolved oxygen will be measured with the hand-held meter next to the data logger before and after pulling the data logger out of the water for cleaning. If the RPD between the data logger data and the hand-held meter data are not within the greater of +/- 0.5 mg/L or 5% for DO or the greater of +/- 0.2°C or 5% for water temperature, the data logger will be retrieved from the site and re-calibrated.

Laboratory Accuracy Objectives. Laboratory accuracy is assessed through the use of known standards, such as Laboratory Control Samples (LCS), and matrix and analytical spikes. Accuracy within the laboratory is expressed in terms of percent recovery (%R). Specific laboratory accuracy requirements are discussed in the applicable analytical Standard Operating Procedure and/or laboratory Quality Assurance Plan. Accuracy goals with acceptance limits for applicable analytical methods are provided in Table 6.

In addition, a limited number of PE samples (one per sampling event) will be used as a double-blind evaluation on the respective laboratory's performances for the following parameters: total phosphorus (TP), total orthophosphate (TOP), dissolved nitrate/nitrite (NO_{23}), and dissolved total ammonia (dNH_4). The PE samples will be purchased from an outside PE manufacturer and will be provided with a known quantity of analyte.

One set of PE samples will be incorporated within the batch of river samples and submitted blindly to the laboratories during each sampling event. The laboratory's analytical results will be compared to the known analyte concentrations provided by the PE manufacturer.

7.2.3 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained for that measurement under normal conditions. Events

that may result in a reduction in measurement completeness include sample breakage during shipment, inaccessibility to proposed sampling location, and sampling equipment errors.

Field Completeness Objectives

Field completeness is a measure of how many valid results were obtained from field measurements. The Field Sampling Plan (Appendix H) specifies the number of field and laboratory measurements to be made during the program. The completeness criterion for all in situ measurements (including continuous dissolved oxygen, temperature) and analytical analyses is 90 percent (i.e., 90 percent of the planned samples must be collected and accepted for analysis) during sampling events.

The completeness criteria may also be violated if a group of samples is missing from one sampling region, such as one sampling reach or all source characterization samples, even if the missing samples total less than 10 percent of the samples collected during the event.

Resampling may be required if the completeness criteria are not met for a specific field activity. In the event of a catastrophic failure (one site or loss of all samples for an analyte), it will be resampled if feasible. Best professional judgment will be used in utilizing resampled data due to likely differences in environmental conditions.

Laboratory Completeness Objectives

Laboratory completeness is a measure of the amount of valid measurements obtained from all the samples submitted by the Project Team for each sampling activity. The laboratory completeness criterion is 95 percent. Note that the number of sampling events may be reduced due to unforeseen conditions, including pandemics.

7.2.4 Representativeness

Representativeness expresses the degree to which data accurately and precisely typify a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. One of the primary objectives of this field sampling program is to obtain water quality data that is representative of conditions in the Study Area.

Measures to Ensure Representativeness of Field Data

Representativeness is dependent upon the proper design of the field sampling program. These performance criteria will be met by ensuring that the sampling protocols listed in the FSP are followed. Additionally, the FSP will be developed considering the DQOs established herein and the appropriateness of sampling locations, sampling protocols, and water quality constituents. The sampling network designed and specified in the FSP will provide data representative of the designated study area for the expressed purposes of the water quality and flow monitoring activities.

Measures to Ensure Representativeness of Laboratory Data

Representativeness in the laboratory is ensured by the use of proper analytical procedures, following “good laboratory practices,” meeting sample holding times, and analyzing and assessing field duplicates. Upper Blackstone and EAL have Quality Assurance Plans and follow written SOPs for each analytical analysis.

7.2.5 Comparability

Comparability is an expression of the confidence with which one data set can be compared with another. Data collected in one segment of the watershed may be compared to data from another area to allow for the relative comparison of water quality parameters between stations.

Measures to Ensure Comparability of Field Data

Comparability of data is assured by a properly designed field sampling program and is satisfied by following proper sampling protocols as outlined in the FSP. For this program, data comparability is assured by the use of identical sampling, measurement, analytical and data reporting methodologies in accordance with documented procedures.

Measures to Ensure Comparability of Laboratory Data

Comparable analytical data results from employing identical sampling and analytical methods as documented in this QAPP. Comparability of analytical data will be assessed under the supervision of the Project Manager.

8. Training Requirements and Certification

This investigation includes only standard field sampling techniques, field analyses, laboratory analyses, and data evaluation techniques. Specialized training is therefore not required. The UMass Field Program Coordinator is experienced in the standard protocols for surface water sampling using the equipment discussed in this QAPP and associated Field Sampling Plan; however, members of the sampling teams for individual sampling events may require additional training.

Individual certifications relevant to implementation of this plan will thus be conducted as outlined in the SOPs. In general, this will require that members of the project team have read the SOPs and any associated equipment manuals or procedures produced specifically for this project and have demonstrated the ability to follow the outlined procedures.

In addition to training staff in water sampling procedures, a tour of the sampling sites will be completed, if possible, for any new staff. A coordination meeting or conference call will be conducted prior to the commencement of each field sampling event to brief members of the sampling team on any updates to the sampling procedures. A run-through of sampling procedures, QC procedures, and sample-splitting procedures will be part of each training session.

All laboratory personnel are trained in accordance with the procedures outlined in their respective Quality Assurance Project Plans. The QAPPs for the EAL laboratory at UMass and the Upper Blackstone Laboratory have been submitted along with this QAPP under separate cover.

9. Documents and Records

This section of the QAPP describes how project data and information will be documented and tracked from its generation in the field to its final use and storage. This will ensure data integrity and defensibility.

9.1 QAPP Distribution and Version Control

The Project Manager will be responsible for distributing copies of the approved QAPP and any subsequent revisions to individuals on the Distribution List. In addition, UMass will maintain on file a complete copy of the original document and all revisions of the QAPP, including addenda and amendments.

Document control procedures will be used to identify the most current version of the QAPP. Each revision will be differentiated with a new revision number and date. The following document control information is included in the top right-hand corner of each page in this QAPP:

- Title of the document (abbreviated)
- Revision number and document status (i.e., draft, interim, final)
- Date of original or current revision

A Project Personnel Sign-Off Sheet will be used to document that all members of the Project Team have read the QAPP and will perform the tasks as described. UMass will maintain the Sign-Off Sheet. The following information will be required:

- Project personnel name, title, contact number, and signature
- Date QAPP was reviewed
- QAPP acceptable as written (Yes/No)

9.2 Data Reporting and Retention

Proper documentation of field and laboratory activities is essential for the attainment of the Data Quality Objectives outlined for this study. Data reporting is the detailed description of the data deliverables used to completely document the analysis, quality control measures, and calculations.

Data acquired in the field will be reported after reduction and evaluation by the responsible technical staff. Data from laboratory analyses will be reported after the data are reviewed, assessed for quality assurance, and the data usability is assessed based on guidance provided in subsequent sections of this QAPP. Preliminary data will not be released as a part of this Study. All data will be evaluated prior to distribution.

9.2.1 Project Documentation and Records

UMass will maintain a Final Evidence File, which will be the central repository for all documents that constitute evidence relevant to sampling and analysis activities as described in this QAPP and associated

Field Sampling Plan. Table 7 presents a summary of sample collection records, field analysis records, laboratory records, and data assessment records that will be contained in the file.

UMass will have the responsibility of implementing and maintaining a document control system. All members of the Project Team will be responsible for project documents in their possession while working on a particular task.

Electronic copies of all project files and deliverables, such as electronic databases, will be routinely backed-up and archived. The Technical Memorandum, or annual report, to be prepared at the conclusion of the field sampling program will be submitted to Upper Blackstone electronically as text in Microsoft Word. All data, reports, and materials obtained and/or created under this task will be turned over to Upper Blackstone at the completion of the project.

9.2.2 Field Analysis Data Package Deliverables and Reporting Formats

The Field Analysis Data Package Deliverables will include the list of items provided in Table 7 under "*Sample Collection and Field Analysis Records.*" Field crews will be instructed to document all activities associated with site visits and sampling efforts, including unusual and anomalous conditions, which will be used during data interpretation and analyses.

All field documentation will be recorded on standardized data collection forms developed specifically for the Blackstone River Watershed Assessment Study, or in field logbooks.

Field Data Collection Forms

Field data collection forms will be used to document equipment calibration, sample collection activities, field changes to procedures, and habitat and site conditions. Additionally, forms will be completed to document staff training in relevant sampling and monitoring procedures. Copies of the Field Data Collection Forms are included in this document as Appendix E.

The field data collection forms are grouped into the following categories:

- Staff Training and Field Program Coordination (Appendix A)
- Equipment Calibration/Inspection (Appendix B)
- Field Collection Forms (Appendix E)
- Chain of Custody Documents (Appendix F)

Field Logbooks

Field logbooks will be used to document all investigation and data collection activities performed at the site that are not covered by the aforementioned standard forms. The logbooks will be permanently bound and paginated prior to the initial entry for the purpose of identifying missing pages after completion. Logbooks will be maintained by members of the Project Team, in accordance with SOP-DOC-001, "Field Logbook Content and Control."

Table 7: Project Documents and Records

Sample Collection and Field Analysis Records
Field and/or lab logbooks
Field data collection and analysis forms
Chain-of-custody (COC) records
Corrective action reports
Field QC checks and QC sample records
QAPP and Field Sampling Plan
Laboratory Records
COC Records
Data summary reports
Corrective action reports
QC checks and QC sample results
Data Assessment Records
Field sampling audit checklists and reports
Field analytical audit checklists and reports
Fixed laboratory audit checklists and reports
Data validation reports
Corrective action reports
Progress reports
Final reports

9.2.3 Laboratory Data Reporting Package and Reporting Formats

Final laboratory data reports will be issued to the Monitoring Program Coordinator within one to two months of the sample receipt, depending on the constituent. Electronic data deliverables will also be provided whenever possible.

The Laboratory Analysis Data Package Deliverables will be provided in a format similar to that required by EPA's Contract Laboratory Protocol. This includes, but is not limited to the following, as appropriate for the respective analyses:

- Chain-of-custody forms (signed)
- Sample Receipt Log-in and Checklist Forms
- Analytical Results (including time, date, and appropriate qualifiers)
- Method Blank Results and Raw Data
- Sample Matrix Spike/Matrix Spike Duplicate Results and Raw Data (per request)
- Laboratory Control Sample Results and Raw Data (per request)
- Laboratory Duplicate Results and Raw Data (per request)

10. Sampling Process Design

The FSPs will provide specifics as to the type and number of samples required, the exact sampling locations and frequencies, and sampling methods. All field sampling programs developed for the project

will be designed to meet the Data Quality Objectives discussed in Section 7, "Quality Objectives and Criteria."

The following section provides a general overview of sampling network design and rationale for the design developed for the Blackstone River watershed.

10.1 Study Area Definition

For the purposes of this Blackstone River Watershed Assessment Study, the Study Area has been defined as the entire Blackstone River watershed in both Massachusetts and Rhode Island upstream of Slater Mill Dam on Main Street in Pawtucket, Rhode Island, as shown in Figure 1-3. The Study Area consists of the Blackstone River and its tributaries in addition to lakes and reservoirs in the watershed.

The focus of the Blackstone River Watershed Assessment Study is to evaluate the overall health of the Blackstone River and to understand the river response to upgrades and nutrient optimization at the Upper Blackstone WWTF. To achieve this goal, we have selected monitoring locations at key mainstem monitoring locations upstream and downstream of the WWTF effluent channel. The six Massachusetts monitoring locations (W0680, UBWPAD2, W1258, W1242, W0767, and W1779) are located in a section of the Blackstone River with few major tributary inputs, so the addition of tributary sampling would not significantly change the understanding of water quality dynamics along this section of river.

The FSPs will provide detail regarding the specific study area definitions for each phase of the sampling program.

10.2 Field Monitoring Activities

Field monitoring activities anticipated under Upper Blackstone FSPs include:

- Routine in-stream water quality sampling and subsequent laboratory analysis for a select set of parameters
- Measurement of a select set of parameters with hand-held meters
- Continuous monitoring for temperature and dissolved oxygen during the months of June through October.

The water quality parameters selected for analysis in this study were chosen based on the DQOs described in Section 7. The focus of the 2020 - 2022 QAPP is on nutrients and associated indicators of river biological health such as dissolved oxygen.

Table 8 provides a summary of the field and analytical analyses included as part of the Blackstone River Watershed Assessment Study. All water columns samples will consist of discrete samples - no composite or flow-weighted sampling is planned.

Water temperature, dissolved oxygen, and pH will be measured in the field at each sampling site with a hand-held meter. Measurements will be recorded on the field data sheet.

Table 8: Anticipated Field and Analytical Analyses

Field Measurements
Water Temperature Dissolved Oxygen pH
Analytical Measurements
Nutrients and Impacts Total Phosphorus (TP) Total Orthophosphate (TOP) Dissolved Nitrate/Nitrite (dNO_{23}) Dissolved Ammonia-N (dNH_4) Total and Total Dissolved Nitrogen (TN, TDN) Particulate Organic Nitrogen (PON) Total Suspended Solids (TSS) Specific Conductance (SC) Chlorophyll-a

In addition, four data loggers will be deployed in June to continuously measure water temperature and dissolved oxygen at four monitoring sites. The data loggers will be removed in late October.

Nutrient sampling will be confined to mainstem run-of-river locations, including some located a short distance downstream from major impoundments. Samples will be collected routinely each month for nutrients, including phosphorus, nitrogen, and chlorophyll-a, regardless of weather conditions. Monthly sampling will typically occur April through November. Three Rhode Island sites along the mainstem of the Blackstone River will be co-sampled with the Narragansett Bay Commission (NBC) following the handling procedures outlined per this QAPP, with field splits sent to both the NBC and Upper Blackstone laboratories for analysis.

Samples will be analyzed at either the Upper Blackstone laboratory, the UMass Dartmouth Coastal Systems Program Analysis Laboratory or the UMass Environmental Analysis Laboratory depending on parameter. At *all locations*:

- Samples retained at UB will be analyzed for total suspended solids (TSS), total orthophosphate (TOP), and specific conductance (SC);
- Samples sent to EAL will be analyzed for chlorophyll-a (chl-a) and total phosphorus (TP);
- Samples sent to UMD will be analyzed for dissolved total ammonia nitrogen (dNH_4), dissolved nitrite/nitrate nitrogen (dNO_{23}), particulate organic nitrogen (PON), and total dissolved nitrogen (TDN), while total nitrogen (TN) will be calculated, Table 9.

Specific details regarding the sampling schedule, the number and type of samples required, and the sampling locations and frequencies will be discussed further in the respective annual Field Sampling Plans developed for this project.

Table 9: Parameters calculated based on lab results

Lab	Parameter	Calculation[1]
UMD	Total Nitrogen	TN = TDN + PON

1: Half the detection limit will be utilized in the calculation when laboratories report results for constituent parameters below the reporting limit.

10.3 Adequate Conditions for Sampling

Water column measurements and samples for nutrients, field parameters, and chlorophyll-a will be collected on a set day each month selected to coincide with monitoring conducted by NBC. Sampling will occur regardless of environmental conditions. Sampling will typically occur on a Wednesday, but some changes to the schedule may occur due to state holidays.

11. Sampling Methods

This section describes the procedures for collecting samples and identifies the specific sampling equipment and performance requirements, sample preservation requirements, and decontamination procedures. Also addressed are the procedures for identifying sampling or measurement system failures and for implementing corrective actions.

11.1 Sample Collection, Preparation, and Decontamination Procedures

Table 10 provides a summary of the specific SOPs that may be used during the field monitoring program; copies of these SOPs are provided in the appendices. The use of SOPs will ensure the collection of accurate, precise, and representative samples, as well as helping to ensure data comparability and usability. It is anticipated that personnel will have project specific recommendations for update of the SOPs. These recommendations will be incorporated as appropriate into the current SOPs and made part of the project record.

The field program will not require the use of any new or innovative procedures or sampling techniques. Study area-specific sample collection and preparation procedures will be provided in the annual Field Sampling Plans; these documents will reference the SOPs as appropriate.

Table 10: Summary of SOPs for Sample and Measurement Collection

Document Name	Title
SOP-DOC-001	Field Notebooks – Contents and Control
Step-by-Step Field Sampling Instructions	Field Sampling Protocol
SOP-FLD-013	Collecting Field Parameters Using a Hand-held Multiparameter Probe
SOP-FLD-014	Field Measurement of Water Temperature and Dissolved Oxygen with Hobo Data Logger

11.1.1 Manual Sampling

Samples will be collected manually. This is an acceptable method for the analytes covered under this QAPP because contact with air will not impair integrity of the samples.

Manual bulk sample containers as well as aliquot bottles will be prepared as specified by the analytical laboratory for each analyte. Bulk sample bottles that are reused for each event will be washed with non-phosphate detergent, and then filled with DI water for storage between sampling events. The conductivity of the DI water in the bottle will be checked prior to use to ensure no leaching from the bottle has occurred. Standard procedure will be to dispose of the DI storage water after testing for conductivity the week of sampling, and then to pre-rinse the bulk sample bottles three times with stream water prior to collecting the sample. Aliquot bottles will be prepared and tested the same way, regardless of whether they are re-used or discarded after a single use.

Typically one bulk sample will be collected and aliquots for the individual laboratory analyses will be prepared from this bulk sample. After collection, all samples will be cooled to 4 $\pm$2°C, or as otherwise directed by the analytical lab, and secured for storage and transport as soon as possible. Samples for chlorophyll-a analysis will be collected separately in a dark bottle to prevent light penetration. One field split and one field duplicate will be collected during each routine sampling event and analyzed for the same parameters as the regular samples at those sites. Splits will consist of separate aliquots taken from the same sample bottle and sent to the lab as an individual aliquot (field split). Duplicates will consist of bulk samples collected side by side (field duplicates) and processed as individual aliquots. Each laboratory will be expected to also run laboratory duplicates (from a single aliquot bottle).

Samples will be collected directly from the river, by using a pole from shore, or by sampling container or pump from a bridge When samples are to be collected directly from shallow streams or rivers (wading), the sampling location will be approached from downstream. The water sample will be collected upstream and perpendicular to the sampler's position to avoid contamination. The sample will be collected by grasping the bottle at its base, submerging it in the water with the mouth pointing upstream (so that any contamination from the sampler's hand or the outside of the bottle is washed away from the bottle), and allowing the bottle to fill. Ideally the bottle cap will be removed after the bottle is submerged in the water, and the mouth of the bottle will be kept under the surface as it is

filling. While filling, the inside of the bottle cap and bottle inlet will be kept free from contamination; the bottle cap will not be set down nor the inside surface touched. The cap will be loosely tightened while the bottle is underwater and then removed from the stream. If necessary, a small portion of the sample will be discarded to ensure sufficient airspace at the top of the bottle (approximately one inch). If samples are collected using a pole from the bank, the sample bottle is securely affixed to the pole and is submerged in the river. Finally, samples are collected from bridges using a a sampling container. The sampling container is a Nalgene 4-L wide-mouth HDPE bottle attached to a rope and reel. It is used every collection at W0767, W1242 and W1258. The sampling container is washed and rinsed in the lab in the same manner as bulk bottles, and rinsed three times with river water at the sampling site before collecting a sample. See the Field Sampling Plan in Appendix H for a detailed description of sampling steps. At the three sites co-sampled with NBC staff, the Upper Blackstone samples will be filled using a peristaltic pump fitted with clean tubing provided by NBC. The field sampling sheet will indicate the sampling methodology used at each site.

11.1.2 Filtration

Table 11 provides an overview of the preparation of filtered samples. Samples at all sites will be field filtered with Millipore (SLGP033RS) 0.22-micron filter units attached to a Millex-GP syringe for analysis of the nitrogen series at UMD. A new syringe and filter unit will be utilized at each site. Each syringe will be rinsed with sample water then filled with a filter attached. The filter will be primed by wasting 20 mL of sample through the filter. The sample bottle will be rinsed with the next 20 mL through the syringe, then the remaining 20 mL will be added to the bottle as a filtered sample. The filter will be removed from the syringe and replaced with a clean filter. The syringe will again be filled with sample water, then 20 mL wasted to prime the filter, and the remaining 40mL added to the sample bottle. Once per collection, a field blank sample is filtered on site in the same manner as regular river samples.

Samples for chlorophyll-a analysis will be filtered as soon as possible, generally within 4 hours, through a 47 mm diameter Whatman GF/F 0.7 µm pore size glass microfiber filter in the lab. Filtering for chlorophyll-a will be conducted at the Upper Blackstone lab rather than in the field in order to more carefully control environmental conditions, such as exposure to sunlight, during filtering than could be in the field.

Table 11: *Summary of Sample Filtration*

Parameter	Filter	Sites	Filtering location	Staff filtering
dNO_{23}	0.22 µm	All	Field	UMass (5 sites), UB (4 sites)
dNH_4	0.22 µm	All	Field	UMass (5 sites), UB (4 sites)
TDN	0.22 µm	All	Field	UMass (5 sites), UB (4 sites)
Chl-a[1]	0.7 µm	All	UB Lab	UMass

[1] Sample analyzed is filter residue, not the filtrate.

11.1.3 Stream Mixing Conditions

To avoid potential incomplete mixing, all sampling locations will be selected such that they are hydraulically uniform, sufficiently distant from point sources and tributary confluences, and downstream of sufficient ripples to be well mixed.

11.1.4 Decontamination Procedures

All materials used during the collection of water quality samples will be decontaminated (washed with non-phosphate detergent) between samples and after use according to the appropriate SOP and as summarized in Table 12. The bottles will be filled with DI water after washing and the conductivity tested after 24-hours. Bottles with conductivity results above 2 microsiemens will be rejected. Bottles that pass will be emptied, allowed to air dry, then capped and stored for the next event. All aliquot bottles, with the exception of those received from UMD, will be similarly washed, tested, and dried. At least two spare bottles will be available each sampling trip in case of mishap.

Table 12: *Sampling Container Decontamination Procedures*

Sample type	Container	Decontamination	Staff
Sampling bucket	4 L, plastic	Phosphate-free soap	UMass
Bulk sample container	4 L and 6 L, plastic	Phosphate-free soap	UMass
Chl-a	500 mL, amber plastic	Phosphate-free soap	UMass
TP	125 mL, amber plastic	Phosphate-free soap and acid wash	UMass
TOP	237 mL, plastic	New, DI rinse	UMass
TSS, SC	1 L, plastic	New, DI rinse	UMass
dNH_4, dNO_{23}, TDN	60 mL, plastic	Acid wash	UMD
PON	1 L, plastic	Acid wash	UMD

11.2 Sampling SOP Modifications

The SOPs provided in the Compendium to this QAPP have been adopted from the standard operating procedures used by various members of the Project Team, the USGS, state environmental protection agencies, and various sources.

11.3 Sampling/Measurement System Failure Response and Corrective Action

This section describes the sample and measurement system failure response and corrective action procedures that will be undertaken during field and laboratory activities.

11.3.1 Field Corrective Actions

Variation from established procedure requirements may be necessary due to unique circumstances encountered on individual projects. Corrective action in the field may be required when a modification is made to the sampling network (i.e., due to changes in the frequency or number of samples taken or changes in sampling locations), or when sampling procedures or field analytical methods require modifications due to unexpected conditions.

Any member of the Project Team may identify a problem requiring corrective action; the field staff in consultation with the Monitoring Program Coordinator will then recommend the correction action to the Project Manager. The Project Manager will approve the corrective measure, which will be implemented by the members of the Project Team. The Project Manager will inform Upper Blackstone and the Monitoring Program Coordinator of the problem and corrective action.

The Project Manager may authorize field staff to initiate variations as necessary. If practical, the request for variation shall be reviewed by the Project Manager prior to implementation, as discussed above. If prior review is not possible, the variation may be implemented immediately at the direction of the Monitoring Program Coordinator, provided that the Project Manager is notified of the variation within 24 hours of implementation, and the Field Change Request is forwarded to the Project Manager and QA Manager for review within two working days of implementation. If the variation is unacceptable to either reviewer, the activity shall be re-performed or action shall be taken as indicated in the "Comments" section of the Field Change Request.

All variations from established procedures shall be documented on the Field Change Request forms and reviewed by the Project Manager and the Monitoring Program Coordinator. All sampling or measurement system failures and resulting corrective actions will also be accurately documented in the field logbooks. All completed Field Change Requests shall be maintained in the project records. A Field Change Request form can be found in Appendix E.

11.3.4 Laboratory Corrective Actions

Corrective action in the laboratory may occur prior to, during, or after initial analyses. A number of conditions, such as broken sample containers, multiple phases, low/high pH readings, and potentially high concentration samples may be identified during sample log-in or just prior to analysis. The bench chemist will identify the need for corrective action. The Lab Manager or Technical Manager, in consultation with the laboratory staff, will approve the required corrective action for implementation by the laboratory staff.

All corrective actions shall be performed prior to the release of the data from the laboratory. The corrective action will be documented in both the laboratory's corrective action file and the narrative data report sent from to the Project Manager. If the corrective action does not rectify the situation, the laboratory will contact the Project Manager.

12. Sample Handling and Custody

This section of the QAPP describes the procedures by which sample custody will be maintained by all members of the Project Team and by the analytical laboratories. Also described are the sample handling and transport procedures that will be employed throughout the project.

12.1 Sample Labeling

Sample labels will be attached to individual sample aliquots for each investigation or quality control sample. The Monitoring Program Coordinator or a designated Task Leader will be responsible for ensuring that all lab processing labels are affixed to the aliquot bottles prior to event mobilization. Alternatively, labels may be affixed when processing samples. These may facilitate filling in additional information, such as the sample collection time and sampler name, which may be difficult if labels are wet. The decision on when to affix laboratory processing labels will be dictated by the number of aliquots and samples collected, the experience of the Field Team, and the need to minimize the potential for mislabeling.

Large volume sample bottles will be used to collect water (unless otherwise noted for select analytes) either directly from the river, with a sampling pole, a bucket, or via a pump and tubing. These bottles will thus also need to be labeled. The Monitoring Program Coordinator or designated staff will be responsible for printing these labels. Field staff will be responsible for affixing the labels when samples are collected (by hand) or set up in preparation for event sampling.

Each label will contain the following information:

- Sampling site ID - Sites co-located with former MassDEP sampling locations will utilize the MassDEP site ID; because sampling sites may change from year to year, the list of sampling site IDs is not provided in the QAPP, but in the annual FSP
- Additional fields will be appended to the sample site ID to identify the type of sample:
  - G = Grab sample
  - FS = Field split
  - FD = Field duplicate
  - LB = EAL lab blank
  - FB = EAL field blank
  - B9 = Blank, SMAST 60 mL pre-filled, left unopened
  - B10 = Blank, SMAST 1 L pre-filled, left unopened
  - B11 = Blank, 60 mL bottle left unopened, returned empty to UMD
  - EB = Equipment blank
- P = Performance evaluation sample
- Sampling date and time
- Aliquot labels will also include:

- The lab running the analyses
- The parameters to be analyzed and associated method and detection limit
- Preservation information
- Filtration information, and
- Bottle type.

Additional detail regarding the sample labeling system is provided in the FSP, including example labels.

12.2 Chain-of-Custody Procedures

Each sample must be properly documented to ensure the timely analysis of all parameters requested and to track the progress of the samples in the laboratory. To this end, chain-of-custody forms will be completed for all samples collected. Copies of the chain of custody forms are included in Appendix F. The forms will be filled out by the respective sampling teams at the end of each sampling round or as sample processing occurs, if the forms cannot be protected from inclement weather. When transferring sample custody, the individuals relinquishing and receiving the samples will sign, date, and note the time on the record.

The forms document the transfer of sample custody from the sampler to another person, to the permanent or mobile laboratory, or to/from a secure storage area. Representatives from both the Project Team and the laboratories will retain a copy of the forms. The chain-of-custody forms will be kept until all data has been received from the laboratories.

Specific laboratory custody procedures are described in Upper Blackstone's, UMD’s, and EAL's Quality Assurance Plans, including:

- Chain-of-custody procedures for assuming control of field samples,
- Detailed sample log-in procedures,
- Detailed internal sample tracking procedures,
- Procedures for internal transfer of sample custody,
- Specifications for sample storage,
- Disposal procedures for samples, extracts, and digestables, and
- Procedures for custody of analytical data and final data storage.

12.3 Sample Handling and Packaging

All grab samples will be collected in clean, bulk sample bottles prepared by UMass in accordance with the applicable SOPs (and briefly described above). This includes acid washing for TP sampling bottles. Water samples will be placed as soon as possible in coolers with sufficient ice to meet holding requirements. To ensure proper temperature storage of samples on sampling day, a 500 mL bottle filled with tap water will be added to each cooler before setting out to sample. The temperature of the water in this bottle will be measured when the cooler arrives at the UB laboratory.

At the UB laboratory, aliquots for individual analyses will be processed as soon as possible from the main sample. All aliquots will be preserved in accordance with specified analytical guidelines.

Table 13 summarizes the required sample volumes, collection containers, holding times, and preservatives for each water quality parameter. The column denoted "Group" identifies the aliquot bottle from which water for each analysis will be drawn. Additional information is provided in the respective laboratory and field SOPs for each analyte. Lab SOP requirements take precedence over those listed in either this QAPP or the field SOPs.

The split samples will be placed in separate coolers from the main samples that are being processed. A chain-of-custody form for the samples will be placed in a waterproof, plastic bag and affixed to the inside cover of the cooler. The logistics of delivering samples to the labs is described in detail in the Field Sampling Plan.

Table 13*:* Summary of Analyte Collection Container, Holding Time, and Preservative

Analysis	Lab	Container	Handling & Preservation	Holding Time
TOP	UB	237 mL, plastic	Store at ≤6°C	48 hours
TSS	UB	1 L, plastic	Store at ≤6°C	7 days
SC	UB	1 L, plastic	Store at ≤6°C	28 days
Chl-a[1]	EAL	1 L, plastic	0.7 µm pore size glass microfiber filter, dry filter and freeze, store in dark, discard filtrate	21 days[2] (hold time up to 3 months acceptable)
TP	EAL	125 mL, plastic acid washed	TP: freeze	1 year
PON	UMD	1 L, Plastic	Store 4±2°C. Transport to UMD (lab filtered by UMD; filter analyzed, filtrate discarded)	48 hours
dNH_4, dNO_{23}, TDN	UMD	60 mL, Plastic	0.22 µm filter. Store filtrate 4±2°C. Transport to UMD	48 hours

1 Sample analyzed is filter residue, not the filtrate

2 Filters are analyzed within 21 days according to the EAL QAPP, however historical method development testing within EAL showed that samples could reliably be held up to 3 months (personal communication with Paul Godfrey, prior WRRC Director and EAL Lab Manager)

13. Analytical Methods

Analytical methods are written instructions that describe how to prepare a sample for analysis, prepare and calibrate test equipment, perform the test, and calculate results. This section of the QAPP identifies the analytical field and laboratory measurements that will be made in support of the Blackstone River Watershed Assessment Study. Detailed information on field measurement techniques is provided in the Field Sampling Plan and referenced Standard Operating Procedures (SOPs); all laboratory methods are documented in the applicable SOPs (see SOP Compendium).

13.1 Laboratory Analytical Methods

Upper Blackstone, UMD and EAL will provide effective and timely analyses of the environmental samples collected under the Blackstone River Watershed Assessment Study. The required turnaround time for laboratory reports to be provided to the Project Team is one to two months. Whenever possible, Electronic Data Deliverables shall be provided.

Table 14 presents a summary of the analytical methods, method detection limits and respective analyzing laboratory for each water quality parameter of interest.

Method Detection Limits (MDLs) are the lowest values at which a parameter can be measured using the reference method. The MDL is defined as the constituent concentration that, when processed through the complete method, produces a signal with 99 percent probability that it is different from the blank.

MDLs are developed for each particular analyte of interest and are established as targets for ensuring that the data quality obtained is adequate for interpreting the data; these MDLs are the minimum to be achieved by the laboratories. The reporting limit (RL) is defined as the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. For this project, laboratories will be responsible for calculating the RL for each analysis batch, and will report out values below their RL as “BRL.” In the database for the project, these data points will be flagged with the code “LT” (less than) and the detection limit value from Table 14 listed as the result. This value will be used in plotting; half of the MDL will be utilized for calculations.

Table 14: Summary of Analytical Methods, Laboratory Responsibilities, and Detection Limits

Upper Blackstone Clean Water		
Parameter	Method	Minimum Detection Limit
TOP	Hach 8048	20 ppb[4]
TSS	USGS I-3765-85	2 ppm
Conductivity	STD Method 2510B	0.0 µS/cm
UMass EAL		
Parameter	Method	Minimum Detection Limit
TP	STD Method 20th ed., 4500P	2 ppb
Chl-a[1c]	STD Method 20th ed., 10200 H	1 ppb
UMass Dartmouth		
Parameter	Method	Minimum Detection Limit/Minimum Reporting Limit
dNH_4[1d]	STD Method 20th ed, 4500-NH3-F	1.4 ppb/2.8 ppb
dNO_{23}[1d]	STD Method 19th ed, 4500-NO3-F	3.5 ppb/7 ppb
TDN[1d]	STD Method 19h ed, 4500-Norg	5.3 ppb/10.3 ppb
PON	EPA 440.0	10 ppb

[1] Filtration for dissolved nutrients varies by lab as detailed below.

[a] Starting in 2015, NBC moved to lab filtration for their dissolved constituents utilizing 0.45 micron filters.

[c] Filtered in the lab within 4-hours of sample collection with Whatman GF/F 47 mm, 0.70 micron filter.

[d] Field filtered utilizing Millipore (SLGP033RS), Millex-GP Syringe 0.22-micron filter units.

[3] Laboratories will be responsible for calculating the RL for each analysis batch, and will report out values below their RL as "BRL.". In the database for the project, these data points will be flagged with the code "LT" (less than) and the detection limit value listed as the result. This value will be use in plotting; half of the MDL will be utilized for calculations.

[4] The Upper Blackstone lab has worked to achieve the lowest detection limit possible with their existing equipment and methodologies, however the labs primary focus is analysis of WWTF effluent. It is acknowledged that these DLs are high for riverine analysis.

Analytical methods will be performed in accordance with the applicable laboratory SOP (Table 15). The laboratory SOPs have been identified as SOP-EAL for the Environmental Analysis Lab at UMass, SOP-UMD for the UMass Dartmouth Lab, SOP-UB for the Upper Blackstone Laboratory. All equipment requirements are specified in the respective SOPs. No nonstandard laboratory analyses will be required as part of this study.

Failures in the laboratory analytical system will be addressed in accordance with Section 11.3.4, "Laboratory Corrective Actions." This section also specifies the individuals responsible for corrective action and how the effectiveness of the corrective action will be determined and documented.

Table 15: Analytical Laboratory Standard Operating Procedures (SOPs)

SOP Number	Parameter	Title
EAL Lab		
SOP-EAL-001	NA	Sample Preparation, Filtering, and Digestion
SOP-EAL-002	Chlorophyll-a	Determination of Chlorophyll-a
SOP-EAL-003	Phosphorus	Total Phosphorus Determination
UMD Lab		
SOP-UMD-001	Ammonia	Laboratory SOP: Ammonium
SOP-UMD-002	Nitrate+Nitrite	Laboratory SOP: Nitrate+Nitrite
SOP-UMD-003	Total Nitrogen/Total Dissolved Nitrogen	Laboratory SOP: Total Nitrogen/Total Dissolved Nitrogen
SOP-UMD-004	Particulate Organic Nitrogen	Laboratory SOP: Particulate Organic Carbon and Nitrogen Analysis
Upper Blackstone Lab		
SOP-UB-004	Orthophosphate	Determination Orthophosphate Hach 8048
SOP-UB-007	Total Suspended Solids	Total Suspended Solids Dried at 103 – 105°C, SM 2540 D
SOP-UB-008	Specific Conductance	Measuring conductivity in the lab with Hach 40 D Multimeter with CDC401 probe

13.2 Field Parameter Measurement Methods

Field parameters (temperature, dissolved oxygen concentration, dissolved oxygen percent saturation, and pH) will be collected at each site using a hand-held multiparameter sonde. The instrument specifications, analytical methodologies, detection limits, instrument range, and instrument precision are listed in Table 16. Measurements will be collected using a Hach HQ40D portable multiparameter probe with probes measuring pH, dissolved oxygen, and temperature.

Table 16: Field Analytical Method Instrument Specifications

Parameter	Method	Minimum Detection Limit	Range	Precision
Dissolved oxygen concentration	ASTM D888-09	0.1 mg/L	0.1 – 20.0 mg/L	+/- 0.1 mg/L, 0 to 8 mg/L, +/- 0.2 mg/L, > 8 mg/L
Temperature	SM 2550 B	0°C	0 – 50°C	+/- 0.3°C
pH	SM 4500-H+B	2 units	2 – 14 SU	+/- 0.02 units

13.3 In Situ Meter Measurement Methods

Continuous temperature and dissolved oxygen are collected at four locations. The instrument specifications, analytical methodologies, detection limits, instrument range, and instrument precision are listed in Table 17. Measurements will be collected using an Onset HOBO U26-001 Dissolved Oxygen Data Logger with probes measuring dissolved oxygen and temperature.

Table 17: In Situ Meter Analytical Method Instrument Specifications

Parameter	Method	Minimum Detection Limit	Range	Precision
Dissolved oxygen concentration	ASTM D888-05	0 mg/L	0 – 30.0 mg/L	+/- 0.2 mg/L, 0 to 8 mg/L, +/- 0.5 mg/L, 8 to 20 mg/L
Temperature	SM 2550	-5°C	-5 – 40°C	+/- 0.2°C

14. Quality Control

Quality Control (QC) is the system of technical activities that measures the performance of a process. Internal QC checks will be performed for sampling, field, and laboratory analysis to verify compliance with project investigation requirements in accordance with the Data Quality Objectives and Measurement Performance Criteria established in Section 7, “Quality Objectives and Criteria.”

This following section describes the general QC procedures that have been established for the Blackstone River Watershed Assessment Study; specific information as to the location and types of quality control checks is provided in the Field Sampling Plan.

14.1 Field Sampling Quality Control Checks

The desired field precision, accuracy, and field blank cleanliness for each parameter based on the quality objectives set forth in this QAPP is provided in Table 5 and Table 6. Precision and accuracy will be calculated in accordance with the procedures established in Section 7, “Quality Criteria and Objectives.” Outlier data points will be considered on an individual basis and may be qualified depending on both upstream and downstream data measurements and on concentrations measured at different times, as applicable.

Sampling quality control will be assessed based on the use of field duplicates and field blanks that will be prepared in the field and transported to the subcontractor laboratories in accordance with standard

procedures. The respective laboratories will analyze the QC samples in accordance with the analytical methods at the method-required frequency.

Nutrient QAQC samples will consist of at least 1 field duplicate, 1 field split, 1 aliquot bottle blank, and 1 bulk sample bottle blank each sampling run, as described in more detail below. Additional blanks and duplicates will be added if positive blanks or duplicates outside of the acceptable precision range are noted.

14.2 Field Measurements Quality Control Checks

For hand-held meter field measured parameters, DO and pH accuracy will be established with calibration of the meters performed each sampling day before setting out to the sampling locations. In addition, measurements will be taken in buffers and air-saturated water with each meter at the lab at the end of the sampling day. Additionally, the meter probes will be checked for pH accuracy by measuring a QC sample provided by EAL.

Temperature accuracy will be established by comparing the measurements taken with the meters in an ice bath and at room temperature with an NIST-certified thermometer at the start and end of the sampling season.

Precision will be measured by comparing temperature, DO, and pH measurements side by side with both meters in the laboratory in a beaker filled with tap water or leftover river samples.

For Data Logger measurements, DO and temperature accuracy will be established with calibration of the data loggers prior to deployment. During the sampling season (at least biweekly), measurements of water temperature and dissolved oxygen will be taken with a hand-held meter next to the data logger at each site. The data will be downloaded from the logger, and results compared between data logger and hand-held meter. The difference between the hand-held meter and the data logger indicates the cumulative impact of fouling and meter calibration drift and will be used to evaluate meter precision. Note that the data loggers take readings every 15 minutes, so the readings between logger and hand-held meter may not be taken at the exact same time.

In addition, the data loggers will be pulled out of their housing (at least biweekly) and cleaned. To evaluate meter calibration drift, water temperature and dissolved oxygen will be measured with the hand-held meter next to the data logger before and after pulling the data logger out of the water for cleaning. If the RPD between the data logger data and the hand-held meter data are not within the greater of +/- 0.3 mg/L or 5% for DO or the greater of +/- 0.2°C or 5% for water temperature, the data logger will be retrieved from the site and re-calibrated. At the end of the season, when the data loggers are pulled out of the water until the following year, the loggers' DO and temperature are checked against the hand-held meter using river water in a bucket.

14.2.1 Field Duplicates

Field duplicates are co-located samples collected simultaneously at given sample locations/times. The duplicates will be carried through all phases of the sampling and analytical procedures in an identical manner to provide overall precision information for each sampling event; these samples will be submitted blindly to the laboratory. Duplicates for manual samples will be collected for all parameters analyzed in the field at a frequency of at least ten percent, or one duplicate per 10 samples.

14.2.2 Field Splits

Field splits are duplicates for laboratory analysis split from the same original bulk sample volume into separate aliquot containers. The splits will be carried through all phases of the sample processing and analytical procedures in an identical manner to provide overall precision information for each sampling event. Splits will be collected for all parameters analyzed in the field at a frequency of ten percent, or one duplicate per 10 samples.

14.2.3 Field Blanks

Field blanks will consist of laboratory grade water from multiple labs. See Section 12.1 for a list of the blank designations associated with water from each lab. The blanks will be preserved as appropriate, will accompany the samples during transport to the laboratory, and will be analyzed as appropriate. Samples will be submitted blindly to the laboratory at a rate of at least ten percent, or one blank per 10 samples. Two types of blanks will be processed each sampling period. The first type, the Lab Blank, will consist of aliquot bottles filled directly from the laboratory water source for each parameter. These blanks will provide information on both the quality of the laboratory water as well as an indication of the potential for sample contamination due to leaching from the bottles or during laboratory processing. The second type, or Field Blank, will be prepared during the sample processing stage of the field-monitoring program. Prior to sampling, one of the bulk sampling bottles will be filled with laboratory water. This bulk sample blank will travel with the field crew during sampling and will be transferred to another bulk bottle in the field, then split into separate aliquot containers for laboratory analysis back in the laboratory at Upper Blackstone. These blanks will provide information on the potential for sample contamination due to leaching from the bulk sampling bottles as well as during collection and processing of the aliquots.

14.2.4 Field Analytical Quality Control Checks

Quality control checks on all instruments used to conduct field measurements will be conducted on a pre-determined basis; specific procedures will be discussed further in Sections 15.1 and 15.2.

14.3 Laboratory Quality Control Check

Upper Blackstone, EAL and UMD will use the procedures outlined in their respective Quality Assurance (QA) Plans to ensure the reliability and validity of analytical results. Copies of these Plans have been submitted along with this QAPP under separate cover.

Compliance with the QA Plans is coordinated and monitored by the respective laboratory's QA Officer. QC samples prepared by the laboratories may include the following, as specified in the respective Plans:

- Laboratory duplicates and blanks
- Matrix spikes and matrix spike duplicates (MS/MSDs)
- Laboratory Control Standard and Laboratory Control Standard Duplicates (LCS/LCSDs)

Additional information regarding laboratory QC procedures is provided in the specific analytical SOPs (see SOP Compendium). Specific criteria for the evaluation of laboratory precision and accuracy are provided in Section 7, "Quality Objectives and Criteria," and Table 6. Any samples analyzed in

nonconformance with the QC criteria will be reanalyzed in the respective laboratory if sufficient sample volume is available and the sample is still within acceptable hold time limits.

We will also purchase Performance Evaluation samples and send these to the labs blind. Performance Evaluation Tests (PETs) will be run for chlorophyll-a, TOP, TP, dNH_4, and dNO_{23}. Concentrations of the PETs will be diluted to reflect the range of concentrations expected in the river based on historical data, with a different value each month. We will utilize the results for these samples to better understand laboratory accuracy as well as differences in the inter-laboratory results.

15. Instrument/Equipment Testing, Inspection, and Maintenance

This section of the QAPP describes the procedures and documentation activities that will be performed during the field sampling program to ensure that all equipment is in working order.

15.1 Field Instruments and Equipment

The inspection, testing, calibration, and maintenance of all field equipment and instruments will be performed in accordance with the applicable SOPs as noted in Section 2.4.1.

In all cases, specific preventative maintenance procedures as defined by the respective manufacturers will be followed. Additionally, field notes from previous sampling events will be reviewed by the respective field crew and the Field Program Coordinator**,** or designated substitutes, to ensure that any previous equipment problems have been identified, and that all necessary repairs have been made.

The Field Program Coordinator, or a designated substitute, will be responsible for testing, inspection, and maintenance of all equipment prior to mobilization. The designated Project Team member will then be responsible for completing the Equipment Inspection, Testing, and Maintenance Sheets during mobilization. An example is provided in the Field Sampling Plan.

15.2 Laboratory Instruments

Each laboratory will perform routine preventative maintenance in accordance with their respective Quality Assurance Plans and with manufacturer's specifications to minimize the occurrence of instrument failure and other system malfunctions. Each laboratory will maintain factory-trained repair staff with in-house spare parts or will maintain service contracts with applicable vendors.

Records of preventative maintenance, equipment repairs and replacement, and documentation of maintenance procedures will be maintained by the designed laboratory Quality Assurance Officer, and subject to auditing by the Project Team.

16. Instrument/Equipment Calibration and Frequency

This section describes the calibration procedures that will be followed for all equipment used to conduct field and laboratory analyses to maintain reliable and accurate measurement results. All calibrations will be performed in accordance with manufacturer's recommendations.

16.1 Field Instruments and Equipment

In-situ collection of chlorophyll-a, nitrogen, and phosphate data is beyond the current scope of this study. Any further water column data collection for these parameters will be accompanied by an amendment to the QAPP. Field equipment will consist of sampling apparatus and meters.

Two Hach HQ 40 D handheld meters will be used to collect DO and pH measurements in the field. They will be calibrated the morning of each sampling day by the UB staff at the UB facility. Calibration will be documented in Upper Blackstone's calibration logbook.

In June, Onset HOBO Dissolved Oxygen (U26-001) data loggers will be deployed at four sites (W0680, UWPAD2, W1258 and Depot). They will be calibrated before deployment, and recalibrated during the monitoring season as needed.

The Field Program Coordinator, or designated others, will be responsible for ensuring that all equipment has met the required calibration standards prior to event mobilization. In the event that an internally calibrated field instrument fails to meet calibration/check-out procedures, it will be returned to the manufacturer for service.

16.2 Laboratory Instruments/Equipment

Calibration procedures and frequencies of all laboratory equipment will be performed in accordance with the respective laboratory's Quality Assurance Plans, manufacturer's specifications, analytical SOPs, and written procedures approved by laboratory management. Records of calibration method and frequency will be filed and maintained by the designated laboratory Quality Assurance Officers; these may be subject to auditing by the Project Team.

17. Inspection and Acceptance of Supplies and Consumables

All supplies to be used during the field sampling program will be inspected prior to acceptance to ensure that they are in satisfactory condition and free of defects or contamination in accordance with the methods specified in Table 18.

Table 18: Summary of Supplies and Inspection Requirements

Critical Supplies and Consumables	Inspection Requirements and Acceptance Criteria
Sample bottles	Visually inspected upon receipt for cracks, breakage, cleanliness, and preservation solution (as needed)
Chemicals and reagents	Visually inspected for proper labeling, expiration dates, and approximate grade
Sampling equipment	Visually inspected for obvious defects, damage, and contamination

The Monitoring Program Coordinator, or her designee, will be responsible for ensuring the acceptability of all material to be used during field activities prior to event mobilization and for implementing corrective action, if necessary. Designated personnel from Upper Blackstone and EAL will be responsible for the inspection and acceptance of all material relating to laboratory analysis.

18. Data Acquisition

All environmental measurements performed under this activity will be taken directly by the Project Team and subcontracted laboratories. Flow measurements at all stream locations other than USGS streamflow gaging sites will be estimated indirectly based on hydrologic hydraulic model data in combination with observed flow conditions at the USGS Woonsocket and Millbury stream gauging locations.

Water quality data collected by other studies and volunteer monitoring groups may be reviewed and used to evaluate general background conditions and historical trends. Since the sampling procedures and protocol for these data may have differed from the procedures specified in this QAPP, care will be given in interpreting and drawing conclusions from the data.

19. Data Management

This section describes the data management procedures that will be followed in the collection, review, and reduction of all environmental data collected as a part of the Blackstone River Watershed Assessment Study field sampling program.

19.1 Data Recording, Handling, and Tracking

This section details the computerized and manual data recording, handling, and tracking procedures that will be used during the sampling program.

19.1.1 Data Recording and Tracking

Field Data. Field environmental measurements collected by the Project Team during sampling events will be recorded in field logbooks and field data collection forms in accordance with guidance provided in Section 9, "Documents and Records." Upon completion of the sampling event, the data collected will be transposed to a project-specific electronic database, the format of which is discussed in section 19.1.2. The transfer of data from paper (*i.e.* logbooks or collection forms) to electronic format will be performed by the Data and Document Custodian; a second individual will then spot check the entries.

Copies of all field data will be maintained by UMass in a "Final Evidence" File in accordance with the document retention and control guidelines discussed in Section 9.2.

Laboratory Data. Laboratory results will be reported in accordance with the guidance provided in Section 9.2, "Data Reporting and Retention." All information related to sample analysis will be documented in controlled laboratory logbooks, instrument printouts, or other approved forms in accordance with the laboratory's Quality Assurance Plan. Analytical laboratory records will be reviewed by the respective laboratory Quality Assurance Officer, and subject to auditing by the Project Team.

Prior to releasing the final data, each laboratory will employ a tiered review process. Each analyst will be responsible for reviewing the analytical and quality control that he/she has generated; the analyst will verify that:

- The appropriate methodology has been used,
- Instrumentation and equipment was functioning properly,
- QC analyses were performed at the proper frequency and the analyses met the acceptance criteria,
- Samples were analyzed within the required holding times,
- All analytes were determined within the calibration range,
- Matrix interference problems were confirmed,
- Method specific analytical requirements were met, and
- Calculations, dilution factors, and detection limits were verified.

The raw data will then be released to the respective area supervisor who will also review the data for attainment of quality control criteria as required in the applicable standard method and for overall reasonableness. The area supervisor will be responsible for generating the data summary report, which will be reviewed by the laboratory Quality Assurance Officer. This review will verify that the report format and content meet the client specifications, that the data were reported correctly, and that analytical and quality control problems were addressed and documented in the file and summary report (if appropriate). Upon acceptance of the preliminary reports by the QA Officer, the final reports will be generated and signed by the Laboratory Project Manager.

Following the receipt of the data reports by the Project Manager or her designee, all results will be transposed or uploaded to the electronic database developed for the project by a member of the

Project Team. Data transcription will be spot checked by a second member of the Team. The final database will include all the data provided by the laboratories, as well as laboratory-provided data flags, including:

- Concentrations below the required detection limits,
- Estimated concentration due to poor relative percent difference,
- Estimated concentration due to poor spike recovery or other outlying QC data, and
- Concentration of chemical also found in laboratory blank.

19.1.2 Data Handling

All data gathered or generated as part of the Field Sampling Plan will be entered into a project-specific database, developed using Microsoft Excel. Data will be organized according to the unique sampling station locations (*i.e.,* Station ID) provided in the Field Sampling Plan. Each site will be referenced based on its latitude and longitude. The database will include at a minimum:

- Station ID,
- Station longitude and latitude, and
- Along stream river mile.

The above information will remain constant between sampling events and thus will be maintained in a separate datasheet. For each collected sample, the following information at a minimum will be included:

- Station ID,
- Sampling Date (MM-DD-YYYY),
- QC sample type, if applicable,
- Parameter ID,
- Analytical results (i.e. constituent concentration),
- Units,
- Reporting limits,
- Data Qualifier (Table 18), and
- Brief field or laboratory notes (as applicable).

Additional information contained in the field and laboratory data sheets may also be converted into a separate electronic file as deemed necessary. These data include:

- Sample collection time,

- Analysis date and time,
- Stream stage at time of sample, and
- Sample method (i.e. manual in-stream or manual from bridge)

Field and laboratory analytical data will be flagged based on the results of the data evaluation described in Section 22. Table 19 presents a summary of the data qualifiers or "flags" that will be used throughout the database. For ease of data presentation for annual reports, the data may be coded through highlights and appropriate notes provided to indicate the qualifiers. Data input to the master project database, however, will be coded with the data qualifiers.

Table 19: Summary of Data Qualifiers

Flag	Description
LT	The material was analyzed for, but was not detected above the level of the associated value. The associated value is either the sample quantification limit or the sample detection limit
R	The data are rejected
NC	No code; no other codes apply
PB	Positive blank; the blank in question has a value above the MDL/RL
BD	% relative difference for field duplicate is more the +/- 20% out of bounds
EPT	% relative difference for performance test is more than +/- 20% out of bounds
BS	% relative difference for field split is more the +/- 20% out of bounds
NA	No data available
LO	Flagged by lab's internal QAQC data as possible outlier
Calc-adj	Calculated value is based on a data value changed due to a PB

Data may be rejected for a variety of reasons, including positive detections in associated blanks, discrepancies between the total and dissolved fraction of an analyte, precision and accuracy outside of the acceptable project limits, or failure of performance evaluation tests. Typically all data for an associated parameter on a given date will be flagged due to these conditions. In some instances, such as due to internal laboratory QAQC data, only samples analyzed after a problem is detected may be flagged. Data validation and usability are discussed in Section 22.

An entry in the database will be made for each parameter that was scheduled to be collected. The analytical results of parameters for which no data are available will be recorded as "NA" and will be

flagged as noted in Table 20, which presents a summary of additional data descriptors which will be used to record missing results.

Table 20: Additional Data Descriptors

Flag	Description
V	Validated by laboratory
IV	Invalidated by laboratory (exceeded holding limit, not preserved correctly, etc.)
ML	Sample mishandled by laboratory (sample dropped)
MF	Sample mishandled in field (i.e. bottle dropped or broken)
NR	Not recorded

Data collected by other studies and volunteer monitoring groups may also be added to the database as the information becomes available to the project team. The data will be flagged as being collected during a separate field program. The data will be reported and cited, as necessary, to support evaluations and conclusions made during the Blackstone River Watershed Assessment Study.

All electronic data files will be stored and maintained in accordance with the procedures detailed in Section 9, “Documents and Records.”

20. Assessment and Response Actions

This section of the QAPP addresses the activities required for assessing the effectiveness of the field sampling program implementation and associated quality assurance and control activities. The purpose of the assessment is to ensure that the QAPP is implemented as prescribed and that appropriate responses are in place to address any non-conformances and deviations from the QAPP.

20.1 Assessments and Response Actions

Performance and system audits of both laboratory and field activities will be conducted to verify that sampling and analysis are performed in accordance with the procedures established in this QAPP and corresponding Field Sampling Plan. Field and laboratory performance audits are performed as an independent evaluation, through a review of internal quality control checks and procedures, of the data being generated. System audits are conducted as an onsite review and evaluation of facilities, instrumentation, quality control practices, data validation, and documentation practices.

20.2 Field Audits

Internal system and performance audits of field activities (sampling and measurement) will be conducted by the Quality Assurance Manager for the project. The scope of these audits may include, but is not limited to:

- Review of field sampling and measurement records,
- Review of field instrument operating records,
- Observation of sample collection, handling, and packaging procedures,
- Maintenance of QA procedures, and
- Chain-of-custody procedures.

Field audits typically occur at the onset of field operations to verify that all established procedures are implemented. The Technical Reviewer will handle audits of this nature. The Data Review audits will involve review of field measurement records, instrumentation calibration records, and sample documentation and will be handled by the Data Reviewer. These audits will occur throughout the project.

20.3 Laboratory Audits

Internal system and performance audits will be conducted by the respective laboratories in accordance with their specified Quality Assurance Plans. The type and frequency of these audits is dictated in their Plans.

Additionally, external laboratory audits may be conducted by the Project Team if problems with the data are observed, such as errors in a laboratory's internal sample tracking.

20.4 Audit Reporting and Corrective Action

Audit reports will be generated by the responsible party (*i.e.* QA Manager) at the completion of each assessment. The audit report will identify proficiencies, deficiencies, and opportunities for improvement, as applicable.

Corrective action includes the process of identifying, recommending, approving, and implementing measures to counter unacceptable procedures or practices that result in data quality beyond the required quality control performance standards. Such actions may occur during field activities, laboratory analyses, data evaluation, and data assessment.

For noncompliance problems, a formal corrective action program will be determined and implemented at the time the problem is identified. Any nonconformance with the established quality control procedures in the QAPP and Field Sampling Plan will be identified and corrected in accordance with the QAPP. The Project Manager, or an approved substitute, will issue a Nonconformance Report for each condition. All corrective actions will be further documented in the QA section of the project deliverables.

20.4.1 Field Corrective Action

Corrective actions in the field will be implemented on a case-by-case basis. Minor response actions taken in the field to immediately correct a problem will be discussed with the respective Field Program Coordinator and documented in the field logbook. The corrective action will be verbally relayed to the Project Manager and a Field Change Form will be filled out. Major corrective actions taken in the field will require approval by the Field Program Coordinator and Project Manager prior to implementation. Such actions may include revising procedures in the field, resampling, or retesting. A Field Change Form will also be filled out.

20.4.2 Laboratory Corrective Action

Corrective action undertaken by the laboratories will be completed in accordance with the procedures outlined in each lab's Quality Assurance Plan. All corrective actions will be reported to the Project Manager and will be documented in the respective data reports for each sampling round. The laboratories will also be required to take and document corrective actions for problems identified by the Project Team.

21. Reports

During the active phases of the sampling project, UMass will submit quarterly status reports to CDM Smith and Upper Blackstone identifying the activities performed, planned activities, and updated schedules. Any issues that are encountered in between the regular reporting will be addressed through personal communication, emails, or memos as appropriate. UMass and CDM Smith will be in communication during the sampling season on a weekly to monthly basis. The Project Team will also develop annual reports to summarize the sampling events and environmental data obtained during the sampling program.

Copies of the quality assurance reports will be provided to the Upper Blackstone Technical Manager and the Lab QA Manager when data or measurement quality problems are encountered. As previously noted, all corrective actions and nonconformance problems will be documented in the field logbooks and Nonconformance Reports. These will be further detailed in the task deliverable. The project data will be submitted to MassDEP and to EPA's WQX, and annual data reports will be shared with MassDEP along with the submitted data.

22. Data Review, Verification, and Validation

This section of the QAPP addresses the data review, verification, and validation procedures and criteria to be performed by the Project Team. These procedures and criteria will identify and qualify data that do not meet the established measurement performance criteria.

One hundred percent of the data collected as part of this program will be evaluated to determine its precision, accuracy, representativeness, completeness, and comparability to field QC samples.

If extreme data problems are identified during the evaluation process, EPA and MassDEP will be notified to determine if 10 percent of the data packages should be validated in order to assure that no global data problems exist. Additional information on the evaluation methods for water quality samples analyzed in the laboratory is provided in Section 23.

22.1 Laboratory Data

Table 21 and Table 22 provide a summary of the criteria that will be used during the evaluation process to accept, reject, or qualify the data, as per the data qualifiers listed in Table 15. This table will be updated as necessary and the QAPP amended to reflect updated analysis methods.

Table 21: Data Evaluation and Validation Criteria (Part I)

PARAMETER (METHODS)	TECHNICAL HOLDING TIME	LAB CALIBRATION		BLANKS	LAB PRECISION
		INITIAL	CONTINUING		
INORGANIC PARAMETERS	Method specific (2)	Calibration curves will be evaluated for applicable methods as per laboratory specific SOPs. Data not meeting internal laboratory controls will not be reported.		< MRL If criteria not met, data for that parameter/data are coded "PB" and 5 x Rule applied (3). Data calculated from results flagged with a "PB" are flagged "Calc-adj" to indicate the calculated value is based on a data value changed due to a "PB"	As per Section 1.4.2 %RPD ≤ 20% Internal lab check

FOOTNOTES

(1) All criteria are for surface water samples unless otherwise noted.

(2) See Table 13 for holding times

(3) 5 x Rule: The highest detected concentration in a blank sample is multiplied by 5. This establishes an action level. All positive sample results for the analyte detected in the blank that are below this action level are qualified as BRL (below reporting limit). If PB, data that are ≥ 5 x PB will be flagged. Data that are ≤ 5x PB will be flagged and censored

Table 22: Data Evaluation and Validation Criteria (Part II)

PARAMETER (METHODS)	LABORATORY PERFORMANCE EVALUATION CRITERIA	LABORATORY DUPLICATES	LAB MATRIX SPIKES & MATRIX SPIKE DUPLICATES (MS/MSD)	FIELD DUPLICATES and SPLITS
INORGANIC PARAMETERS	%R 80 – 120% If laboratory fails this criterion for a blind performance test, data for that parameter/date are coded "EPT"	%RPD ≤ 20% Internal lab check – Any data reported by labs as questionable due to their internal review flagged "LO"	%R 80 – 120% Internal lab check - Any data reported by labs as questionable due to their internal review flagged "LO"	%RPD ≤ 30% If criteria not met, data for that parameter/date are coded but reported: "BS" – field split out of bounds; "BD" – field duplicate out of bounds

22.2 Data Loggers

The continuous meter data will be corrected for sensor drift following the USGS procedures in TM 1-D3 (Wagner *et al.*, 2006) at the end of the sampling program. These procedures describe when data correction is required and the maximum allowable deviation from the calibration before the data should be censored. Table 23 presents the thresholds for which data correction is required. Correction is required if the deviation between the Data Logger and hand-held meter collected from the side-by-side measurements in the river differs by the greater of the absolute temperature/concentration or percent difference. If the deviation is less than the threshold in Table 23 then the data are used without correction.

Table 23: Data Logger Correction Criteria

PARAMETER	CRITERIA – CORRECTION REQUIRED
TEMPERATURE	+/- 0.2°C or 5% (greater of)
DISSOLVED OXYGEN	+/- 0.3 mg/L or 5% (greater of)

Correction should be completed using a two-point linear algorithm, assuming that the rate of drift is constant between calibration sample points. The percentage error at each calibration point is calculated as:

$$\%C_d = 100\left(\frac{V_s - V_c}{V_c}\right)$$

where V_s is the value of the DO calibration measurement using the hand-held probe and V_c is the continuous meter reading at the same time. The percentage error should be linearly interpolated between the two sampling points, and the continuous data adjusted by the linearly interpolated percentage error. The final result is an adjusted dataset that matches the calibration points.

The data quality of the corrected dataset should be flagged based on the following criteria (Table 24).

Table 24: Continuous Meter Data Quality Flags

DATA TYPE	MEASUREMENT TYPE	EXCELLENT	GOOD	FAIR	POOR	NOT VALID
DISSOLVED OXYGEN	Conc. or % Diff.	≤ ± 0.3 mg/l or ≤ ± 5%	± 0.3-0.5 mg/l or ± 5-10 %	± 0.5-0.8 mg/l or ± 10-15%	± 0.8-2 mg/l or ± 15-20%	> 2 mg/l or > 20%
TEMPERATURE		≤ ± 0.2°C	± 0.2 – 0.5°C	± 0.5 – 0.8°C	± 0.8 – 2.0°C	> 2.0°C

Data that exceed the maximum allowable limits (flagged as "not valid") will be censored. Both the raw dataset and the corrected dataset will be maintained and submitted to MassDEP.

23. Verification and Validation Methods

One hundred percent of the data and field QC samples will be evaluated for precision, accuracy, representativeness, completeness, comparability, and sensitivity in accordance with the "Region I, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses." The evaluation process will include a review of the following, as appropriate:

- Sample holding times,
- Sample preservation methods,
- Method preparation blanks,
- Laboratory duplicates,
- Matrix Spikes (MS) and/or Matrix Spike Duplicates (MSD)[2],
- Laboratory Control Samples (LCS) and/or Laboratory Control Sample Duplicates (LCSD)[3],
- Sampling and analytical procedures,
- Data usability,
- Method detection limits and reporting limits,
- Field blanks,
- Field duplicates,
- Field splits, and

[2] These data reviewed internally by labs prior to release of data

- Performance Evaluation (PE) sample results (limited).

During data evaluation, analytical data will be qualified as specified in Table 20 through Table 24. A data evaluation summary report will be generated at the completion of the evaluation effort to document the data precision, accuracy, completeness, representativeness, and comparability; an assessment of the overall data usability will also be presented. Included in an appendix to this report will be the specific sample delivery group (SDG) evaluation reports presented in tabular format; an example table is provided as Table 25.

The need for corrective action may be identified during either data evaluation or data assessment. Potential types of corrective action may include resampling by the field team (if possible) or reanalysis of samples by the subcontracted laboratory. These actions are dependent upon the ability to mobilize the field team and whether or not the data is necessary to meet the specified Data Quality Objectives.

If a Project Team assessor identifies a needed corrective action, the Project Manager will be responsible for approving the implementation of the response action. Problems that may be attributed to laboratory quality assurance issues will be brought to the attention of the laboratory's Quality Assurance Officer, who will determine what, if any, action is required. The laboratory QA Officer will be responsible for implementing and reporting the corrective action.

Table 25: Example Data Evaluation Table for Water Quality Measurements

		Precision	Accuracy	Representativeness		
Sample ID	**Collection Date/Time**	**Field Dup. Analyses %RPD**	**Perf. Eval. Test %R**	**Holding Times**	**Pres.**	**Blanks**
R116G	10/17/14 9:15 AM	9% **Acceptable**	89% **Acceptable**	Acceptable	Acceptable	Acceptable

24. Reconciliation with User Requirements

One hundred percent of the analytical data from the subcontracted laboratories will be evaluated. The Project Team will determine which data are usable for their intended purposes, as defined by the Data Quality Objectives established in Section 7.1. This review will consist of the following steps:

- Review Data Quality Objectives and sampling design,
- Conduct preliminary data review,
- Identify data limitations, and
- Draw conclusions from the data.

The measured environmental and streamflow data will be compared to the applicable water quality standards for Massachusetts and Rhode Island, as appropriate. The findings of the data reconciliation will be presented in a data report to be developed annually at the conclusion of the sampling program.

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Appendix A

Staff Training & Checklists

1 - Personnel Contact List
2 - Personnel Training and Certification
3 - Field Sampling Bottles Checklist
4 - Field Sampling Supplies Checklist
5 - Equipment Hand-off Checklist
6 - UMass Sampling Coordination Checklist

2020 Blackstone River Project Team Contact Information

Name/Organization	Role	Contact
UMass: Marie-Françoise Hatte Cameron Richards	Principal Investigator Field Sampling Assistance QAQC Review EAL Lab Coordinator Field Program Coordinator Document & Data Custodian Primary Field Sampler	mfhatte@umass.edu 413.545.5531 (w) 413.768.8402 (c) cameronr@umass.edu 413.545.5979 (w) 978.732.4007 (c)
CDM Smith: Kristina Masterson Zach Eichenwald	Program Management & Technical Oversight "	MastersonKK@cdmsmith.com 617.452.6284 (w) 978.618.6646 (c) eichenwaldzt@cdmsmith 508.654.2866 (c)
Upper Blackstone: Timothy Loftus Sharon Lawson Denise Prouty Cindy D'Alessandro Rick Vaudry Ornela Piluri Devon Avery	 Upper Blackstone Lab Manager Upper Blackstone Sampling and Lab Assistance " " " " "	TLoftus@ubcleanwater.org (774.312.3956) slawson@ubcleanwater.org (774.696.8423 Sharon) dprouty@ubcleanwater.org (508.523.9538 Denise) CD'Alessandro@ubcleanwater.org (508.769.4125 Cindy) RVaudry@ubcleanwater.org (401.580.7175 Rick) opiluri@ubcleanwater.org (508.981.5540 Ornela) davery@ubcleanwater.org (774.482.0568 Devon)
UMD: Sara Sampieri Horvet Dr. David Schlezinger Brian Howes	 UMD Lab Coordinator UMD Lab Director UMD Lab QA Officer	508.910.6325 (w) 508-985-8468 (c) ssampieri@umassd.edu dschlezinger@umassd.edu bhowes@umassd.edu
NBC: Karen Cortes Eliza Moore John Motta Luis Cruz Molly Welsh Sara Nadeau Bekki Songolo Jeff Tortorella	 Asst Mgr, Environmental. Monitoring Sr. Environmental Scientist Manager, Environmental Monitoring Environmental Scientist Environmental Scientist Field Supervisor	 Karen.cortes@narrabay.com 401.461.8848 ext. 274 eliza.moore@narrabay.com 401.461-8848, ext. 267 401.641.2709 401.641.1635 401.641.3274 401.461.3274 401.461.2709 401.461.1635

Personnel Training and Certification

Two lines for each - first line date, second line signature (initials)

Year: _____

	Review of Documentation					Cleaning			Sampling		Other Training
Staff Member	QAPP	FSP	SOPs	Manuals & other docs	Calibration	Equipment Cleaning	Bottle Wash	Acid Wash	Set-up	Manual	Pre-Sampling Refresher

Lab / Analyte	Type	Fill in Field	Fill at EAL	Fill at UB (Aliquot Split)	**Total Needed (Plus extras)**	Ready for Event
UMD Bottles						
dNH_4/dNO_{23}/TDN (.22µm)	60 ml	12	2 (P,LB)	0	**14+2**	□
POCN	1 L bottle	0	1 (LB)	12	**13+2**	□
UB Bottles						
TOP	237 ml jug	0	2 (P,LB)	12	**14+2**	□
TSS/SC	1L plastic jug	0	1 (LB)	12	**13+2**	□
EAL Bottles						
Chl-a	1 L, amber plastic	11	1 (LB)	0	**13+2**	□
TP	125ml acid washed, amber	0	2 (P,LB)	12	**13+2**	□
NBC Bottles						
dNO_{23}/dNH_4/dOrthoP PT	1L plastic jug	0	1	0	**1**	□
Bulk Bottles						
RI sites bulk	6 L carboy	3	0	0	**3**	□
MA sites bulk	4 L bottle	8	0	0	**8+2**	□
DI water for blanks	4 L bottle	0	1 (DI for FB)	0	**1**	□
TSS/SC split bulk	2 L bottle	1	0	0	**1**	□

Supplies		Need in Field	Need in Lab	Extras	**Total Needed (Incl. extras)**	Ready for Event
$MgCO_3$ solution	Small bottle of solution	0	1	0	**1**	□
47mm, 0.70 micron filters	Whatman GF/F	0	15	5	**20**	□
0.22 µm filters - Upper Loop	Millipore SLGP033RS	6 to 7	0	5	**12**	□
0.22 µm filters - Lower Loop	Millipore SLGP033RS	5 to 6	0	5	**11**	□
plastic syringes - Upper Loop	BD 309653	6 to 7	0	3	**10**	□
plastic syringes - Lower Loop	BD 309653	5 to 6	0	3	**9**	□

Note: Add 1 to all bottle and filter numbers in April for the Equipment Blank. If equipment blank needed beyond April, again add 1 to bottle and filter numbers.

Field Sampling Checklist

General Supplies	
Sampling pole	◻
2-L sampling bucket, rope, reel*	◻
Filter drier*	◻
Forceps*	◻
2 plastic flasks for chl-a*	◻
2 vacuum funnels for chl-a*	◻
Tin foil*	◻
Squeeze bottle DI*	◻
500 mL graduated cylinder*	◻
Hand sanitizer	◻
zip ties	◻
Latex Gloves	◻
Clip board	◻
Sharpies & Pens/Pencils	◻
Poison Ivy Wipes	◻
Poison Ivy Tarp	◻
Poison Ivy Suits	◻
Bug Repellant	◻
Forms	
Sampling Sites & Naming Convention	◻
EAL COC	◻
UB COC	◻
UMD COC	◻
NBC COC (for PET) sample	◻
Bulk_Sample_Collection_DataSheet	◻
River Field Data Sheets	◻
Site driving directions	◻
Step-by-Step Field Sampling directions	◻
Step-by-Step Lab Aliquots directions	◻
EquipmentProblemSheet	◻
FieldChangeRequestSheet	◻
Contact List	◻
Labels Bulk Chla	◻
Labels Chl a Filters	◻
Labels EAL TP Aliquots	◻
Labels Lab Water	◻
Labels Bulk Samples	◻

*April only. Will remain at UB lab for duration of sampling season

UMass - UB Crew Equipment Hand-off Checklist

UMass to UB:

- ☐ Clipboard with:
  - □ Field sheets for the 4 Lower Loop sites
  - □ 2 NBC CoC sheets
  - □ Bulk bottle CoC
  - □ Meter SOP
  - □ Field Log Book
  - □ Field Sampling Guide
  - □ Equipment Problem Report Sheet
  - □ Field Change Request Form
  - □ Site Directions
  - □ Extra labels
- ☐ Performance test sample for NBC
- ☐ Ziploc bag with 0.22 micron filters, syringes
- ☐ Bulk sampling bottles (3 6L with spout for RI, 1 4L for W1779)
- ☐ 4 bags of field bottles (one for each site)
- ☐ Bag with spare bottles
- ☐ Gloves
- ☐ Paper towels/wipes

If doing LB, FB at Lower Loop site:

- ☐ Pre-filled LB samples
- ☐ Bag of FB field bottles
- ☐ Empty 4L bulk bottle for FB
- ☐ 4L bulk bottle filled with DI water to pour into empty FB 4L bulk
- ☐ 1L chl-a bottle filled with DI water to pour into empty FB 1L chl-a bottle

If doing FS (split) at lower loop site

- ☐ 2L bulk bottle for TSS/SC

If doing FD (duplicate) at lower loop site

- ☐ Bag of FD field bottles
- ☐ Empty 4L bulk bottle for FD

UB to UMass:

- ☐ Hand-held meter with probes, kimwipes, and filled DI wash bottle
- ☐ Ice packs
- ☐ Two 1 gallon jugs of DI water if UMass is doing EB

UB Crew Equipment to bring up from UB building:

- ☐ Sampling pole
- ☐ Sampling bucket with rope and reel
- ☐ 2 large coolers

UB – UMass Sampling Coordination Checklist

Prior to sampling season:

- ☐ 1-month prior to sampling season start
  - Contact Karen Cortes at NBC (kcortes@narrabay.com) to find out when they plan to sample for April-November.
  - Share tentative sampling dates for the year based on NBC sampling plans.
  - Update training materials
  - Order bottles from Quality Containers of New England, if needed
  - Order performance test standards from Advanced Analytical Solutions
  - Order 0.22 micron filters from Fisher Scientific
  - Ensure all reagents and equipment for chlorophyll-a and total phosphorus analyses are fully stocked at EAL
  - Schedule and hold refresher training for all samplers either by conference call or in-person meeting
  - Train any new staff members

For each sampling event:

- ☐ 2-3 weeks prior to sampling
  - Create new folder for the month's chains of custody (/Blackstone/Blackstone 2020/Blackstone 2020 Forms/Chain of Custody Forms/)
    - First update "Sites_Naming Convention_QC History" file by picking which sites will have the P, FD, FS, LB, and FB QCs. First month have an EB as well. (Rotate them around so each site gets each QC type once by the end of the year. Be sure to split QCs between the two groups fairly evenly each month (RMSD, R116, RMSL and W1779 is one group and the rest of the sites are the other group)
    - Update all chains of custody with the upcoming sampling date and the correct QCs
    - Print two copies of CoCs (one for each group's clipboards). Print each lab's CoC on a different color paper to help identify them on sampling day.
      - RI sampling crew signs both NBC CoCs and keeps one, lower loop crew keeps the other
      - Be sure to print entire workbook (all 3 pages) for UMass Darmouth CoC
  - Create new folder for the month's bottle labels (/Blackstone/Blackstone 2020/Blackstone 2020 Forms/Labels/)
    - Update all label files with the correct QCs
    - Print labels using either Avery 5522 label paper or Avery 5520 label paper
    - Chlorophyll filters labels can go in the UMass sampler's clipboard or the box containing chlorophyll supplies (they will be filled out and attached to the aluminum foil containing the dry chlorophyll filters)
  - Have student wash bulk sampling bottles and other bottles needed for sampling event (see Sample volumes 2020.docx in /Blackstone 2020 Forms/Guides and Checklists/)
  - Contact Sara Horvet at UMass Dartmouth (ssampieri@umassd.edu) requesting bottles. (22 of the 60mL bottles, 15 of the 1L bottles)
- ☐ 1-2 weeks prior to sampling
  - Label sample bottles or have student label sample bottles

        - Chlorophyll split (FS) label goes on same sample bottle as regular (G) chlorophyll label. Both samples (G and FS) will be filtered from the same bottle.
        - Chl-a preserved labels will go on 500mL brown bottles
        - In UMD 500mL labels file, one label says "500mL for NBC." Attach this label to one of the "milk jug" bottles and that will be the bottle used for the performance test sent to NBC. Sample must be handed off to RI sampling crew when meeting in the morning.
        - In bulk labels file:
            - Split label (FS) goes on 2L round bulk bottle. This bottle will be used for the regular and split TSS/SC samples. All other lab aliquots will be filled from the regular bulk bottle for that site.
            - The duplicate (FD) label goes on a 4L bulk bottle which will be collected alongside the regular bulk bottle in the field.
            - The field blank (FB) label goes on a 4L bulk bottle and at the site, pour the blank water from the "EAL Lab DI Water (Pour into FB bulk bottle)" bottle into the FB bulk bottle.
            - The label "EAL Lab DI Water (Pour into FB Chl-a bottle)" will go on a 1L brown Nalgene bottle. Fill it with DI water and at the FB sampling site, pour that blank water into the chlorophyll FB bottle.
            - The label "EAL Lab DI Water (Pour into FB bulk bottle)" will go on a 4L bulk bottle. Fill it with DI water and at the FB sampling site, pour that blank water into the FB bulk bottle.
    - Once bottles are labeled, place them in bags for easy organization.
        - One set of bags contains sample bottles filled in the field
            - 1L chlorophyll-a bottle, 60mL nitrogen bottle
            - Put RMSD, R116, RMSL, and W1779 bags in one tub for Lower Loop crew (Upper Blackstone staff)
            - Put W1242, W1258, W0767, UBWPAD2, and W0680 field bags in one tub for Upper Loop crew (UMass staff)
        - One set of bags contains aliquot bottles to be filled at the UB lab from bulk bottles:
            - 125mL TP bottle, 1L TSS/SC bottle, 237mL TOP bottle, 1L POCN bottle, isotope bottles for Dave Boutt (one per site, no QCs)
            - Lab aliquot bags can be put in one large tub and left in Upper Blackstone lab when you arrive in the morning
        - For site with split (FS), include in aliquots bag both regular grab sample (-G-) and split (-FS-) bottles, as the G and FS are filled from the same sources
        - For duplicates (-FD-), you'll have a separate bag since they are two distinct samples from the same site
        - There are no LB bags because those bottles are pre-filled at EAL
        - Create bags for FB field and aliquot bottles at the site chosen that month
    - Prepare all sampling supplies (Use "Sampling Supplies Checklist.xlsx" in /Blackstone 2020/Blackstone 2020 Forms/Guides and Checklists/)
        - Bring small handheld cooler for bringing samples back to UMass
        - Bring cooler from UMass Dartmouth to mail samples to them
        - Large wheeled cooler for 6L bulk bottles is kept at Upper Blackstone in basement
    - Separate supplies into different tubs/piles for RI sampling crew (Lower loop, UB staff) and UMass sampling crew (upper loop).

- UMass and UB Lab Manager (Tim Loftus) talk and confirm sampling plans. Alternative contact will be Sharon Lawson.
- Contact Karen at NBC to confirm co-sampling date (kcortes@narrabay.com)
- Reserve vehicle from Enterprise (call or use "Reservations" link on this site: https://www.umass.edu/transportation/car-rentals-0) and send email confirmation to Christine Przewoznik (cprzewoz@cns.umass.edu) for a PO number, or charge to your travel credit card.

☐ Monday of week of sampling,
- Send reminder of sampling plans to UB and NBC

☐ Day before sampling
- Create performance test standards and fill performance test bottles (those with "-P-" as the sample type)
- Fill LB bottles with DI water
- Fill 1L brown Nalgene bottle labeled "EAL Lab DI Water (Pour into FB Chl-a bottle)" with DI water
- Fill 4L square bulk bottle labeled "EAL Lab DI Water (Pour into FB bulk bottle)" with DI water.
- Pick up vehicle from Enterprise and load all equipment in it.
  - Put filled bottles in cooler with ice packs
  - Use "Sampling Supplies Checklist.xlsx" in /Blackstone 2020/Blackstone 2020 Forms/Guides and Checklists/ to ensure all supplies are loaded

☐ Day of sampling
- Meet at 7 am at UB main building (park in rear of building)
- UMass brings into lab bottles for aliquot splitting
- UB staff park UB truck next to UMass vehicle
- UB and UMass staff transfer equipment for sampling as needed to UB vehicle (check boxes on UMass to UB Crew Hand-off Checklist)
- Get ice packs for all coolers from freezer in basement of UB facility
- ~7:30 am departure for sampling
  - Typically UMass will sample Upper Loop and UB will sample Lower Loop
- 8:30 am, UB staff meet NBC staff at Slater Mill Dam sampling site unless alternative arrangements have been made
  - UB staff transfer P sample and associated chain of custody to NBC staff
  - Two copies of chain of custody will be available, both must be signed by UB as "release" and NBC as "acceptor"
  - UB staff will retain one copy and give to UMass upon return to District
- ~11am, UMass returns to District lab to start chlorophyll-a sample filtering
- ~12:30 pm, UB staff return to District lab
- UMass will process chlorophyll-a samples until done
- UB staff or UMass assistant will prepare nutrient aliquots until done
- UMass and UB staff will jointly coordinate preparation of aliquots for delivery to appropriate labs
  - 1 cooler to UMass Dartmouth
  - 1 cooler to UMass Amherst (EAL)
  - TSS/SC and TOP samples stay at UB
- Chain of custody documents will be finalized
  - UB staff will check and sign chain of custody release line.
  - UMass staff will sign CoC acceptance line for EAL form

        - Tim will sign CoC acceptance line for UB form
        - Acceptance line for UMD form will be left blank; UMD will email copy of final form once signed by their staff
    - UB staff will drop-off UMD cooler at Fed Ex location for shipping
    - UMass staff will reload equipment and aliquots for EAL into van for return to UMass
    - UMass staff unload equipment at UMass
    - UMass staff places TP samples and chlorophyll filters in the freezer
    - UMass staff returns vehicle to Enterprise

- ☐ After sampling
    - UB staff completes analysis of TOP, DOP, SC, and TSS and sends results to UMass Amherst
    - UMass Dartmouth completes analysis of dNH_4, dNO_{23}, PON, and TN, and sends results to UMass Amherst
    - UMass Amherst analyzes chlorophyll-a and total phosphorus samples
    - Give UMass student field sheets to enter into spreadsheet (/Blackstone/Blackstone 2020/Blackstone 2020 Forms/Field Sampling Notes 2020.xlsx)
    - Give UMass student yellow field log books to enter into spreadsheet (/Blackstone/Blackstone 2020/Blackstone 2020 Forms/Field Sampling Book 2020.xlsx)
    - UMass student enters all lab data into Data Summary Data file, MassDEP file, and EPA WQX file
    - UMass student adds all documents from the month into the 2020 Evidence file
    - Deliver isotope samples (15mL bottles) to David Boutt. Contact Marsha Allen (mkallen@umass.edu) to coordinate drop-off
        - At end of sampling season, send Dave Boutt a spreadsheet with probe results for all sites with dates and times.

Appendix B

Equipment Calibration/Inspection Forms

1 - Meter Calibration Form - DO
2 - Meter Calibration Record - pH
3 - Hand-held Meters QC Forms

Daily D.O. River Field

Meter Calibration Record - Hach HQ40d Multi DO

			water saturated air reading (before/after sampling event) (Northern)		Ideal slope 100% +/- 30			water saturated air reading (before/after sampling event) (Southern)		Ideal slope 100% +/- 30
Date	Initials	% Slope	Before	After	Notes		% Slope	Before	After	Notes

RIVER pH METERS CALIBRATIONS RECORD

(3 point pH calibration using buffers 4, 7 and 10)

NORTHERN									SOUTHERN						
		buffer reading (before/after sampling event)							buffer reading before/after sampling event)						
DATE	Initials	7		4		10		% Slope	7		4		10		% Slope
		Before	After	Before	After	Before	After		Before	After	Before	After	Before	After	

Hand-Held Meters QC Form

Date	Sample	Initials	Upper Loop (Northern) Meter				Lower Loop (Southern) Meter				expected value	acceptable range	
			Temp (°C)	DO (mg/L)	DO (% sat)	pH	Temp (°C)	DO (mg/L)	DO (% sat)	pH			

River pH Meters Calibration Record

Date	Initials	Upper Loop (Northern) Meter				Lower Loop (Southern) Meter			
		% Slope	4 Buffer	7 Buffer	10 Buffer	% Slope	4 Buffer	7 Buffer	10 Buffer

River DO Meters Calibration Record

Date	Initials	Upper Loop (Northern) Meter			Lower Loop (Southern) Meter		
		% Air Saturated Slope	% Air Saturation Reading		% Air Saturated Slope	% Air Saturation Reading	
			Before	After		Before	After

Appendix C

Sampling Sites

1 - Sites Naming Convention
2 - Sampling Driving Directions
3 - QC Site Assignment

BLACKSTONE RIVER SITES – Sample Naming Convention

Sample ID	Waterbody Segment
RMSD-h	Slater Mill Dam Pawtucket, RI (Historical site on bank) *(41.876909, -71.381940)*
RMSD-n	Slater Mill Dam, Pawtucket, RI (New site on bridge) *(41.879836, -71.381556)*
R116	Rte 116 Bikepath bridge Pawtucket, RI *(41.938066, -71.433769)*
RMSL	State Line, RI *(42.009974, -71.529313)*
W1779	Below Rice City Pond Sluice Gates Hartford St., Uxbridge *(42.09727, -71.62241)*
W0767	USGS gage 01110500 Sutton St. Bridge, Northbridge, MA *(42.153966, -71.652452)*
W1242	Route 122A Grafton, MA *(42.17704, -71.68796)*
W1258	Central Cemetery Waters Street, Millbury, MA *(42.19373, -71.76603)*
UBWPAD2	Below Confluence UBWPAD and Blackstone River Millbury, MA *(42.20702, -71.78154)*
W0680	New Millbury St Bridge Worcester, MA *(42.22784, -71.78762)*
B	Blanks not associated with a site
G	Grab sample
FS	Field split
FD	Field duplicate
LB	Lab blank (EAL DI)
FB	Field blank (EAL DI)
EB	Equipment blank
B3	Lab blank (UBWPAD DI)
B4	Field blank (UBWPAD DI)
B5	Lab blank – unwashed bottle (UMD DI)
B6	Field blank – unwashed bottle (UMD DI)
B7	Field blank – washed 60mL and leftover water in 1L for POCN (UMD DI)
B8	Blank, bottle washed by EAL, returned empty
B9	Blank, pre-filled, left unopened
B10	Blank, 1L pre-filled, left unopened (UMD DI)
P	Performance Evaluation Sample

Sampling Site Details

UB: 50 US-20, Millbury, MA (Use 7 Nippnapp Trail, Millbury, MA for GPS directions)

Sample Site	Waterbody Segment	Coordinates
RMSDh[1] RMSDn[2]	Slater Mill Dam Pawtucket, RI	*(41.876909, -71.381940)*[1] *(41.879836, -71.381556)*[2]
R116	Rte 116 Bikepath Bridge Pawtucket, RI	*(41.938066, -71.433769)*
RMSL	State Line RI	*(42.009974, -71.529313)*
W1779	Below Rice City Pond Sluice Gates Hartford St., Uxbridge, MA	*(42.09727, -71.62241)*
W0767	USGS gage 01110500 near Sutton St. Bridge Northbridge, MA	*(42.153996, -71.652438)*
W1242	Route 122A Grafton, MA	*(42.17704, -71.68796)*
W1258	Central Cemetery Waters Street, Millbury, MA	*(42.19373, -71.76603)*
UBWPAD2	Below Confluence UB effluent and Blackstone River Millbury, MA	*(42.20702, -71.78154)*
W0680	New Millbury St. Bridge Worcester, MA	*(42.22784, -71.78762)*

[1] Historical site
[2] New site at Exchange St Bridge

UB toy Slater Mill Dam (Historical site)

1. Leave plant and turn left onto Route 20
2. Take immediate right at light to head towards entrance to I-90 (Pike)
3. Go past entrance to I-90 and take exit on right to Rt-146 S
4. Continue on RI-146 S into Rhode Island
5. Take the RI-15/Mineral Springs Ave exit
6. Turn left on to Mineral Springs Ave/RI-15. Continue to follow RI-15 E
7. Continue straight for as long as possible, staying straight to go onto Church St.SML
8. At T-intersections, turn left onto Park Place E
9. Turn right onto Main
10. Go across bridge staying to the left.
11. Turn left onto School Street for 1 block, taking next left to go around the block and down the hill back to the river.
12. Park on the LHS of Broadway.
13. Dam across the street.

BE CAREFUL CROSSING STREET – CARS MOVE FAST AROUND THE CORNER AND IT IS A BLIND TURN.

To reach the new site at Exchange Street Bridge:
Head west on Broadway
Turn right onto Main St.
Turn right on to Roosevelt Ave
Turn right onto Exchange St.
Park on the right side of the bridge and sample from that side.

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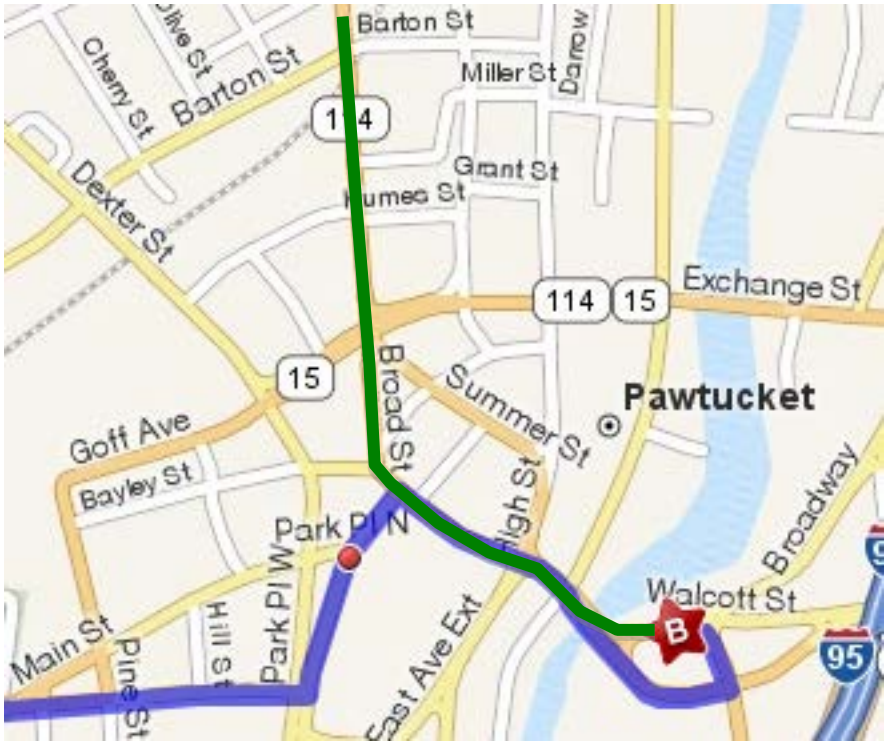
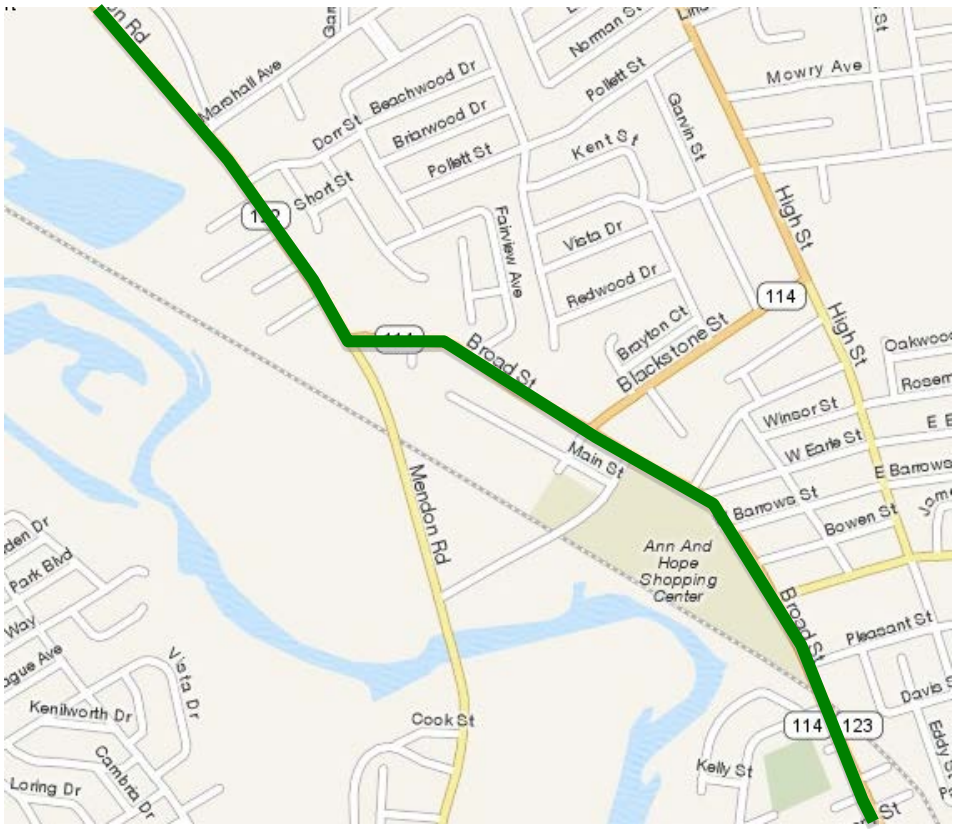
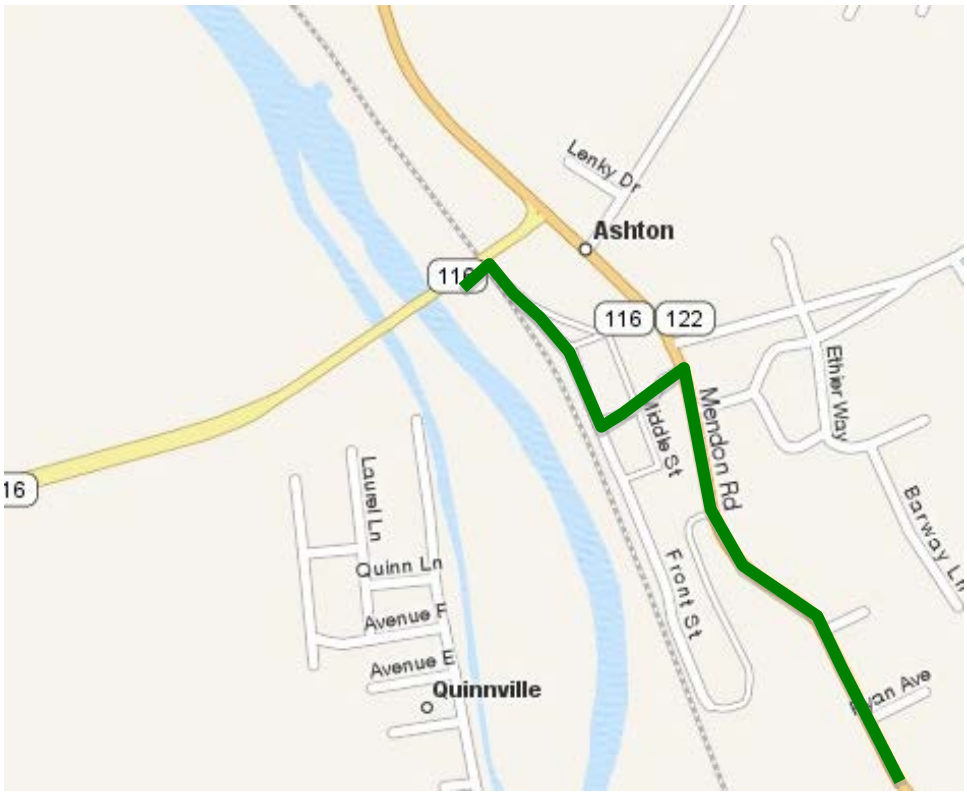
Slater Mill Dam to Rt. 116 Bikepath Bridge (George Washington Highway)

1. Return to Main Street and turn right.
2. Go straight up the hill, verging to the right at the top go onto Broad Street, Route 114.
3. Stay on Broad Street (merges with Rt 123)
4. Turn right onto Rt. 122/Mendon Rd when Broad Street ends.
5. Turn left into the Loft Apartment/Mill Shops near Middle St. and Front St.
6. Park under highway bridge and collect sample from bikepath bridge







Rt. 116 Bikepath Bridge to MA/RI State Line

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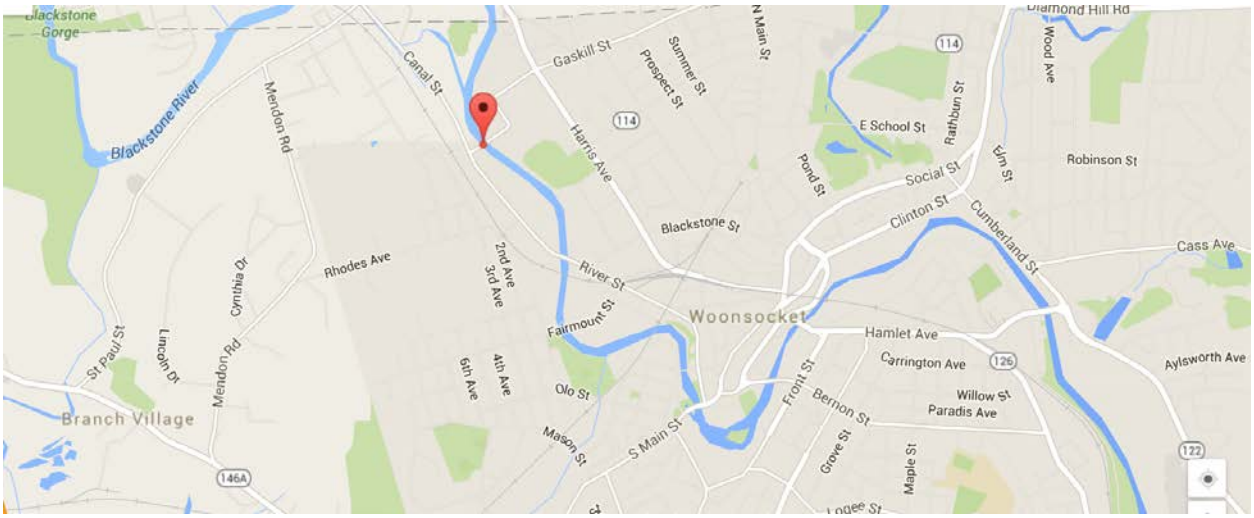
1. Exit shops area and turn left back onto Rt. 122/Mendon Rd.
2. Continue on Rt. 122 into Woonsocket.
3. Verge left to stay on Rt. 122/Cumberland Rd when Mendon Rd turns to the right
4. Turn left onto Hamlet Ave/Rt. 122/Rt. 126, crossing the river
5. Continue on Hamlet Ave/Rt. 122 until cross river again.
6. After crossing river, continue straight, up the hill on the one way street (High Street) past the historic train station (and big bear wooden statue).
7. Continue to the end of High St./122
8. Turn right onto River Street
9. Cross River, continuing on River Street to the Singleton Street bridge
10. Sample from bridge

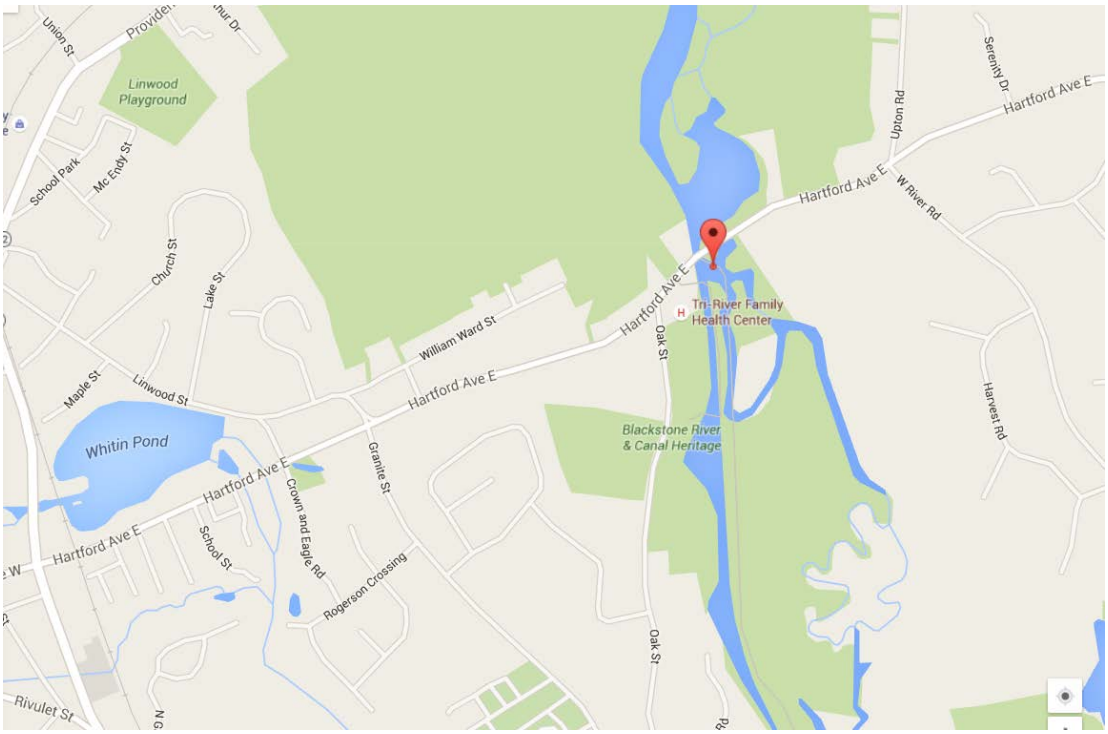


Directions to return directly to Rt. 146:

1. Head southwest on Singleton St toward Canal St
2. Turn right onto Canal St
3. Turn left onto St Paul St
4. Turn right onto Rhode Island 146A N/State Hwy 146A N
5. Merge onto RI-146 N via the ramp to Worcester

MA/RI State Line to Rice City Pond

1. Turn around on Singleton Street in order to turn right onto Canal Street
2. Briefly turn left onto St. Paul Street, then immediately right again to stay on Canal Street.
3. Cross the river and continue straight to stop sign.
4. Turn left onto Route 122
5. Continue on Route 122 through Uxbridge and into North Uxbridge.
6. Turn right onto E. Hartford Ave
7. Continue on E. Hartford Ave across Mumford River and through stop sign.
8. When road starts to go downhill, turn right onto Oak Street (sign for River Bend Farm and conservation area).
9. Turn left into medical practices offices. Park in far corner near canal/river park.



RCP back to Rte 146:

1. Go out of parking lot and turn right onto Oak St, then left back onto Hartford Ave.
2. Continue on Hartford Ave then go right at the light onto Rte 122 North
3. Continue on 122 to Northbridge and go left onto Sutton St. It becomes Central Turnpike and will take you to the exit for Rte 146 N.

To get to RCP from Rte 146

1. Take Exit 3 (Uxbridge), Douglas Street
2. Turn left onto Rt. 122 N.
3. Travel north short ways until East Hartford Ave

Rice City Pond to W0767 (Sutton St. Bridge)

1. Retrace path to Hartford Ave and return to Rt. 122
2. Turn right onto Rt. 122N
3. Follow Rt. 122N to Sutton St on left
4. Left onto Sutton St then park on bridge
5. Sample from downstream side of bridge
6. Old site (through 2018): Park behind the apartment building on the left, and sample from the bank

Sutton St Bridge to Rt. 122A Bridge

3. Return to Rt. 122
4. Turn left onto Rt. 122N
5. Continue on Rt. 122N, verge left onto Rt. 122A
6. Park in shopping area lot on left just before the bridge
7. Sample from downstream side of bridge

To get to Rt. 122A bridge from Rt. 146

1. Turn left onto Boston Rd from 146 (Pizza place on RHS)
2. Follow Boston Rd to 122A
3. Turn right onto Rt. 122A south
4. Continue to bridge over Blackstone River

Rt. 122A Bridge to Central Cemetery

1. Leave parking lot turning left to continue on Rt. 122A North
2. Merge left to continue onto Rt. 122A/Canal St./Elm St in Millbury
3. Verge right to stay on Rt. 122A up the hill
4. Turn right onto North Main Street
5. Take next left onto West Street
6. At stop sign, turn right on Waters Street and park in Cake Shop Café
7. Sample from upstream side of the bridge

To get to Central Cemetery from Rt. 146

1. Take Elm St. exit, immediately past gas station/donut shop
2. Turn left at end of the ramp onto Elm Street
8. Cross river and take immediate left onto River Street
9. Continue on River Street to stop sign
10. Turn left onto Waters Street, park Cake Shop Café
11. Sample from upstream side of the bridge

Central Cemetery to UBWPAD Confluence (UBWPAD2 site)

1. Leave site and turn right onto River Street at stop sign.

W:\WRRC\Water Resources\Blackstone\Document Originals\Sampling Sites Directions and Maps\Sampling Driving Directions.docx

2. At end of River St., turn right onto Elm Street
3. Cross river and then turn left for the Route 146 entrance
4. Follow Rt. 146, taking the I-90 interchange exit
5. Stay right to stay on Route 20 Connector
6. At second set of lights, turn left onto Route 20 West/Washington St.
7. Continue past the plant and turn left onto Greenwood Street
8. Continue straight on the I-90 overpass
9. Before bridge over the Blackstone River (white house like business on left that used to sell antiques) turn left and take the access road along the Kettle Brook diversion.
10. Park down dirt path and cross railroad tracks on foot, following path to gain access to bike path
11. Once on bike path, go right down the path until you see a clearing in the brush on your right. The point of entry will be marked with blue plastic colored ribbon. Go into the woods towards the river. The sampling spot will be marked with the same color ribbon.

UB Plant to UBWPAD2 sampling site

1. Leave plant and turn right onto Route 20 West/Washington St.
2. At light, turn left onto Greenwood Street
3. Continue straight on the I-90 overpass

4. Before bride over the Blackstone River (white house like business on left that used to sell antiques) turn left and take the access road along the Kettle Brook diversion.
5. Park down dirt path and cross railroad tracks on foot, following path to gain access to bike path.

UB Plant to New Millbury Street Bridge

1. Leave plant and turn right onto Route 20 West/Washington St.
2. At light, turn right onto Greenwood Street
3. In Quinsigamond Village, turn right onto Blackstone River Road
4. Go past Imperial Distributors
5. At light, turn onto Tobiason Boland Way
6. Turn left into large store (old Sam's) parking lot, and drive all around the building until you see dumpsters
7. Park near dumpsters, walk to fence where there is a gate
8. Walk left on the bike path
9. Go through gate (use key to lock if necessary)
10. Sample under bridge

Stebbins St
Falmouth St
Ekman St
Halmstad St
Kosta St
Jay St
Greenwood St
Gibbs St
146
St Louis St
Millbury St
QUINSIGAMOND VILLAGE
11
Arnold Rd
Southwest Cutoff
Rogers St
A
Route 20 Conn
10

QC Samples Site Assignment								
QC	**April**	**May**	**June**	**July**	**August**	**September**	**October**	**November**
P	RMSD	W0680	R116	UBWPAD2	RMSL	W1242	W1779	W1258
LB	W1779	W0767	W0680	RSMD	UBWPAD2	R116	W1242	RMSL
FB	W1258	RMSL	W1258	W1779	W0767	RSMD	W0680	UBWPAD2
EB	W1242	?	x	x	x	x	x	x
FD	R116	W1779	W1242	RMSL	W0680	W0767	RSMD	UBWPAD2
FS	W0680	UBWPAD2	RSMD	W0767	W1779	W1258	RMSL	R116

Appendix D

Standard Operating Procedures for Sample Collection & Aliquot Splitting

1 - SOP-DOC-001 – Field Notebooks – Content and Control
2 - Step-by-Step Field Sampling Instructions
3 - Step-by-Step Lab Aliquots
4 – Hand-held Meter: Field Measurement of Temperature, Dissolved Oxygen, and pH
5 – Field Measurement of Water Temperature and Dissolved Oxygen with Hobo Data Logger

RECORD OF REVISIONS

SOP-DOC-001
Field Notebooks – Content and Control
Revision Level -1-

Page	*Section*	*Description of Revision*
Throughout		Editorial

Rev. Level – 0- July 2004
Rev. Level – 1- July 2014

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FIELD NOTEBOOKS – CONTENT AND CONTROL

1. Objective

The objective of this standard operating procedure (SOP) is to set criteria for content entry and form of field notebooks for the Blackstone River field monitoring project. Field notebooks are an essential tool to document field activities for historical and legal purposes.

2. Preparation

In addition to this SOP, site personnel responsible for maintaining logbooks must be familiar with all procedures applicable to the field activity being performed. These procedures should be consulted as necessary to obtain specific information about equipment and supplies, health and safety, sample collection, packaging, decontamination, and documentation. Each Field Crew member will receive copies of these procedures; master copies of the procedures will be located at UMass.

Information pertinent to the field work will be recorded in bound and numbered project-specific field notebooks. The pages in these field notebooks will be numbered. Due to the number of field monitoring sites, each individual site will be grouped with others in a logical fashion and the group assigned to a specific notebook. Prior to use in the field, each field notebook will be appropriately labeled with a document control number. The document control number shall appear both on the cover and first page of the field notebook and shall include a volume number, if necessary. The following information will also be recorded on the first pages of the field notebook:

- ◻ Project Name
- ◻ Field notebook document control number
- ◻ Name and contact information of Project Manager and Field Program Coordinator
- ◻ Start date
- ◻ Field monitoring sites covered by the field notebook

Sufficient blank pages will be left prior to the first field note entry to facilitate updating field crew information. Prior to use, the remaining pages of the field notebooks will be divided into sections, leaving sufficient blank pages between sections. Each section will be assigned to a specific monitoring location and numbered sequentially based on the monitoring location identifier. Field records will be retained for a minimum of seven years after the completion of the project.

3. Operation

All field notes must be legible and written in indelible black or blue ink pen. Errors should be crossed out with a single line and initialed. Each field entry should be placed in the appropriate section of the field notebook for the location and at a minimum contain the following information:

- Date;
- Project and monitoring site location identifier;
- Purpose of site visit (*i.e.* maintenance, dry- or wet-weather sampling);

- Names and affiliations of field crew at location and their designated initials;
- Name of individual making entry;
- Description of work being performed that day;
- Time of each data entry in military units;
- Weather conditions on site;
- Visual observations;
- Pertinent field data (and any other measurements) including equipment calibration details (field and laboratory);
- List of any Field Forms, completed as part of the activities, where additional information may be found (no need to duplicate);
- Serial/tracking numbers, if any, on seals, transportation cases, equipment and or documentation (e.g., carrier air bills or chain of custody documents);
- Summary of problems encountered and corrective actions;
- Sketches as appropriate;
- Photographs taken, including date, time, direction faced, description of subject or activity, sequential number of the photo and film roll number will be recorded in the field notebook.

If data collection forms are specified by an activity-specific plan, this information need not be duplicated in the logbook. However, any such forms used to record site information must be referenced in the logbook by date and a document control number.

A new page will be started for each unique set of entries. However, notes regarding a wet-weather sampling event that extends over several hours or days will be considered a single set of entries and thus will not be entered on the same page. At the end of their entry, each notebook recorder will sign out by printing their name, then providing their signature with the date. A new author will note their name as described above prior to their entry.

Any deviations from the project scope of work, health and safety issues, or other warranting information should be recorded in the field book, and the project manager should be contacted immediately.

4. Quality Control

Periodically the individual responsible for the field notebooks will ensure that all entries have been appropriately recorded, signed, and dated, and that any corrections were made properly. Completed logbooks shall be submitted to the records files. No pages shall be removed from the field notebook.

Step-by-Step Field Sampling Guide

Prior to sampling: Calibrate DO & pH Probes at Upper Blackstone Lab

For RI Sites: *Give NBC the PT Sample (500mL) in cooler, along with a Chain of Custody sheet. NBC and UB sign both CoC copies, one goes with NBC, the other one stays with UB.*

Put on clean pair of nitrile gloves at each site.

- ☐ 1 (6L) Carboy (Bulk Sample) for each site
- ☐ 1 (1L) brown Nalgene bottle for the chlorophyll sample
- ☐ 1 60 mL bottle for UMD filtered sample

- ☐ Measure Water Temperature, pH, and DO in mg/L and % saturation with Hach meter and record on field data sheet. Circle "River" or "Sampling Container" on field data sheet. (Where probe can't reach the river, take a sample with sampling container and take measurements in container).
- ☐ Rinse all three bottles 3x with river sample water
- ☐ Fill brown 1L chlorophyll bottle
- ☐ Fill Carboy ~ ¾ full
- ☐ **Shake carboy !**
- ☐ NBC takes their sample from this carboy
- ☐ Fill out field data sheet
- ☐ Ask NBC folks for their Sonde readings (Water Temperature, DO, pH, and chl), and record on the field data sheet
- ☐ For 60mL NH_4/NO_{23}/TDN samples to be sent to UMassD (All sampling sites):
    - o Rinse clean syringe 3 times with water from bulk sample bottle. Attach 0.22 micron filter to syringe and fill with water from bulk sample bottle by removing plunger, pouring into barrel, and replacing plunger.
    - o Filter 20mL of sample through the disposable 0.22 micron filter housing and discard. Then, filter 20mL into the 60mL bottle to rinse bottle and discard. Then use the remaining 20mL water in the syringe to filter into the 60mL sample bottle.
    - o Remove filter from syringe and replace with new 0.22 micron filter. Filter 20mL of sample through disposable 0.22 micron filter housing and discard. Then use the remaining 40mL water in the syringe to fill the 60mL bottle that contains 20mL of sample from first 0.22 micron filter.
    - o Use new clean syringes and filters for each site.
- ☐ Record the sampling date and time on the Bulk Sampling COC – Make sure all bottles are labeled with date and time of sampling!
- ☐ All samples go back in the coolers for transport back to the lab

For MA Sites:

- ☐ 1 (4L) Square bulk sample bottle for each site
- ☐ 1 (1L) brown Nalgene bottle for the chlorophyll sample
- ☐ 1 60 mL bottle for UMD filtered sample
- ☐ Measure Water Temperature, pH, and DO in mg/L and % saturation with Hach meter and record on field data sheet. Circle "River" or "Sampling Container" on field data sheet. (Where probe can't reach the river, take a sample with sampling container and take measurements in container).
- ☐ If using, rinse sampling bottle on pole or reel 3 times with river water

- ☐ Rinse sample bottles 3x with river sample water
- ☐ Fill 4L bottle
- ☐ Fill brown 1L chlorophyll bottle
- ☐ Each crew: take meter measurements from both the river and the sampling container at <u>one site</u> (of your choice).
- ☐ Fill out field data sheet
- ☐ For samples to be sent to UMassD (All sampling sites):
    - Rinse clean syringe 3 times with water from bulk sample bottle. Attach 0.22 micron filter to syringe and fill with water from bulk sample bottle by removing plunger, pouring into barrel, and replacing plunger.
    - Filter 20mL of sample through the disposable 0.22 micron filter housing and discard. Then, filter 20mL into the 60mL bottle to rinse bottle and discard. Then use the remaining 20mL water in the syringe to filter into the 60mL sample bottle.
    - Remove filter from syringe and replace with new 0.22 micron filter. Filter 20mL of sample through disposable 0.22 micron filter housing and discard. Then use the remaining 40mL water in the syringe to fill the 60mL bottle that contains 20mL of sample from first 0.22 micron filter.
- ☐ Record the sampling date and time on the Bulk Sampling COC – Make sure bottles are labeled with date and time of sampling!
- ☐ All samples go back in the coolers for transport back to the lab
- ☐ **ONLY AT W1779:** Walk to the middle of the bridge on Hartford Drive (wear a yellow vest) on the upstream side, and take photos of the pond to document presence/abundance of algae and aquatic macrophytes. Photos will be emailed to UMass.

For QA/QC Samples:

- ☐ Samples marked "FD" are Field Duplicates. FD sample should be taken immediately after the regular ("G"') sample.
- ☐ Samples marked "FS" are Field Splits. Make sure you collect enough sample water – fill bottles and fill an extra 2L bottle at the sampling site for MA sites. That 2L bottle will be split into the TSS/SC sample and TSS/SC field split sample.
- ☐ Field Blanks (FB)– Make sure the Blank DI Water gets poured into the corresponding Bulk Sample Bottle in the field, at the sampling site.
- ☐ Lab Blanks (LB) are already filled and should accompany you on the entire field trip, in cooler

Site Specific instructions:

- ☐ W0680 – Get key from UBWPAD; Use sampling pole *
- ☐ UBWPAD2 – Use the sampling pole* *Watch out for poison ivy here*
- ☐ W1258 – Use bridge sampler (4L Bottle that is attached to a rope and reel)
- ☐ W1242 – Use bridge sampler
- ☐ W0767 – Use bridge sampler
- ☐ W1779 – Use sampling pole

*If using the sampling pole to fill the 4L bottle, attach the clean 1L brown bottle to the pole, rise 3x with river water, then fill the 4L bottle with the river water. Once the 4L bottle is filled, fill the brown bottle again and cap. That will be your chlorophyll sample.

Step-by-Step Directions – Lab Procedures for Aliquot Splitting

1. Work with other crew member to bring in bulk sample bottles
    - 6-L and 4-L bulk bottles and 1-L brown bottles to UB lab
    - 1-L bottles go to one designated bench and bulk bottles go to another

2. Take the Bulk Sample Bottle Chain-of-Custody to fill out EAL Chlorophyll Chain-of-Custody (fill in sample collection times)

3. Take the Bulk Sample Bottle Chain-of-Custody to bench with bulk bottles and use it to fill in the sample collection times on the:
    - UB Chain-of-Custody
    - EAL Chain-of-Custody
    - UMassD Chain-of-Custody

4. There will be bags labeled for each sampling site [there are 9 sites (split in site bag) plus 1 field blank and a filed duplicate bag]. Each bag will contain labeled bottles:
    - One 1 L jug (TSS/SC) – (for field split, will have a 2L bottle to split into two 1L bottles)
    - One 237 mL bottle (TOP)
    - One 1L Nalgene bottle (POCN) (For UMassD)
    - One 125 mL brown bottle filled with DI water (TP) (EAL)

5. The bottles for field splits will be in the bag with the chosen site for that week's QC.
    - **The two TSS/SC bottles should be filled from the round 2L bulk bottle**
    - The other samples and splits should come from the large bulk sample bottle for the site

6. Set aside the set of bottles for the site that will also have a blank
    - One 1 L jug
    - One 237 mL bottle
    - One 60 mL bottle (UMassD)

7. Fill in the correct sample collection time on all of the aliquot labels. You may choose to do these all at once, or one site at a time as you fill the aliquots

8. Set up 2 boxes for the aliquots, 1 for TSS/SC, 1 for TOP (if there aren't any boxes right there, ask UB lab staff)
    - Small cooler for POCN & 60mL bottles.
    - TP 125ml EAL bottles in the freezer

9. Starting at RMSD:
    - Double check label on bulk and aliquots to make sure they match (site and time)
    - Snap off the bottle cap rings so you can easily open the aliquot bottles
    - Loosen or remove the caps and set to the side
    - **Invert the bulk bottle 10 times** to make sure it is fully mixed
    - Rinse each aliquot bottle once with a small amount of sample
    - Fill the aliquot bottles, always in the same order – 1 L jug, 1 L Nalgene bottle, 237mL, & 125 mL bottles.

- If it is a field split site, fill the same types of bottles in sequence (e.g., 1 L jug “G” sample, then 1 L jug “FS” sample before filling the 1L Nalgene bottle etc…)
- Reshake/mix bulk sample bottles between filling each bottle, if needed cap the aliquot bottles as soon as possible
- Repeat this process with the next sample.
- Set unused bulk sample back in cooler

10. Sign and date chain-of-custody for UB
    - Make sure to fill in samplers’ initials
    - Place in one of the UB cardboard boxes
    - Move both boxes to refrigerator

11. Sign and date chain-of-custody for UMassD
    - Place 1 L Nalgene bottles and 60 mL aliquot bottles in cooler
    - Pack with ice
    - Ship FedEx to UMassD at address on cover sheet of chain of custody

12. Cleanup
    - Once you are sure you have all the aliquots, empty the remaining sample water from the bulk bottles
    - Place empty bulk bottles in cooler or bag to return to UMass
    - Put all ice bottles back in freezer at UB (keep a few to bring back to UMass)
    - Wipe down counters

13. Remove EAL TP bottles from freezer
    - Place in cooler with ice
    - Deliver back to freezer at UMass Amherst (EAL)

14. Place chlorophyll-a filters in cooler
    - Deliver to freezer at UMass Amherst (EAL)

SOP-FLD-013

Field Measurement of Temperature, Dissolved Oxygen, and pH

Field Measurement of Temperature, Dissolved Oxygen, and pH

Overview

This procedure describes how to measure dissolved oxygen and pH in the field using a Hach HQ 40 D Multimeter.

1. Field Equipment List

___ 1 Hach HQ 40 D Multimeter

___ 1 DO probe

___ 1 pH probe

___ 1 Erlenmeyer flask containing water saturated air

___ Field Sheet

___ Wash bottle filled with DI water

___ Kim wipes

2. Meter Calibration

2.1 This is done in the lab before going to sampling sites.

2.2 Oxygen probe:

2.2.1 REMOVE the DO Probe from Erlenmeyer flask containing water saturated air; carefully DRY the probe cap with Kim wipe, and put the probe back to the Flask.

2.2.3 Allow five minutes to saturate the flask air with water.

2.2.4 Turn the Meter ON by pushing “power” button.

2.2.5 Push “UP/DOWN” key to bring the display as "single" for mg/L.

2.2.6 Push BLUE/LEFT key for "calibrate''.

2.2.7 Push GREEN/RIGHT key for "Read''. The display shows "stabilizing" and a progress bar as the probes stabilizes. When the reading is stable, the display shows the DO reading as X.XX %.

2.2.8 Push “DONE” key to view the calibration summary: read the "slope'' as %; For example, 90.3%. Percent saturation should read 100% ± 30%. If slope is not within these limits, follow these steps:

2.2.8.1 Recalibrate
2.2.8.2 Check probe for damage, replace if damaged
2.2.8.3 Clean probe, recalibrate
2.2.8.4 Replace probe.

2.2.9 Push “STORE” button to accept the calibration. The meter is now ready for DO measurement.

2.3 pH probe

2.3.1 Remove the pH probe from overnight storage by turning the probe storage bottle counterclockwise

2.3.2 Rinse the probe with deionized water; carefully DRY the probe cap with Kim wipe;

2.3.3 Prepare the fresh buffers of pH = 7, 4, and 10 in separate beakers with stir bars

2.3.4 Rinse the probe with pH 7 rinse solution;

2.3.5 Put the probe in beaker containing buffer 7 and stir the buffer; condition the probe for several minutes in the buffer;

2.3.6 Turn the HACH Meter ON by pushing "power"' button;

2.3.7 Push "UP/DOWN" key to bring the display as ''single'" for pH;

2.3.8 Push BLUE/LEFT key for "calibrate'';

2.3.9 Push GREEN/RIGHT key for “Read”; the display shows "stabilizing" and a progress bar; as the probes stabilizes. When the reading is stable, the display will ask for the next buffer;

2.3.10 Rinse the probe with DI water then with buffer 4 rinse solution, then Put the probe in beaker containing buffer 4 and stir the buffer; condition the probe for several minutes in buffer;

2.3.11 Push "READ''; once the reading is stable, the display will ask for next buffer;

2.3.12 Rinse the probe with DI water, then with pH= 10 rinse solution, then put the probe in beaker containing buffer 10 and stir the buffer; Condition the probe for several minutes in buffer;

2.3.13 Push "READ''; once the reading is stable the display will ask for next buffer;

2.3.14 Push ''DONE'' key to view the calibration summary; read the "slope" as %; As for example, 99%; The acceptable slope range is 98 – 102%. If slope is not within this range, consult the meter manual.

2.3.15 Push "STORE" button to accept the calibration and the Meter is now ready for pH.

STANDARD OPERATING PROCEDURES

Blackstone River Water Quality Monitoring Program

Field Measurement of Water Temperature and Dissolved Oxygen with Hobo Data Logger

SOP-FLD-014

November 2019

Overview

This procedure describes how to measure water temperature and dissolved oxygen in the field using a HOBO Dissolved Oxygen Logger (U26-001).

Calibration

1. At the start of the season, install a new Dissolved Oxygen Sensor Cap (U26-RDOB-1) on the data logger.
2. You will need tap water, the calibration boot and sponge supplied with the logger, and a source for current barometric pressure at your current location.
3. You will need an NIST-traceable thermometer to calibrate for temperature.
4. You will also need sodium sulfite solution (U26-CAL-SOL) and a 3-inch beaker for calibrating to 0% saturation.
5. You will need the computer where you have installed the HOBOware software.
6. Follow the HOBO Dissolved Oxygen Logger (U26-100) Manual's instructions for 'Calibrating the Logger with the Lab Calibration Tool.'

Launching the Logger

After calibration, the logger must be launched to configure it before deployment in the field.

1. You need the computer where you have installed the HOBOware software.
2. Follow the HOBO Dissolved Oxygen Logger (U26-100) Manual's instructions for 'Launching the Logger.'
3. Select a logging interval of 15 minutes and record in the field notebook the hour minutes that the logger will read. For example, 0:05 minutes; 0:20 minutes; 0:35 minutes; and 0:50 minutes of every hour.
4. Choose a starting time that allows for enough time to arrive and deploy the logger at the sampling site.

Deploying the Logger

1. Install an anti-fouling guard (U26-GUARD-2) over the data logger tip.
2. Insert the logger into the protective housing secured to a cement block. Use a premade stainless steel cable with crimped end loops and a marine-grade lock to secure the data logger in the housing. Attach one end of another premade stainless steel cable with crimped end loops to the lock and the other end to a nearby tree. Make sure the cable is long enough to reach the location of the housing placement and has enough slack for housing movement during high water flows.
3. Place the protective housing/data logger unit on the river bottom out of direct sunlight, making sure it is fully submerged, preferably at least one foot below the water surface and no more than 3 feet deep.
4. Orientate the logger so that the sensor is pointing into the current.
5. Hide from view the wire cable in the water with rocks and with vegetation on the land.
6. Take a GPS reading at the data logger location
7. Note in field book the data logger ID number, depth of water to river bottom, and depth of water to top of data logger.

Field QC

Preferably weekly, but least biweekly, visit each site, bringing a calibrated hand-held Temp and DO meter and:

1. Record water temperature and dissolved oxygen (in mg/L) as close to the data logger probe tip as possible. Write results in Field Log Book.
2. Remove the logger from its housing and clean the probe tip.
3. Place the data logger and hand-held meter probe in a bucket of river water from the site.
4. Measure the DO/temp with the hand-held at the same time that the data logger was scheduled to take a reading.
5. Record hand-held measurements in Field Log Book with the date and time measurements were taken.
6. Download data logger to the shuttle.

Removing the Logger

At the end of the sampling season, remove the logger after performing a final QC check as described in previous section.

Back in the office, use the computer program to stop the logger.

Clean the probes and housing for storage.

3.0 Measurement Protocol

3.1 Rinse the probe cap with deionized water.
3.2 Lower the probe into the river, where samples are taken, just below the water surface.
3.3 Push "READ" key; the display will show '"stabilizing" and a progress bar. The display will show lock icon when the reading stabilizes. (Wait at least 3 minutes for stabilization to occur)
3.4 Write the measurements for temperature and pH on the field sheet.
3.5 Select the button with a wrench on it (full access options)
3.6 Select “LD0101 settings” (DO Probe)
3.7 Select “modify current settings”
3.8 Select “units mg/L or %”
3.9 Select “mg/L” and write the measurement for DO concentration on the field sheet.
3.10 Repeat steps 3.4 through 3.7 for % DO saturation
3.11 When the measurements are done, rinse the probe caps with deionized water, and place them in their sleeves.

Appendix E

Field Collection Forms

1 - Blackstone River Collector Sheets (MA & RI)
2 - Bulk Sample Collection Data Sheet
3 - Equipment Problem Report Sheet
4 – Field Change Request Sheet

Blackstone River Field Sheet

Organization: MA WRRC / UB **Site ID:** _____ **Date:** _____ **Time:** _____

River Name: Blackstone **Site Name:** _____

Town: _____ **Sampling Crew:** _____

Sample Type: ☐ G ☐ FB ☐ FD ☐ FS ☐ EB

Photos taken? ☐ yes ☐ no

Multimeter Measurements: **Temp:** _____ **pH:** _____ **DO (mg/L):** _____ **DO (% sat):** _____ **River**

Multimeter Measurements: **Temp:** _____ **pH:** _____ **DO (mg/L):** _____ **DO (% sat):** _____ **Samp. Cont.**

Air Temperature: (ºC) **River Water Level:** ☐ Low ☐ Normal ☐ High

Current weather:
- ☐ Clear
- ☐ Partly sunny
- ☐ Partly cloudy
- ☐ Overcast
- ☐ Foggy
- ☐ Drizzly
- ☐ Light rain
- ☐ Heavy rain
- ☐ Sleet
- ☐ Snow

Wind Conditions:
- ☐ Calm (0-2 km/h)
- ☐ Slight breeze (2-8 km/h)
- ☐ Moderate Winds (8-25 km/h)
- ☐ Gusty (15-40 km/h)
- ☐ Storm winds (>40 km/h)
- ☐ Strong gusts (25-40 km/h)

Water Clarity:
(check all that apply)
- ☐ Clear
- ☐ Suspended solids / murky
- ☐ Slightly turbid
- ☐ Highly cloudy

Water Color:
- ☐ Clear/blue
- ☐ Grayish
- ☐ Light yellow/tan
- ☐ Dark tan
- ☐ Light green tint
- ☐ Green
- ☐ Brownish
- ☐ Blue-green
- ☐ Reddish/ blackish
- ☐ Other:

Water Odor:
- ☐ None
- ☐ Sulfide (rotten eggs)
- ☐ Chlorine
- ☐ Petroleum
- ☐ Musty (basement)
- ☐ Rotting vegetables
- ☐ Septic
- ☐ Other:

Presence of Algae
(check all that apply)
- ☐ None
- ☐ Unobservable
- ☐ Sparse (0-25%)
- ☐ Moderate (25-75%)
- ☐ Dense (75-100%)
- ☐ Suspended
- ☐ Floating

Density of Aquatic Plants
- ☐ None
- ☐ Unobservable
- ☐ Sparse (0-25%)
- ☐ Moderate (25-75%)
- ☐ Dense (75-100%)
- ☐ Emergent
- ☐ Floating
- ☐ Submerged

Scum(s) ☐ yes ☐ no (include oil sheens, pollen/dust blankets and similar floating layers that reduce aesthetics)

Description of Scum(s):

Observed Use(s) (include indications of use even if use is not observed): ☐ none ☐ swimming ☐ boating ☐ water intake ☐ fishing ☐ other

Description of Observed Use(s):

Objectional Deposits: ☐ none ☐ floating ☐ sunken ☐ garbage/trash ☐ flocculent mass (rust colored or other) ☐ other

Description of Objectionable Deposits:

Shoreline Erosion: ☐ yes ☐ no

Description of Erosion:

Wildlife Sightings ☐ none ☐ fish ☐ mammals ☐ birds ☐ reptiles ☐ waterfowl ☐ amphibians ☐ other

Description of Wildlife Sightings :

Potential Pollution Source: ☐ none ☐ waste outfall pipes ☐ garbage/trash dumping ☐ green lawns ☐ construction ☐ shoreline residences ☐ land clearing

Description of Potential Pollution Sources:

Blackstone River Field Sheet

Instream NBC Data Chl: _____

H_2O Temp (°C): pH: DO(mg/L): DO(%):

River Name: Blackstone **Site Name:** _____

Town: _____ **Sampling Crew:** _____

Sample Type: ☐ G ☐ FB ☐ FD ☐ FS ☐ EB

Photos taken? ☐ yes ☐ no

Multimeter Measurements: **Temp:** _____ **pH:** _____ **DO (mg/L):** _____ **DO (% sat):** _____ **River**

Multimeter Measurements: **Temp:** _____ **pH:** _____ **DO (mg/L):** _____ **DO (% sat):** _____ **Samp. Cont.**

Air Temperature: (ºC) **River Water Level:** ☐ Low ☐ Normal ☐ High

Current weather:
- ☐ Clear
- ☐ Partly sunny
- ☐ Partly cloudy
- ☐ Overcast
- ☐ Foggy
- ☐ Drizzly
- ☐ Light rain
- ☐ Heavy rain
- ☐ Sleet
- ☐ Snow

Wind Conditions:
- ☐ Calm (0-2 km/h)
- ☐ Slight breeze (2-8 km/h)
- ☐ Moderate Winds (8-25 km/h)
- ☐ Gusty (15-40 km/h)
- ☐ Storm winds (>40 km/h)
- ☐ Strong gusts (25-40 km/h)

Water Clarity:
(check all that apply)
- ☐ Clear
- ☐ Suspended solids / murky
- ☐ Slightly turbid
- ☐ Highly cloudy

Water Color:
- ☐ Clear/blue
- ☐ Grayish
- ☐ Light yellow/tan
- ☐ Dark tan
- ☐ Light green tint
- ☐ Green
- ☐ Brownish
- ☐ Blue-green
- ☐ Reddish/ blackish
- ☐ Other:

Water Odor:
- ☐ None
- ☐ Sulfide (rotten eggs)
- ☐ Chlorine
- ☐ Petroleum
- ☐ Musty (basement)
- ☐ Rotting vegetables
- ☐ Septic
- ☐ Other:

Presence of Algae
(check all that apply)
- ☐ None
- ☐ Unobservable
- ☐ Sparse (0-25%)
- ☐ Moderate (25-75%)
- ☐ Dense (75-100%)
- ☐ Suspended
- ☐ Floating

Density of Aquatic Plants
- ☐ None
- ☐ Unobservable
- ☐ Sparse (0-25%)
- ☐ Moderate (25-75%)
- ☐ Dense (75-100%)
- ☐ Emergent
- ☐ Floating
- ☐ Submerged

Scum(s) ☐ yes ☐ no (include oil sheens, pollen/dust blankets and similar floating layers that reduce aesthetics)

Description of Scum(s):

Observed Use(s) (include indications of use even if use is not observed): ☐ none ☐ swimming ☐ boating ☐ water intake ☐ fishing ☐ other

Description of Observed Use(s):

Objectional Deposits: ☐ none ☐ floating ☐ sunken ☐ garbage/trash ☐ flocculent mass (rust colored or other) ☐ other

Description of Objectionable Deposits:

Shoreline Erosion: ☐ yes ☐ no

Description of Erosion:

Wildlife Sightings ☐ none ☐ fish ☐ mammals ☐ birds ☐ reptiles ☐ waterfowl ☐ amphibians ☐ other

Description of Wildlife Sightings :

Potential Pollution Source: ☐ none ☐ waste outfall pipes ☐ garbage/trash dumping ☐ green lawns ☐ construction ☐ shoreline residences ☐ land clearing

Description of Potential Pollution Sources:

Bulk Sample Collection Data Sheet -

Event Date: _____

Event Type

- ☐ **Dry-weather**
- ☐ **Wet-weather**
- ☐ **Routine (monthly)**

Cooler ID	Temp (°C) Start	Temp (°C) End

Field Crew: _____

_____

Note collector with *

Processing Crew: _____

_____

Page ____ of ____

No. Field Blanks

No. Field Splits *(Scheduled No.)*

Nutrients
Chlorophyll-a

Sample ID	Collection Date and Time	[2]Processing Date and Time	Bottles filled in the field: [5]Chlorophyll-a (1L amber: EAL)	Bottles filled in the field: [8]Bulk Sample Volume	Bottles filled in the field: .22µm dNH4/dNO32/TDN(60mL: UMD)	Lab aliquots from bulk (✓= pre-filled): TSS/SC (1 L: UB)	Lab aliquots from bulk (✓= pre-filled): TP (125 mL: EAL)	Lab aliquots from bulk (✓= pre-filled): TOP (237 mL: UB)	Lab aliquots from bulk (✓= pre-filled): POCN (1 L: UMD)	PT Only: dNO23/dNH3/dOP (500mL: NBC)	QA/QC[4]: Blank	QA/QC[4]: Field Split	QA/QC[4]: Field Duplicate	Total # of Field Bottles	Total # of Lab Bottles	Notes[6]
RMSDh-G				6L												
RMSDn-G				6L												
R116-G				6L												
RMSL-G				6L												
W1779-G				4L												
W0767-G				4L												
W1242-G				4L												
W1258-G				4L												
UBWPAD2-G				4L												
W0680-G				4L												
RMSD-P					✓		✓	✓		✓						Standard
W1779-LB			✓		✓	✓	✓	✓	✓		•					EAL DI
W0767-FB				4L												Empty
				4L							•					EAL DI
W1258-FS				2L								•				
RMSL-FD				4L									•			

Notes:

2 Processing time is time when bulk sample is split.
3 Analyte/Bottle Group volume and preservative notes subject to change. Labs for each noted.
4 QA/QC samples will have a unique ID# on chains. Leave blank lines before and after to ensure processing crew sees request.
5 Bulk sample collected in 1 L amber plastic; filtered through 0.07 micron glass fiber filter, dried, stored in foil, frozen as soon as possible.
6 Chlorophyll-a QCs do not require a second 1 L amber plastic bottle. Only one bottle is needed per site.
7 Location of duplicates, splits, and blanks changes each event.
8 2L bulk for splitting into two TSS 1L sample bottles. The other splits come from the same large 4 L (MA) or 6 L (RI) bottle as regular samp
9 Use two 1 Gallon bottles of UB DI water for EB field blank

CHAIN OF CUSTODY FORM

Fill in the Date and Time, and Sign in the Released/Received Columns. Mark if sample was cool or warm.

SAMPLE ID (Bottle ID)	RELEASED BY FIELD COLLECTOR: Signature/Date/Time	RELEASED BY PROCESSING CREW: Signature/Date/Time	Samples split to Aliquots, Lab COCs complete, Remaining bulk sample disposed of
All samples listed on front of sheet.			
	Date: Time:	Date: Time:	
	Sample: cool warm (circle one)	Sample: cool warm (circle one)	

Equipment Problem Report Sheet

Equipment Type: _____
Serial Number: _____
Site: _____

Date: _____ **Time:** _____

Problem Reported by: _____

Sampling Event (if applicable): _____

Define the Problem: _____

Proposed Corrective Action: _____

Corrective Action Implemented? YES NO

If NO, why not? _____

Follow-up: If problem was not corrected in the field, what was done as follow-up corrective action? _____

Date: _____ **Time:** _____

Name: _____ **Signature:** _____

Field Change Request Form

Date: _____ **Time:** _____

Problem Reported by (print and sign): _____

Sampling Event (if applicable): _____ **Site:** _____

Define the Problem: _____

Proposed Corrective Action: _____

Authorized Prior to Implementation? **YES** **NO**

PRIOR AUTHORIZATION
Prior authorization received from:* _____

Method of prior authorization:
- ☐ **Phone**
- ☐ **In-person**
- ☐ **Other (Specify)** _____

NO PRIOR AUTHORIZATION
- ☐ **Project Manager notified of variation** **Date:**_____ **Time:** _____
- ☐ **Field Change Request forwarded** **Date:**_____ **Time:** _____

Corrective Action Implemented? **YES** **NO**

If NO, why not? _____

Follow-up: If problem was not corrected in the field, what was done as follow-up corrective action? _____

Project Manager Review and Approval

Date: _____ **Time:**_____

Name: _____ **Signature:** _____

*** Authorizing individual to initial**

Appendix F

Field Collection Forms

1 - Blackstone River Collector Sheets (MA & RI)
2 - Bulk Sample Collection Data Sheet
3 - Equipment Problem Report Sheet
4 – Field Change Request Sheet

EAL Chain of Custody

Date Rec'd in Lab: **PAGE 1 OF 1**

Client Information	Project Information	Report Information Data Delivery
UMass Amherst/Marie-Francoise Hatte	**Project Name:** Blackstone River Study	☐ Email Expected Date: 30 days
Massachusetts WRRC	**Project Location**: MA & RI	☐ Other
209 Agriculture Engineering Building 250 Natural Resources Way	Blackstone River Mainstem	**Due Date:**
Amherst, MA 01003	Comments (e.g., detection limits):	
413.545.5531 or 413.545.5979	Lowest possible d.l. for parameter available.	
mfhatte@umass.edu		

EAL Lab ID	Sample ID	Collection Date	Collection Time	Sample Matrix	Sampler's Initials	Chlorophyll (dried Filter)	TP (125 mL, acid washed)	DP (125 mL, acid washed)	Sample Notes
LB1	Lab Blank 1	10/9/2019		S.W.		x			
RMSD	RMSD-G-LF70	10/9/2019		S.W.		x			
RMSD	RMSD-G-UF	10/9/2019		S.W.			x		
R116	R116-G-LF70	10/9/2019		S.W.		x			
R116	R116-G-UF	10/9/2019		S.W.			x		
R116	R116-FD-LF70	10/9/2019		S.W.		x			
R116	R116-FD-UF	10/9/2019		S.W.			x		
RMSL	RMSL-G-LF70	10/9/2019		S.W.		x			
RMSL	RMSL-G-UF	10/9/2019		S.W.			x		
W1779	W1779-G-LF70	10/9/2019		S.W.		x			
W1779	W1779-G-UF	10/9/2019		S.W.			x		
W1779	W1779-P-NA	10/9/2019		S.W.				x	
W0767	W0767-G-LF70	10/9/2019		S.W.		x			
W0767	W0767-G-UF	10/9/2019		S.W.			x		
W0767	W0767-BANK-G-LF70	10/9/2019		S.W.		x			
W0767	W0767-BANK-G-UF	10/9/2019		S.W.			x		
W0767	W0767-FS-LF70	10/9/2019		S.W.		x			
W0767	W0767-FS-UF	10/9/2019		S.W.			x		
W1242	W1242-G-LF70	10/9/2019		S.W.		x			
W1242	W1242-G-UF	10/9/2019		S.W.			x		
W1242	W1242-FB-LF70	10/9/2019		S.W.		x			
W1242	W1242-FB-UF	10/9/2019		S.W.			x		
W1258	W1258-G-LF70	10/9/2019		S.W.		x			
W1258	W1258-G-UF	10/9/2019		S.W.			x		
UBWPAD2	UBWPAD2-G-LF70	10/9/2019		S.W.		x			
UBWPAD2	UBWPAD2-G-UF	10/9/2019		S.W.			x		
W0680	W0680-G-LF70	10/9/2019		S.W.		x			
W0680	W0680-G-UF	10/9/2019		S.W.			x		
W0680	W0680-LB-LF70	10/9/2019		S.W.		x			
W0680	W0680-LB-UF	10/9/2019		S.W.			x		
LB2	Lab Blank 2	10/9/2019		S.W.		x			
Relinquished By:		**Date/Time**		**Total number**		16	14	1	
				Preservative	Freeze	☐	☐	☐	
					None	☐	☐	☐	
Received By:		**Date/Time**		**Filtered**	Filtered	☐	☐	☐	
					Not Filtered	☐	☐	☐	

Upper Blackstone Chain of Custody

Date Rec'd in Lab: **PAGE 1 OF 1**

Client Information	Project Information	Report Information Data Delivery
UMass Amherst/Marie-Francoise Hatte	**Project Name:** Blackstone River Study	☐ Email Expected Date: 30 days
Massachusetts WRRC	**Project Location**: MA & RI	**Due Date:**
209 Agriculture Engineering Building 250 Natural Resources Way	Blackstone River Mainstem	
Amherst, MA 01003	Comments: Lowest possible d.l. for parameter available.	
413.545.5531 or 413.545.5979	mfhatte@umass.edu	

UB Lab ID	Sample ID	Collection Date	Collection Time	Sample Matrix	Sampler's Initials		TSS , SC	TP, TKN, NO23, TAM	TOP	DP, dNO23, dTAM, dTKN	DOP	DP, dTKN	dNO23, dTAM	Sample Notes
RMSD	**RMSD-G-UF**	10/9/2019		S.W.			x		x					
R116	**R116-G-UF**	10/9/2019		S.W.			x		x					
RMSL	**RMSL-G-UF**	10/9/2019		S.W.			x		x					
W1779	**W1779-G-UF**	10/9/2019		S.W.			x		x					
W0767	**W0767-G-UF**	10/9/2019		S.W.			x		x					
W0767	**W0767-BANK-G-UF**	10/9/2019		S.W.			x		x					
W1242	**W1242-G-UF**	10/9/2019		S.W.			x		x					
W1258	**W1258-G-UF**	10/9/2019		S.W.			x		x					
UBWPAD2	**UBWPAD2-G-UF**	10/9/2019		S.W.			x		x					
W0680	**W0680-G-UF**	10/9/2019		S.W.			x		x					
W1779	**W1779-P-NA**	10/9/2019		S.W.							x			Dissolved std.
R116	**R116-FD-UF**	10/9/2019		S.W.			x		x					
W0767	**W0767-FS-UF**	10/9/2019		S.W.			x		x					
W0680	**W0680-LB-NA**	10/9/2019		S.W.			x		x					
W1242	**W1242-FB-UF**	10/9/2019		S.W.			x		x					
						Total number:	14		14		1			
Relinquished By:	**Date/Time**			**Container Type**		Plastic (vol)	1L	500ml	237ml	500ml	237ml	237ml	237ml	
				Preservative		Preserved	☐	☐	☐	☐	☐	☐	☐	
				(H2SO4)		Not Preserved	☒	☐	☒	☐	☒	☐	☐	
Received By:	**Date/Time**			**Filtered**		Filtered	☐	☐	☐	☐	☒	☐	☐	
				0.45 micron		Not Filtered	☒	☐	☒	☐	☐	☐	☐	

Blackstone River Water Quality Monitoring Chain of Custody

Upper Blackstone Clean Water, 50 Route 20
Millbury, MA 01527-2199

Send to:
Coastal Systems Program
706 South Rodney French Blvd
New Bedford, Ma 02744
Attn: Dr. David Schlezinger
Office: 508-910-6314
Lab:

Delivered to UB by: _____ _____ _____
Name Date Time

Received by: _____ _____ _____
Name Date Time

Sent to UMass Dartmouth by: _____ _____ _____
Name Date Time

Received by: _____ _____ _____
Name Date Time

Project Information - Required	
Contact Name:	Marie-Francoise Hatte (project lead contact)
Contact Address:	Massachusetts WRRC, 250 Natural Resources Way Ag Engineering, Room 209, Amherst, MA 01003
Contact Email:	mfhatte@umass.edu
Date samples shipped:	
Project Name:	Blackstone R Water Quality Monitoring
Project Location/Area:	Blackstone River
Project State:	Massachusetts & Rhode Island
Project Country (if outside US)	
Brief Project Description:	Water quality sampling in support of the Blackstone R modeling project.
Data Priority	

Funding Agent (billing)

Karla Sangrey, Director
Upper Blackstone Clean Water, 50 Route 20
Millbury, MA 01527-2199
ksangray@ubwpad.org

UMD Chain of Custody

COASTAL SYSTEMS GROUP LABORATORY

Personnel Contacts

RECEIVED		RECEIVED	
name		name	
date		date	time
COLLECTED		CONTACT	
name	UMass Amherst	name	UMass Amherst/Marie-Francoise Hatte
date	local	phone	413.545.5531 or 413.545.5979

Sample Notes

Special notes/ Sample Handling	Total number of samples:	**29**
	Number of 60mL bottles:	**15**
	Number of 1L bottles:	**14**

Sample Status

Sample ID	Sample Date	NH4	NO3/NO2	TDN	POCN
		60 mL bottle			1 L bottle
RMSD-G-FF22	10/9/2019	X	X	X	
RMSD-G-FR	10/9/2019				X
RMSL-G-FF22	10/9/2019	X	X	X	
RMSL-G-FR	10/9/2019				X
R116-G-FF22	10/9/2019	X	X	X	
R116-G-FR	10/9/2019				X
R116-FD-FF22	10/9/2019	X	X	X	
R116-FD-FR	10/9/2019				X
W1779-G-FF22	10/9/2019	X	X	X	
W1779-G-FR	10/9/2019				X
W1779-P-NA	10/9/2019	X	X	X	
W0767-G-FF22	10/9/2019	X	X	X	
W0767-G-FR	10/9/2019				X
W0767-BANK-G-FF22	10/9/2019	X	X	X	
W0767-BANK-G-FR	10/9/2019				X
W0767-FS-FF22	10/9/2019	X	X	X	
W0767-FS-FR	10/9/2019				X
W1242-G-FF22	10/9/2019	X	X	X	
W1242-G-FR	10/9/2019				X
W1242-FB-FF22	10/9/2019	X	X	X	
W1242-FB-FR	10/9/2019				X
W1258-G-FF22	10/9/2019	X	X	X	
W1258-G-FR	10/9/2019				X
UBWPAD2-G-FF22	10/9/2019	X	X	X	
UBWPAD2-G-FR	10/9/2019				X
W0680-G-FF22	10/9/2019	X	X	X	
W0680-G-FR	10/9/2019				X
W0680-LB-NA	10/9/2019	X	X	X	
W0680-LB-FR	10/9/2019				X

Appendix G

Lab QAPPs and Standard Operating Procedures for Laboratory Analyses

1 - EAL QAPP 2019 (includes SOPs)
2 - UMD Coastal Systems Program Lab QA Plan 2020 (includes SOPs)
3 - Upper Blackstone Laboratory SOPs
4 - Field Change Request Sheet

Quality Assurance Program Plan

For

Environmental Analysis Laboratory
University of Massachusetts Amherst

Prepared by: Cameron Richards & MF Hatte
May 6, 2019

_____, Date: _____
WRRC Interim Director: Marie-Françoise Hatte, 413-545-5531, mfhatte@umass.edu
Water Resources Research Center, 250 Natural Resources Way, Amherst, MA 01003

_____, Date: _____
Laboratory Manager: Cameron Richards, 413-545-5979, cameronr@umass.edu
Water Resources Research Center, 250 Natural Resources Way, Amherst, MA 01003

_____, Date: _____
MassDEP QA Officer: Richard Chase, 508-767-2859, richard.f.chase@state.ma.us
MassDEP, 8 New Bond Street, Worcester, MA 01606

1. LAB ORGANIZATION

The Environmental Analysis Laboratory (EAL) at the University of Massachusetts Amherst supports the research, education, and outreach roles of the University by providing chemical and physical analysis of water for public agencies, University researchers, and other clients.

The EAL was created in 1984 by the Massachusetts Water Resources Research Center to assist the Acid Rain Monitoring Project by analyzing more than 40,000 ARM samples for a suite of 21 parameters. Since 1988, the Lab has provided services to a wide range of off-campus and on-campus researchers. Past clients include the U.S. Environmental Protection Agency, New England Interstate Water Pollution Control Commission, Greater Springfield Housing Program, Massachusetts Division of Fisheries and Wildlife, Massachusetts Department of Environmental Protection, Living Lakes Corporation, State of West Virginia, and a number of Universities and Colleges. The Lab is located on the first floor of the Goessmann Chemistry Building on the UMass Amherst. The core personnel of the EAL are listed below along with their responsibilities.

1.1 Laboratory Manager: The *Lab Manager* is responsible for the day-to-day management of the EAL and also serves as the chief analyst. The Manager oversees methods development, standard operating procedures, and major equipment purchases, and ensures that the lab is able to handle the number of samples submitted while maintaining the accuracy and precision goals of the quality assurance plan. The Laboratory Manager also oversees all aspects of daily quality control in the lab including performing analyses, supervision of student laboratory technicians, and sample distribution. The Manager is responsible for the acceptance of samples received by the lab, security and documentation for chain-of-custody samples, sample tracking, data validation, inspection and maintenance of laboratory notebooks, log books, and control charts. The Manager oversees the work of student laboratory technicians conducting sample analyses, including set up and calibration of instruments, recording batch and sample IDs, and checking for problems during runs. The Laboratory Manager reports analytical results to the laboratory's clients and keeps records of all analyses.

1.2 WRRC Director: In consultation with the Lab Manager, the *WRRC Director* is responsible for the overall program management, integration, and activities conducted by the EAL staff. This includes budget preparation, authorization of grants and allocation of resources. The WRRC Director, with the support of the Lab Manager, is responsible for overall program direction and administration of the EAL. The Director is responsible for negotiations between outside contractors, state, and federal agencies and the University. The Director is the Supervisor mentioned in this document.

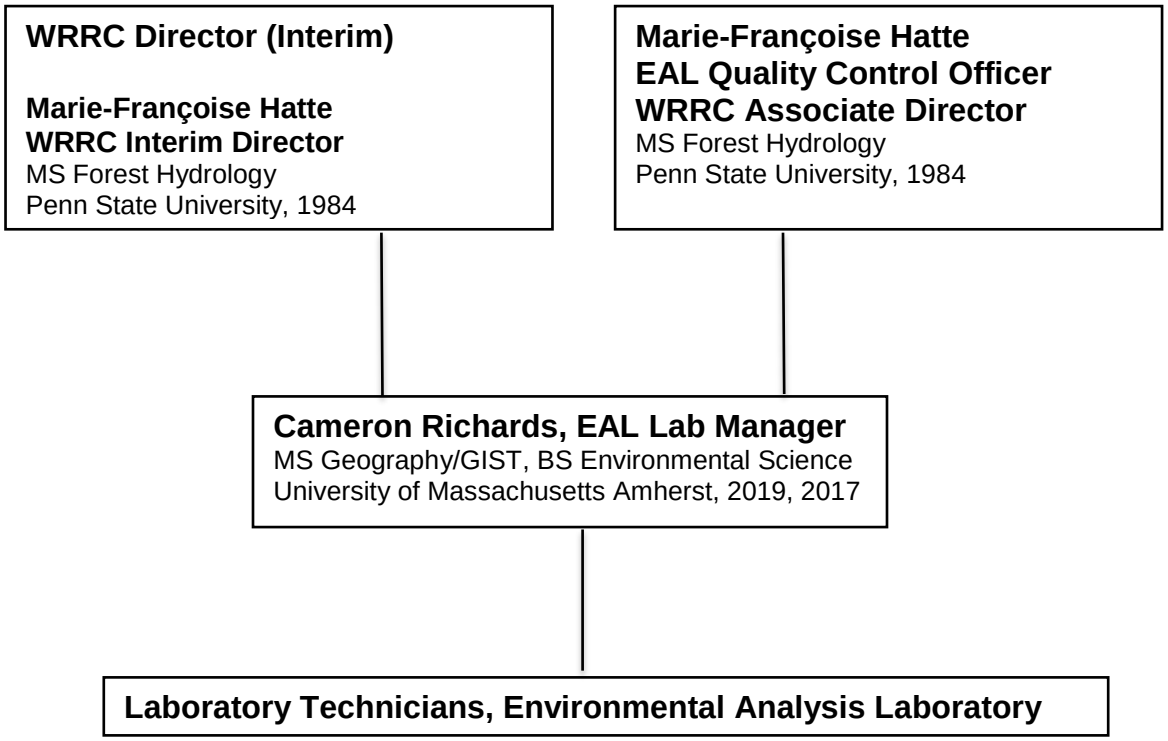
1.3 Quality Control Officer: The *QC Officer* has the responsibility to monitor the performance of the lab and ensure that the laboratory is meeting all of the required

performance criteria. This includes summarizing results of both internal and external audits, performance evaluation samples, and reporting general laboratory performance on quality control checks such as conductivity checks. The QC Officer must review the quality control for all data and approve release of the data from the lab. Each data report sent out by the QC Officer will also be accompanied by appropriate data summarizing the data quality. Currently this position is held by the WRRC Director.

1.4 Laboratory Technicians: Depending on the laboratory workload, the lab may employ lab technicians. These will usually be UMass undergraduate students interested in obtaining laboratory experience. Under the supervision of the Lab Manager, they will perform the analysis of samples, including set up and calibration of the instruments, recording batch and sample IDs and checking for obvious problems (over calibration, poor accuracy on internal standards, spikes and duplicates, high blanks or contamination) during the run. Also included are responsibilities for cleaning, acid-washing, and rinsing of the glass and plastic-ware in the lab and entering all batch information for each run into the appropriate lab notebooks.

1.5 Job Descriptions: Job descriptions for the EAL staff are maintained by the University of Massachusetts and updated according to University rules.

Figure 1.1 Organizational Chart



1.6 Equipment List

- pH meters - Orion Research 940, Beckman Coulter pH1410
- Conductance – Oakton, Acorn Series Con6, 2008
- UV-visible Spectrophotometer, Shimadzu UV-1800, up to 10 cm path length
- Centrifuge – Damen/IEC Division, I.E.C. HN-S
- Autoclave – All American No. 50x

2. QUALITY ASSURANCE OBJECTIVES

The data quality objectives are to provide contract agencies with data of known accuracy and precision for water samples within specified holding times. The EAL also provides summaries of data quality for each batch of samples as well as summaries of overall data quality. A batch is defined as a group of 20 or fewer samples analyzed with a single calibration. The specific types of data quality objectives are:

2.1 Accuracy: Accuracy is determined by how close to the true or expected value the reported values are. Accuracy objectives for each of the analyses are shown in Table 2.1.

2.2 Precision: Precision is determined by how close replicate samples or split samples agree with each other. Precision objectives for each analysis are shown in Table 2.1

2.3 Detection Limits: Detection limits must be reported so that the lowest level of detection for each analysis is known. By comparing a result to the specified detection limit, it can be reliably determined if the analyte is present. Detection limit objectives for each analysis are shown in Table 2.1

2.4 Holding Times: Each analysis must be completed on each sample within the specified holding time. This holding time starts from the time of sampling and may vary depending on the type of analysis. Holding times are listed in Table 4.1.

Table 2.1 EAL Data Quality Objectives
Goals for minimum analytical detection limits, accuracy and relative precision of duplicates.

Parameter	Units	Detection Limit	Reporting Limit	Accuracy*	Precision*
Alkalinity	mg/L	---	---	10%	10%
Chlorophyll	µg/L	1	1	10%	10%
Oxygen - dissolved	mg/L	0.1	0.1	10%	10%
pH	pH	---	---	±0.10	±0.05
Phosphorus - total	µg/L	2	8	10%	10%

**Accuracy and precision for samples >10X the detection limit.*

3. GENERAL LABORATORY OPERATION

3.1 Laboratory Training Requirements: All laboratory staff is required to attend a 2-hour Laboratory and Fire Safety Training through the University of Massachusetts' Environmental Health and Safety Department. The Laboratory Manager will train the analytical staff. Table 3.1 outlines the training program summary.

Table 3.1: Training Program Summary

Task and Type of Training	Frequency of Training and by Whom
Field sampling	Project Manager
Laboratory Safety	Annually, University of Massachusetts office of Environmental Health and Safety
Water chemistry analysis	Immediately prior to initiation by Laboratory Manager
Visual observation	Immediately prior to initiation by Project Manager
Data management	As needed by Laboratory Manager and Project Manager
Data interpretation	As needed by Project Manager

3.2 Reagents: Analytical reagent grade chemicals or certified standard solutions will be used for all analyses. Standard solutions are purchased as certified standard solutions from reputable chemical companies. Subsequent dilutions of these standards are carried out with

calibrated auto-pipettes and class A volumetric flasks. The auto-pipettes are calibrated yearly by an outside calibration service.

3.3 Analytical Electronic Balance: A Mettler AJ100 electronic balance is used in the measurement of reagent grade dry chemicals. Balance calibration is checked before use with Class S certified weights of 30mg and 10g. Each time the balance is used the results of the calibration are noted with the date and operator initials in the general lab notebook.

3.34 Safety: Laboratory safety is our primary concern and is prerequisite for stable, efficient operation of the lab. The University Department of Environmental Health and Safety is responsible for general safety regulations on campus. Our laboratory personnel are responsible for safety activities within the lab itself. Required safety information is readily available in the lab in a notebook provided by Environmental Health and Safety. Right to Know (111F Mass. General Law) is posted on the inside of the lab door.

All hazardous materials are safely stored in appropriate cabinets (organics, acids and bases are separate), all lab personnel are trained in safe laboratory practices including the use of safety equipment, and keep supplies of safety equipment and clothing in stock.

All hazardous wastes are disposed of in accordance with state and federal law and a separate covered container for glass or other sharp wastes is kept. All spills are cleaned up immediately by the person responsible. Medical aid is provided for injuries and all serious accidents and injuries are reported to the Environmental Health and Safety Office.

The following schedule will be used for safety checks:

a) Annual checks: University Department of Environmental Health and safety will check flow rates in the fume hoods, test fire alarms, check pressure in fire extinguishers and test personnel showers.
b) Semi-annual checks: Check supplies of pipet bulbs, bicarbonate for acid spills, plastic gloves, goggles, aprons, and contents of the first aid kit for gauze, bandages and antiseptics. Test operation of eye wash stations. Results of these tests are recorded in the laboratory notebook.

3.4 Reagent Water: Water used in laboratory analyses is deionized using a Millipore Synergy UV Water Purification System (Part No. SYNS0HF00). This system creates Type I grade reagent water.

3.5 Washing and Rinsing of Labware: Glassware and plasticware will be washed in warm phosphate-free detergent solution and thoroughly rinsed, first with distilled water. Both glassware and plasticware are acid rinsed in 1:1 HCl acid then rinsed 3 times with deionized Type I reagent water. Bottles are then filled with Type I reagent water. After 48 hours, the conductivity of the water in each bottle is checked. If the conductivity is greater than 2 μS/cm, the bottle is washed again. Bottles are air dried and capped until needed.

3.6 SOPs with Dates of Last Revision

Standard operating procedures for analysis are shown in Appendix A. Current copies of all SOPs are maintained in the lab and in the QC Manager's files. Each SOP is reviewed annually or sooner if needed and revised as changes in equipment or procedure are made. Revisions are signed by the QC Officer.

4. SAMPLE COLLECTION, PRESERVATION, CUSTODY AND HANDLING

Sample integrity is maintained by the use of appropriate containers, unique sample ID codes listed on sample labels, approved sample collectors, proper preservatives and storage for samples. In addition, our technicians are trained to avoid sample contamination in the lab by appropriate laboratory techniques (e.g. using clean glassware, pouring off sub-samples from sample bottles, and maintaining rigorous documentation). Specific procedures are discussed below.

4.1 Sample Collector: The EAL is an analysis laboratory and the staff at the EAL do not collect samples unless special requests are made. Our clients are responsible for sample collection by appropriate methods. The EAL will provide appropriate bottles (pre-cleaned, and pre-labeled) and preservatives, on request, along with appropriate sampling documentation and instructions according to the following protocol. The sample collector is responsible for following the appropriate sampling procedure and must fill out the documentation on the analysis request form, including chain-of-custody, if required, and insure prompt preservation (see Table 6.1) and transportation to the EAL lab.

4.2 Sample Receipt: Upon arrival, sample bottles are inspected for leakage, suspended solids or other unusual conditions and the samples are logged into a master log data file. First the sample is assigned a unique sample ID number. The location, type, date and time of collection and analyses requested are recorded in the master log data file. The chain-of-custody (if required) is signed and filed, and the analysis request form is signed by the person receiving samples. Both the analysis request form and chain-of-custody form are filed in the laboratory.

4.3 Rejection of Samples: Samples taken for compliance purposes will be rejected if they were not collected by an approved collector as described above, or do not meet the criteria for containers, preservation, and holding times for certified analyses as specified in Table 4.1. Suspect samples (e.g. samples with unusual color, volume, sediment, or samples with loose caps) are received by the lab but are noted in the logbook and the Laboratory Manager is notified. The Laboratory Manager then calls the client for a new sample, such as in the case of chain-of-custody samples, or permission to proceed with the analysis if the condition of the suspect sample is adequately explained (e.g. a small volume was used deliberately). In either case the result is noted in the logbook and the sample is flagged (see data flags).

4.4 Chain of Custody: The Environmental Analysis Laboratory (EAL) will maintain chain-of-custody when requested. Upon request, sample bottles will be prepared, pre-labeled, and will be delivered to the sampler in a sealed container along with the analysis request form and the chain-of-custody document (see Appendix B for samples of the bottle label, chain-of-custody document, and analysis

request form).

Upon collection and appropriate preservation, the sampler is required to record in indelible ink the required information on the sample label, the analysis request form and the chain-of-custody form. The sampler must indicate if he/she is a state approved sampler on the analysis request form and include their or her signature on both the chain-of-custody form and the analysis request form. Each person who accepts the samples must also sign for them on the chain-of-custody document, and must retain control of the samples to insure sample integrity until the samples are ultimately relinquished and signed over to the Laboratory Manager, or in their absence, an authorized laboratory technician. Samples can be delivered by registered mail with return receipt requested if the samples and documentation are enclosed in a secure, sealed container which would indicate evidence of tampering. Such sealed containers must be inspected and evidence of tampering noted by the laboratory personnel in the logbook, then the package is opened and the chain-of-custody document signed and the samples are recorded in the logbook. The final signed chain-of-custody document is filed at the EAL laboratory and a copy of the form is sent back to the sampler. Once received by the laboratory, the samples are stored, either in the refrigerator, or in a locked desk drawer, depending on storage requirements.

Only the Laboratory Manager or authorized technician will have access to the secure storage areas. Each time the samples are removed for analysis the time, date, sample ID number along with the analysis requested and technician's name and signature are recorded in the chain-of-custody logbook. An appropriate subsample is taken and labeled and the original sample returned to the secure storage area while the technician immediately performs the analysis requested. When all requested analyses are finished and approved by the QC Officer, the Laboratory Manager destroys the sample and records the time and date and sample ID number in the logbook with their signature. If at any time the requirements for chain-of-custody are not met, the Laboratory Manager will note the irregularities in the chain-of-custody notebook, request new samples and request permission of the QC Officer to destroy the suspect samples. An example of the chain-of-custody form is shown in Appendix B.

4.5 Sample Records: Records of sample receipt, record of custody, storage conditions and dates of sample analysis are also maintained by the Laboratory Manager.

Table 4.1 Sample Containers, Preservatives and Holding Times

Contaminant	Preservative	Container[1]	Holding Time[2]
Alkalinity	Cool to 4°C	P or G	14 days
Chlorophyll a (filters)	None	Foil	Fresh - immediately Frozen - 21 days Air-dried - 15 days
Color (Spectrophotometric)	Cool to 4°C	P or G	48 h
Conductivity	Cool to 4°C	P or G	28 days
Oxygen-dissolved	$MnSO_4$, alkali-iodide Sulfuric or sulfamic acid	G	8 hours
pH	Cool to 4°C	P or G (no head space)	48 hours
Phosphorus-total or dissolved	Frozen	P	12 months

[1]Plastic (P) or glass (G) containers, cleaned as described previously. Plastic will be used unless otherwise requested.
[2]In all cases samples will be analyzed as soon after collection as possible.

5. CALIBRATION PROCEDURES

The calibration procedure for all inorganic chemistry (except pH, see Section 7.8) uses a calibration blank prepared with reagent grade deionized water. Overall linearity is checked annually on each instrument with the use of 3 standards and a calibration blank. In all cases certified stock standard solutions along with blanks are used. Response of the quality control check solutions (QCCS) are checked prior to the run and entered into the control charts and notes. Specific calibration procedures are described in the SOPs (Appendix A).

6. ANALYTICAL PROCEDURES AND METHODS

6.1 Sample Analysis

A list of analytical methods is given in Table 6.1. Unless otherwise stated the methods follow EPA guidelines and the instruction manuals for each instrument. The detailed Standard Operating Procedure (SOP) for each analyte is given in Appendix A. Holding times and detection limits generally follow EPA recommendations (see sections 2 and 4). General procedures are described here. The technician in charge of the analysis retrieves each sample batch (20 or fewer samples) and enters these into the analysis log along with QCCS samples, spike additions, blanks, duplicates and internal QC check solutions and detection limit QC solutions. Samples are digested, if required, and analyzed, according to protocols

listed in Appendix A, Standard Operating Procedures. Immediate checks on quality control for the batch are performed on the run by checking the measured concentrations against the expected values of the QCCS (see below). Any problems in the run (e.g. sample concentration exceeds standard operating range or other samples requiring reanalysis are flagged and noted in the logbook along with analysis time, date, and analyst's name).

Table 6.1 Analytes and Methodology

Parameter	MCL mg/L	Method	EAL SOP Date	Approval Status & Date
Alkalinity	---	Potentiometric titration, EPA 310.1	Rev. 0: 11/3/2001	Approved 11/28/2001
Chlorophyll	---	SM 10200H	Rev. 0: 11/13/2001; Rev. 1: 7/1/2013 Rev. 2: 4/18/2017	Rev. 0 Approved 11/26/2001; Rev. 1 Approved 7/2/2013; Rev. 2 Approval Pending
Color	15*	EPA 110.3, SM 2120C		
Conductivity	---	SM 2510B		
Oxygen - dissolved	---	EPA 353.3	Rev. 0: 11/13/2001	Rev. 0 Approved 11/26/2001
pH	6.5-8.5*	Electrometric, EPA 150.1	Rev. 0: 11/3/2001	Approved 11/28/2001
Phosphorus - total	---	SM 4500-P E	Rev. 1: 2/20/2013 Rev. 2: 4/30/2018	Approved 2/20/2013; Rev. 2 Approval Pending

Key:

SM = Standard Methods for the Examination of Water and Wastewater, 22nd edition, A.P.H.A., A.W.W.A., W.P.C.F., 2012.

EPA = Methods for Chemical Analysis of Water and Wastes, EPA, 1999

* = Secondary Standard

7. INTERNAL QUALITY CONTROL

7.1 Overview. Internal quality control procedures depend on the analysis. Generally these include the comparison of spike additions, blanks, duplicates and internal QC check solutions, and detection limit QC solutions with expected values. Table 7.1 summarizes the procedures used for internal quality control conducted by the EAL. The types of quality control samples are listed below.

7.2 QCCS. The QCCS are standards prepared from a different source (a different chemical company) so that problems with purity or dilution are not duplicated in the calibration standards.

7.3 Blanks: Blanks are prepared from deionized water with only the necessary reagents added. The results of blank analyses should be within 2 times the detection limit.

7.4 Matrix Spikes: The matrix spike is a small volume of concentrated standard solution added to an aliquot of a chosen sample. The volume of the spike is chosen to minimize dilution effects of the spike on the sample aliquot. The results of the analysis of this sample are compared to those expected from

the aliquot of the original sample plus the spike addition.

Percent spike recoveries are calculated from:

$$\% \text{ spike recovery} = \frac{[\text{Spiked sample}]-[\text{unspiked sample}]}{[\text{amount of spike}]} \times 100$$

If the result is not within 15% of the expected 100% recovery of the spike the analysis is suspended and two additional samples are spiked. If these do note pass the above test, then the analysis is halted until the problem with the method is resolved, or the entire batch must be analyzed by standard additions as described in section 104C of Standard Methods (1980). All spike recoveries are noted in the notebook.

7.5 Detection Limits: Detection limit standards are dilute solutions prepared from stock solutions, with concentrations generally within 1 to 5 times the concentration of the calculated detection limit. The results of these solutions are compiled by the QC Officer to obtain detection limits. Detection limits are determined as the one-sided 99% confidence limit of a blank given the standard deviation of 7 detection limit standard solutions (based on Glaser *et al*., Trace analyses for wastewaters. ES&T 1981). The 99% confidence limit is calculated from:

$$\text{Detection limit} = T^* (s)$$

where T = 3.143 (Student T value based on 6 DF and the 0.01 α level, one sided test)
s = standard deviation of 7 DL samples.

Detection limit objectives for each analysis are shown in Table 2.1. All results are reported down to the MDL levels. Accuracy and precision goals are also listed in Table 2.1.

7.6 Split Sample Duplicates: Split sample duplicates are prepared by taking an aliquot from a randomly chosen sample and analyzing it as a regular sample. The error between the sample and duplicate is recorded and plotted on the control charts. Results falling outside the limits of Table 4.1 or outside the control limits of the control chart are noted in logbook and appropriate action is taken.

7.7 Control Charts: Data for QCCS, spike recoveries and duplicate precision are plotted individually on control charts as each batch is completed. A batch whose value on the control chart lies outside the warning limits (95% Confidence Interval) serves to warn the analyst to recheck the procedure. A QCCS outside the control limits (99% Confidence Interval) requires that the analyst immediately stop the analysis, recalibrate and rerun the batch. The 99% two-sided confidence intervals are calculated from:

$$X \pm T^*(s/\%n)$$

where X = mean
T = student T value based on n-1 DF and the 0.01 α level, (two-sided test).

s = standard deviation
n = number of samples

For any QC sample that falls outside the 99% control limits, the appropriate data flags must be set for all samples in the batch, the problem noted in the logbook and corrective action must be taken by the Supervisor.

7.8 QC for pH and Alkalinity: pH and alkalinity measurements by their nature do not have a 'detection limit,' and normal QC tests such as blanks and spikes are not run. Instead, the pH meter is standardized by certified pH 7 buffer and the slope adjusted with a certified pH 4 buffers. QC checks are made as listed in Table 7.1 and detailed in Appendix A, Standard Operating Procedures.

Table 7.1 Batch Quality Control Checks

Unless otherwise noted, each QC check is run once per batch of no more than 20 samples.

Parameter or Method	QC Check	Control Limits	Corrective action
Alkalinity, pH	1. Titrant standardization cross-check. Once per month.	1. Relative difference <5%.	1. Restandardize titrants.
	2. Electrode calibration (Nernstian response check). Once per month.	2. Slope = 1.0± 0.05.	2. Recalibrate or replace electrode.
	3. pH QCCS (pH 4 and 7) analysis. Once per batch.	3. pH 4 = 4.00± 0.05. pH 7 = 7.00 ± 0.05.	3. Recalibrate electrode.
	4. Duplicate analysis. Once per batch.	4. RSD ± 10%.	4. Refine analytical technique. Analyze another duplicate.
Total phosphorus (TP)	1a. Initial QCCS analysis (calibration and verification) 1b. Continuing QCCS analysis (every 20 samples).	1. The 99% CI.	1a. Prepare new standards and recalibrate 1b. Recalibrate. Reanalyze associated samples.
	2. Detection limit determination (seven DL QAs quarterly).	2. DL < values in Table 2.1.	2. Optimize instrumentation and technique.
	3. Blank analysis. Once per batch.	3. Blank ±2*DL	3. Determine and eliminate contamination source. Prepare fresh blank solution. Reanalyze associated samples.
	4. Duplicate analysis. Once per batch.	4. The 99% CI on Control Chart, Duplicate precision (RSD) ± values given in Table 2.1.	4. Investigate and eliminate source of imprecision. Analyze another duplicate.
	5. Matrix spike. Once per batch.	5. The 99% CI on Control Chart, % Recovery = 100± 15%. Except TP = 100 ± 20%.	5. Analyze 2 additional spikes. If one or both outside control limits, analyze sample batch by method of standard additions.

8. DATA VALIDATION

During the analysis of samples, the technician completing sample analysis is responsible for recording any problems with meeting measurement performance criteria and/or instrument operational issues. Any failure of a sample to meet defined measurement performance criteria is recorded and the data flagged for further review upon data entry and final data validation.

The data validation process starts once the data has been produced and it is entered into Microsoft Excel files. After data has been entered into the appropriate file, laboratory staff completes an initial check to be sure all data was entered correctly. Then, the Laboratory Manager checks the data entered for errors and corrects any that are found. Outliers and inconsistencies are flagged for further review. Data are compared to values obtained for similar samples analyzed in the past. The decision to discard data is made by the Laboratory Manager.

The Quality Control Officer checks each batch to see that the QCCS, the matrix spike recovery and the duplicates were within acceptable limits. Samples in a batch that fail the QCCS test are flagged as failed and are marked for reanalysis. Samples in a batch failing the spike recovery or duplicate tests are flagged appropriately. Any substitutions of re-analyzed data are noted in the data flags.

9. QUALITY ASSURANCE AND SYSTEM AUDIT

Performance Evaluation Audits: The EAL has participated in several external quality assurance programs. These include DEP quality control audits when submitting the updated SOP for total phosphorus and audits performed with other university laboratories across New England. Occasionally, additional audits are conducted on EPA acid precipitation studies, USGS NSRW audits and other audits as requested.

10. EQUIPMENT MAINTENANCE

Schedule of maintenance varies for the different instruments. By design, the components of some instruments need to be replaced on a regular schedule. We follow the manufacturer recommendations for this. These typically include such things as: filling solution in reference electrodes, cartridges for the deionizer. Simple electronic repairs are conducted by an experienced electronics specialist on campus. Other instrument repairs are conducted by the manufacturers repair specialists.

11. CORRECTIVE ACTIONS

Quality control for each batch is the responsibility of the Laboratory Manager. Corrective actions are classified into four types, Technician, Supervisor, Quality Control, and Program actions as follows:

11.1 Technician Actions: In the case of suspected errors arising during the course of a run (contamination of blanks, inability to correctly determine standard check solutions, etc.), immediate corrective actions may be taken by the technician. Corrective actions include but are not limited to:

checking purity of water supply, rechecking standards, recalibration of the instrument and rerunning the batch. Both the problem and the corrective action are noted in the log book.

11.2 Supervisor Actions: In case of errors such as poor spike recoveries, duplicates failing QC tests, or control chart drift, the Supervisor may assist the technician in identifying the problem with the instrument or the procedure and take appropriate action. This may be as simple as increasing the routine maintenance schedule or it may involve recalibration or replacement by the manufacturer. Once the problem has been rectified, the Laboratory Manager will have the batches with failed QC tests run again. Notes on the problems and the solutions are noted in the log book.

11.3 Quality Control Actions: Should the lab show poor performance on audit or double blind QC samples, the quality control officer will send a performance report to all personnel and meet with the Lab Manager to discuss the problems and suggest changes in procedures or changes in instrumentation. Routine analysis may be suspended while the problem is located and resolved. Problems and changes are reported in the quality assurance reports and in the lab notebook. Analyses can resume when the Laboratory Manager obtains written permission from the QC Officer.

11.4 Program Actions: The quality control reports are discussed at the annual laboratory meeting and a plan of action is agreed upon at that time. Any changes in methods, instruments, or procedures are proposed and discussed. If changes are agreed upon, a written plan of action is then given to the Laboratory Manager and any new changes to the quality assurance plan are made and the Director, QC Officer, and Laboratory Manager must all sign the new version. The new standard operating procedures are sent to the state laboratory certifying agent.

12. DATA AND RECORD MANAGEMENT AND REPORTING

Private clients, utilities, state and local officials and the US EPA receive similar data reporting packages. They receive a cover letter, data report as described below. System QC statistics are not provided unless specifically requested.

12.1 Data Storage: Files are transferred from the instruments as Excel data files on both an internal server and an external hard drive. The relevant laboratory analysis notes are transferred as electronic files and a laboratory notebook is also maintained.

12.2 Archiving: All of the original Excel files are archived for future reference. In addition, all computer files are backed up by the Laboratory Manager in case of disk failure.

12.3 Data Report: The data report includes:

a) cover letter-- which explains the data and quality control reports and describes the method of analysis and the laboratory and persons responsible for the analyses.
b) copy of the request for analysis-- includes the date, place, time of sampling, type of sample (e.g. grab, composite, check sample etc.), preservative added and name of sampler, and date and time of receipt of samples in lab.

c) copy of the chain-of-custody (if required).
d) quality control report-- a summary of batch QC statistics which details accuracy of outside quality control check solutions, duplicate precision, spike recovery and holding time summaries.
e) data-- a hard copy of the data including data flags and date of each analysis, printed from the database manager. Data reported to DEP will use DEP forms in Appendix B.

12.4 System QC Statistics: The QC Officer is required to summarize the results of the internal quality control program, internal audits and external performance evaluation audits in an annual report to the Director. This will include a summary of the accuracy of the outside QC solutions, duplicate precision, spike recovery, and detection limits. At least once a year the laboratory staff meets to discuss the quality report and suggest changes or improvements to the methods or equipment.

REFERENCES

APHA. 1998. Standard Methods for the Examination of Water and Wastewater, 20th ed. American Public Health Association, the American Water Works Association and the Water Environment Federation.

EPA. 1999. Methods and Guidance for Analysis of Water. United States Environmental Protection Agency, Office of Water, Washington, D.C., EPA 821-C-99-004, June 1999.

Glaser, J.A., *et al*. "*Trace Analysis for Wastewaters*," *Environmental Science and Technology*, 15, 1426 *(*1981*)*

APPENDIX A. STANDARD OPERATING PROCEDURES

A1. Sample Preparation, Filtering, and Digestion
A2. Chlorophyll a Determination
A3. Total Phosphorous Determination
A4. Color Determination
A5. Dissolved Oxygen Determination
A6. pH Determination
A7. Alkalinity Determination

A1. SAMPLE PREPARATION, FILTERING AND DIGESTION

_____

Signature Title Revision Date

For analysis of pH and alkalinity, no sample preparation is needed. For the analysis of dissolved metals, filtration is required. For the analysis of total metals, digestion is required if the turbidity is greater than 1 NTU.

1. Sample Filtration: Samples for dissolved analyses must be filtered through a 0.45 :m membrane filter. We follow methods described in EPA (1983) method 200.7 section 8.2.1. A new filter should be placed onto a clean filtering apparatus and attached to a clean filtering flask. The filtering flask is attached to the vacuum pump. Fifty ml of sample is filtered under low vacuum. This filtrate is used to rinse the flask and is discarded. The filtering flask is reattached to the vacuum pump and the required amount of sample is filtered (e.g. approximately 100 ml). A small amount of final filtrate is used to rinse a clean filtrate sample bottle and the rinse water discarded. The remainder of the sample is transferred to the filtrate sample bottle and labeled as "filtered", and the information from the original sample is copied onto the label as well. If not previously acidified the sample must be acidified to a pH of 2 or less with (1+1) HNO_3 (normally 3ml per liter are sufficient). The used filter is discarded and filter apparatus must be thoroughly rinsed with pure water between samples.

2. Turbidity: Plug in the HF Scientific DRT-15C Turbidimeter and turn range to 20. The special sample bottles must be clean as dust will affect the readings. Insert reference standard into sample holder, cover with sample cover and adjust the REF. ADJ. knob to the correct standard reading. Remove standard. Shake sample, wait for bubbles to disappear, and pour into clean sample bottle. Place bottle in instrument, cover and read turbidity. Record turbidity in log notebook.

3. Total Metals Digestion: Digestion is required for total metals if the turbidity is greater than one. If the turbidity is less than one, the value must be entered into the lab notebook. For digestion we follow the methods listed in EPA (1983) method 200.7 section 9.3. From the unfiltered sample bottle measure 100ml into a clean, labeled Griffin beaker. Add 3ml of conc. HNO_3. Place on a hot plate and evaporate to near dryness without boiling. Cool and add 5ml HNO_3, cover with clean watch glass and reflux on hot plate, adding additional acid as needed until digestion is complete (digestate is light in color and color stable). Evaporate to near dryness and cool. Add 10ml of 1+1 HCl and 15ml of deionized water and warm for 15 min. to dissolve precipitates. Cool and wash down sides of beaker with deionized water and filter to remove insoluble material. Adjust sample volume to 100 ml with deionized water. If required, store sample in clean bottle labeled 'digested' along with sample information.

A2. Chlorophyll-a Determination

Revision 04/18/2017

_____ _____
Travis Drury, UMass Environmental Analysis Laboratory Date
209 Ag Engineering UMass Amherst, MA 01003 413.545.5979

_____ _____
Richard Chase, MassDEP, Division of Watershed Management Date
627 Main St. 2nd floor Worcester, MA 01608 508.767.2859

_____ _____
Mark Mattson, MassDEP, Division of Watershed Management Date
627 Main St. 2nd floor Worcester, MA 01608 508.767.2868

1.0 Overview

This procedure describes how to perform laboratory analysis of a water sample for Chlorophyll *a*. The estimated low level detection limit (MDL) is 1 µg/l.

Chlorophyll samples are provided as material filtered on a Whatman GF/F filter 0.7µm), folded, dried and wrapped in a labeled aluminum foil sheet.

The method followed is described in Standard Methods, 20th edition as method 10200H.

2.0 Equipment List

- Tissue grinder or Mortar & pestle — glass & glass, glass and Teflon, or ceramic (60 mL)
- Centrifuge tubes with caps — 15 ml conical bottom to fit centrifuge, scribed line at 15 ml. Snap-on caps provide a wider mouth. Calibrated tubes are very expensive. Disposable tubes work as well but must be calibrated carefully to 15 mL. A small file or Dremel tool with cutting disk can be used to mark the tubes. Each tube should be calibrated using an accurate pipette or small graduated cylinder
- Squeeze bottle for 90% acetone
- 10 or 15 mL graduated cylinder
- 90% acetone, reagent grade acetone diluted with distilled or deionized water. Acetone is a hazardous material; avoid contact and dispose of properly
- Powder funnel to fit in the centrifuge tubes with a little room for air to escape when a liquid is poured through the funnel
- Test tube holder for the centrifuge tubes

- Centrifuge capable of 500 Gs. Typically, centrifuges with angled tube holders will not develop enough centrifugal force. Only those holders that permit the tubes to spin horizontally should be used
- Refrigerator where samples may be steeped for at least 24 hours in the dark
- Spectrophotometer with 2 nm or smaller resolution and capable of making readings at 664, 665, and 750 nm that holds a 5 cm cell. A Shimadzu UV1800 is currently being used by EAL
- 0.5N HCl and eye dropper
- Disposable pipettes
- Calculator or computer

3.0 Safety

3.1 The University Department of Environmental Health and Safety is responsible for general safety regulations on campus. Our laboratory personnel is responsible for safety activities within the lab itself. Required safety information is readily available in the lab in a notebook provided by Environmental Health and Safety. Right to Know (111F Mass. General Law) is posted on the inside of the lab door.

3.1.1 All hazardous materials are safely stored in appropriate cabinets (organics, acids and bases are separate). All lab personnel are trained in safe laboratory practices including the use of safety equipment. Supplies of safety equipment and clothing are kept in stock.

3.1.2 All hazardous wastes are disposed of in accordance with state and federal law and a separate covered container for glass or other sharp wastes is kept. The person responsible cleans up all spills immediately. Medical aid is provided for injuries and all serious accidents and injuries are reported to the Environmental Health and Safety Office.

3.1.3 The following schedule is used for safety checks:

a) Annual checks: University Department of Environmental Health and Safety will check flow rates in the fume hoods, test fire alarms, check pressure in fire extinguishers and test personnel showers.

b) Semi-annual checks: Check supplies of pipet bulbs, bicarbonate for acid spills, plastic gloves, goggles, aprons, and contents of the first aid kit for gauze, bandages and antiseptics. Test operation of eye wash stations. Results of these tests are recorded in the laboratory notebook.

3.2 Personal Safety

3.2.1 Eye and face protection must be worn in the laboratory when there is a potential for contact with hazardous chemicals or other agents (e.g., non

ionizing radiation, biohazardous materials, flying objects). All protective eye and face wear meet American National Standards Institute ANSI Z 87.1, 1989 standards.

3.2.2 Laboratory coats and shoes (not open sandals) are worn when performing laboratory work. Coats, aprons and gloves are removed when leaving the laboratory. Gloves are be replaced immediately if they are contaminated or torn. In situations involving extremely hazardous chemicals, double gloves are used. Gloves are carefully selected for their degradation and permeation characteristics to provide proper protection.

3.2.3 All work with corrosive, flammable, odoriferous, toxic or other dangerous materials is conducted only in the properly operating chemical fume hood.

4.0 Sample handling protocol

4.1 After following the Standard Operating Procedure Lakes-8 For Chlorophyll *a* (Massachusetts Water Watch Partnership, Amherst, MA 2001), the samples are delivered to the laboratory.

4.2 Samples are logged in and placed in the freezer immediately upon arrival at the laboratory.

4.3 Samples are analyzed within 21 days. Results include qualifiers for any improper sample preservation that may have taken place.

5.0 Analytical Procedure

This analysis uses hazardous substances; observe all laboratory safety protocols. Wear appropriate safety gear – e.g. Latex or latex alternative gloves, safety glasses, and lab coat. See Section 3.

5.1 Preparation of Samples

Solutions: 90% Acetone Solution (10% Deionized Water) in a squirt bottle

It is very important that exposure of the pigment to light be minimized. The grinding should be done in subdued lighting, if possible. Transport of samples should be done quickly or shaded against light. Avoid full daylight. Steeping must be done in the dark. During spectrophotometric readings, samples waiting for measurement should be kept in the dark. **It is suggested that samples be placed in a box.**

5.1.1 **Grinding**

5.1.1.1 Record all data that is listed on the sample container label and record the number of the centrifuge tube to be used for the sample. **This includes sample ID, date collected, and amount of water filtered.**

5.1.1.2 Remove the filter from the aluminum foil wrapper. It should be folded in half. Do not unfold the filter. **Record the appearance of the filter.**

5.1.1.3 Using a ceramic mortar and pestle, place folded filter in bottom of the mortar.

5.1.1.4 Add 6 to 7 mL of 90% acetone and begin grinding. If you use more acetone, there is a danger of exceeding the 15 mL limit in the centrifuge tubes. This volume must be exact. Exact volume not needed in this step, however. If you use less than 6 mL, the difficulty of pouring the slurry into the funnel without leaving significant residue behind increases. The filters should be ground until they are a fine slurry of glass fibers. Chunks of filter should be ground further.

5.1.1.5 Ready the centrifuge tube (double check that the tube number agrees with that already written on the lab sheet) and funnel.

5.1.1.6 Pour the contents of the mortar into the centrifuge tube. The trick is to pour the contents of the mortar fairly quickly into the center of the funnel. However, if the funnel is placed in the centrifuge tube so that air cannot escape around it, an air lock will occur and liquid sample will possibly be lost. Using as little as possible 90% acetone from the squeeze bottle, rinse the pestle, mortar and funnel of all filter fibers, in that order and pouring from one to the other to minimize rinse volume. Be very careful to minimize rinsing so that the 15 mL volume in the centrifuge tube is not exceeded. (If a mistake occurs, corrections can be made later, but with additional trouble.)

5.1.1.7 Bring the level of liquid in the centrifuge tube exactly to the scribed mark (15 mL) by carefully adding acetone from the squirt bottle. If some filter material is on the sidewalls of the mortar or on the pestle, wash carefully with a few more milliliters of acetone and transfer into centrifuge tube. Cap the tube and place sample into the refrigerator or into a dark, covered box as they are ground so that samples are not exposed to light for significant amounts of time. Note time when sample is placed in refrigerator.

5.1.1.8 Rinse mortar, pestle and funnel with acetone. Acetone is a hazardous material; it should not be disposed of in the sink. Acetone should be disposed of following the protocols outlined in the Laboratory Health and Safety Manual (UMass EHS 2000).

5.1.1.9 Repeat process for other samples.

5.1.2 **Steeping**

5.1.2.1 Place samples in refrigerator at 40° F and in the dark overnight. The minimum steeping time is 2 hours. 8 to 12 hours steeping time is preferable.

5.1.3 **Centrifugation**

5.1.3.1 Remove only the number of samples that centrifuge will hold in one batch from the refrigerator. Carefully slosh the liquid slightly around the upper part of the tube to rinse any filter fragments into the liquid. Install tubes in the centrifuge. **Make sure that there is even distribution of mass in the centrifuge. This may require placing centrifuge tubes with 15 milliliters of water into the empty slots of the centrifuge if there are an odd number of samples.**

5.1.3.2 Centrifuge at 500 Gs or 3000 rpm for 20 minutes.

5.1.3.3 Remove tubes from the centrifuge. Tubes may be returned to the refrigerator while another centrifuge batch is prepared, but must be kept in the dark.

5.2 Preparing the Spectrophotometer

5.2.1 Start the spectrophotometer and wait 5 minutes for the self-diagnostic program to run. Allow the spectrophotometer to "warm up" for 20 minutes prior to beginning the analysis.

5.2.2 Fill the two 5 cm cells with reagent blank (90% Acetone solution).

5.2.3 Press F4 to connect the spectrophotometer to the computer.

5.2.4 On the computer, open the UVProbe program.

5.2.5 On the "Instrument" tab near the bottom left of the screen, right click and press "activate"

5.2.6 Press Connect

5.2.7 Press File, then Open.

5.2.8 Look in the "Methods" folder and press "Chlorophyll".

5.2.9 Press Open. You should now have the spectrophotometric absorbance readings at 750 nm, 665 nm, and 664 nm.

5.2.10 Now save this page in UVProbe by pressing "Save As" and naming your data sheet, preparing it for the new data.

5.2.11 With the (2) 5cm reagent blank cells in the instrument, press "Baseline".

5.2.12 Verify that reagent blank shows no absorption by typing in "blank" in the Sample ID section of the Sample table and click "Read Sample". If it does show absorption, then press "Autozero." The cells must be impeccably

clean for each and every measurement. Wipe the outside optical surfaces softly with a lint free tissue before each reading. Care in filling the cells will minimize the problem.

5.2.13 Appropriately dispose of the acetone used for the blank.

5.3 Analyzing Samples

5.3.1 Carefully decant the acetone-extracted pigment in the centrifuge tube into the spectrophotometer cell without disturbing the sediment at the bottom of the tube. Be sure that the level of liquid in the spectrophotometric cell is well above the light path, i.e. the cell is filled to the neck of the filling ports.

5.3.2 On the computer, in UVProbe, Sample Table, type in your Sample ID.

5.3.3 Press “Read Sample” to make a spectrophotometric absorbance reading at 750 nm, 665 nm, and 664 nm. The absorbance values will be recorded in the program. *Do not exceed an absorbance of 1.0 for your 665 readings. If you do, dilute the sample by an exact amount and filter less sample the next time. If the sample is diluted, be sure to compensate for this in the calculation step. Samples with readings below 0.1 absorbance units will not be reliable. Record results.

5.3.4 With the current sample still in the spectrophotometer, the next sample ID in your Sample Table should be “Sample ID_A” denoting whatever name you choose for your sample ID_Acidified.

5.3.5 Add two drops of 0.5N HCl and set timer for 90 seconds. Gently agitate using a clean disposable pipette for each sample.

5.3.6 After 90 seconds, press “Read Sample” to make a spectrophotometric absorbance reading at 750 nm, 665 nm, and 664 nm. This will give you your “sample acidified” reading.

5.3.7 Properly dispose of the sample and rinse the cell with 90% acetone.

5.3.8 Analyze the remaining samples in the same manner.

5.3.9 After the last sample, press Save, then Disconnect.

5.3.10 Clean cells and fill with deionized water.

5.4 Results

5.4.1 The following must be known exactly for the calculation of chlorophyll and phaeophytin:

- Absorbance at 665 nm, 664 nm, and 750 nm. Please note:
    - “na” indicates “non-acidified sample”
    - “a” indicates “acidified sample”
- Volume of sample filtered

- Volume of the sample in the centrifuge tube (15 mL)
- Path length of the spectrophotometric cell (5 cm)
- I.D. number of the sample (centrifuge tube number) that relates to where and when the sample was collected.

5.4.2 Subtract the 750na nm absorbance from the 664na absorbance to get the 664nacor (non-acidified corrected) absorbance value; subtract the 750a from the 665a absorbance to get the 665acor (acidified corrected) absorbance value.

5.4.2.1 Calculate chlorophyll by the following formula (SM 10200H, APHA 2012):

$$\boldsymbol{Chlorophyll}\ \mathbf{a}\ (\boldsymbol{\mu g/L}) = \frac{\mathbf{11} \times \mathbf{2.43} \times (\mathbf{664}\boldsymbol{nacor} - \mathbf{665}\boldsymbol{acor}) \times \boldsymbol{volume\ extracted}\ (\boldsymbol{mL})}{\frac{\boldsymbol{volume\ filtered}\ (\boldsymbol{mL})}{\mathbf{1000}} \times \boldsymbol{cell\ path\ length}\ (\boldsymbol{cm})}$$

5.4.2.2 Calculate phaeophytin by the following formula (SM 10200H, APHA 2012):

$$\boldsymbol{Pheophytin}\ \mathbf{a}\ (\boldsymbol{\mu g/L}) = \frac{\mathbf{11} \times \mathbf{2.43} \times [(\mathbf{1.7} \times \mathbf{665}\boldsymbol{acor}) - \mathbf{664}\boldsymbol{nacor}] \times \boldsymbol{volume\ extracted}\ (\boldsymbol{mL})}{\frac{\boldsymbol{volume\ filtered}\ (\boldsymbol{mL})}{\mathbf{1000}} \times \boldsymbol{cell\ path\ length}\ (\boldsymbol{cm})}$$

5.4.2.3 Where 664nacor is the corrected non-acidified absorbance at 664 nm, 665acor is the corrected acidified absorbance at 665 nm; Volume extracted will be 15 mL, and cell path length is 5 cm.

5.4.2.4 Write the calculated values for chlorophyll *a* and phaeophytin *a* on the lab sheets

6.0 Quality Control

6.1 General Quality Control Procedure

The accuracy of the sample measurements will be determined by comparing the concentration of chlorophyll check samples (Turner Design, Inc.) to the calculated concentration. The check sample values should fall within 20% of the standard calibration readings. If this level of accuracy is not met then the source of the error must be identified before further analyses are done. If the project data objectives allow it, a larger percent error may be acceptable.

6.2 Laboratory Blanks

A laboratory blank is the first and last filter extracted of a sample set. The laboratory blank is made by running 500mL deionized water through a 0.7µm

glass fiber filter, folded in half, air dried according to MWWP protocols, and frozen until use. It is used to check for contamination of the reagents or apparatus. This laboratory blank filter is extracted and analyzed similarly to a sample filter. If the sample value is greater than 1 µg/L then the samples for that day must be re-run or their data annotated and judgment made as to whether the data objectives are still met.

6.3 Duplicate Samples

One duplicate sample must be run for every ten samples analyzed. The duplicate sample is split from the same field sample bottle. Otherwise, it is treated the same as the other samples in the batch. The split sample is considered a lab duplicate, since it results in a duplicate filter for analysis. Field duplicates using separate sample bottles are also recommended. These are the responsibility of the sampler and will be treated as a normal sample.

The precision for these samples will be determined by calculating their relative percent difference (RPD).

$$RPD = \frac{(Sample - Duplicate)}{\frac{(Sample + Duplicate)}{2}} \times 100$$

The RPD should not exceed 20%.

7.0 Reporting

7.1 Results of Chlorophyll *a* analyses are recorded and calculated in an excel spreadsheet.

7.2 Results are presented in a table that includes the Sample ID, the Chlorophyll *a* value and the Phaeophytin *a* value unless a different format is requested.

Site ID	Date Sampled	Chlorophyll *a* (µg/L)	Phaeophytin *a* (µg/L)

7.3 Results that have values less than 1 µg/L are considered to be below the detection limit and are labeled “BDL”.

8.0 Interferences

8.1 High concentrations of humic acids can cause interference because they fluoresce at the same wavelengths as the chlorophyll *a*. Other substances that fluoresce in the red region of the light spectrum may interfere with chlorophyll *a* measurement.

8.2 Phaeophytin *a* (a degradation product of chlorophyll *a*) and chlorophyll *a* are measured at similar wavelengths. This can result in an overestimation of chlorophyll *a* measurement if you are using the acidification method for chlorophyll *a* analysis. A correction formula is used to adjust for this problem. These formulas are provided in Standard Methods (American Public Health Assoc., 1981).

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A3. Total Phosphorous Determination

Revision 04/30/2018

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Travis Drury, UMass Environmental Analysis Laboratory Date
209 Ag Engineering UMass Amherst, MA 01003 413.545.5979

_____ _____

Richard Chase, MassDEP, Division of Watershed Management Date
627 Main St. 2nd floor Worcester, MA 01608 508.767.2859

_____ _____

Mark Mattson, MassDEP, Division of Watershed Management Date
627 Main St. 2nd floor Worcester, MA 01608 508.767.2868

1.0 Overview

This procedure describes how to perform laboratory analysis of a water sample for Total Phosphorous.

2.0 Equipment List

___ Acid-washed glassware and pipette tips
___ Pipettes, calibrated yearly
___ 70mL capacity, digestible, screw top sample tubes with mark at 50 mL
___ Autoclave
___ Spectrophotometer; Shimadzu model UV-1800 with optically matched 5 cm path length cells

3.0 Safety

3.1 The University Department of Environmental Health and Safety is responsible for general safety regulations on campus. Our laboratory personnel are responsible for safety activities within the lab itself. Required safety information is readily available in the lab in a notebook provided by Environmental Health and Safety. Right to Know (111F Mass. General Law) is posted on the inside of the lab door.

3.1.1 All hazardous materials are safely stored in appropriate cabinets (organics, acids and bases are separate), train all lab personnel in safe laboratory practices including the use of safety equipment, and keep supplies of safety equipment and clothing in stock.

3.1.2 All hazardous wastes are disposed of in accordance with state and federal

law and a separate covered container for glass or other sharp wastes is kept. All spills are cleaned up immediately by the person responsible. Medical aid is provided for injuries and all serious accidents and injuries are reported to the Environmental Health and Safety Office.

3.1.3 The following schedule is used for safety checks:
a) Annual checks: University Department of Environmental Health and safety will check flow rates in the fume hoods, test fire alarms, check pressure in fire extinguishers and test personnel showers.
b) Semi-annual checks: Check supplies of pipet bulbs, bicarbonate for acid spills, plastic gloves, goggles, aprons, and contents of the first aid kit for gauze, bandages and antiseptics. Test operation of eye wash stations. Results of these tests are recorded in the laboratory notebook.

3.2 Personal Safety

3.2.1 Eye and face protection must be worn in the laboratory when there is a potential for contact with hazardous chemicals or other agents (e.g., non ionizing radiation, biohazardous materials, flying objects.) Please note that all protective eye and face wear should meet American National Standards Institute ANSI Z 87.1, 1989 standards.

3.2.2 Laboratory coats and shoes (not open sandals) should be worn when performing laboratory work. Coats, aprons and gloves should be removed when leaving the laboratory. Gloves should be replaced immediately if they are contaminated or torn. In situations involving extremely hazardous chemicals, double gloves are recommended. Gloves should be carefully selected for their degradation and permeation characteristics to provide proper protection.

3.2.3 All work with corrosive, flammable, odoriferous, toxic or other dangerous materials shall be conducted only in a properly operating chemical fume hood, gas cabinet, or glovebox.

4.0 Sample handling protocol

4.1 Samples will be frozen and transported to the laboratory, frozen, in light-blocking polyethylene bottles.

4.2 Samples will be logged in and placed in the freezer immediately upon arrival at the laboratory.

4.3 Samples will be analyzed within one year or less according to the needs of the project.

4.4 Results will include qualifiers for any improper sample preservation that may have taken place.

5.0 Analytical Procedure

5.1 Preparation of Samples

5.1.1 Thaw frozen samples in a warm water bath.

5.1.2 Shake each sample upside down to suspend solids immediately prior to pouring any/all aliquots when sub-sampling.

5.2 Digestion Tube Preparation

5.2.1 Wash with hot water and phosphate-free detergent, rinse with distilled water.

5.2.2 Acid wash in 50%HCl.

Dip the test tube mouth in the acid after pouring the acid out.

5.2.3 Rinse 3 times in distilled, once in deionized water.

5.3 Laboratory Equipment Preparation

5.3.1 For any glassware, lids, stirrers, and balanceware that comes into contact with the reagents, their components, or the samples wash with hot water and phosphate-free detergent, rinse with distilled water

5.3.2 Acid wash in 50% HCL

5.3.3 Rinse 3 times in distilled, once in deionized water.

5.4 Preparation of Reagents

This analysis uses hazardous substances; observe all laboratory safety protocols. Wear appropriate safety gear – e.g. Latex or latex alternative gloves, safety glasses, and lab coat. See Section 3.

5.4.1 Solutions

5.4.1.1 Persulfate: Make a scoop out of a piece of disposable pipette tip. It should deliver 0.3-0.35 g of powdered Potassium Persulfate. Sodium persulfate is also acceptable.

5.4.1.2 Sulfuric acid, 10.7N, for digestion: Slowly add 30 mL of concentrated H_2SO_4 to 60 mL deionized water, then dilute to 100 mL with deionized water.

5.4.1.3 Sulfuric acid, 5N, for colorimetric analysis: Dilute 7 mL concentrated H2SO4 to 50 mL with deionized water.

5.4.1.4 Antimony potassium tartrate solution: Dissolve 1.3715g $K(SbO)C_4H_4O_6 \cdot ½ H_2O$ in 400 mL deionized water in a 500 mL volumetric flask and dilute to volume. Store in a glass-stoppered bottle.

5.4.1.5 Ammonium molybdate solution: Dissolve 20 g $(NH_4)_6Mo_7O_{24} \cdot 4H2O$ in 500 mL deionized water. Store in a glass-stoppered bottle.

5.4.1.6 Ascorbic acid, 0.1M: Dissolve 1.76g ascorbic acid in 100mL deionized water. The solution is stable for 1 week at 4°C.

5.4.2 Combined Reagent

5.4.2.1 After all reagents have reached room temperature, mix in the following order and proportions for 100 mL of combined reagent: 50 mL sulfuric acid 5N, 5 mL antimony potassium tartrate solution, 15 mL ammonium molybdate solution, and 30 mL ascorbic acid solution.

5.4.2.2 Mix after the addition of each reagent. If turbidity forms, shake and let stand for a few minutes until turbidity disappears before proceeding.

5.4.2.3 The combined reagent is stable for 4 hours.

5.5 Preparation of Standards, 25ppm P Solution

For each standard solution, start with a 100mL clean, acid-washed volumetric flask except for the 7.5 µg/L standard which is produced in a 500mL clean, acid-washed volumetric flask. Fill with 50mL deionized water. Ricca 25ppm P as Phosphate standard is used to prepare the seven standards as P.

5.5.1 Pipette 150 µL of standard 25ppm P solution into the volumetric flask. Add deionized water for a total of 500 mL to produce a 7.5 µg/l standard as P.

5.5.2 Pipette 50 µL of standard 25ppm P solution into the volumetric flask. Add deionized water for a total of 100 mL to produce a 12.5 µg/l standard as P.

5.5.3 Pipette 100 µL of standard 25ppm P solution into the volumetric flask. Add deionized water for a total of 100 mL to produce a 25 µg/l standard as P.

5.5.4 Pipette 200 µL of standard 25ppm P solution into the volumetric flask. Add deionized water for a total of 100 mL to produce a 50 µg/l standard as P.

5.5.5 Pipette 400 µL of standard 25ppm P_4 solution into the volumetric flask. Add deionized water for a total of 100 mL to produce a 100 µg/l standard as P.

5.5.6 Pipette 1000 µL of standard 25ppm P solution into the volumetric flask. Add deionized water for a total of 100 mL to produce a 250 µg/l standard as P.

5.5.7 Pipette 2000 µL of standard 25ppm P solution into the volumetric flask. Add deionized water for a total of 100 mL to produce a 500 µg/l standard as P.

5.6 Preparing Samples for Digestion

5.6.1 Arrange samples in a logical order and enter identities into a logbook.

5.6.2 Rack the blank and standard tubes to bracket the samples.

5.6.3 For the blanks, pipette totally 30mL of deionized water, 10 mL each pipette, into the digestion tubes.

5.6.4 For each standard, pipette totally 30mL of the standard solution, 10 mL each pipette, into the digestion tubes. Use fresh, previously acid-washed, DI-rinsed, and air-dried pipette tip for each standard.

5.6.5 Shake each sample well. Pipette totally 30mL of sample from sample bottle, 10 mL each pipette. Swirl/shake well before each time to suspend solids. Use fresh, previously acid-washed, DI-rinsed, and air-dried pipette tip for each sample.

5.6.6 Add one drop of phenolphthalein to each tube. Swirl and look for a pink color.

5.6.7 To any tubes that show a pink color, add enough drops of sulfuric acid solution for digestion to barely discharge all pink color. This occurs infrequently and the number of drops should be noted in the logbook.

5.6.8 Add to each tube, including blanks and standards, 0.6 mL sulfuric acid solution for digestion and 1 scoop equal to .3g of dry Potassium Persulfate.

5.6.9 Loosely cap all tubes.

5.7 Digesting Samples

5.7.1 Check to see that all tubes are loosely capped.

5.7.2 Put sample tubes carefully in steel buckets that will fit in the autoclave being used. All tubes should be very nearly vertical. Rinse and fill autoclave with distilled water just to the level of the rack.

5.7.3 Turn on. Allow to preheat.

5.7.4 Put samples in autoclave, place inner lid on top of tubes to keep caps in place.

5.7.5 Cover, and start tightening screws in pairs. Allow autoclave to vent for 20 minutes.

5.7.6 Close the pressure vent. After another 10 minutes, finish tightening screws. Pressure should begin to build immediately.

5.7.7 The samples should digest at 15lb/sq. inch of pressure for 40 minutes.

5.7.8 Cock the pressure release and allow to return to ambient pressure.

5.7.9 Remove sample bucket with tubes and rinse the outside wall of the sample tubes with cold tap water to return to ambient temperature.

5.8 Preparing the spectrophotometer

5.8.1 Power on. Instrument will warm up and go through a self-diagnostic program. Allow the spectrophotometer to “warm up” for 20 minutes prior to beginning the analysis.

5.8.2 Flush and fill both cells with deionized water. Clean thoroughly with a lint-free lens cloth. Replace cells in holders.

5.8.3 Press F4 on the spectrophotometer to connect it to the computer.

5.8.4 On the computer, open the UVProbe program.

5.8.4.1 On the “Instrument” tab near the bottom left of the screen, right click and press “activate”

5.8.4.2 Press Connect

5.8.4.3 Press File, then Open.

5.8.4.4 Look in the “Methods” folder and press “Total Phosphorus”.

5.8.4.5 Press Open. You should now have the spectrophotometric absorbance reading (WL) at 880 nm.

5.8.4.6 Now save this page in UVProbe by pressing “Save As” and naming your data sheet, preparing it for the new data.

5.8.4.7 With the (2) 5cm reagent blank cells in the instrument, press “Baseline”.

5.8.4.8 Verify that reagent blank shows no absorption by typing in “blank” in the Sample ID section of the Sample table and click “Read Sample”. If it does show absorption, then press Autozero. The cells must be impeccably clean for every measurement. Wipe the outside optical surfaces softly with a lint free tissue before each reading. Care in filling the cells will minimize the problem.

5.8.4.9 Appropriately dispose of the deionized water used for the blank.

When using this instrument, clean cell windows of ANY dust, smudges, moisture, etc. before each measurement. The slightest trace of dirt will give an incorrect result. Sample level in the cell must be even with the shoulders of the upright tubes.

5.9 Analyzing samples

Wear appropriate safety gear when handling hazardous materials.

5.9.1 Add one more drop of phenolphthalein indicator to each digestion tube.

5.9.2 Neutralize to faint pink color with 1N sodium hydroxide.

5.9.3 Make each sample up to 50 mL with deionized water by adding deionized water until sample is level with 50 mL mark on sample tube.

5.9.4 Add 8 mL Combined Reagent to the first tube from an acid-washed pipet a mix thoroughly. Note time and set a 2 minute timer.

5.9.5 Addition of reagent will be in 2-minute intervals, and the elapsed time between addition of reagent and reading in the spectrophotometer will be 21 minutes. Therefore, if the first tube is set up at 2:00, it will be read at 2:21, and the next tube will be set up at 2:02 to be read at 2:23. Record start/end times in the logbook.

5.9.6 Rinse combined reagent pipet between samples with deionized water to prevent contamination.

5.9.7 To fill the spectrophotometer cell with the first sample, remove it carefully from its holder and pour out the deionized water that was used to calibrate

the instrument. Rinse with a small amount of sample then fill. Align cell with the same orientation for each reading.

5.9.8 To read sample, press START/STOP on the spectrophotometer and record absorbance in logbook.

5.9.9 After each sample, flush for 10 seconds with distilled water at tap pressure, flush quickly with deionized water from a squeeze bottle, then rinse with a small amount of the next sample to be analyzed.

5.9.10 Log results in a permanently bound logbook.

6.0 Quality Control

6.1 Method Blank

6.1.1 Method blanks will be created by pipetting 30mL of deionized water into clean, acid-washed sample tubes.

6.1.2 Blanks will be carried through entire process as if they were regular samples.

6.1.3 At least two blanks will be analyzed in each batch of samples, one at the beginning and one at the end of the batch.

6.1.4 Blank results should be less than one-half the reporting limit. Any value above this level should be examined for contamination.

6.1.5 Any blank result at or above the reporting level will result in immediate corrective action, including re-analyzing the sample batch.

6.2 Laboratory-Fortified Blank (Outside check)

6.2.1 Standard calibration curve calculations will be checked with a Laboratory-fortified blank (LFB) made from a different source of P standard and diluted to approximately the middle of the calibration range.

6.2.2 Pipette 50 µL of Ricca 100ppm P as Phosphate standard into a sample tube containing 30 mL of DI blank water.

6.2.3 The concentration is 166.4 µg/L in 30.05 mL

6.2.4 Correcting for the volume increase by multiplying the concentration by (30 mL /30.05 mL), the results should read 166.7 µg/L.

6.2.5 Tolerance for the LFB is +/- 10%.

6.3 Quality Control Sample

6.3.1 At least one blind quality control sample will be acquired from Massachusetts Department of Environmental Protection and analyzed each year.

6.3.2 Sample will be analyzed by the same procedure as a normal environmental sample.

6.3.3 Results will be reported to Mass DEP to determine if they are within acceptable +/- 10% limits.

6.4 Performance Test

6.4.1 At least one performance test using an outside phosphorus source will be run with each sample batch.

6.4.2 The performance test will be created by diluting the Complex Nutrients sample from Advanced Analytical Solutions to a value within the calibration curve.

6.4.3 Sample values will vary throughout the year to cover a variety of levels within the calibration curve.

6.4.4 Tolerance for the performance test is +/- 10%.

6.5 Duplicates

6.5.1 One duplicate sample must be run for every ten samples analyzed. The duplicate sample is split from the same field sample bottle. Otherwise, it is treated the same as the other samples in the batch.

6.5.2 Field duplicates are recommended. These are the responsibility of the sampler and will be treated as a normal sample.

6.5.3 Relative percent difference will be calculated using the following formula:

$$\frac{|sample\ result - duplicate\ result|}{[(sample\ result + duplicate\ result)/2]} \times 100$$

6.5.4 Tolerance is +/- 10% relative difference for duplicates.

6.6 Laboratory-Fortified Matrix (Spike)

6.6.1 One Laboratory-fortified matrix (LFM) sample will be run for every ten samples analyzed. The LFM sample is split from the same field sample bottle, and a known quantity of P is added to test for the presence of matrix interference. This quantity should be between 50% and 200% of the level expected to be present in the sample.

6.6.2 Pipette 50 µL of Ricca 25ppm P as Phosphate standard into a sample tube containing a split from a field sample and analyze as normal.

6.6.3 The percent recovery will be calculated using the formula:

$$\frac{\left([LFM\ value] \times (\frac{30\ mL}{30.005\ mL})\ (dilution\ correction)\right) - [Sample\ concentration]}{41.67\ (concentration\ added\ to\ sample\ with\ spike)} \times 100$$

6.6.4 Tolerance is +/- 20% recovery for laboratory-fortified matrix samples.

6.7 Method Detection Level

6.7.1 Three Detection Level Checks will be run for each calibration using the 7.5 µg/L standard created in section 5.4.1. Add 30ml of this solution to clean sample tube. Do the same for 2 more tubes.

6.7.2 Use the three Detection Level Checks from this experiment and three from each of the previous two tests, so that there are 9 in total. The standard deviation of the 9 values is then determined.

6.7.3 Multiplying the standard deviation by 2.896 (one-sided t-table value for 8 degrees of freedom at the 99% confidence level) will give the calculated Method Detection Level.

7.0 Calibration & Results

7.1 Calibration Curve

7.1.1 Absorbance of standard concentrations, when plotted, should result in a straight line. A linear calibration curve will be calculated from the following standards: Blank (0 µg/L), 7.5 µg/L, 12.5 µg/L, 25 µg/L, 50 µg/L, 100 µg/L, 250 µg/L and 500 µg/L.

7.1.2 The correlation coefficient should be greater than or equal to 0.995.

7.1.3 The concentrations of each standard in the calibration curve will be back-calculated and the values should agree with the true concentrations within +/- 20%.

7.1.4 Using the equation from the calibration curve, sample results will be calculated for P concentration in µg/L. These results are reported "as P."

7.2 Results

7.2.1 The results will be reported down to the reporting limit (RL), equal to the lowest standard in the calibration curve, or the method detection level (MDL), whichever is higher.

8.0 Interferences

8.1 Improperly taken samples, specifically, those containing solids such as excess sediment (that would not be present in a properly collected sample) will show positive error. Solid pieces of organic matter, if included in the digest, will produce an artificially high concentration of phosphorous in the digestate. Suspended sediment in the cell will scatter light and give a false high reading. Interferences can be reduced by removing large particles, but it is ultimately the responsibility of the field sampler to provide samples as free from sediments as possible, unless they are actually part of the representative sample (such as sediment-laden stormwater samples). Analyzed TP samples shall ensure inclusion of the particulate fraction via sufficient sample mixing prior to the taking of any/all sub-samples. Results should note the presence of any large organic materials that were present in the raw samples.

8.2 Arsenates at concentrations as low as 0.1 mg/l, react with molybdate reagent to produce a blue color resulting in positive interference in colorimetric analysis at 880 nm.

8.3 Nitrite and hexavalent chromium interfere to give low analytical results at concentrations as low as 1.0 mg/l.

References:

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University of Massachusetts Office of Environmental Health and Safety, 2000. Laboratory Health and Safety Manual, University of Massachusetts, Amherst, MA

Environmental Protection Agency (USEPA), 2012, ***Water: Monitoring & Assessment, 5.6 Phosphorus.*** http://water.epa.gov/type/rsl/monitoring/vms56.cfm

A4. EAL Color SOP

Updated: 3/28/19

Travis Drury, EAL Laboratory Manager

1.1 Creating Standards

1.1.1 Create standards using Hach Color Standard Solution 500 Platinum Cobalt Units (PCU) (Hach 1414-53)

1.1.2 Standards are created for 50 PCU, 250 PCU, and 500 PCU

50 PCU standard	5 ml (500 PCU solution) std + 95 ml DI water
250 PCU standard	50 ml (500 PCU solution) + 50 ml DI Water
500 PCU standard	100 ml 500 PCU solution, no dilution

1.2 Preparing the Spectrophotometer

1.2.1 Start the spectrophotometer and wait 5 minutes for the self-diagnostic program to run. Allow the spectrophotometer to "warm up" for 20 minutes prior to beginning the analysis.

1.2.2 Fill the two 5 cm cells with reagent blank (DI water).

1.2.3 Press F4 to connect the spectrophotometer to the computer.

1.2.4 On the computer, open the UVProbe program.

1.2.5 Press Connect at bottom of window

1.2.6 Press File, then Open.

1.2.7 Look in the "Methods" folder and press "ARM Color".

1.2.8 Press Open. You should now have the spectrophotometric absorbance readings at 425nm.

1.2.9 Now save this page in UVProbe by pressing "Save As" and naming your data sheet, preparing it for the new data.

1.2.10 With the (2) 5cm reagent blank cells in the instrument, press "Baseline".

1.2.11 Verify that reagent blank shows no absorption by typing in "blank" in the Sample ID section of the Sample table and click "Read Sample". If it does show absorption, then press "Autozero." The cells must be impeccably clean for each and every measurement. Wipe the outside optical surfaces softly with a lint free tissue before each reading. Care in filling the cells will minimize the problem.

1.3 Analyzing Samples

1.3.1 In Standard Table in UVProbe, add the following under Sample ID:

1.3.1.1 0 PCU

1.3.1.2 50 PCU

1.3.1.3 250 PCU

1.3.1.4 500 PCU

1.3.2 Enter sample names under Sample ID in Sample Table

1.3.3 With deionized water in the spectrophotometer cell, click in the Standard Table and then click “Read Std.” button to record a value for the “0 PCU” standard

1.3.4 Empty cell and fill with 50 PCU standard

1.3.5 Click Read Standard

1.3.6 Empty cell and rinse with deionized water

1.3.7 Repeat procedure for 250 and 500 PCU standards

1.3.8 After standards are analyzed, empty cell, rinse with DI water and fill with first sample

1.3.9 Click in Sample Table, then click “Read Unk.” Button to read the first sample.

1.3.10 Empty cell, rinse with deionized water, and fill with next sample.

1.3.11 Analyze the remaining samples in the same manner.

1.3.12 After the last sample, press Save, then Disconnect.

1.3.13 Clean cells and fill with deionized water.

A5. DISSOLVED OXYGEN DETERMINATION

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Signature Title Revision Date

(These instructions assume that all three reagents have already been added to a sample collected, and you are now ready to titrate a 100ml sample --*text in italics is for titrating 50ml*).

1) Select a 0.2N Sodium Thiosulfate Titration cartridge.
2) Insert a clean delivery tube into the titration cartridge.
3) Attach the cartridge to the body of the digital titrator.
4) Hold the titrator with the cartridge pointing up. Turn the delivery knob to eject air and a few drops of titrant - until there are no more bubbles present in the deliver tube or the cartridge. Reset the digit counter to 0.
5) Rinse a 100 ml *(50ml)* graduated cylinder with a small amount of sample from your sample bottle.
6) Pour 100 mls *(50ml)* of your "fixed" sample into the graduated cylinder.
7) Rinse out a a 250 ml *(100ml)* erlenmeyer flask or 250 ml *(100ml)* beaker with distilled water
8) Transfer the sample from the cylinder into the beaker. Place the beaker on a white surface. Immerse the delivery tube tip in the solution and swirl the flask (or use a magnetic stirrer) while turning the delivery knob. Titrate to a pale yellow color.
9) Add a few drops of Starch Indicator Solution - enough to turn the sample a deep blue - and swirl to mix.
10) Continue to titrate to a colorless endpoint. **Go slowly as you near the colorless point**, waiting a few seconds between each added drop. If you see any “swirl” in your sample as you are adding titrant, keep titrating. Record the digits required. Deliver another few digits, one at a time. If no further color change (or no swirl) is noted, use the first recorded number as your value. Otherwise, use the last digit at which a color change was noted.

<u>11) Calculate mg/l of DO:</u>

DO = Digits Required x .02 for 100 ml samples.

DO = Digits Required x .04 for 50 ml samples.

Troubleshooting the DO analysis procedure.

1) Some brown particles may remain when sample is ready for titration. This can cause variable results because chemicals in the sample are now unevenly concentrated.

TO AVOID THIS: Carefully observe the BOD bottle after adding all three reagents. If particles are visible, or if there is a deposit on the bottom of the bottle, try shaking the bottle to dissolve any remaining solid matter. If this doesn't work, use a plastic, teflon or stainless steel stirring rod or spatula to stir up the bottom sediments. This should allow the acid in the solution to fully dissolve the particles. You are then ready to titrate.

NOTE: Make sure you rinse the stirring rod well after trying this, to avoid corrosion of your utensil.

2) If your results seem totally off-base, check to see you are using the correct Sodium Thiosulfate cartridge. Some folks have been known to use a sulfuric acid cartridge by mistake.

3) Sometimes an old cartridge can give an inaccurate reading, particularly if it has been left uncapped and allowed to evaporate somewhat. If you suspect the cartridge, try using a new one.

4) If you are consistently low on quality control samples, you may be measuring too small a sample. Make sure that the meniscus in the graduated cylinder is resting on top of the mark, not at the mark. You may also be stopping the titration too soon. Look down on your sample and beware of any swirl happening as you add a drop. As long as you see a swirl, the titration is not finished.

A6. PH DETERMINATION

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Signature Title Revision Date

The following SOP is for the Corning Model 101 pH meter. Two buffer calibration is always used. The meter is equipped with an electrode pair consisting of a glass sensing electrode and a calomel reference electrode.

1. Material Needed:

pH meter, equipped with a glass-calomel electrode pair
4M KCl (without AgCl)
Standard buffers, pH 7.00 and pH 4.01
Check Solution, pH 4.7
Magnetic Stirrer, and micro-stirbars
Thermometer

2. Set up:

a) Visually check the reference electrode before use to determine that it has an adequate supply of electrolyte. If not, fill to just below the fill-hole with 4M KCl without silver chloride.
b) Allow samples and buffers to adjust to room temperature.
c) Set the temperature adjustment to read the temperature of the buffers and sample(s). Record temperature in pH log book.

3. Calibration of Meter:

a) Remove the electrode pair from the storage solution. Rinse each electrode 3-4 times with pure water using a squeeze bottle. Blot (DO NOT WIPE) the electrodes dry using a Kim-Wipe.
b) Lower the electrodes into the beaker of pH 7.00 buffer, which contains a micro-stirbar. Adjust the magnetic stirrer to slowly stir the solution. Depress the RUN button on the meter. Wait for about 1 min. for the reading to stabilize. If, when stable, the display does not show 7.00 rotate the center knob of the CALIBRATION control until the display reads 7.00. Raise the electrodes rinse with water and blot dry with a Kim-Wipe.
c) Lower the electrodes into the pH 4.01 buffer solution. Adjust the stirrer to slowly stir the solution. Wait about 1 min. for the display to stabilize. If, when stable, the display does not read 4.01, use the SLOPE knob to make the display read 4.01. Raise the electrodes, rinse and blot dry as before. The slope should read between 92 and 102 percent. If the slope is outside these limits, see the Lab Supervisor.
d) Lower the electrodes into the pH 4.7 Check Solution (Note 1), stir and wait for about 1 min. or until the display is stable. This solution should read 4.70 $\pm$ 0.05. If a reading within these limits is obtained, the electrodes are functioning properly and you may proceed with the pH measurement of samples. If the Check Solution reads outside these limits, see the Lab Supervisor.
e) Record the results of the slope check and pH 4.7 check in the pH log book along with the meter name, date, time, and analyst signature.

4. Measurement of pH:

a) Sample pH is measured following the general procedures given above for calibration. The rinsed and dried (blotted) electrodes are lowered into a beaker containing enough sample to cover the bottom of the electrodes. A micro-stirbar is added and the stirrer adjusted to stir slowly. The meter must be in the RUN mode.

b) Wait 2-3 minutes or until a stable display is obtained. Record the sample ID and measured pH value into the pH log book. All entries must be dated and signed by the operator.

c) If multiple samples are to be run, the electrodes must be rinsed and dried between each sample and a duplicate sample must be analyzed for pH in each batch of 20 or fewer samples. Follow QAQC listed in Chapter 8.8.

d) If a large number of samples are to be measured, the Check Solution (pH 4.7) should be read after every 10 samples and the reading obtained entered into the log book. If the reading is outside the 4.7 $\pm$ 0.05 limits, recalibrate the electrodes and re-read the check solution. If the Check Solution still reads outside the acceptable limits, see the Lab Supervisor.

5. Shutdown:

After all samples are measured, the electrodes should be rinsed and lowered into the storage solution. Depress the STANDBY button on the meter.

Note 1: The pH 4.7 Check Solution is made by diluting 0.10 mL of 0.1 N HCl to 500 ML in a vol. flask using pure water.

A7. ALKALINITY DETERMINATION

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Signature Title Revision Date

Alkalinity is a measure of the capacity of a water to receive inputs of strong acid before suffering a marked decrease in pH. In this laboratory Alkalinity is often referred to as Acid Neutralizing Capacity, ANC. We follow EPA (1983) method 310.1. The determination results are expressed as $CaCO_3$ mg/L.

1. **Materials Needed:**

pH meter, calibrated before use; see SOP for pH for calibration
Hach Digital Titrator with 0.16 N H_2SO_4 cartridge.
Magnetic stirrer, with micro-stirbar
Beakers, 125-150 mL
Graduated cylinder, 100 mL
Deionized rinse water (pure water)

2. **Titration Startup**:

a) Set up the pH meter as described under the pH SOP. Be sure the graduated cylinder and beaker are clean and rinsed three times with deionized water. It is not necessary for the beaker to be dry if the liquid present is deionized water. Rinse the graduated cylinder with three small portions (ca 10 mL) of the sample to be measured. Carefully measure 100 mL of sample in the graduated cylinder and transfer the contents into the sample beaker. Add the stirbar and stir at medium speed; avoid stirring that produces a vortex. Depress the RUN button on the pH meter.

b) Allow the electrodes to equilibrate with the sample until a stable reading is obtained. The initial sample pH is not needed for Alkalinity, but check to see if pH is requested for the sample. If so, record the initial pH in the Alkalinity log book, along with the sample ID.

c) Check the digital titrator to be sure that the appropriate cartridge is in place (0.16 N acid) and that the plunger is contact with the plug in the cartridge and that air bubbles are out of the dispensing tip. Turn the unit with the delivery tip up to check for air in the cartridge. If present, dispense with the tip held upward until the air is expelled. Then, turn the delivery knob until titrant flows freely from the tip. Rinse the delivery tip thoroughly with pure water and set the counter to zero. The titrator is now ready for use.

3**. Titration:**

a) Add 0.16 N acid from the digital titrator by rotating the end knob. Add acid until the pH reaches pH 4.5 (Note 1). Record the exact pH to two decimal places and the number of digits required to reach pH 4.5 in the Alkalinity log book. If the digits are equal to or greater than 200 (20 mg $CaCO_3$/L) then calculate alkalinity with the high alkalinity calculations, below, skip step b, and continue with step c.

b) If digits are less than 200 to a pH of 4.5 then record digits to 4.5 in log book under A, and carefully continue addition of acid until the sample pH reaches pH 4.2 (Note 1). Record the exact pH value to two decimal places and the <u>total digits</u> added to pH 4.2 in the Alkalinity log book.

c) Carefully rinse the beakers, stir-bar, titration tip, and graduated cylinder with pure water before

analysis of the next sample. Follow QAQC protocols listed in Chapter 8.8.

4. Calculations (100 mL sample):

High alkalinity samples (greater than 20 mg/L):

digits*0.1= mg $CaCO_3$/L

Low alkalinity samples (less than 20 mg/L):

A = digits required to reach pH 4.5
B = total digits to reach pH 4.2

(2A - B) x 0.1 = mg $CaCO_3$/L

Note 1: For low alkalinity samples it is not necessary to reach exactly pH 4.5 for the initial end-point. An initial end-point within 0.2 pH units is acceptable, but the actual pH reached must be accurately recorded to two decimal points. The second pH reached MUST BE EXACTLY 0.3 pH UNITS LOWER. For example, if the first pH reached was pH 4.57, the second value must be carefully brought to pH 4.27.

APPENDIX B. EXAMPLE LABELS, AND FORMS

Figure B1. Sample Identification Tag Example

Environmental Analysis Lab, UMass Amherst **EAL ID#** Phone 413-545-5979			
Client or Company Name	**Circle Analyses Requested**		
	pH		
Sample Location:	Alk		
	TP		
Time (HH:MM am/pm; Date (MM/DD/YY)	Chl *a*		
	D.O.		
Sample Type:	Color		
	Cond.		
Sampler Signature:			
Comments:	Preservatives:		

Figure B2. Chain-of-Custody Document

CHAIN-OF-CUSTODY

Environmental Analysis Lab, University of Massachusetts Amherst, 413-545-5979

Client: Sampler's Signature:_____

Sample ID	Station Location	Date, Time	Type	#Bottles	Analyses	Comments

Relinquished by: Signature	Received by: Signature	Date/Time
Relinquished by: Signature	Received by: Signature	Date/Time
Relinquished by: Signature	Received by: Signature	Date/Time
Relinquished by: Signature	Received @Lab: Signature	Date/Time

Distribution: Original--Accompany Shipment, File at EAL. Duplicate--Accompany Shipment, Return to Client

Comments:

Figure B3. Analysis Request Form

Analysis Request

Environmental Analysis Lab, University of Massachusetts Amherst, Phone: 413-545-5979

Client: Samplers Signature:
Certified Analyses Requested? Yes No Chain-of-Custody Requested? Yes No

Sample ID	Station Location	Date, Time	Type	#Bottles	Analyses	Comments/Preservatives

Relinquished by: Signature	Received by: Signature	Date/Time
Relinquished by: Signature	Received by: Signature	Date/Time
Relinquished by: Signature	Received by: Signature	Date/Time
Relinquished by: Signature	Received @Lab: Signature	Date/Time

Comments:

SMAST

COASTAL SYSTEMS PROGRAM
Analytical Facility
Laboratory Quality Assurance Plan

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This Document has been compiled by the University of Massachusetts – Dartmouth
School of Marine Science and Technology (SMAST)
Coastal Systems Laboratory

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Coastal Systems Analytical Facility
Summary of Laboratory Quality Assurance Plan

Revised January 13, 2020

Coastal Systems Program

Dr. Brian L. Howes, Program Manager
School for Marine Science and Technology

Overview:
The Coastal Systems Program was established to provide research quality information to address the growing ecological degradation of coastal ecosystems. The goal of the Program is to fill the niche between basic and applied research to provide high quality scientific support for management of coastal ecosystems (bays, harbors, wetlands and watersheds). The Coastal Systems Program is one of five research area programs within SMAST which uses state-of-the-art instrumentation and methodologies to address specific coastal problems, while simultaneously producing new knowledge of the functioning of coastal systems. Staff seek projects which allow new applications of current basic research techniques and explore new approaches for addressing growing coastal issues in 4 major program areas: shallow water ecosystems, wetlands, groundwater and innovative wastewater technologies.

The Coastal Systems Program maintains staff scientists and research support personnel who are supplemented on a project basis by scientists from academic and research institutions throughout the U.S. The laboratory maintains the capability of analyzing a wide-spectrum of biogeochemical parameters relating to water quality, nutrient related ecological health and coastal pollution. In addition, a variety of autonomous field instruments for biological and chemical rate measurements required for determining nutrient thresholds of coastal systems are available. The laboratory also provides technical and analytical support to water quality monitoring programs and peripheral research efforts. The Center trains environmental scientists at the undergraduate, graduate and professional levels using ongoing projects as "real-life" classrooms.

SMAST staff have played central roles in ecological monitoring programs in Massachusetts Bay (MWRA), Buzzards Bay, Nantucket Harbor, Montego Bay etc. In addition, SMAST scientists have on-going monitoring programs of wetlands and coastal embayments within the region from which to conduct comparative assessments relative to the recovery or decline of embayments of interest. These programs include a continuous (30yr) record of production and species distribution in the Great Sippewissett Saltmarsh. SMAST is the logistical, educational and data synthesis center for water quality monitoring throughout S.E. Massachusetts. In addition to regional studies, Coastal Systems Program personnel conduct coastal research world-wide with studies in Antarctica to the central Pacific Ocean and the Black Sea. SMAST scientists provide a reservoir of world-class expertise that can be brought in to address specific program needs. SMAST laboratory capabilities include the following: coastal ecosystem level ecology, wetlands ecology, fish population biology, ornithology, phytoplankton ecology, benthic ecology, biogeochemistry, marine physiology (toxics), eelgrass ecology, data management, physical oceanography and hydrology. SMAST has full computing, GIS and modeling capabilities, which provide integrated data-management. In addition, SMAST is an academic center, which provides undergraduate and graduate research programs.

Program Areas:
Coastal Waters -- These systems range from small bays and harbors to larger embayments (Buzzards Bay, Montego Bay, Peconic Bay) to more open continental shelf waters (to ca. 300 meters). The Center and its associated laboratories will have the capability to conduct watershed loading analyses and impacts of both biogeochemical (organic matter, nutrients etc) and toxic materials on receiving waters. Whole ecosystem analysis is required for evaluation of nutrient loading rates, siting of discharges and development of conservation and remediation plans. This includes large scale water quality programs covering more than 50 embayments in S.E. Massachusetts as well as international water quality programs. The research team has proven capabilities in producing integrated evaluations of existing systems and predictive assessments of future conditions.

Wetlands -- This area focuses on both saltwater and freshwater wetland ecology and hydrology. The Program has played a central role in evaluating the impacts of nutrients and wastewater on all ecological levels (bacteria to birds) and the effects of surface and sub-surface hydrology on wetland plant growth and development. Most recently the research staff have been conducting research into the role of coastal wetlands in preventing the negative impacts of nutrient loading to coastal waters through the interception of groundwater transported nutrients from coastal development. We have also collaborated with State and local governments in an effort to document the negative impacts of tidal restrictions on coastal wetlands and to recommend solutions to restore ecological health to these habitats.

Groundwater -- Groundwater is the major pathway of nutrient and chemical contamination of coastal waters. The new field of biological transformation of contaminants in groundwater systems is critical for both understanding transport and designing remediation. SMAST and associated scientists have extensive expertise in contaminant transport and transformation in groundwater systems.

Innovative Wastewater Technologies -- Wastewater is the major source of nutrient-related water quality problems in coastal waters world-wide. Innovative technologies are currently being developed which remove nutrients before wastewater discharge. Center staff have been working for almost a decade evaluating tertiary treatment systems of intermediate scale and on-site denitrifying septic systems. In non-urban coastal regions on-site septic discharges account for more than half of the terrestrial nutrient inputs to receiving waters. Ecological management of coastal systems requires a thorough understanding of the functioning and efficiency of these technologies.

Analytical Facility:
The biogeochemistry laboratory of the Coastal Systems Program has been conducting research on coastal ecosystems for ca. 20 years. It provides the analytical capability required for quantitative ecological research in the coastal zone. It is part of the School of Marine Science and Technology, University of Massachusetts, a new marine research institute located on Clark's Point in New Bedford, Mass. Our analytical laboratory supports our research programs funded by NSF, EPA, NOAA-Sea Grant, NOAA-Estuarine Programs,

DEP, MCZM, EOEA Massachusetts Watershed Initiative, Mass Bays Program, and various states and cities. In addition, “public sector” projects are occasionally supported analytically or by specialists in ecological processes related to environmental health. The techniques and approaches employed are generally state-of-art, basic research methods.

The Coastal Systems Program maintains on-site capabilities for laboratory chemical analyses, ecological rate measurements, remotely deployed moored instrumentation and personnel and equipment required for a suite of field sampling designs.

We investigate nutrient related water quality issues, providing information fundamental to developing data based management plans for the protection of our nearshore coastal waters. Using a coupled watershed to coastal waters approach, studies involve investigation of nutrient inputs, transformations and losses from their sources to their ultimate fate and impact on the marine environment. These studies include a significant focus on wetlands ecology (existing at the interface between watersheds and their associated water bodies) and innovative waste treatment technologies to minimize the potential impact of human waste disposal on coastal ecological health. Communities representing over half of the coastal embayments in Massachusetts currently use data generated by our laboratory for management and policy decisions regarding restoration and remediation of affected sites, modeling of environmental systems and monitoring. Specialized laboratory and field instrumentation allows us to monitor environmental parameters in wastewater and natural waters (both fresh and, salt, surface and ground). Such parameters include inorganic and organic nutrients, plant pigments, environmental gasses (O_2 N_2, N_2O, CO_2, etc.), sulfur species and physical parameters such as light intensity, tide stage, current speed-direction, temperature and salinity.

Nutrients are measured using a variety of state-of-the-art methods and instruments. The Facility is continually upgrading its instrumentation to provide high quality water quality results at low cost. Due to the large number of samples processed, many instruments are interfaced with computers to allow greater accuracy and ease of data transfer. Specialized instrumentation, such as auto-analyzers, fluorometers, gas chromatographs and spectrophotometers are utilized to provide highly sensitive measurements of various nutrients and gases frequently found at very low concentrations in the natural environment. All analytical methods have the required sensitivity for detection of analytes in natural waters (salt and fresh). We currently run over 30,000 chemical assays each year.

The Coastal Systems Analytical Facility is situated within the School for Marine Science and Technology (SMAST), UMass Dartmouth, a new state-of-the-art marine laboratory located on Clark's Point, New Bedford. SMAST consists of 16 laboratories supporting over 50 research and teaching faculty and their technical staff and students. SMAST also supports a fabrication shop and a state-of-the-art acoustic-optical test facility.

The Coastal Systems Program within SMAST is fully equipped for the field and analytical requirements of coastal research including: automated nutrient analyzers (LACHAT), field (SeaTech) fluorometers, ion (Dionex) & gas (ECD, TCD, FID) chromatographs, CTD's (Seabird), LECO Total Sulfur Analyzer, water and sediment sampling gear, field automated samplers (ISCO), Marsh-McBurney electromagnetic flow meters, field moorings for oxygen, temperature, salinity, depth (Endeco/YSI) and current (Sontek), and 4 small coastal vessels

(15’ to 22’). Specific to nutrient related research are the automated nutrient analyzers, Turner AU10 laboratory fluorometer, Radiometer SB10 potentiometric oxygen titrator, Buchler Chloridometer, Eh and pH electrodes and meters, scanning spectrophotometers (Spectronic 2000 & Spectronic 801), CO_2 Infrared analyzers, Perkin Elmer PE2400 automated CHN analyzer, plus the full suite of analytical balances, drying ovens, autoclaves, walk-in freezers & refrigerators, radiochemistry laboratory, glove boxes, and Niskin and pump samplers. All field and laboratory equipment is available to support data collection for basic and applied research projects and to support environmental management of coastal systems.

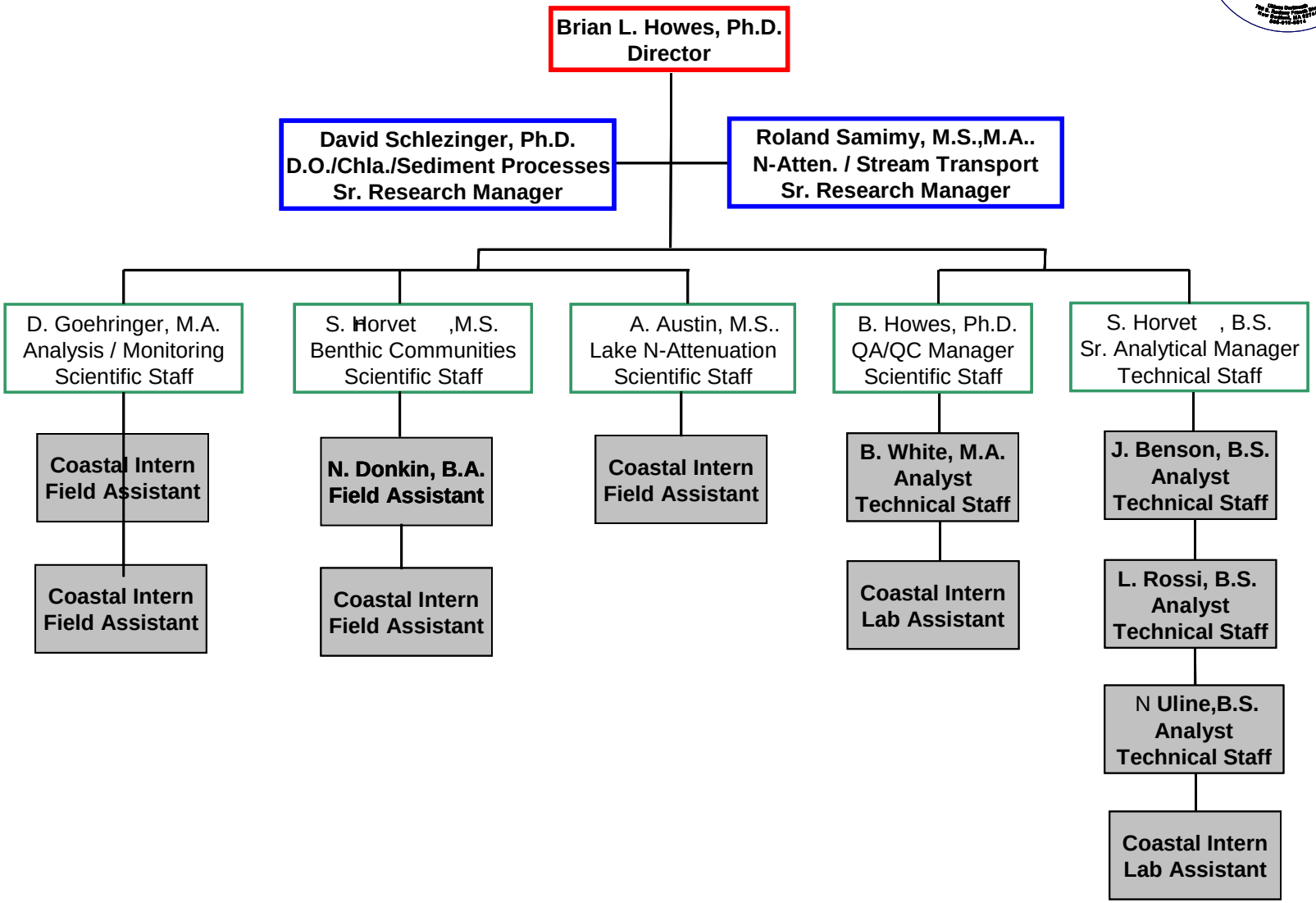
1. Laboratory Organization and Responsibility

a. Include a chart or table showing the laboratory organization and lines of responsibility, including QA managers:

The Coastal Systems Program is a year-round research program supported by full time analytical facility. The staff is composed of professional staff, graduate students and laboratory assistants. Due to the seasonal nature of the projects, which the Program undertakes, additional field assistants are brought on from May – September each year. All personnel assist in field projects as required. The laboratory organizational chart, the year-round personnel and their programmatic positions and primary responsibilities are given below:

Coastal Systems Program Organizational Structure

SMAST
University of Massachusetts Dartmouth
The School for Marine Science and Technology



b. Key individuals who are responsible for ensuring the production of valid measurements and the routine assessment of measurement systems for precision and accuracy (e.g., the persons responsible for internal audits and reviews of the implementation of the plan and its requirements):

All Coastal Systems Program (CSP) full-time personnel are responsible at some level for QA, maintenance of instrumentation and routine assessment of the precision and accuracy relative to the assays which they perform. The full scientific staff, with brief descriptions of their areas of expertise is given in the next section below. Key personnel responsible for internal audits and reviews of different areas of CSP operations are senior staff, all with graduate degrees related to the area of analytical field for which they are responsible. In addition, they all have several years (generally 10 or more) of relevant experience. The duties specifically include the maintenance and calibration of instrumentation within their technical field. These personnel are as follows:

Dr. Brian L. Howes: overall QA goals and implementation of the plan.

Dr. Brian L. Howes: analytical QA Officer with day-to-day laboratory QA oversight and assessment relative to nutrient chemistries.

Ms. Sara Horvet: oversees general nutrient chemistry activities and works with Dr. Howes on QA issues.

Dr. David R. Schlezinger: QA issues and operations related to dissolved oxygen and moored autonomous instrumentation.

Mr. Roland Samimy: QA issues and operations related to surface water flow instrumentation.

Seasonal Personnel:
Summer graduate and undergraduate interns are hired for general support during the intense data collection period, May – September. The general support personnel work under the direct and immediate supervision of CSP Technical Leads and Specialists. The selection of the interns is based on competitive review of applications and their having suitable basic science backgrounds to be able to assist senior scientists with field data collection, sample collection or laboratory work. Roles vary based upon program needs.

c. Job descriptions of the personnel and training to keep personnel updated on regulations and methodology, and proficiency of laboratory personnel for the methods they perform:

Coastal Systems Program personnel have analytical and QA responsibilities apportioned in direct relation to their training and expertise. Senior staff are directly responsible for quality assurance procedures and implementation of this plan. They

have graduate degrees and have developed and/or extensively used the analytical protocols for which they currently have QA responsibility. Senior staff have over 10 years (many more than 18 yrs) of direct experience in their related area. CSP is part of the graduate School for Marine Science and Technology. CSP staff take part in training programs offered on lab analytical methodologies and are required to keep abreast of new developments in instrumentation and assays. Each person has a job description on file with UMD Human Resources and at SMAST.

Technical staff are trained on CSP procedures and protocols within the laboratory. They do not conduct assays until they show competence in different procedural steps. The Laboratory Manager and Sr. Analyst have several years of training in their respective assays, training attained by working with senior staff and skilled analytical chemists. All other Technical staff work directly with the Manager and senior staff (who provide constant oversight during the performance of tasks). The Technical staff perform sample prep and laboratory maintenance (glassware prep, sample filtration, Xeroxing, etc).

In addition to training and oversight by CSP senior personnel, all personnel are given laboratory safety training with appropriate laboratory procedures by the University Safety Office. This training is supplemented by a specific CSP Safety workshop. Both the CSP Program Manager and Laboratory Manager have HAZWOPER training (40 hr course).

Scientific Staff and Job Descriptions:

Senior Staff:
Director Coastal Systems Programt: Dr. Brian Howes, overall programmatic oversight, data review and synthesis, Coastal Ecologist/Biogeochemist.

Technical Lead - Moorings/Sediment Processes: Dr. David Schlezinger, oversight of field mooring programs and sediment process level studies, data review and synthesis. Biogeochemist/Instrumentation.

Technical Lead – Stream Transport & Natural Attenuation Program: Mr. Roland Samimy (M.A., M.S.), oversight and conduct of stream gauging, nutrient and bacterial sampling, data review & synthesis. Hydrologist/Environmental Policy Specialist

Laboratory QC Manager, Wetlands Scientist & Bacterial Assessment Technical Specialist: Dr. Brian Howes, day-to-day oversight of laboratory quality assurance, QA/QC synthesis and data management and performance of data integration and synthesis on bacterial contamination in coastal waters.

Laboratory Senior Analyst & Monitoring Liaison: Ms. Dale Goehringer (M.A.), nutrient analyst and liaison with embayment and lake monitoring programs. Wetland Ecologist/Analyst.

Technical Staff:
Laboratory Manager: Ms. Sara Horvet, coordination and conduct of laboratory analyses, field nutrient sampling. Sr. Analyst/Coordinator.

Laboratory Analyst & Field Operations Manager (Natural Attenuation/Lakes): Nick Uline, performance of POC/PON elemental analysis and oversight of wetland and lake projects relating to nitrogen cycling. Biogeochemist/Analyst.

Sr. Laboratory Analyst: Ms. Jennifer Benson, conduct of laboratory assays and water column sampling. Analyst.

Laboratory Analyst: Ms. Shalan McDonnough, conduct of laboratory assays & water column sampling. Analyst.

Laboratory Analyst: Ms. Leanne Rossi, laboratory & field assistance. General Assistant.

2. Coastal Systems Analytical Facility

Laboratory Quality Assurance Quality Control

Excerpted from Laboratory Standard Operating Procedures

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Water Column and Pore Water Analytes

Coastal Systems Analytical Facility
Laboratory SOP: Ammonium

Introduction:
The ammonium ion (NH_4^+) is present in surface water, ground water and the sediment pore waters of both fresh water and marine ecosystems. Samples are pre-filtered through a 0.22 μm membrane filter. Analysis is by the indophenol/hypochlorite method after Scheiner (1976).

Equipment:
Spectrophotometer set at 635nm
1ml repeater Eppendorf pipette or 1ml Eppendorf pipette
Adjustable Oxford Pipette (1-5 ml)
1 Liter, 500 ml and 100 ml volumetric flasks

Quality Assurance/Quality Control

The slope, intercept and r^2 value of the standard curve are recorded each day for each set of samples analyzed. The r^2 value should be between 0.99 and 1.00.
Blanks are run on a minimum of 5% of the sample load and after any samples that are off scale.
Laboratory Duplicates are run on 10% of the samples and must be within 20% of each other.
Field duplicates are collected for 5% of the sample set and must be within 30% of each other.
Analytical duplicates are run on every sample and must be within 10% of each other.

A minimum of 5 check standards are run as samples each day for each set of samples analyzed. Check standard must be between 80 and 120% of the known standard concentration. If the check standard is not between acceptable recovery limits then the problem must be determined, corrected and the check standard re-run so that it falls between 80-120% of the standard concentration value.

Standard Additions are run on at least 5 samples each day for each set of samples analyzed. Standard Additions must be between 80 and 120% recovery to pass. If standard addition is not between acceptable recovery limits then the problem must be determined and std. addition repeated until there is 80-120% recovery. Standard additions are added to a sample such that the volume change is negligible and the spike will fall in the middle of the standard curve range.

Method Detection Limit

The Method Detection Limit (MDL) is 0.1 μM or 0.003 mg/L.

References

Standard Methods for the Examination of Water and Wastewater. 20th edition. Method 4500-NH3-F.

Scheiner, D. 1976. Determination of ammonia and kjeldahl nitrogen by indophenol method. Water Research, 10:31-36.

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Coastal Systems Analytical Facility
Laboratory SOP: Nitrate+Nitrite

Introduction:
Nitrate+nitrite (NO_3+NO_2) are present in surface water, ground water and the sediment pore waters of both fresh water and marine ecosystems. Samples are pre-filtered through a 0.22 μm membrane filter. Analysis is by an auto-analyzer (Lachat) using copperized cadmium reduction and colorimetric assay.

Equipment:
Lachat QuikChem 8000 with filter for 520nm wavelength
1 liter volumetric flasks
2 liter wide mouth plastic bottle
Adjustable Eppendorf Pipette

Quality Assurance/Quality Control

Internally programmed system QA/QC:
Standard curve must have an r value of .9950 or greater.
Residuals greater then 10% are flagged.
Check standards are run every 6 samples and must be within 10% of expected values.
A column check using a known NO_2 standard is run at the beginning of the tray and must give an efficiency greater than 88%.
Field duplicates are collected for 5% of the sample set and must be within 30% of each other.
Lab duplicates are run every fifth sample and must be with 20% of each other for the system to be in control.
Blanks are run twice per sample set.
Standard additions are run every ninth sample and must have recovery of 80-120% to pass.

Method	0-10uM Method	0-50uM Method	0-700uM Method
Sample volume (ml)	5ml	5ml	5ml
Spike: ml of 5,000uM stock NO_3 to add	2.5ul Gives 5uM spike	10ul Gives 10uM spike	100ul Gives 100uM spike

If standard addition is not between acceptable recovery limits then the analysis is out of control and the problem must be determined and std. addition repeated until there is 80-120% recovery.
Standard additions are added to a sample such that the volume change is negligible

and the spike will fall in the middle of the standard curve range.

Method Detection Limit

The Method Detection Limit (MDL) is 0.25uM or 0.0035 mg/L.

Interferences

Sample turbidity, concentrations of iron, copper or other metals above several mg/L, oil and grease and residual chlorine can interfere with this analysis. Sample turbidity can be eliminated by filtration and by settling. Metal interferences can be removed by the addition of EDTA into the buffer. Oil and grease can be removed by distillation.

References

Standard Methods for the Examination of Water and Wastewater, 19th edition. Method 4500-NO3-F.

Lachat Autoanalysis procedures based upon the following techniques:
Wood, E., F. Armstrong and F. Richards. 1967. Determination of nitrate in sea water by cadmium copper reduction to nitrite. J. Mar. Biol. Ass. U.K. 47:23-31.

Bendschneider, K. and R. Robinson. 1952. A new spectrophotometric method for the determination of nitrite in seawater. J. Mar. Res. 11:87-96.

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Coastal Systems Analytical Facility
Laboratory SOP: Total Nitrogen/Total Dissolved Nitrogen

Introduction:
Total nitrogen/total dissolved nitrogen in natural waters is analyzed by persulfate digestion as modified from Lachat Instruments Division of Zellweger Analytics Inc. Samples for total dissolved nitrogen are filtered through a 0.22 μm membrane filter. Both filtered and unfiltered samples can be oxidized to nitrate and then analyzed using the nitrate/nitrite method described in this manual.

Equipment:
Autoclave
Autoclavable 25 x 125 mm screw cap test tubes
1 liter class A Volumetric Flasks
Transfer Pipettes (disposable), 10-25 ml
Adjustable Eppendorf Pipettes, 100-1000 uL

Quality Assurance/Quality Control
Method Detection Limit

The Method Detection Limit (MDL) is 0.4 μM or 0.005 mg/L.

Blanks:
3 oxidizer and 2 MilliQ blanks are digested with each sample set.
Field duplicates are collected for 5% of the sample set and must be within 30% of each other.
Standard additions are run on 10% of samples and must have recovery of 80-120% to pass.

References

Standard Methods for the Examination of Water and Wastewater. 19th edition. Method 4500-Norg.

D'Elia, C.F., P.A. Stuedler and N. Corwin. 1977. Determination of total nitrogen in aqueous samples using persulfate digestion. Limnol. Oceanogr. 22: 760-764.

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Coastal System Analytical Facility
Laboratory SOP: Particulate Organic Carbon and Nitrogen Analysis

Introduction:
Particulate organic carbon and nitrogen (PC/PN) determinations are made on sediments, algae, organic solids, and filtered suspended solids, with a Perkin Elmer 2400 elemental analyzer. The analyzer uses the micro-Dumas combustion technique where solids are combusted with oxygen in the presence of a catalyst, separated, and content determined by thermal conductivity (Kirsten, 1983). This is the method of choice in all aquatic research, both fresh and salt water.

Equipment:
PE 2400 CHN elemental analyzer
PE AD-6 ultramicroautobalance (±1 g)
Convection oven (60 °C)
Muffle furnace (485 °C)
Centrifuge
Vacuum filtration setup
Graduated cylinders (500 mL)
Plastic snap closure petri dishes (4.5 cm)
Adjustable pipette
Glass grinding rod

Quality Assurance/Quality Control

The elemental analyzer is calibrated with blank pre-combusted filters and with acetanilide standard. This is equivalent to "making" the standards in the same matrix as the sample. Acetanilide is the analytical community choice for CHN standards and while it is routinely used, periodically certified standard coal is used for confirmation. In addition, differing amounts of standard are routinely assayed. Blanks and standards are run after every 8 samples. Precision is usually < ± 10 ug.

Field duplicates are collected for 5% of the sample set and should be within 30% of each other.

Method Detection Limit

The method detection limit for this assay is 3 μg.

References
EPA Method 440.0
Kirsten, W. 1983. Organic Elemental Analysis: Ultramicro, Micro, and Trace Methods. Academic Press/Harcourt Brace Jovanovich, NY.
Perkin-Elmer Model 2400 CHN Analyzer Technical Manual.

3. Field Sampling Procedures-

a. Description of required preservation, proper containers, correct sample container cleaning procedures, sample holding times from collection to analysis, and sample shipping and storage conditions is presented in the Coastal Systems Program Laboratory Standard Operating Procedures

Table 3-1 Nutrient and Bacteria Sample Holding and Preservation Methods

Parameter	Matrix[a]	Sample Volume/ Container	Maximum Holding Time	Processing/ Preservation	Units
Nutrients:					
Nitrate + Nitrite	1	60 ml polyethylene acid-washed	28 days (frozen)	Field filter, store dark at -20°C in Lab[b]	μg/l
Ammonium	1	60 ml polyethylene acid-washed	24 hours (4C)	Field filter, store on ice in dark	μg/l
Total dissolved N	1	1L polyethylene acid-washed	28 days (frozen)	Field filter, store on ice in dark	μg/l
Particulate C& N	1	1L polyethylene acid-washed	28 days	Collect on ashed Filter in Lab, Dry and Store in dessicator	μg/l

[a] Matrix 1 = Freshwater
[b] USGS Central Laboratory had determined that freezing filtered samples for nitrate+nitrite is acceptable, without acidification (Avanzino and Kennedy 1993).

b. Chain of Custody Forms.

Copies of Chain of Custody Forms are in available from the Coastal Systems Laboratory (Lab 114).

c. Sample Check-in when they arrive at the lab for proper containers, temperature and proper preservation (e.g., pH, chlorine residual).

All samples assayed by the Coastal Systems Analytical Facility at SMAST or its collaborating laboratories (eg. Barnstable County Department of Health and Environment Laboratory), require completed Chain of Custody forms before accepting samples. Upon arrival at the CSP Facility, samples are cross-checked to COC's by laboratory personnel under the supervision of the Laboratory Manager and with the person delivering the samples. Both the original COC and a copy are signed by the Lab Manager. The original of the form is then given to the CSP Technical Specialist or

external client and the copy is kept on file in the Analytical Facility (by the Lab Manager, Rm 114).

4. Laboratory Sample Handling Procedures

a. Data Handling

The CSP Analytical Facility uses bound laboratory note books, filled out in ink, with entries dated and signed by the appropriate analyst. A secure, password protected, electronic data base is also used for parallel storage of data (i.e. both are used for each data set, but the hardcopy data files only contain raw analytical data).

b. Storage of Unprocessed and Processed Samples:

Processed and unprocessed individually labeled samples are sorted by project, put into labeled closed polyethlene containers and stored either in a walk-in cold room set at 4°C or a walk-in freezer set at –20°C. Both the cold room and freezer are located away from the analytical laboratory. Both of these units have recording temperature displays and temperature alarms. Individual freezers are used for "special" samples (eg. Wastewater or chlorophyll assay). Cross contamination of samples is not generally an issue with embayment samples as they are typically of the same relative type and concentration. The CSP Laboratory does not typically handle high concentration wastes stream samples, as its assays are geared to natural waters.

c. Sample Storage/Assay Times:

All short (<7 day) holding time assays are run within 24 hours of entering the laboratory, with the exception of bacteria samples (<6 hr) and redox sensitive assays which are assayed immediately upon collection. This practice requires coordination between field and laboratory personnel, but is routine given its nearly 2 decades of implementation. Samples with longer holding times (>7 days) are tracked based upon chain of custody forms.

d. Maintenance of Sample Inegrity, (e.g., by tracking samples from receipt by laboratory through analysis to disposal);

Samples are accepted with a chain of custody form. The samples are then placed within closed polyethene boxes by project (labeled on the outside of the box. Each bottle is also individually labeled with the project id, date and sample specific information. Records of samples to be assayed are kept to guide assay prioritization. When samples are assayed (generally in batches by project), they are marked "run", the data are placed in the data books and in electronic data base and cross-checked to the original COC forms. The residual sample is returned to holding and kept until the final QA review and acceptance of the data. Sample disposal is conducted jointly by a team consisting of the Laboratory Manager, Analytical QA Officer and CSP Program Manager.

All sample and waste disposal is performed to EPA procedures as directed by the University of Massachusetts Dartmouth's Safety Officer. Procedures are routinely reviewed and final disposal if performed by the UMD Safety Office.

e. Criteria for rejection of samples which do not meet shipping, holding time and/or preservation requirements and procedures for notification of sample originators.

Samples which do not have proper Chain of Custody forms are not accepted into the laboratory. Any samples which arrive at the laboratory that appear to be compromised in any way (beyond holding time, preservation inadequate to ensure sample integrity, unfiltered dissolved nutrient samples, etc) are set aside. The CSP Program Manager or Analytical QA Manager or appropriate senior staff (specific to technical expertise required to judge) are consulted by the Laboratory Manager or Sr. Analyst. If the sample then judged to be compromised the appropriate CSP field personnel, NGO Director, project manager (research, private firm, agency) are notified by telephone immediately. The general laboratory policy is to NOT run compromised samples but to re-collect them appropriately. "It is better to have No Data, than Bad Data."

1. Calibration Procedures for Chemistry

a. Type of calibration used for each method and frequency of use;

Laboratory analytical instruments are calibrated for each analytical run and standards are run as part of the Facility's analytical process. The instruments are also serviced by factory representatives if they fall outside of factory specifications. Balances and spectrophotometers are checked weekly with calibration standards.
Details are provided in the specific analytical procedures documented in the Coastal Systems Program Laboratory Quality Assurance Plan.

Complete standard curves are generated for each analytical run for Ammonium and Orthophosphate. If more than a 10-fold range of concentrations are encountered in the samples, then both a high and low standard curve is created. In all cases the standards are prepared new each day and are chosen to give at least 5 points over the sample concentration range. Standards well above the sample range are not used. Nitrate+Nitrite (run in duplicate) by autoanalysis has additional standards run before and after every five (5) samples. Failure of these additional standards (run as samples) to agree within 10% of their known value halts the assay line for complete recalibration and the re-running of the last sample set.

For nitrate+nitrite, dissolved ammonium, dissolved organic nitrogen, and ortho-phosphate, non-automated assays are all run in duplicate (at a frequency of at least 10% of the samples) with a <5% tolerance between duplicates required for acceptance. After completion of analyses, remaining sample is frozen, for possible reanalysis if required. Oxygen analyses are performed within the headspace overlying the sediments using a stirred oxygen electrode. The electrode is calibrated at known

oxygen concentrations, at the incubation temperature and salinity prior to and after each measurement. The calibrated electrode reading must be within 0.2 mg/L of the standard for a headspace measurement to be accepted.

b. Standards' Source, Age, Storage, Labeling;

The standards appropriate for each assay are given in the SOP for that assay. The standards used by the CSP Laboratory are either purchased as “Certified Standards” for a particular assay (for example specific conductivity) or are constituted by the Laboratory Manager, Sr. Analyst or Senior Staff from the appropriate “reagent grade” chemicals. If the latter is performed the chemical bottle is sequestered for standard preparation only.

All standards and stock standards are labeled with the person who made them, date, concentration, and chemical content. Typically the SOP’s require daily or weekly replacement of non-stock standards. New standards are always cross-checked to old standards before use in sample assay.

c. Control Charts.

Assay specific control charts or tables are based upon the standard curves conducted for each assay. Since full standard curves are generally created each day, the control chart approach has been modified to accommodate this information. A more traditional control approach is used for the POC/PON assay that does more single standard calibration.

2. Data Reduction, Validation, Reporting and Verification

Nutrient data are recorded in laboratory notebooks at the Coastal Systems Analytical Facility (both data and chain of custody forms are filed). Sampling personnel check that all data are accurate and legible before transferring it to the monitoring coordinator and/or laboratory supporting the specific monitoring program. All data entry is checked by two laboratory personnel and the QA/QC checks are completed by the Project QA Officer (A.4 Project Organization and Responsibilities.)

The Technical Manager is asked to check that all data are accurate and legible before making copies for the Project Library. All data are reviewed by the Technical Manager. The data are stored on CD-ROM with copies held by the Analytical Facility and the Technical Manager at the SMAST Project Library. Hard copies of data are also maintained by the same persons.

a. Describe Data Reduction Process;

Raw data are maintained in duplicate notebooks. Data reduction involves the process of converting raw numbers into data that have direct chemical meaning or can be compared statistically. Calculation to concentration is done in an adjacent column for easy comparison. The calculation is based upon the regression equation calculated from the chemical standards. The results are reported in terms of concentration, as means and standard errors. All data are subject to 100% check at all stages by the Project Technical Director (B. Howes), the technical lead in N-regeneration (D. Schlezinger), the Coastal Systems Lab Manager (Sara Horvet), and the Lab Coordinator for water quality monitoring (D. Goehringer). All data reported are reviewed to check for errors in transcription, calculation, or computer input. If data points are judged to be aberrant, the reserved sample is reanalyzed. Data are also reviewed for adherence to analytical protocols and to pre-established criteria (e.g., holding times, surrogate recoveries, initial and continuing calibration, matrix spikes, laboratory duplicates, blank contamination). Students t-test for paired samples, analysis of variance, are used for interpretation. Data are transcribed only for the statistical analysis and each point is checked for accuracy. Sample logs associated with field and laboratory custody and tracking are maintained in the project files.

b. Data Evaluation Process;

For data to be reported to CSP collaborative projects requires standard data entry checks by two laboratory personnel and the QA/QC checks are completed by the CSP QA Manager. After clearing these checks all data are then reviewed jointly by the CSP Program Manager and the Laboratory Manager for assessment of biogeochemical, ecological and sampling issues. This latter review generally suggests potential problems with sampling methodology or contamination not part of Laboratory QA/QC evaluation.

c. Reporting Procedures, including Format;

Data reports are made generally via electronic delivery of digitial data sets (typically Excel Spreadsheets). Issues of contamination, sample handling, etc. are made both in a column in the spreadsheet paired to the specific sample and in textual form in the cover letter. Significant issues or “interesting” results are discussed with the recipient project manager (by telephone) either by the CSP Program Manager or the Laboratory Manager or the QA Manager.

d. Procedure for Data Corrections.

If data errors are found (transcription, calculation, etc) on reported data, the CSP Program Manager or Laboratory Manager contact the recipient project manager immediately. A new data report is generated and the data base is corrected (and noted). Data errors found during data review are corrected in all copies and in the database and noted. In addition, the associated personnel are contacted and notified of the error and proper procedure to be followed. Personnel involved with multiple errors are generally re-trained on the full procedure and must re-qualify for that assay.

3. Quality Control

Data quality objectives have been selected to fit with the concentrations and natural variability found within the tidal estuarine environments throughout southeastern Massachusetts. The minimum performance criteria for nutrient and bacterial sampling are given in **Table 7-1**, below.

Table 7-1. Analytical Procedures/Quality Control Samples

Parameter	Essential or Correlative data	Method	Detection Limits	QC Samples	Acceptable %Recovery
Nitrate + Nitrite-	**Essential**	**LACHAT Autoanalyzer[a]** (Cd Reduction)	**0.25 µM**	**Lab Dups** **Field Dups** **Matrix Spike**	**± 20%** **± 30%** **± 80%-120%**
Ammonium-	**Essential**	**Indophenol[b]**	**0.25 µM**	**Lab Dups** **Field Dups** **Matrix Spike**	**± 20%** **± 30%** **± 80%-120%**
Total Dissolved Nitrogen	**Essential**	**Persulfate digestion[d]**	**0.4 µM**	**Lab Dups** **Field Dups** **Matrix Spike**	**± 20%** **± 30%** **± 80%-120%**
Particulate Nitrogen & Carbon -	**Essential**	**Elemental analysis[f], 440.0**	**10 µg**	**Field Dups** **Internal Check Std**	**± 30%** **± 95%-105%**

a Standard Methods 19th Edition, Method 4500-NO3-F using Lachat Autoanalysis procedures based upon:
Wood, E., F. Armstrong and F. Richards. 1967. Determination of nitrate in sea water by cadmium copper reduction to nitrite. J. Mar. Biol. Ass. U.K. 47:23-31.
Bendschneider, K. and R. Robinson. 1952. A new spectrophotometric method for the determination of nitrite in sea water. J. Mar. Res. 11:87-96.
b Standard Methods 19th Edition, Method 4500-NH3-F and Schneider, D. 1976. Determination of ammonia and Kjeldahl nitrogen by indophenol method. Water Resources 10:31-36.
d Standard Methods 19th Edition, Method 4500-Norg-D D'Elia, C.F., P.A. Steudler and N. Corwin. 1977. Determination of total nitrogen in aqueous samples using persulfate digestion. Limnol. Oceanogr. 22:760-764.
e Parsons, T.R., Y. Maita and C. Lalli. 1989. Manual of Chemical and Biological Methods for seawater analysis. Pergamon Press, 173 pp.
f Perkin-Elmer Model 2400 CHN Analyzer Technical Manual.

a. Quality Control Procedures used for all Analytical Procedures. Parameters for chemistry include:

- **<u>instrument performance check standards</u>**
  The nutrient analyses follow standard laboratory procedures. In the analysis of field samples, for each chemical assay, a complete standard curve is generated for each analytical run (see Section 5a). In addition to the R^2 criterion, each curve is visually inspected to determine that each standard, especially the lower standards, lie close to the curve. Check standards are run after every 10-15 samples to determine that the instrument has maintained its calibration. Nitrate+Nitrite (run in duplicate) and Particulate C & N by autoanalysis have additional standards run before and after every five (5-6) samples. Failure of these additional "check" standards (run as samples) to agree within 10% of their known value halts the assay line for complete recalibration and the re-running of the last sample set. These "check" standards are used to adjust the calculated sample values for instrument efficiency. For all assays, "check" standards are run at the end of each run and compared to the standard curve.
  The usable measurement range for each chemical assay is only within the linear range as determined from least squares linear regression of laboratory standard curves. Concentrations above the linear range require standard dilutions for acceptable analysis. Since high values can be readily diluted and re-assayed the same day, the upper range of measurement is variable. Sample dilutions attempt to bring the concentration of the diluted sample into the middle of the linear range for the assay. The natural range for any analyte is typically less than 1000 fold.

- **<u>frequency of determination of method detection limit (MDL) calculations:</u>** MDL studies are conducted during the winter (January-March) of each year.

- **<u>calibration, internal and surrogate standards;</u>**
  The precision of each laboratory chemical assay needs to have been determined from duplicate assays of five standards. The field precision is from duplicate assay of five blind field duplicates. The precision is calculated as the relative percent difference (RPD). An additional estimate of precision is determined from the R^2 of the linear regression of each set of standards (N>5).

- **<u>laboratory reagent blanks;</u>**
  Calibration blanks are prepared and analyzed simultaneously with the creation of each standard curve that is created for each sample series. In addition, reagent blanks are prepared and analyzed with each new batch of reagent. These blanks are compared to previous data on blanks to evaluate the potential of contamination and the standard curve compared to previous records. If this initial blank and standard curve are deemed

satisfactory, samples using the new reagent batch can then be analyzed.

- **laboratory duplicates;**
  For nitrate+nitrite, dissolved ammonium, total dissolved nitrogen, ortho-phosphate, and total phosphorus, all are assayed in duplicate at a frequency of 10% of the samples and with a 20% tolerance between duplicates required for acceptance. After completion of analyses, the remaining sample is frozen, for possible reanalysis if required (and appropriate). For the particulate analyses (PN, PC), only field duplicates and laboratory standards can be assayed as the analysis consumes the entire sample.

- **field duplicates;**
  For nitrate+nitrite, dissolved ammonium, total dissolved nitrogen, ortho-phosphate, total phosphorus and particulate organic carbon and nitrogen, field duplicates are collected at a frequency of 5% of the samples and with a 30% tolerance between duplicates required for acceptance.

- ***quality control and proficiency testing samples;***
  Accuracy is determined from the analysis of standards for the standard curves and use of Performance and Evaluation Samples (Ultra Scientific Inc.). Accuracy is determined as the RPD of the assay of five standards run as samples within a series of analytical runs. This is compared to the RPD of five sets of Performance and Evaluation Samples. In addition, the accuracy of the method within the sample matrix is “checked” using the results and RPD of five matrix spikes experiments (standard additions) for comparison to the results and RPD of the standards, where appropriate. As available (eg. PC/PN not available, Total C is not appropriate for Particulate C evaluation), Performance and Evaluation Samples for the nutrient assays are purchased and run during the course of this study. These data are used to evaluate the accuracy of the SMAST laboratory.

- ***laboratory fortified blanks and laboratory fortified sample matrices;***
  Spiked samples are periodically analyzed as analytical checks in dissolved ammonium, nitrate+nitrite, total dissolved nitrogen, total phosphorus and ortho-phosphate assays. Spiked samples are not widely run, as the standards are made up in the same matrix as the samples. Not all analytes are amenable to matrix spikes (eg. PC/PN). Greater numbers of spiked samples are sometimes run as unknowns, similar to field duplicates. Recovery of spikes must be within 80%-120% of expected to meet QA. Spikes for PN/PC samples are not available. Therefore, PC/PN at known concentrations is added directly to filters. This is done during machine calibration as an internal QA check after every fifth field sample assayed.

- ***initial demonstrations of method capability;***
  When a new assay is brought on-line, performance studies are conducted

in a variety of matrices. These studies include MDL and interference testing. In addition, effects of matrix and pH on the rate and degree of color are generally tested, where appropriate. In addition, senior staff conduct a full literature review and discussions with other research laboratories conducting the assay.

4. Schedule of Internal Audits

March-April and October-November

5. Preventive Maintenance Procedures and Schedules

All instruments are situated, maintained and serviced as per manufacturer instructions. The major automated instruments have manufacturer service contracts. Most preventative maintenance procedures focus on cleaning after each use and maintaining the proper laboratory environment. Instruments requiring factory-level calibration are either sent to the factory for re-calibration on a 1-2 year basis (CTD) or when CSP checking calibration (generally with each use) find a calibration issue. All instruments are returned to the factory if drift or CSP calibration issues are detected. Flow meters are checked in a research quality flume and are factory calibrated. Additional, maintenance/calibration procedures are indicated within specific SOP's.

6. Corrective Action Contingencies

a. Obtaining unacceptable results from analysis of lab QC checks and personnel responsible for corrective actions:

There are (1) instrument, (2) analytical and (3) process level issues relating to unacceptable results. When unacceptable results are found the CSP Program Manager (Dr. B.L. Howes), QA Manager (Dr. B.L. Howes), and Laboratory Manager (Ms. S. Horvet), sometimes in concert with specific senior staff (see Section 1c), review the case. The review generally follows the sequence of checking the data flow from raw data entry through final data report; discussing the process and procedures followed with the analyst and supervisor; evaluation of standards; evaluation of instrument for calibration/drift/sensitivity. In addition, if samples are involved, the residual archived sample is examined unusual characteristics (for color, turbidity etc). The data report is held until QC issues are resolved and QC of sample assay results is assured.

b. Documentation of Corrective Actions.

For the 3 areas in which corrective actions may be taken:
(1) instrument - If an instrument needs repair, maintenance or recalibration this is done immediately and the action and date noted in the lab notebook and on the instrument itself.
(2) analytical – if there is an analytical problem, the corrective action (if systemic) is made to the SOP and noted in the laboratory notebook.

(3) process-level – if the QA issue stems from the analyst technique, then the analyst is re-trained in the entire procedure or re-assigned.

7. Record Keeping Procedures

a. Procedures and documentation:

Hardcopy data: raw data books, field datasheets, Chain of Custody forms are held in data notebooks by the Laboratory Manager. Analytical data sheets, field datasheets, COC's, electronic spreadsheets, calculation sheets are annotated with the personnel's name and date when they were created and modified (when and by whom). The proper filing and archiving of data and forms is continuously checked by the Laboratory Manager and the CSP Program Manager and the QA Manager. Record keeping issues are immediately brought to the attention of all staff to ensure that proper procedures are followed.

b. Security policy of electronic databases:

Electronic databases are held both on the access protected hard-drives of the Laboratory Manager and/or QA Manager. In addition, immediate backup is held on the SMAST central computer which is maintained by professional full-time CIT staff. CD copies are also generally created for larger projects.

Conductivity

DOC316.53.01199

USEPA Direct Measurement Method[1, 2]

Method 8160

0.01 µS/cm to 200.0 mS/cm

Conductivity Probe

Scope and application: For water and wastewater.

[1] USEPA accepted for reporting for Standard Method 2510-B
[2] Procedure is equivalent to Standard Method 2510-B for wastewater.

Test preparation

Instrument-specific information

This procedure is applicable to the meters and probes that are shown in Table 1. Procedures for other meters and probes can be different.

Table 1 Instrument-specific information

Meter	Probe
HQ14d portable single input, conductivity HQ30d portable single input, multi-parameter HQ40d portable dual input, multi-parameter HQ430d benchtop single input, multi-parameter HQ440d benchtop dual input, multi-parameter	IntelliCAL CDC401 Conductivity
sensION™+ MM156 portable pH/EC/DO	sensION+ 5049 multi-parameter
sensION™+ EC5 portable conductivity sensION™+ MM150 portable pH/ORP/EC	sensION+ 5048, 5059, 5060 or 5062 Conductivity
sensION™+ EC7 lab conductivity sensION™+ EC71 GLP lab conductivity sensION™+ MM374 lab dual input, pH/mV/EC/ISE sensION™+ MM378 lab dual input, pH/ISE/EC/DO	sensION+ 5070 Conductivity

Before starting

Refer to the meter documentation for meter settings and operation. Refer to probe documentation for probe preparation, maintenance and storage information.
Prepare the probe before initial use. Refer to probe documentation.
When an IntelliCAL™ probe is connected to an HQd meter, the meter automatically identifies the measurement parameter and is prepared for use.
Small differences in concentration between samples can increase the stabilization time. Make sure to condition the probe correctly. Try different stir rates to see if the stabilization time decreases.
If solutions are not at the reference temperature, the meter automatically adjusts the conductivity value to the value at the reference temperature.
Measurement errors can occur if the correct temperature correction value is not selected. Refer to Table 2 on page 3 for typical temperature correction values.
Do not touch the tip of the probe.
The cell constant is derived from the calibration standard.
Do not dilute conductivity standards and samples.
For the most accurate results with high conductivity samples, calibrate the cell constant or check the accuracy of the meter with a 111.3 mS/cm (1 Demal) certified conductivity standard.

Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

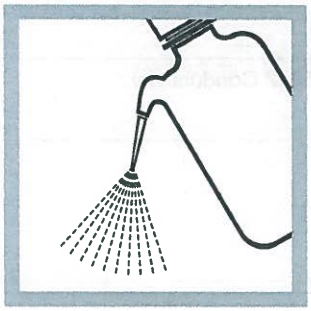
Description	Quantity
Beaker, 100 mL, polypropylene	1
Wash bottle with deionized water	1
Conductivity standard solution (refer to Recommended standards on page 5)	1

Refer to Consumables and replacement items on page 4 for order information.

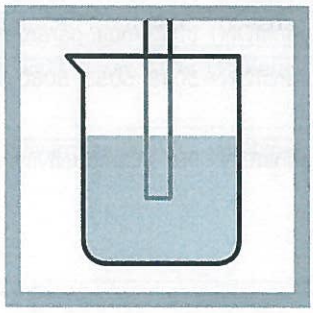
Sample collection and storage

- Collect samples in clean glass or plastic bottles.
- To preserve samples for later analysis, keep the samples at or below 6 °C (43 °F) for a minimum of 24 hours.
- Let the sample temperature increase to room temperature before analysis.

Test procedure

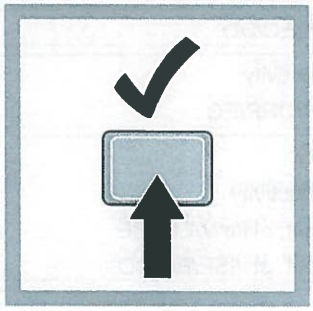


1. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

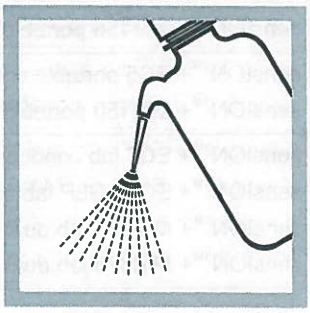


2. Laboratory test: Put the probe in a beaker that contains the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip. Stir the sample at a slow to moderate rate.
Field test: Put the probe in the sample. Move the probe up and down to remove bubbles from the electrode.

Make sure to put the temperature sensor fully in the sample.



3. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.



4. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

Conversions

Table 2 shows the conversions to change the readings on the display to other conductivity units.

Table 2 Unit conversion

From	To	Use this equation
mS/cm	µS/cm	mS/cm × 1000
µS/cm	mS/cm	µS/cm × 0.001
µS/cm	µmhos/cm	µS/cm × 1
mS/cm	mmhos/cm	mS/cm × 1
µS/cm	mg/L TDS	µS/cm × 0.64[1]
g/L TDS	mg/L TDS	g/L TDS × 1000
mS/cm	g/L TDS	mS/cm × 0.64
mg/L TDS	g/L TDS	mg/L TDS × 0.001
mg/L TDS	gpg TDS	mg/L TDS × 0.05842
g/L TDS	gpg TDS	g/L TDS × 58.42
µS/cm	ohms cm	1,000,000 ÷ µS/cm
mS/cm	ohms cm	1,000 ÷ mS/cm

Temperature correction

Table 3 shows typical temperature correction values for selected solutions from the linear temperature correction option.

Table 3 Temperature correction

Solution	Percent per °C
Ultrapure water	4.55
Salt (NaCl)	2.125
NaOH	1.72
Dilute ammonia	1.8810
10% HCl	1.325
5% sulfuric acid	0.9698

Interferences

To remove the conductivity that occurs from hydroxide ions, adjust the sample pH as follows:

1. Add 4 drops of phenolphthalein indicator solution to 50 mL of sample. The sample becomes pink.
2. Add 1 drop of gallic acid solution at a time until the pink color is gone.
3. Measure the conductivity.

Accuracy check

Standard solution method

Use the standard solution method to validate the test procedure, the reagents (if applicable) and the instrument.

Items to collect:

- Sodium chloride standard solution with a conductivity value that is near the value of typical samples

[1] TDS is an empirically-derived value from the conductivity measurement. Select a value of 0.5 for simplicity and suitability to a wide variety of waters.

1. Use the test procedure to measure the concentration of the standard solution.
2. Compare the expected result to the actual result.

Clean the probe

Clean the probe when:

- Drifting/inaccurate readings occur as a result of contamination on the sensing element or incorrect storage conditions.
- Slow response time occurs as a result of contamination on the sensing element.
- The slope is out of range as a result of contamination on the sensing element.

For general contamination, complete the steps that follow.

1. Rinse the probe with deionized water. Blot dry with a lint-free cloth.
2. If harsh contaminants are attached to the probe, polish the probe tip with a soft cloth or cotton swab to remove the contaminants.
3. Soak the probe in deionized water for 1 minute.

Method performance

The accuracy of the measurements is dependent on many factors that are related with the overall system, which includes the meter, the probe and calibration solutions. Refer to the meter or probe documentation for more information.

Summary of method

Electrolytic conductivity is the movement of ions in a solution, which makes an electrical current and is the reciprocal of the solution resistivity. The ions come from inorganic dissolved solids (e.g., chloride, nitrate, sulfate and phosphate anions and sodium, calcium, magnesium, iron and aluminum cations). Organic material such as oils, phenols, alcohols and sugars do not have sufficient conductivity for a good estimate of the concentration.

Conductivity meters measure the resistance that occurs in an area of the solution that is defined by the physical design of the probe. A voltage is applied between the electrodes, and the voltage decrease caused by the resistance of the solution is used to calculate the conductivity for each centimeter. The basic unit of measure for conductivity is the Siemen (or mho), which is the reciprocal of the ohm. Other common units for aqueous solutions are milliSiemens/cm (10^{-3} S or mS/cm) and microSiemens/cm (10^{-6} S or µS/cm).

Consumables and replacement items

HQd meters and probes

Description	Unit	Item no.
HQ14d portable single input, conductivity meter	each	HQ14D53201000
HQ30d portable single input, multi-parameter meter	each	HQ30D53000000
HQ40d portable dual input, multi-parameter meter	each	HQ40D53000000
HQ430d benchtop single input, multi-parameter meter	each	HQ430D
HQ440d benchtop dual input, multi-parameter meter	each	HQ440D
IntelliCAL™ standard conductivity probe, 1 m cable	each	CDC40101
IntelliCAL™ standard conductivity probe, 3 m cable	each	CDC40103
IntelliCAL™ rugged conductivity probe, 5 m cable	each	CDC40105
IntelliCAL™ rugged conductivity probe, 10 m cable	each	CDC40110
IntelliCAL™ rugged conductivity probe, 15 m cable	each	CDC40115
IntelliCAL™ rugged conductivity probe, 30 m cable	each	CDC40130

sensION+ meters and probes

Description	Unit	Item no.
sensION™+ EC7 lab conductivity meter	each	LPV3010.97.0002
sensION™+ EC71 GLP lab conductivity meter	each	LPV3110.97.0002
sensION™+ MM374 lab dual input, pH/mV/EC/ISE meter	each	LPV4110.97.0002
sensION™+ MM378 lab dual input, pH/ISE/EC/DO meter	each	LPV4130.97.0002
sensION™+ 5048 portable multi-parameter (pH, conductivity, ORP and temperature) probe	each	LZW5048.97.0002
sensION™+ 5049 portable multi-parameter (pH, conductivity, dissolved oxygen and temperature) probe	each	LZW5049.97.0002
sensION™+ 5059 portable multi-parameter (pH, conductivity and temperature) probe	each	LZW5059.97.0002
sensION™+ 5060 portable platinum conductivity cell probe	each	LZW5060.97.0002
sensION™+ 5062 portable titanium conductivity cell probe	each	LZW5062.97.0002
sensION™+ 5070 laboratory platinum conductivity cell probe	each	LZW5070.97.0002

Recommended standards

Description	Unit	Item no.
NaCl conductivity standards:		
Sodium chloride standard solution, 180 ± 10 mS/cm, 90 ± 1 mg/L TDS	100 mL	2307542
Sodium chloride standard solution, 1000 ± 10 mS per cm, 500 ± 5 mg/L TDS	100 mL	1440042
Sodium chloride standard solution, 1990 ± 20 mS/cm, 995 ± 10 mg/L TDS	100 mL	210542
Sodium chloride standard solution, 18,000 ± 50 mS/cm, 9000 ± 25 mg/L TDS	100 mL	2307442
KCl conductivity standards:		
KCl, 0.1 M, 12.88 mS/cm at 25 °C (77 °F)	500 mL	C20C250
KCl, 0.01 M, 1413 µS/cm at 25 °C (77 °F)	500 mL	C20C270
KCl, 0.001 M, 148 µS/cm at 25 °C (77 °F)	500 mL	C20C280
Certified conductivity standards:		
KCl, 1 Demal, 111.3 mS/cm ± 0.5% at 25 °C (77 °F)	500 mL	S51M001
KCl, 0.1 Demal, 12.85 mS/cm ± 0.35% at 25 °C (77 °F)	500 mL	S51M002
KCl, 0.01 Demal, 1408 mS/cm ± 0.5% at 25 °C (77 °F)	500 mL	S51M003
NaCl, 0.05%, 1015 µS/cm ± 0.5% at 25 °C (77 °F)	500 mL	S51M004

Optional reagents and accessories

Description	Unit	Item no.
Beaker, polypropylene, 100-mL	each	108042
Gallic acid solution	50 mL SCDB	1442326
Hydrochloric Acid Solution, 6 N, 1:1	500 mL	88449
Phenolphthalein indicator solution	15 mL SCDB	16236
Wash bottle, 125-mL	each	62014
Water, deionized	4 L	27256

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – **Call toll-free 800-227-4224**
Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
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WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

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03/2015, Edition 8

User Manual

Conductivity Probe: Model CDC40101, CDC40103, CDC40105, CDC40110, CDC40115 or CDC40130

Safety information

Precautionary labels

Read all labels and tags attached to the instrument. Personal injury or damage to the instrument could occur if not observed. A symbol on the instrument is referenced in the manual with a precautionary statement.

	Electrical equipment marked with this symbol may not be disposed of in European public disposal systems after 12 August of 2005. In conformity with European local and national regulations (EU Directive 2002/96/EC), European electrical equipment users must now return old or end-of-life equipment to the Producer for disposal at no charge to the user. ***Note:*** *For return for recycling, please contact the equipment producer or supplier for instructions on how to return end-of-life equipment, producer-supplied electrical accessories, and all auxiliary items for proper disposal.*

Specifications

Note: *Specifications are subject to change without notice.*

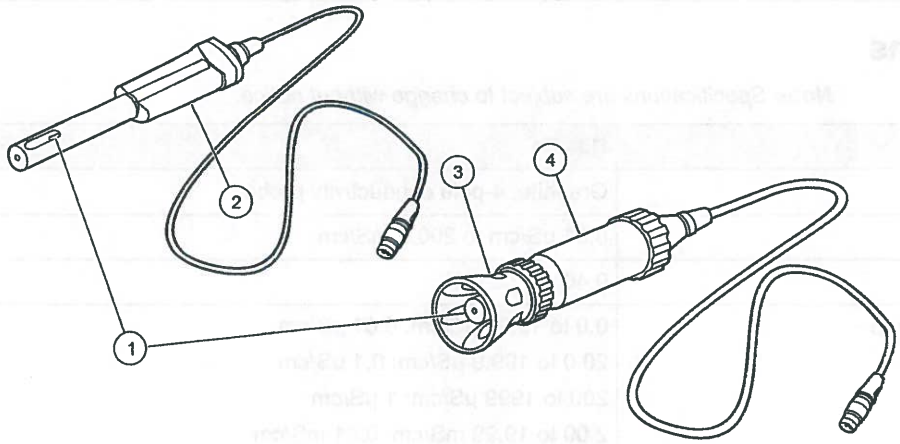
Specifications	Details
Probe type	Graphite, 4-pole conductivity probe
Conductivity range	0.01 µS/cm to 200.0 mS/cm
Cell constant	0.40 cm^{-1} ±10%
Conductivity resolution	0.0 to 19.99 µS/cm: 0.01 µS/cm 20.0 to 199.9 µS/cm: 0.1 µS/cm 200 to 1999 µS/cm: 1 µS/cm 2.00 to 19.99 mS/cm: 0.01 mS/cm 20.0 to 200.0 mS/cm: 0.1 mS/cm
Conductivity accuracy	±0.5% of reading
TDS (total dissolved solids) range	0 to 50,000 mg/L as NaCl
TDS resolution	0.0 to 19.99 mg/L: 0.01 mg/L 200 to 1999 mg/L: 1 mg/L 2.00 to 19.99 g/L: 0.01 g/L 20.0 to 50.0 g/L: 0.1 g/L
TDS accuracy	±0.5% of reading
Sample salinity range	0 to 42 (ppt) (‰)
Salinity resolution	0.01 parts per thousand (ppt) (‰)
Salinity accuracy	±1 parts per thousand (ppt) (‰)
Temperature accuracy	±0.3 °C (±0.54 °F)
Operating temperature range	-10 to 110 °C (14 to 230 °F)
Storage temperature range	5 to 40 °C (41 to 104 °F)
Minimum sample depth	45 mm (1.77 in.)
Dimensions (standard)	Diameter: 15 mm (0.59 in.) Length: 184 mm (7.24 in.) Cable length: 1 or 3 m (3.28 or 9.84 ft)

Specifications	Details
Dimensions (rugged)	Diameter: 46 mm (1.81 in.) Length: 223 mm (8.73 in.) Cable length: 5, 10, 15 or 30 m (16.40, 32.81, 49.21 or 98.42 ft)
Cable connection	M12 digital output and connector compatible with HQd meters

Product overview

The CDC401 series probe is a graphite, 4-pole conductivity probe (Figure 1). The CDC40101 or CDC40103 standard conductivity probe is available with a 1 or 3 m (3.28 or 9.84 ft) cable and is intended for laboratory use. The CDC40105, CDC40110, CDC40115 or CDC40130 rugged conductivity probe is available with a 5, 10, 15 or 30 m (16.40, 32.81, 49.21 or 98.42 ft) cable. The probe measures electrical conductivity, salinity, resistivity or total dissolved solids (TDS) in wastewater, drinking water and general applications.

Figure 1 Probe overview



1 Temperature sensor and 4-pole graphite design conductivity cell	**3** Shroud (rugged model)
2 Standard probe (1 or 3 meter cable)	**4** Rugged probe (5, 10, 15, or 30 meter cable)

Calibration

Before calibration:
The probe must have the correct service-life time stamp. Set the date and time in the meter before the probe is attached.
It is not necessary to recalibrate when moving a calibrated probe from one HQd meter to another if the additional meter is configured to use the same calibration options.
To view the current calibration, push 🗁, select View Probe Data, then select View Current Calibration.
If any two probes are connected, push the **UP** or **DOWN** arrow to change to the single display mode in order to show the Calibrate option.
If a rugged probe, remove the shroud from the probe (refer to Remove the shroud on page 8).

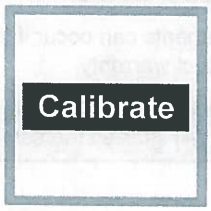
Calibration notes:

- Do not touch the tip of the probe.
- Additional conductivity standards can be selected in the Calibration Options menu.
- The cell constant is derived from the calibration standard.
- Do not dilute conductivity standards and samples.

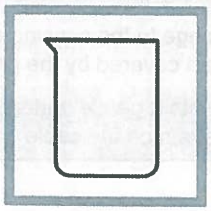
- The meter will automatically correct the calibration measurement to the selected reference temperature (20 or 25 °C) using the default NaCl-based, non-linear temperature coefficient. Settings can be changed in the CDC401 Calibration Options menu.
- The calibration is recorded in the probe and the data log. The calibration is also sent to a PC, printer or flash memory stick if connected.
- Air bubbles under the sensor tip when submerged can cause slow response or error in measurement. If bubbles are present, gently shake the probe until bubbles are removed.
- If a calibration error occurs, refer to Troubleshooting on page 9.

Calibration procedure:

1. Connect the probe to the meter. Make sure that the cable locking nut is securely connected to the meter. Turn on the meter.

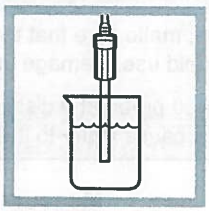


2. Push **Calibrate**. The display shows the conductivity standard solution that is necessary for calibration.



3. Add fresh conductivity standard solution to a beaker or an appropriate container.

4. Rinse the probe with deionized water. Blot dry with a lint-free cloth.



5. Put the probe in the standard solution and stir gently. Make sure that the temperature sensor is completely submerged.

6. Push **Read**. Stir gently. The display will show "Stabilizing" and a progress bar as the probe stabilizes in the standard. The display shows the standard solution value that has just been read and shows the temperature corrected value when the reading is stable.

7. Push **Done** to view the calibration summary.

8. Push **Store** to accept the calibration and return to the measurement mode. If a rugged probe, install the shroud on the probe (refer to Install the shroud on page 9).

Sample measurement

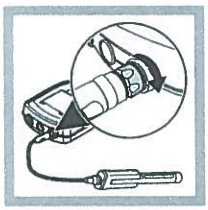
Before measurement:
The probe must have the correct service-life time stamp. Set the date and time in the meter before the probe is attached.
If complete traceability is necessary, enter a sample ID and operator ID before measurement. Refer to the HQd meter manual for more information.
To display other parameters (TDS, salinity or resistivity), push 🔧, select CDC401 Settings and then Current Method.
When using the CDC401 probe with the LDO101 probe to do auto salinity correction, set the CDC401 probe to measure salinity. Refer to Change measurement options on page 6.
Regular calibration is required for the best measurement accuracy (refer to Calibration on page 2).
If a rugged probe, make sure that the shroud is installed. Damage to the sensing elements can occur if the shroud is not installed during field use. Damage under these conditions is not covered by the product warranty.
To deploy a rugged probe at a distance, toss the probe body with a gentle underhand throw. Do not swing the probe by the cable as this may cause injury to the user, will cause severe strain on the cable and will shorten the service life of the probe.

Measurement notes:

- Do not touch the tip of the probe.
- Stabilization times with smaller concentration changes generally will be longer and can be minimized by correct stirring and conditioning. Experiment to determine the correct stir rate if necessary.
- Data is automatically stored in the data log when **Press to Read** or **Interval** is selected in the Measurement Mode. When **Continuous** is selected, data will only be stored when **Store** is selected.
- Air bubbles under the sensor tip when submerged can cause slow response or error in measurement. If bubbles are present, gently shake the probe until bubbles are removed.
- If a measurement error occurs, refer to Troubleshooting on page 9.

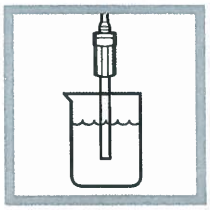
Measurement procedure:

Note: *Procedure also applies for rugged model probes.*



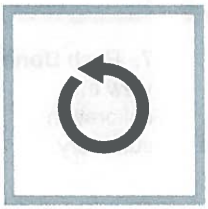
1. Connect the probe to the meter. Make sure that the cable locking nut is securely connected to the meter. Turn on the meter.

2. Rinse the probe with deionized water. Blot dry with a lint-free cloth.



3. Put the probe into the sample so that the temperature sensor is completely submerged. Do not put the probe on the bottom or sides of the container.

4. Push **Read.** The display will show "Stabilizing" and a progress bar as the probe stabilizes in the sample. The display will show the lock icon when the reading stabilizes. The measurement is automatically corrected to the selected reference temperature (20 or 25 °C).



5. Repeat steps 2 - 4 for additional measurements. When measurements are done, store the probe (refer to Storage on page 9).

Run a check standard

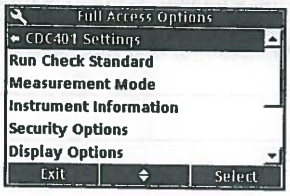
The run check standard feature validates instrument performance between sample measurements. Use the run check standard feature for periodic or user-defined interval measurements of a traceable standard solution. Set the criteria for check standards from the CDC401 Settings menu.

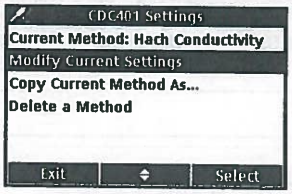
Note: *Access control must be off or a valid password must be entered before any of the check standard method options can be changed.*

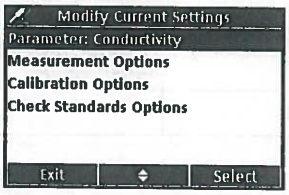
1. Push . The Full Access Options menu is shown.
2. Select Run Check Standard.
   Note: *Select the correct probe if two probes are connected to the meter.*
3. Get the standard solution shown on the display.
4. Rinse the probe with deionized water. Blot dry with a lint-free cloth.
5. Put the probe in the standard solution until the temperature sensor is completely submerged. Move the probe up or down or gently tap on the beaker to remove air bubbles from the probe.
6. Push **Read**. The display will show "Stabilizing" and a progress bar as the reading stabilizes. The display shows the value of the check standard and either Check Standard Passed or Check Standard Failed.
7. If the display shows **Check Standard Passed**, the check standard measurement is within the accepted limits set by the administrative user. Select **Done** to continue with the sample measurement.
8. If the display shows **Check Standard Failed**, the measurement is outside of accepted limits set by the administrative user and a recalibration is recommended. If the acceptance criteria is set to Cal Expires on Failure: Yes, the display shows the calibration icon and a question mark until the probe is recalibrated. To correct the probe calibration and status indicator, calibrate the probe (refer to Calibration on page 2).

Advanced operation

Parameter-specific settings can be changed through the Full Access Options menu. Details about menu navigation, available options and how to change them are given in the screens, tables and procedures throughout this section.







The settings that can be changed are shown in Table 1.

Table 1 Parameter-specific settings

Setting	Options
Parameter	• Conductivity • Salinity • TDS • Resistivity
Measurement Options	• Units • Measurement limits • Temperature correction • Correction factor (if linear temperature correction is selected) • Reference temperature (if a temperature correction is selected)

Table 1 Parameter-specific settings (continued)

Setting	Options
Calibration Options	• Standard • Calibration reminder • Standard units (if Custom option is selected) • Standard value (if Custom option is selected) • Reference temperature (if Custom option is selected) • Temperature correction (if Custom option is selected)
Check Standards Options	• Standard solution for calibration verification • Reminder • Acceptance criteria

Change measurement options

Methods are groups of default or user-defined settings relevant to specific applications. If the meter is set to the default method and the Modify Current Settings option is chosen, a prompt for a new name is shown after the changes are entered. The settings are saved with this name to distinguish them from the default method settings, which cannot be changed. A saved method can be used instead of multiple adjustments to the individual settings. Changes made to a user defined method are automatically saved with the existing name. Multiple methods can be saved for the same probe on each meter.

Table 2 lists the five default methods available for the CDC401 conductivity cell.

Table 2 Default methods

Options	Description
Hach Conductivity	Default method with conductivity measurement values. Conductivity is typically used for natural water samples.
Hach TDS	Default method with TDS measurement values. TDS is typically used to estimate the amount of total dissolved solids in the sample. The conductivity value is also shown in the Detailed Reading screen.
Hach Salinity	Default method with salinity measurement values. Salinity is typically used for samples with a high salt content, such as sea water. The conductivity value will also be shown in the Detailed Reading screen.
Hach Resistivity	Default method with resistivity measurement values. Resistivity is typically used for ultra pure water applications.
Default	—

1. Make sure a probe is connected to the meter.
2. Push and select CDC401 Settings.
3. Select Modify Current Settings.
4. Select Parameter to change the parameter that is shown in the display.
5. Select Measurement Options and update the settings:

Option	Description
Units—Conductivity	Sets the units for conductivity—Auto (default), µS/cm or mS/cm. When Auto is selected, the units will automatically change to mS/cm when the sample conductivity is high and µS/cm when the conductivity is low. Select µS/cm or mS/cm to always show the same units.
Units—Salinity	Sets the units for salinity—‰ (default), g/kg, <unitless> or ppt (parts per thousand).

Option	Description
Measurement Limits	Sets the measurement limits—Lower limit (default: 0.01 µS/cm; 0 ‰) or Upper limit (default: 400000.00 µS/cm; 42 ‰). The measurement limits can be set to match the acceptable values for the sample. When the measurement is above the upper limit setting or below the lower limit setting, the meter shows an "Out of limits" message. This message is an alert to a potential problem with the process conditions.
Temperature Correction	Sets the temperature correction—None, Linear, NaCl non-linear (default) or Natural Water. The conductivity of a sample changes when the temperature changes. Temperature correction shows the conductivity at the user-selected reference temperature. Temperature correction can be changed or turned off when the parameter is set to conductivity, TDS or resistivity.
Correction Factor	When the temperature correction is set to linear, this sets a correction factor based on the sample type—% per °C (default: 1.90% per °C). The correction factor may need to be identified experimentally. For example, the factor for ultrapure water is 4.55% per °C and the factor for NaCl salt solution 2.125% per °C.
Reference Temperature	When the parameter is set to conductivity, TDS or resistivity, sets the reference temperature for temperature correction—20 °C or 25 °C (default).
TDS Form	When the parameter is set to TDS, sets the conversion factor from conductivity to total dissolved solids—NaCl (default, factor 0.5) or Custom. To change the factor, select Custom and enter the conversion factor and temperature correction information. ***Note:*** *Labels and options may vary depending on the units selected.*

6. If prompted, enter a name for the new method settings. Additional changes made to the settings of an existing method are automatically saved with the same method name.
7. Push **EXIT** until the meter returns to the measurement mode.

Change calibration options

1. Make sure a probe is connected to the meter.
2. Push ⚙ and select CDC401 Settings.
3. Select Modify Current Settings.
4. Select Calibration Options and update the settings:

Option	Description
Standard	Sets the conductivity calibration standard— • 1 D KCl, 111.3 mS/cm, 25 °C • 0.1 D KCl, 12.85 mS/cm, 25 °C • 0.01 D KCl, 1408 µS/cm, 25 °C • 0.1 M KCl, 12.88 mS/cm, 25 °C • 0.01 M KCl, 1413 µS/cm, 25 °C • 0.001 M KCl, 146.93 µS/cm, 25 °C • NaCl, 18 mS/cm, 25 °C • NaCl, 1000 µS/cm, 25 °C • NaCl, 25 µS/cm, 25 °C • NaCl, 0.05%, 1015 µS/cm, 25 °C • Seawater (S=35) • Custom

Option	Description
Standard Units	When Standard is set to Custom, sets the units for the custom calibration standard.
Standard Value	When Standard is set to Custom, sets the values for the custom calibration standard.
Reference Temperature	When Standard is set to Custom, sets the reference temperature for the custom calibration standard.
Temperature Correction	When Standard is set to Custom, sets the temperature correction for the custom calibration standard.

5. Select Calibration Reminder and update the settings:

Option	Description
Reminder Repeat	Meter will make an audible sound when calibration is due and repeat the sound at selected interval—Off, 2 h, 4 h, 8 h, 2 d, 5 d or 7 d.
Expires	Calibration expires after the selected time—Immediately, Reminder + 30 min, Reminder + 1 h, Reminder + 2 h or Continue Reading. ***Note:*** *The meter cannot be used to read samples after calibration has expired unless Continue Reading is selected.*

6. If prompted, enter a name for the new method settings. Additional changes made to the settings of an existing method are automatically saved with the same method name.
7. Push **EXIT** until the meter returns to the measurement mode.

Maintenance

Clean the probe

Clean the probe when:

- Drifting/inaccurate readings or slow stabilization time occurs as a result of mineral or sample buildup on the electrodes.
- The slope is out of range as a result of mineral or sample buildup on the electrodes.

Before a rugged probe can be cleaned, the shroud must be removed (refer to Remove the shroud on page 8). Install the shroud after the probe is clean (refer to Install the shroud on page 9).

For general contaminants:

1. Rinse the probe with deionized water and blot dry with a lint-free cloth.

For greases and oils:

1. Soak the glass bulb in a warm detergent solution for up to 2 hours.
2. Rinse or soak the probe for 1 minute in deionized water.
3. Blot dry with a lint-free cloth.

For mineral buildup:

1. Soak the probe in a dilute 10% hydrochloric acid (HCl) solution for no more than 5 minutes.
2. Rinse or soak the probe for 1 minute in deionized water.
3. Blot dry with a lint-free cloth.

Remove the shroud

1. Loosen and remove the locking ring.
2. Slide the shroud and locking ring off the probe.

Install the shroud

1. Put the locking ring on the probe with the threads toward the probe.
2. Slide the shroud on the probe until it is against the locking groove.
3. Hand-tighten the locking ring on the shroud.

Storage

Between uses, make sure the probe is dry and store it in ambient conditions. Rugged probes may be stored with the shroud installed if the storage container is sufficiently large.

Troubleshooting

Message or symptom	Possible cause	Action
Probe not supported	Software not updated	To download the most current version of the software, refer to the applicable product page on the manufacturer's website. Refer to the HQd Series meter manual for specific instructions for the meter model.
	HQd meter does not support IntelliCAL® probe	Contact a Technical Support Representative.
Connect a probe or probe requires service	Probe not connected correctly	Disconnect, then connect the probe. Tighten the locking nut.
	Software not updated	To download the most current version of the software, refer to the applicable product page on the manufacturer's website. Refer to the HQd Series meter manual.
	Large number of methods stored on the probe	Continue to let probe connect. Do not disconnect the probe.
	Damaged probe	Make sure there is connectivity with another probe or meter to confirm isolated issue with probe. Contact a Technical Support Representative.
Slow stabilization time	Mineral or sample buildup on electrodes	Clean the probe (refer to Clean the probe on page 8).
	Bubbles trapped under probe tip	Make sure that the sample concentration and temperature are both within the range of the CDC401 probe.
Out of range	Temperature and/or pressure sensor error	Make sure that the temperature and pressure sensors are both reading correctly.
	Damaged probe	Replace the conductivity probe or contact a Technical Support Representative.
	CO2 absorption in LIS/high purity samples	Replace the conductivity probe or contact a Technical Support Representative.
	Bubbles trapped under probe tip	Make sure that the sample concentration and temperature are both within the range of the CDC401 probe.

Message or symptom	Possible cause	Action
Drifting/Inaccurate readings	Incorrect settings	Measurement Options—Make sure that Temp Correction (Correction Factor if not set as NaCl) and reference temperature are both correct.
		Calibration Options—Make sure that Standard Value, Reference Temperature and Temp Correction are all correct.
	Mineral or sample buildup on cell	Clean the probe (refer to Clean the probe on page 8).
	CO2 absorption in LIS/high purity samples	Isolate LIS/high purity samples to prevent sample contamination.
	Bubbles trapped under probe tip	Gently shake the probe until bubbles are removed.
Calibration failed - Out of limits/Out of range	Incorrect settings	Measurement Options—Make sure that Temp Correction (Correction Factor if not set as NaCl) and reference temperature are both correct.
		Calibration Options—Make sure that Standard Value, Reference Temperature and Temp Correction are all correct.

HACH COMPANY World Headquarters
P.O. Box 389, Loveland, CO 80539-0389 U.S.A.
Tel. (970) 669-3050
(800) 227-4224 (U.S.A. only)
Fax (970) 669-2932
orders@hach.com
www.hach.com

HACH LANGE GMBH
Willstätterstraße 11
D-40549 Düsseldorf, Germany
Tel. +49 (0) 2 11 52 88-320
Fax +49 (0) 2 11 52 88-210
info@hach-lange.de
www.hach-lange.de

HACH LANGE Sàrl
6, route de Compois
1222 Vésenaz
SWITZERLAND
Tel. +41 22 594 6400
Fax +41 22 594 6499

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05/2013, Edition 2

User Manual

Luminescent Dissolved Oxygen Probe: Model LDO10101, LDO10103, LDO10105, LDO10110, LDO10115 or LDO10130

Safety information

Precautionary labels

Read all labels and tags attached to the instrument. Personal injury or damage to the instrument could occur if not observed. A symbol on the instrument is referenced in the manual with a precautionary statement.

	Electrical equipment marked with this symbol may not be disposed of in European public disposal systems after 12 August of 2005. In conformity with European local and national regulations (EU Directive 2002/96/EC), European electrical equipment users must now return old or end-of-life equipment to the Producer for disposal at no charge to the user. ***Note:*** *For return for recycling, please contact the equipment producer or supplier for instructions on how to return end-of-life equipment, producer-supplied electrical accessories, and all auxiliary items for proper disposal.*

Specifications

Note: *Specifications are subject to change without notice.*

Specifications	Details
Probe type	Luminescent dissolved oxygen (LDO) probe
Dissolved oxygen range	0.1 to 20.0 mg/L (ppm) 1 to 200% saturation
Dissolved oxygen accuracy	±0.1 mg/L for 0 to 8 mg/L ±0.2 mg/L for greater than 8 mg/L
% saturation resolution	0.1%
Stabilization time	T90% at 10 seconds (when stirred)
Temperature resolution	0.1 °C (0.18 °F)
Temperature accuracy	±0.3 °C (±0.54 °F)
Pressure resolution	1 hPa
Pressure accuracy	±0.8%
Operating temperature range	0 to 50 °C (32 to 122 °F)
Storage temperature range	0 to 40 °C (32 to 104 °F)
Minimum sample depth	25 mm (0.984 in.)
Dimensions (standard)	Diameter: 29 mm (1.14 in.) Length: 191 mm (7.52 in.) Cable length: 1 or 3 m (3.28 or 9.84 ft)
Dimensions (rugged)	Diameter: 46 mm (1.81 in.) Length: 223 mm (8.73 in.) Cable length: 5, 10, 15 or 30 meter (16.40, 32.81, 49.21 or 98.42 ft)
Cable connection	M12 digital output and connector compatible with HQd meters

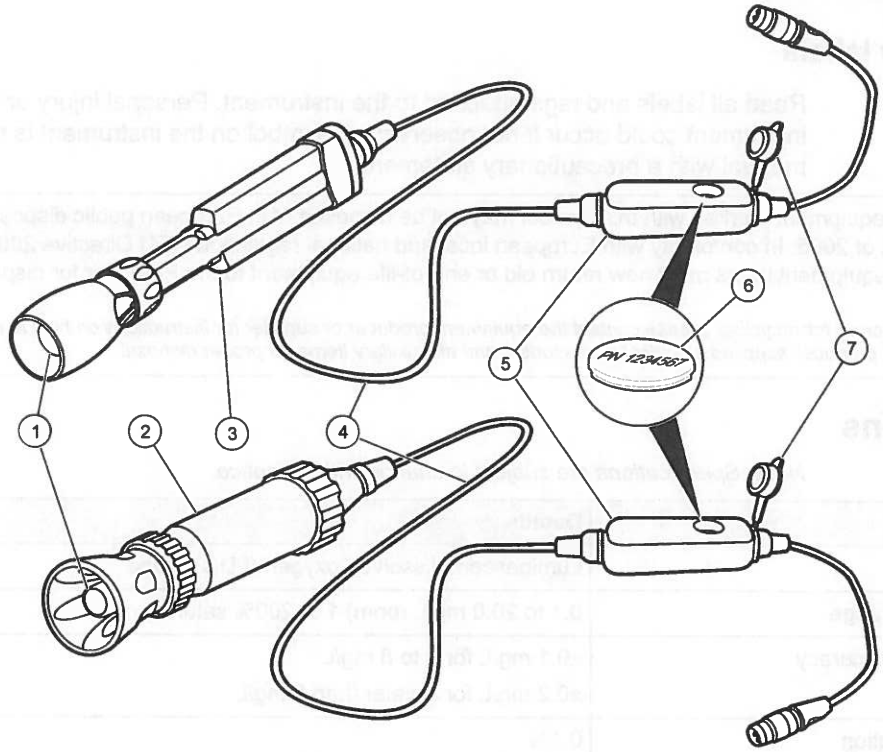
Product overview

The LDO101 series probe is a luminescent dissolved oxygen probe (Figure 1). The LDO10105, LDO10110, LDO10115 or LDO10130 rugged probe is available with a 5, 10, 15 or 30 m (16.40, 32.81, 49.21 or 98.42 ft) cable. The LDO10101 or LDO10103 standard

probe is available with a 1 or 3 m (3.28 or 9.84 ft) cable and is intended for laboratory use. The probe measures the dissolved oxygen concentration in wastewater, drinking water and general applications.

Note: *For BOD applications, use the LBOD10101 probe which has LDO technology and a stirrer.*

Figure 1 Probe overview



1 LDO probe cap	**5** Pressure sensor module
2 Rugged probe (5, 10, 15 or 30 meter cable)	**6** iButton® compartment[1]
3 Standard probe (1 or 3 meter cable)	**7** Pressure sensor module cap
4 Probe cable	

[1] iButton is a registered trademark of Maxim Integrated Products, Inc.

Preparation for use

Note: *Do not touch the probe cap with a hand, fingers or any surface that can scratch the cap.*

Prepare the probe for use before calibration or sample measurement.

1. Make sure that the probe cap and iButton are installed correctly. The iButton label should be up.
2. Make sure that the probe cap and iButton have the same lot code.
3. If a rugged probe, make sure that the shroud is installed before field use (refer to Install the shroud on page 9).

   Note: *Damage to the sensing elements can occur if the shroud is not installed during field use. Damage under these conditions is not covered by the product warranty.*
4. Rinse the probe cap with deionized water. Blot dry with a lint-free cloth.
5. If dissolved oxygen monitoring periods are longer than 6 hours, condition the probe cap for 72 hours. Calibrate the probe once every 8 hours.

   Note: *After 72 hours, the probe cap will reach a fully hydrated state.*

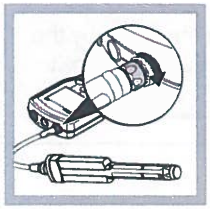
Calibration

Before calibration:
The probe must have the correct service-life time stamp. Set the date and time in the meter before the probe is attached.
It is not necessary to recalibrate when moving a calibrated probe from one HQd meter to another if the additional meter is configured to use the same calibration options.
To view the current calibration, push 🗁, select View Probe Data, then select View Current Calibration.
If any two probes are connected, push the **UP** or **DOWN** arrow to change to the single display mode in order to show the Calibrate option.
Prepare the probe for use (refer to Preparation for use on page 2.
If a rugged probe, remove the shroud from the probe (refer to Remove the shroud on page 9).

Calibration notes:

- % saturation or mg/L calibration methods are available in the Modify Current Settings menu.
- The slope value is the comparison between the latest calibration and the factory calibration shown as a percentage.
- An additional zero point calibration can be added to the calibration routine. Refer to Change calibration options on page 8.
- The calibration is recorded in the probe and the data log. The calibration is also sent to a PC, printer or flash memory stick if connected.
- Air bubbles under the sensor tip when submerged can cause slow response or error in measurement. If bubbles are present, gently shake the probe until bubbles are removed.
- If a calibration error occurs, refer to Troubleshooting on page 10.

Water-saturated air (100%) calibration procedure:



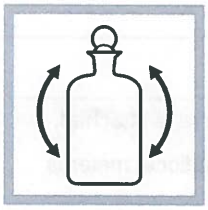
1. Connect the probe to the meter. Make sure that the cable locking nut is securely connected to the meter. Turn on the meter.

2. Push **Calibrate**.

3. Push **Methods**. Select User Cal - 100%. Push **OK**.

4. Rinse the probe cap with deionized water. Blot dry with a lint-free cloth.

5. Add approximately ¼ inch (6.4 mm) of reagent water to a narrow-neck bottle, such as a BOD bottle.



6. Put a stopper in the bottle and shake the bottle vigorously for approximately 30 seconds to saturate the entrapped air with water. Allow up to 30 minutes for contents to equilibrate to room temperature.

7. Remove the stopper. Carefully dry the probe cap with a non-abrasive cloth. Put the probe in the bottle.

8. Push **Read**. The display shows "Stabilizing" and a progress bar as the probe stabilizes. The display shows the standard value when the reading is stable.

9. Push **Done** to view the calibration summary.

10. Push **Store** to accept the calibration and return to the measurement mode. If a rugged probe, install the shroud on the probe (refer to Install the shroud on page 9).

Sample measurement

Before measurement:
The probe must have the correct service-life time stamp. Set the date and time in the meter before the probe is attached.
If complete traceability is necessary, enter a sample ID and operator ID before measurement. Refer to the HQd meter manual for more information.
Regular calibration is required for the best measurement accuracy (refer to Calibration on page 3). Calibrate the probe if accuracy better than ±0.50 mg/L is necessary for the application.
Prepare the probe for use (refer to Preparation for use on page 2).
To deploy a rugged probe at a distance, toss the probe body with a gentle underhand throw. Do not swing the probe by the cable as this may cause injury to the user, will cause severe strain on the cable and will shorten the service life of the cell. Damage under these conditions is not covered by the product warranty.

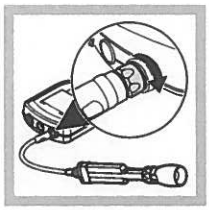
	Do not submerge the pressure sensor module.

Measurement notes:

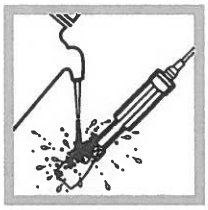
- Stabilization times with smaller concentration changes generally will be longer and can be minimized by correct stirring and conditioning. Experiment to determine the correct stir rate if necessary.
- Salinity affects the concentration of dissolved oxygen in the sample. To correct for salinity effects, refer to Advanced operation on page 6 or do the Auto salinity correction on page 5.
- Data is automatically stored in the data log when **Press to Read** or **Interval** is selected in the Measurement Mode. When **Continuous** is selected, data will only be stored when **Store** is selected.
- Air bubbles under the sensor tip when submerged can cause slow response or error in measurement. If bubbles are present, gently shake the probe until bubbles are removed.
- If a measurement error occurs, refer to Troubleshooting on page 10.

Measurement procedure:

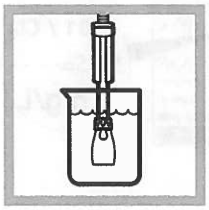
Note: *Procedures also apply for rugged model probes.*



1. Connect the probe to the meter. Make sure that the cable locking nut is securely connected to the meter. Turn on the meter.

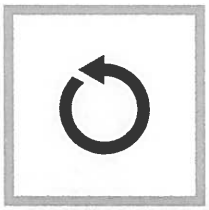


2. Rinse the probe cap with deionized water. Blot dry with a lint-free cloth.



3. Put the probe in the sample and stir gently or add a stir bar. Do not put the probe on the bottom or sides of the container. Stir the sample at a moderate rate or put the probe in flowing conditions.

4. Put the probe in the sample at least 25 mm (0.984 in.) deep. Push **Read**. The display will show "Stabilizing" and a progress bar as the probe stabilizes in the sample. The display will show the lock icon when the reading stabilizes.



5. Repeat steps 2-4 for additional measurements. When measurements are done, store the probe Storage on page 10.

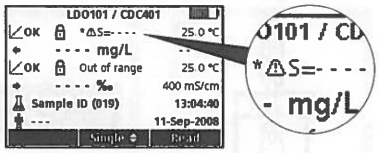
Auto salinity correction

Dissolved substances affect the amount of oxygen water can hold. Manually enter salinity settings for the most accurate dissolved oxygen measurements or use the optional Auto Salinity Correction feature.

The manufacturer recommends using the Auto Salinity Correction feature when measuring dissolved oxygen in samples where salinity varies. Auto salinity correction measures dissolved oxygen through the connection of one LDO101 probe and one CDC401 conductivity cell (set to Salinity parameter). The value obtained by the CDC401 conductivity cell automatically adjusts the salinity value for the LDO101 series probe. Salinity units are represented as parts per thousand (ppt) or (°/°°).

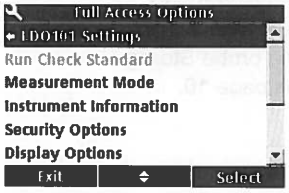
1. Connect the LDO101 probe and CDC401 conductivity cell to the HQd meter. Turn the meter on.
   Note: *Security options must be turned off to use auto salinity correction.*
2. Push and select the CDC401 Settings.
3. Select Current Method, Hach Salinity. Push **OK**.
   Note: *To change more measurement options, choose Modify Current Settings, change the parameter to Salinity and any other desired settings.*
4. Push **EXIT** until the Full Access Options menu is shown.
5. Select LDO101 Settings, Modify Current Settings, Measurement Options, Salinity Correction: Off. Then select Sal Correction Mode: Off. Push the **DOWN** arrow to select Auto (*) - Use CDC401. Push **OK**.
6. Push **EXIT** until the meter returns to the measurement mode. The HQ40d meter is now set up to automatically use the salinity values obtained by the CDC401 with the LDO101 probe. If the salinity value is out of range, the display will show ***S= ----** above the dissolved oxygen reading as shown in Figure 2.
   Note: *The asterisk (*) indicates that salinity is automatically correcting the dissolved oxygen value. No asterisk indicates that salinity is being manually corrected. Warning messages will override the asterisk (*) priority.*

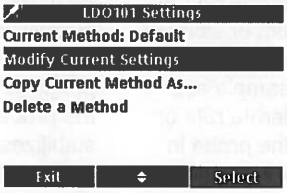
Figure 2 Salinity value out of range

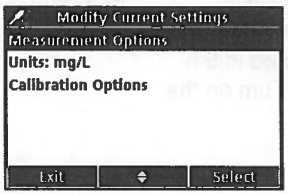


Advanced operation

Parameter-specific settings can be changed through the Full Access Options menu. Details about menu navigation, available options and how to change them are given in the screens, tables and procedures throughout this section.







The settings that can be changed are shown in Table 1.

Table 1 Parameter-specific settings

Setting	Options	Description
Measurement Options	Resolution	Defines measurement resolution
	Measurement Limits	Upper and lower measurement limits
	Salinity Correction	Value for salinity correction
	Pressure Units	Atmospheric pressure units
	Averaging Interval	How often the meter calculates an average readings
Units	mg/L %	Primary unit of measurement
Calibration Options	Calibration	• User 100% • User 100% with 0 • User mg/L • User mg/L with 0 • Factory
	Calibration Reminder	Reminder Repeat—Off, 8 h, 12 h, 1 d, 2 d, 5 d or 7 d
		Expires—Immediately, Reminder + 30 m, Reminder + 1 h, Reminder + 2 h or Continue Reading

Change measurement options

Methods are groups of default or user-defined settings relevant to specific applications. If the meter is set to the default method and the Modify Current Settings option is chosen, a prompt for a new name is shown after the changes are entered. The settings are saved with this name to distinguish them from the default method settings, which cannot be changed. A saved method can be used instead of multiple adjustments to the individual settings. Changes made to a user defined method are automatically saved with the existing name. Multiple methods can be saved for the same probe on each meter.

There are three default methods available for the LDO101 probe:

- Factory Cal (Calibration with default LDO calibration)
- User Calibration—100% (allows user calibration)

- Default

1. Make sure a probe is connected to the meter.
2. Push ✎ and select LDO101 Settings.
3. Select Modify Current Settings.
4. Select Units. Select mg/L (default) or %.
5. Select Measurement Options and update the settings:

Option	Description
Resolution	Sets the resolution: • 0.1—Fast (0.35 mg/L)/min • 0.01—Fast (0.35 mg/L)/min • 0.01—Medium (0.15 mg/L)/min (default), or • 0.01—Slow (0.05 mg/L)/min The resolution affects the number of decimal places and the stabilization time. Higher resolution measurements take more time to stabilize.
Measurement Limits	Set the measurement limits—Lower limit (default: 0.0 mg/L; 0%) or Upper limit (default: 20.0 mg/L; 200%). The measurement limits can be set to match the acceptable values for the sample. When the measurement is above the upper limit setting or below the lower limit setting, the meter shows an "Out of limits" message. This message is an alert to a potential problem with the process conditions.
Salinity Correction	Sets the salinity correction—Off (default), Manual or Auto (connect conductivity probe). Salinity lowers the solubility of dissolved oxygen in water. To correct for salinity in the sample, set salinity correction to manual and then enter the salinity value. ***Note:*** *When the HQ40d meter is used, a conductivity probe can also be connected for automatic salinity measurement and correction. The parameter setting for the conductivity probe must show salinity.*
Salinity Value	Sets the salinity value—‰ (default: 35.0 ‰). When salinity correction is set to manual, sets the salinity value of the sample. Salinity can be measured with a conductivity probe.
Pressure Units	Sets the pressure units—hPa, mBar, inHg or mmHg. The meter shows the atmospheric pressure at the current elevation, which is necessary for accurate measurements. ***Note:*** *This pressure reading will not agree with readings from sources such as weather stations, which report atmospheric pressure at sea level.*
Averaging Interval	Sets the averaging interval—Off, 30, 60, 90 seconds, 3, 5 minutes. The averaging interval is useful for samples that contain a lot of air bubbles, for example in an aeration basin. The air bubbles cause the dissolved oxygen readings to vary greatly from one reading to the next. To make the readings more consistent, increase the averaging interval. The meter will take measurements at the same frequency but show only the average over a longer interval. ***Note:*** *Labels and options may vary depending on the units selected.*

6. If prompted, enter a name for the new method settings. Additional changes made to the settings of an existing method are automatically saved with the same method name.
7. Push **EXIT** until the meter returns to the measurement mode.

Change calibration options

1. Make sure that a probe is connected to the meter.
2. Push ✎ and select LDO101 Settings.
3. Select Modify Current Settings.
4. Select Calibration Options and update the settings:

Option	Description
Calibration	• User—100% (water-saturated air (100%) calibration) • User—100% with 0 (water-saturated air (100%) calibration with 0 point) • User—mg/L (calibration with a specified dissolved oxygen concentration (mg/L) solution) • User—mg/L with 0 (calibration with a specified dissolved oxygen concentration (mg/L) solution with 0 point) • Factory (calibration with the default LDO calibration)
Standard Value	When Calibration is set to mg/L or mg/L with 0, sets the concentration of the solution that will be used for calibration—2.00 to 20.00 mg/L (default=7.00 mg/L)

5. Select Calibration Reminder and update the settings:

Option	Description
Reminder Repeat	Meter will make an audible sound when calibration is due and repeat the sound at selected interval—Off, 8 h, 12 h, 1 d, 2 d, 5 d or 7 d.
Expires	Calibration expires after the selected time—Immediately, Reminder + 30 min, Reminder + 1 h, Reminder + 2 h or Continue Reading. ***Note:*** *The meter cannot be used to read samples after calibration has expired unless Continue Reading is selected.*

6. If prompted, enter a name for the new method settings. Additional changes made to the settings of an existing method are automatically saved with the same method name.
7. Push **EXIT** until the meter goes back to the measurement mode.

Maintenance

Clean the probe

Keep the probe cap free of deposits for the best measurements.

Note: *Do not touch the black colored substrate of the probe cap. Do not use alcohol or other organic solvents to clean the black colored substrate of the probe cap. These solvents cause damage to the probe cap.*

1. Remove the shroud (refer to Remove the shroud on page 9).
2. Gently clean the probe cap with a mild detergent, water and a soft cloth or cotton swab. Do not remove the black colored substrate from the probe cap. Do not scrub the probe cap or lens.
3. If water is present between the probe cap and lens:
   a. Remove the probe cap.
   b. Blot dry the probe cap and lens with a soft dry cloth.
   c. Install the probe cap.
4. Install the shroud (refer to Install the shroud on page 9).

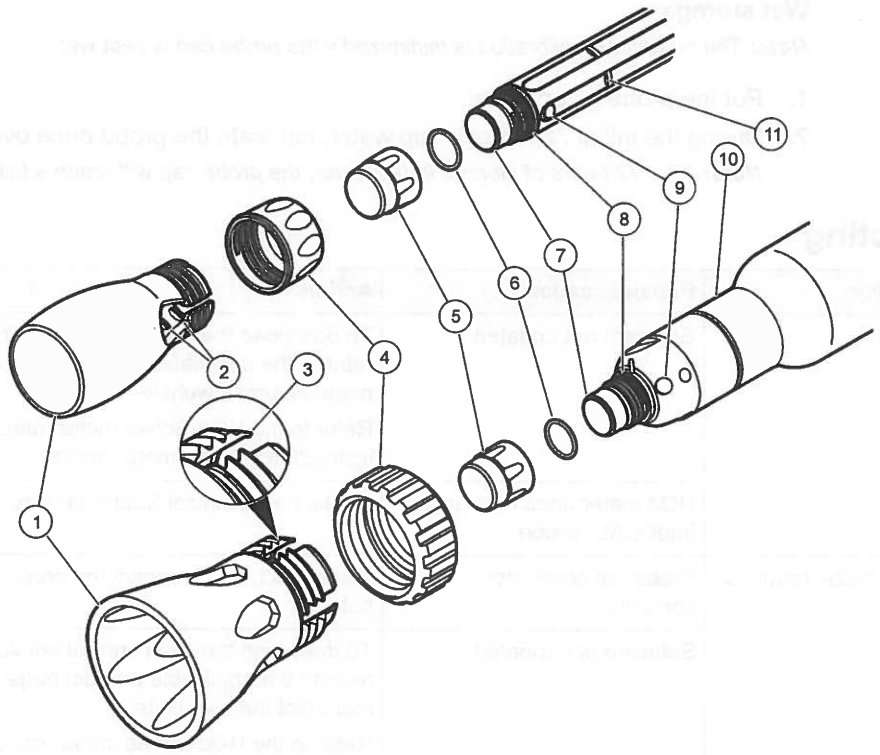
Replace probe cap

The probe cap must be replaced every 365 days or more often if the cap becomes damaged or fouled. The meter will show a reminder message when 30 days of probe service life remains on the probe cap.
For LDO probe cap replacement instructions, refer to the instructions provided with the LDO probe cap replacement kit.

Remove the shroud

1. Loosen and remove the locking ring (Figure 3).
2. Slide the shroud and locking ring off the probe.

Figure 3 Probe exploded view



1 Shroud	**7** Probe lens
2 Locking ridges (8x)	**8** Cap seal
3 Locking rib	**9** Temperature sensor
4 Locking ring	**10** Locking groove
5 Probe cap	**11** Locking ribs (4x)
6 O-ring	

Install the shroud

1. Put the locking ring on the probe with the threads toward the probe cap (Figure 3 on page 9).
2. Slide the shroud on the probe until it is against the locking groove (rugged) or ribs (standard). Slide the standard probe shroud on the standard probe until the inside locking ridges align halfway between the ribs on the probe. Turn the shroud slightly until it is seated.
3. Hand-tighten the locking ring on the shroud.

Storage

- Dry storage—the manufacturer recommends that the probe is stored dry when the probe is used for measurements of short duration (less than 6 hours).
- Wet storage—the probe must be stored wet when the probe is used for monitoring periods longer than 6 hours.

Dry storage

Note: *Rugged probes may be stored dry with the shroud installed if the storage container is sufficiently large.*

1. Rinse the probe with deionized water. Blot dry with a lint-free cloth.
   Note: *The probe must be conditioned again in tap water for at least 30 minutes prior to use.*
2. If a rugged probe, remove the shroud (optional). Refer to Remove the shroud on page 9.

Wet storage

Note: *The need for recalibration is minimized if the probe cap is kept wet.*

1. Put the probe in tap water.
2. During the initial 72 hours in tap water, calibrate the probe once every 8 hours.
   Note: *After 72 hours of storage in tap water, the probe cap will reach a fully hydrated state.*

Troubleshooting

Message or symptom	Possible cause	Action
Probe not supported	Software not updated	To download the most current version of the software, refer to the applicable product page on the manufacturer's website. Refer to the HQd Series meter manual for specific instructions for the meter model.
	HQd meter does not support IntelliCAL® probe	Contact a Technical Support Representative.
Connect a probe or probe requires service	Probe not connected correctly	Disconnect, then connect the probe. Tighten the locking nut.
	Software not updated	To download the most current version of the software, refer to the applicable product page on the manufacturer's website. Refer to the HQd Series meter manual.
	Large number of methods stored on the probe	Continue to let the probe connect. Do not disconnect the probe.
	Damaged probe	Make sure there is connectivity with another probe or meter to confirm isolated issue with probe. Contact a Technical Support Representative.

Message or symptom	Possible cause	Action
Out of range	Probe cap loose, scratched or damaged	Reposition or replace the probe cap.
	Temperature and/or pressure sensor error	Make sure that the temperature and pressure sensors are both reading correctly.[1]
	Damaged probe	Make sure that the blue and red LEDs are both illuminated on the probe. If not, replace the probe or contact a Technical Support Representative.
	Sample outside of specifications	Make sure that the sample concentration, temperature and pressure are within the range of the probe.
	iButton number does not match probe cap lot number	Replace the iButton or probe cap or do a user calibration.
	Bubbles trapped under probe tip	Gently shake the probe until bubbles are removed.
Out of range	Probe cap exposed to direct sunlight	Install the protective shroud.
Slope out of range	Probe not prepared for sample	Let the probe reach equilibrium in a water-saturated air environment and do the calibration again.
	Calibration method settings	Make sure that the calibration standards in the method are correct.
	Probe cap loose, scratched or damaged	Locate and install the iButton that matches the probe cap and replace the probe cap.
	Temperature and pressure errors	Make sure that the temperature and pressure sensors are both reading accurately. Contact a Technical Support Representative.[1]
	LED lights do not function	Contact a Technical Support Representative.
	Bubbles trapped under probe tip	Gently shake the probe until bubbles are removed.
LDO–calibration not supported (factory calibration)	LDO method calibration option is set to Factory.	If user calibration is necessary, change the settings in Calibration Options. Refer to Change calibration options on page 8.
O2 Sensor 0 days remaining	There are 0 days remaining in the life of the probe cap	Replace the probe cap. Calibration will be allowed, however the calibration icon and question mark will be shown on the measurement screen even if the calibration has passed.
	Meter set to incorrect date and time	Disconnect the probe from the meter. Set the correct date and time in the Meter Options menu. Connect the probe and make sure that the message has been removed.
	Software not updated	Update the HQd software to the latest version and test again.
O2 Sensor ## of days remaining	There are 30 days or fewer remaining in the life of the probe cap.	Replace the probe cap soon.

Message or symptom	Possible cause	Action
Calibration failed: outside of acceptance criteria/Temperature out of range/Offset out of limits	Water Saturated air equilibration not reached	Allow longer equilibration time.
	Probe cap loose, scratched, or damaged	Change the location of the probe cap or replace the probe cap.
	Temperature and/or pressure sensor error	Make sure that the temperature and pressure sensors are both reading correctly and within range.[1]
	Damaged probe	Make sure that the blue and red LEDs are both illuminated on the probe. If not, replace the probe or contact a Technical Support Representative.

[1] The pressure as measured by the probe is what is referred to as atmospheric pressure and is not corrected to sea level. Weather station pressures are reported at sea level and commonly referred to as mean sea level pressure. As a result the probe will not read the same as most household or professional barometers or weather station reports (which are compensated) unless reported at sea level. In order to compare the pressure results obtained from the probe barometer and these compensated barometers, it is necessary to first compensate the pressure reported by the probes mathematically.

HACH COMPANY World Headquarters
P.O. Box 389, Loveland, CO 80539-0389 U.S.A.
Tel. (970) 669-3050
(800) 227-4224 (U.S.A. only)
Fax (970) 669-2932
orders@hach.com
www.hach.com

HACH LANGE GMBH
Willstätterstraße 11
D-40549 Düsseldorf, Germany
Tel. +49 (0) 2 11 52 88-320
Fax +49 (0) 2 11 52 88-210
info@hach-lange.de
www.hach-lange.de

HACH LANGE Sàrl
6, route de Compois
1222 Vésenaz
SWITZERLAND
Tel. +41 22 594 6400
Fax +41 22 594 6499

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05/2013, Edition 2

User Manual

Gel-filled pH Probe: Model PHC10101, PHC10103, PHC10105, PHC10110, PHC10115 or PHC10130

Safety information

Precautionary labels

Read all labels and tags attached to the instrument. Personal injury or damage to the instrument could occur if not observed. A symbol on the instrument is referenced in the manual with a precautionary statement.

	Electrical equipment marked with this symbol may not be disposed of in European public disposal systems after 12 August of 2005. In conformity with European local and national regulations (EU Directive 2002/96/EC), European electrical equipment users must now return old or end-of-life equipment to the Producer for disposal at no charge to the user. ***Note:*** *For return for recycling, please contact the equipment producer or supplier for instructions on how to return end-of-life equipment, producer-supplied electrical accessories, and all auxiliary items for proper disposal.*

Specifications

Note: *Specifications are subject to change without notice.*

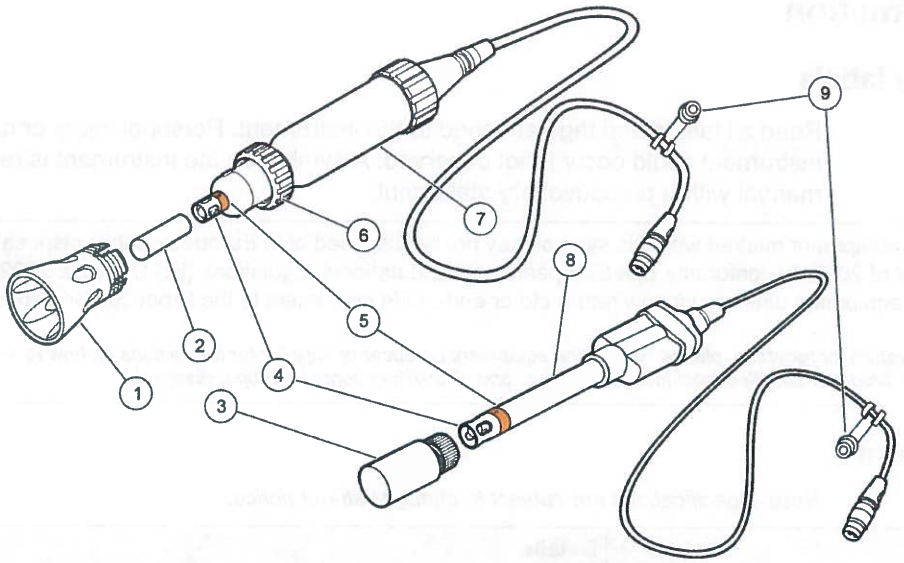
Specifications	Details
Probe type	Digital combination non-refillable, gel-filled probe with double junction reference and built-in temperature sensor
pH range	pH 2 to 14
pH resolution	User-selectable stabilization time and resolution—Fast: 0.1, Fast: 0.01, Medium: 0.01, Slow: 0.01 or Slow: 0.001
Slope	-59 mV/pH (90 to 110% at 25 °C (77 °F) per Nernstian theoretical value)
Operating temperature range	0 to 50 °C (32 to 122 °F)
Storage temperature range	5 to 40 °C (41 to 104 °F)
Junction	Open
Reference type	Ag/AgCl
Sodium (alkalinity) error	-0.6 pH at pH 12.6 in 1 M NaOH
Temperature accuracy	±0.3 °C (±0.54 °F)
Minimum sample depth	20 mm (0.79 in.)
Dimensions (standard)	Diameter: 12 mm (0.47 in.) Length: 175 mm (6.89 in.) Cable length: 1 or 3 m (3.28 or 9.84 ft)
Dimensions (rugged)	Diameter: 46 mm (1.81 in.) Length: 223 mm (8.73 in.) Cable length: 5, 10, 15 or 30 m (16.40, 32.81, 49.21 or 98.42 ft)
Cable connection	M12 digital output and connector compatible with HQd meters

Product overview

The PHC101 series probe is a non-refillable, gel-filled combination pH probe with a built-in temperature sensor (Figure 1). The standard PHC10101 or PHC10103 probe comes with a 1 or 3 m (3.28 or 9.84 ft) cable and is intended for laboratory use. The rugged PHC10105, PHC10110, PHC10115 or PHC10130 comes with a 5, 10, 15 or 30 m (16.40,

32.81, 49.21 or 98.42 ft) cable and is intended for field use. The probe provides pH measurement in wastewater, drinking water and general aqueous applications. The probe is not suitable for use with organic solvents or samples with pH less than 2.

Figure 1 Probe overview



1 Shroud (rugged model)	6 Locking ring (rugged model)
2 Probe storage cap	7 Rugged probe (5, 10, 15 or 30 meter cable)
3 Probe soaker bottle	8 Standard probe (1 or 3 meter cable)
4 Glass bulb and temperature sensor	9 Probe storage cap or soaker bottle holder
5 Reference junctions and protective tape	

Preparation for use

To prepare the probe for initial use:

1. If a rugged probe, remove the shroud and probe storage cap (refer to Remove the shroud on page 10).
2. If a standard probe, turn the probe soaker bottle cap counter-clockwise to loosen the cap. Remove the soaker bottle from the probe.
3. Remove the protective tape from the reference junctions (refer to Figure 1 on page 2). Dispose of the protective tape.
4. If the probe will be used immediately, prepare the probe for calibration or sample measurement.
5. If the probe will not be used immediately, store the probe (refer to Storage on page 10).

To prepare the probe for calibration or sample measurement:

1. If a rugged probe, remove the probe storage cap.
2. If a standard probe, turn the probe soaker bottle cap counter-clockwise to loosen the cap. Remove the soaker bottle from the probe.
3. Rinse the reference junctions and glass bulb thoroughly with deionized water to remove the 3 M KCl solution completely. Blot dry with a lint-free cloth.
4. For the best stabilization time, condition the probe for several minutes in the sample before use.
5. If a rugged probe, make sure that the shroud is installed before field use (refer to Install the shroud on page 10).

***Note:** Damage to the sensing elements can occur if the shroud is not installed during field use. Damage under these conditions is not covered by the product warranty.*

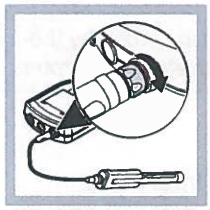
Calibration

Before calibration:
The probe must have the correct service-life time stamp. Set the date and time in the meter before the probe is attached.
It is not necessary to recalibrate when moving a calibrated probe from one HQd meter to another if the additional meter is configured to use the same calibration options.
To view the current calibration, push 🗁, select View Probe Data, then select View Current Calibration.
If any two probes are connected, push the **UP** or **DOWN** arrow to change to the single display mode in order to show the Calibrate option.
Prepare the probe for use (refer to Preparation for use on page 2).
If a rugged probe, remove the shroud from the probe (refer to Remove the shroud on page 10).

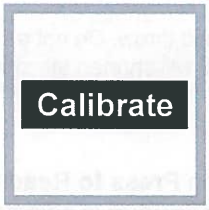
Calibration notes:

- pH buffers can be used in any order. Use buffers that are two pH units apart.
- Additional standard sets along with the minimum number of calibration points can be selected in the Calibration Options. For a two point calibration, it is recommended that two buffers be selected: one with a pH above and one with a pH below the expected sample pH. For a one point calibration, select the buffer nearest to the expected sample pH.
- The calibration is recorded in the probe and the data log. The calibration is also sent to a PC, printer or flash memory stick if connected.
- Air bubbles under the sensor tip when submerged can cause slow response or error in measurement. If bubbles are present, gently shake the probe until bubbles are removed.
- If a calibration error occurs, refer to Troubleshooting on page 10.

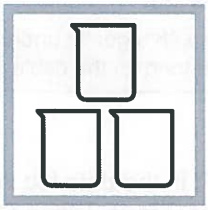
Calibration procedure:



1. Connect the probe to the meter. Make sure that the cable locking nut is securely connected to the meter. Turn on the meter.

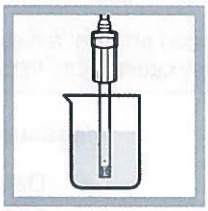


2. Push **Calibrate**. The display shows the buffers that are necessary for calibration.

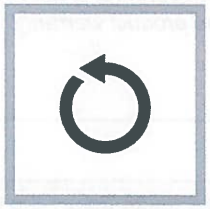


3. Prepare the fresh buffers in separate beakers or appropriate containers.

4. Rinse the probe with deionized water. Blot dry with a lint-free cloth.



5. Put the probe in the pH buffer solution and stir gently. Make sure that the reference junctions are completely submerged. Shake the probe from side to side in the standard solution to refresh the reference junction.



6. Push **Read.** Stir gently. The display will show "Stabilizing" and a progress bar as the probe stabilizes in the standard. The display shows the buffer that has just been read and shows the temperature corrected pH value when the reading is stable.

7. Repeat steps 4 - 6 until the minimum number of calibration points specified in the current method have been collected.

8. Push **Done** to view the calibration summary. The display will not show Done until the minimum number of calibration points have been collected.

9. Push **Store** to accept the calibration and go back to measurement mode. If a rugged probe, install the shroud on the probe (refer to Install the shroud on page 10).

Sample measurement

Before measurement:
The probe must have the correct service-life time stamp. Set the date and time in the meter before the probe is attached.
If complete traceability is necessary, enter a sample ID and operator ID before measurement. Refer to the HQd meter manual for more information.
Regular calibration is required for the best measurement accuracy (refer to Calibration on page 3).
Prepare the probe for use (refer to Preparation for use on page 2).
To deploy a rugged probe at a distance, toss the probe body with a gentle underhand throw. Do not swing the probe by the cable as this may cause injury to the user, will cause severe strain on the cable and will shorten the service life of the probe.

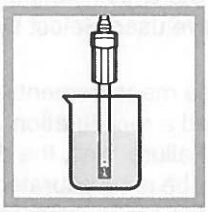
Measurement notes:

- Data is automatically stored in the data log when **Press to Read** or **Interval** is selected in the Measurement Mode. When **Continuous** is selected, data will only be stored when **Store** is selected.
- Air bubbles under the sensor tip when submerged can cause slow response or error in measurement. If bubbles are present, gently shake the probe until bubbles are removed.
- If a measurement error occurs, refer to Troubleshooting on page 10.

Measurement procedure:

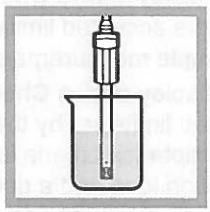
***Note:** Procedure also applies for rugged model probes.*

1. Connect the probe to the meter. Make sure that the cable locking nut is securely connected to the meter. Turn the meter on.



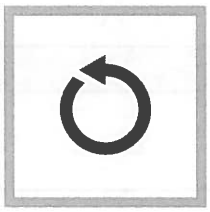
2. For the best stabilization time, condition the probe for several minutes in the sample or in a solution comparable to the sample in terms of pH and ionic strength before the initial sample measurement.

3. Rinse the probe with deionized water, then with the sample. Blot dry with a lint-free cloth.

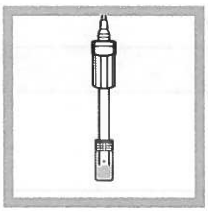


4. Put the probe in the sample and stir gently. Make sure that the reference junctions are completely submerged. Do not put the probe on the bottom or sides of the container. Shake the probe from side to side in the sample to refresh the reference junction.

5. Push **Read**. The display will show "Stabilizing" and a progress bar as the probe stabilizes in the sample. The display will show the lock icon when the reading stabilizes.



6. Repeat steps 3-5 for additional measurements.



7. When measurements are done, store the probe (refer to Storage on page 10).

Run a check standard

The run check standard feature validates instrument performance between sample measurements. Use the run check standard feature for periodic or user-defined interval measurements of a traceable standard solution. Set the criteria for check standards from the PHC101 Settings menu.

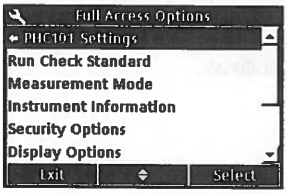
***Note:** Access control must be off or a valid password must be entered before any of the check standard method options can be changed.*

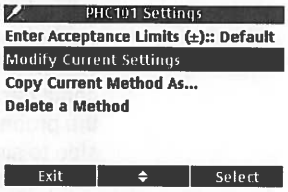
1. Push . The Full Access Options menu is shown.
2. Select Run Check Standard.
   ***Note:** Select the correct probe if two probes are connected to the meter.*
3. Get the standard solution shown on the display.
4. Rinse the probe with deionized water. Blot dry with a lint-free cloth.
5. Put the probe in the standard solution until the temperature sensor is completely submerged. Move the probe up or down or gently tap on the beaker to remove air bubbles from the probe.
6. Push **Read**. The display will show "Stabilizing" and a progress bar as the reading stabilizes. The display shows the value of the check standard and either Check Standard Passed or Check Standard Failed.

7. If the display shows **Check Standard Passed**, the check standard measurement is within the accepted limits set by the administrative user. Select **Done** to continue with the sample measurement.
8. If the display shows **Check Standard Failed**, the measurement is outside of accepted limits set by the administrative user and a recalibration is recommended. If the acceptance criteria is set to Cal Expires on Failure: Yes, the display shows the calibration icon and a question mark until the probe is recalibrated. To correct the probe calibration and status indicator, calibrate the probe (refer to Calibration on page 3).

Advanced operation

Parameter-specific settings can be changed through the Full Access Options menu. Details about menu navigation, available options and how to change them are given in the screens, tables and procedures throughout this section.





The settings that can be changed are shown in Table 1.

Table 1 Parameter-specific settings

Setting	Options
Measurement Options	• Resolution • Upper and lower range limits
Calibration Options	• Buffer set • Buffer set values (if Custom Buffer Set selected) • Reminder • Minimum Cal points • Slope limit
Check Standard Options	• Standard (temperature compensated buffer or custom at 25 °C) • Reminder • Acceptance criteria • Standard value at 25 °C (if custom standard selected)
Units	• pH • mV

Change measurement options

Methods are groups of default or user-defined settings relevant to specific applications. If the meter is set to the default method and the Modify Current Settings option is chosen, a prompt for a new name is shown after the changes are entered. The settings are saved with this name to distinguish them from the default method settings, which cannot be changed. A saved method can be used instead of multiple adjustments to the individual settings. Changes made to a user-defined method are automatically saved with the existing name. Multiple methods can be saved for the same probe on each meter.

1. Make sure a probe is connected to the meter.
2. Push ✎ and select PHC101 Settings.

3. Select Modify Current Settings.
4. Select Units. Select pH (default) or mV.
   Note: *The mV option can be used to find the probe offset in a pH 7 buffer or to measure the slope. Both units are shown when the detail display mode is selected.*
5. Select Measurement Options and update the settings:

Option	Description
Resolution	Sets the resolution: • 0.1pH—Fast • 0.01pH—Fast (default) • 0.01pH—Medium • 0.01pH—Slow, or • 0.001pH—Slow The resolution affects the number of decimal places and the stabilization time. Higher resolution measurements take more time to stabilize. Slower stabilization times provide higher accuracy measurements.
Measurement Limits	Set the measurement limits—Lower limit (default: 2.00 pH) or Upper limit (default: 14.00 pH). The measurement limits can be set to match the acceptable values for the sample. When the measurement is above the upper limit setting or below the lower limit setting, the meter shows an "Out of limits" message. This message is an alert to a potential problem with the process conditions.

6. If prompted, enter a name for the new method settings. Additional changes made to the settings of an existing method are automatically saved with the same method name.
7. Push **EXIT** until the meter returns to the measurement mode.

Change calibration options

1. Make sure a probe is connected to the meter.
2. Push 🔧 and select PHC101 Settings.
3. Select Modify Current Settings.
4. Select Calibration Options and update the settings:

Option	Description
Buffer Set	Sets the temperature compensated buffer set used for calibration— • Color Coded—4.01, 7.00, 10.01 (default) • IUPAC—4.01, 7.00, 10.01, 12.45 • DIN—4.65, 9.23 • IUPAC—4.01, 6.86, 10.01, 12.45 • IUPAC—4.01, 6.86, 9.18, 12.45 • IUPAC—4.01, 7.00, 9.18, 12.45 • Custom Buffer Set (refer to Table 2) Custom buffer sets are characterized at 25 °C (77 °F). Buffer set values are shown on the Calibration Options screen. ***Note:*** *Only the minimum calibration points must be measured for **DONE** to be shown on the calibration screen.*
Buffer Set Values	If the Buffer Set is set to Customer Buffer Set, sets the custom buffer set (refer to Table 2).
Minimum Cal Points	Sets the minimum number of calibration points necessary before a calibration can be completed—1 (default), 2 or 3.
Slope Limit	Sets the slope limit—1% to 10% (acceptable slope criteria, default = 5%). The slope must fall within set limits for successful calibration.

5. Select Calibration Reminder and update the settings:

Option	Description
Reminder Repeat	Meter will make an audible sound when a calibration is due and repeat the sound at the selected interval—Off (default), 2 h, 4 h, 8 h, 2 d, 5 d or 7 d.
Expires	Calibration expires after the selected time—Immediately, Reminder + 30 min, Reminder + 1 h, Reminder + 2 h or Continue Reading. ***Note:*** *The meter cannot be used to read samples after calibration has expired unless Continue Reading is selected.*

6. If prompted, enter a name for the new method settings. Additional changes made to the settings of an existing method are automatically saved with the same method name.
7. Push **EXIT** until the meter returns to the measurement mode.

Table 2 Custom buffer sets

Buffer set values	Option	Description
Std1 Std2 Std3 Std4 Std5	4.01pH—25 °C	Pre-set temperature compensated buffer values. ***Note:*** *Selected standards must differ by a minimum of 2 pH units. For example, if 1.09pH is chosen for the first standard, the second standard must differ by at least 2 pH. Standards that do not meet this minimum will appear gray on the screen and will not be selectable.*
	4.65pH—25 °C	
	6.86pH—25 °C	
	7.00pH—25 °C	
	9.18pH—25 °C	
	9.23pH—25 °C	
	10.01pH—25 °C	
	12.45pH—25 °C	
	Custom Buffer	Custom buffer value. Range = 2.000 pH to 14.000 pH. Custom buffer values are not temperature compensated. Custom buffers should be read at 25 °C.
	No Buffer	Standard is undefined when this option is selected.

Change check standard options

1. Make sure a probe is connected to the meter.
2. Push ✎ and select PHC101 Settings.
3. Select Modify Current Settings.

4. Select Check Standards Options and update the settings:

Option	Description
Standard	Sets the temperature compensated buffer value for check standard— • 4.01pH—25 °C • 4.65pH—25 °C • 6.86pH—25 °C • 7.00pH—25 °C • 9.18pH—25 °C • 9.23pH—25 °C • 10.01pH—25 °C • 12.45pH—25 °C • Custom The standard value is shown on the Check Standard Options screen. No temperature compensation for custom buffers.
Standard Value	When Standard is set to Custom, enter the standard value using the up/down arrow keys.

5. Select Check Standard Reminder and update the settings:

Option	Description
Reminder Repeat	Sets the time interval for the check standard reminder—Off, 30 minutes, 2 h, 4 h, 8 h, 12 h or 24 h.
Allow Defer	Allows the postponement of check standard reminders—Yes or No.

6. Select Acceptance Criteria and update the settings:

Option	Description
Acceptance Limits	Sets the tolerance limits for check standard—0.005pH (default) to 1.000pH.
Cal Expires on Failure	Recalibration required if check standard fails—Yes or No.

7. If prompted, enter a name for the new method settings. Additional changes made to the settings of an existing method are automatically saved with the same method name.
8. Push **EXIT** until the meter returns to the measurement mode.

Maintenance

Clean the probe

Clean the probe when:

- Drifting/inaccurate readings occur as a result of contamination on the glass sensor or the probe being left dry for extended periods of time.
- Slow stabilization time occurs as a result of contamination on the glass sensor.
- A calibration error occurs as a result of contamination on the glass sensor.

Before a rugged probe can be cleaned, the shroud must be removed (refer to Remove the shroud on page 10). Install the shroud after the probe is clean (refer to Install the shroud on page 10).

For general contaminants:

1. Rinse the probe with deionized water and blot dry with a lint-free cloth.
2. Soak the glass bulb for 12 to 16 hours in Hach Electrode Cleaning Solution.
3. Rinse or soak the probe for 1 minute in deionized water.
4. Soak the probe in pH 4 buffer for up to 20 minutes, then rinse with deionized water.
5. Blot dry with a lint-free cloth.

For fats, grease and oils:

1. Soak the glass bulb in a warm detergent solution for up to 2 hours.
2. Rinse or soak the probe for 1 minute in deionized water.
3. Soak the probe in pH 4 buffer for up to 20 minutes, then rinse with deionized water.
4. Blot dry with a lint-free cloth.

Remove the shroud

1. Loosen and remove the locking ring.
2. Slide the shroud and locking ring off the probe.

Install the shroud

1. Put the locking ring on the probe with the threads toward the probe.
2. Slide the shroud on the probe until it is against the locking groove.
3. Hand-tighten the locking ring on the shroud.

Storage

Short-term and long-term storage

For the best probe performance, do not let the reference junction dry out.

1. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.
2. Fill the probe storage cap or soaker bottle half full with Hach Electrode Storage Solution or 3 M potassium chloride (KCl) solution.
3. If a rugged probe, put the probe storage cap on the probe.
4. If a standard probe, put the soaker bottle on the probe and tighten the soaker bottle cap.
5. Make sure that the solution in the storage cap or soaker bottle completely covers the glass bulb and reference junction.

Note: *The probe can also be stored in a sample for up to 2 hours if the sample pH is not high.*

If the glass bulb becomes dry:

1. Soak the probe tip in the 4.01, 7.00 and 10.01 buffers each for 5 minutes.
2. Rinse the probe with deionized water. Blot dry with a lint-free cloth.
3. Calibrate the probe.

Troubleshooting

Message or symptom	Possible cause	Action
Probe not supported	Software not updated	To download the most current version of the software, refer to the applicable product page on the manufacturer's website. Refer to the HQd Series meter manual for specific instructions for the meter model.
	HQd meter does not support IntelliCAL® probe	Contact a Technical Support Representative.

Message or symptom	Possible cause	Action
Connect a probe or probe requires service	Probe not connected properly	Disconnect, then connect the probe. Tighten the locking nut.
	Software not updated	To download the most current version of the software, refer to the applicable product page on the manufacturer's website. Refer to the HQd Series meter manual.
	Large number of methods stored	Continue to let probe connect. Do not disconnect the probe.
	Damaged probe	Make sure there is connectivity with another probe or meter to confirm isolated issue with probe. Contact a Technical Support Representative.
Standard not recognized error	Tape not removed from the reference junctions	Remove the tape.
Standard not recognized error	Probe storage cap or soaker bottle not removed.	Remove the probe storage cap or soaker bottle.
	Incorrect or contaminated buffer solution	Use fresh buffer solution as specified in the method.
pH reading and/or mV reading is same for all solutions	Tape not removed from the reference junctions	Remove the tape.
pH reading and/or mV reading is same for all solutions	Storage cap or soaker bottle not removed	Remove the storage cap or soaker bottle.
	Electrical issue	Contact a Technical Support Representative.
Slow stabilization time	Tape not removed from the reference junctions	Remove the tape.
Slow stabilization time	Contaminated glass sensor	Clean the probe (refer to Clean the probe on page 9).
	Poor contact between reference junction and solution	Shake the probe in the solution from side to side to refresh the reference junction.
	Probe not prepared for sample	For the best stabilization time, soak the probe in the sample for 10 to 15 minutes before doing a sample measurement.
	Low sample temperature or temperature difference between samples	Check the sample temperature. The lower the temperature or the greater the difference of temperatures between samples, the longer the stabilization time will be.
	Air bubbles around inner reference electrode	Gently tap the probe with hand or shake the probe downward to remove any air bubbles.
Calibration errors	Calibration not done correctly	Recalibrate using freshly prepared pH buffers.
	Contaminated glass sensor	Clean the probe (refer to Clean the probe on page 9).
	Slope exceeds the criteria for % of theoretical (as defined in the method slope limit)	1. Widen the slope limits by changing the PHC101 calibration settings and method. 2. Recalibrate the probe. 3. Run a check standard to check the performance of the probe.

Message or symptom	Possible cause	Action
Drifting/Inaccurate readings	Contaminated glass sensor	Clean the probe (refer to Clean the probe on page 9).
	CO_2 absorption (for low ionic strength or high purity sample)	Use the LIS chamber for LIS/high purity samples to keep sample contamination from occuring.
	Air bubbles around inner reference electrode	Rinse the reference junction holes with deionized water and then gently tap the probe with hand or shake the probe to remove any air bubbles.
	Incorrect storage conditions (discolored, contaminated or dried gel)	Clean or condition the probe and do recalibration. The probe may not operate correctly if the probe has been left dry for a long time. Condition the glass sensor and reference junctions again: 1. Soak the probe tip in the 4.01, 7.00 and 10.01 buffers each for 5 minutes. 2. Rinse with deionized water. Blot dry with a lint-free cloth. 3. Calibrate the probe.
	Electromagnetic Forces (EMF) such as voltaic cells, thermoelectric devices, eletrical generators, resistors and transformers.	Do not test in areas where EMF is present. For testing in process units (i.e. spot checking), make sure the equipment is grounded.
Out of range	Measurement value is outside of range	Make sure that the sample is within the range of the probe.
Temperature out of range	Temperature value is outside of range	Make sure that the sample temperature is within the range of the probe.
		Make sure that the temperature sensor is working correctly.
	Measured pH buffer temperature is outside range of the probe	Make sure that the standard temperature is within the range of the probe.
		Make sure that the temperature sensor is working correctly.
	Check standard temperature value is outside of range	Make sure that the Check Standard temperature is within the range of the probe.
Out of limits	Measurement value is outside of measurement limits set in the current method	Make sure that the sample is within the limits of the current method.
		Create a new method with expanded limits.
	Check standard value is outside of limits set in the current method	Make sure that the check standard is within the limits of the current method.
		Create another method that expands the acceptable limits.

HACH COMPANY World Headquarters
P.O. Box 389, Loveland, CO 80539-0389 U.S.A.
Tel. (970) 669-3050
(800) 227-4224 (U.S.A. only)
Fax (970) 669-2932
orders@hach.com
www.hach.com

HACH LANGE GMBH
Willstätterstraße 11
D-40549 Düsseldorf, Germany
Tel. +49 (0) 2 11 52 88-320
Fax +49 (0) 2 11 52 88-210
info@hach-lange.de
www.hach-lange.de

HACH LANGE Sàrl
6, route de Compois
1222 Vésenaz
SWITZERLAND
Tel. +41 22 594 6400
Fax +41 22 594 6499

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05/2013, Edition 2

UBWPAD

UPPER BLACKSTONE WATER POLLUTION ABATEMENT DISTRICT

Standard Operating Procedure

REACTIVE PHOSPHORUS (ORTHOPHOSPHATE)

Finalized Date: March 23, 2015

50 Route 20
Millbury, MA 01527

This procedure is performed as per Hach Method 8048 version 1.0

(Acceptable versions of EPA Method 365.2)

ID# 551 Revision Date 3/21/2015 Revision#

STANDARD OPERATING PROCEDURES

Blackstone River Water Quality Monitoring Program

REACTIVE (orthophosphate) PHOSHORUS

SOP-551

Prepared by: _____ Date: _____

Denise Prouty, UBWPAD Senior Laboratory Technician

Approved by: _____ Date: _____

Debra LaVergne, UBWPAD Lab/Pretreatment Manager

List of Revisions

Revision Date	Revision	Pages #s

Standard Operating Procedures
Reactive (Orthophosphate) Phosphorus
(Hach 8048)

1.0 EQUIPMENT & SUPPLIES

1.1 Hach DR3800 Spectrophotometer
Hach Low Range Reactive Phosphorus TNT Reagent Set
Deionized water
Test tube rack
Hach variable volume 1-10ml pipette
Hach pipet tips 1-10ml
Kimwipes

2.0 PROCEDURE

2.1 Press power pad on back of machine. Machine will perform a self-test. The display will show a MAIN MENU. FAVORITE PROGRAMS need to highlight 535 P REACT. PV TNT 1.63 mg/L making sure program is reading in "P" not "P043-" START

2.2 Reactive Phosphorus vials are stored in the cabinet beneath the phosphorus test work area. Place as many vials as needed into a tube rack (located in the middle drawer directly above the cabinet). Also take out as many reagent powder pillows as needed. Generally, the volume of a sample needed to run a reactive P test is 5 mL Volumes may need to be adjusted as to the type of sample that is being run.

2.3 Fill one (1) vial with 5mls of DI water. This is your reagent blank.

2.4 Fill the remaining vials with the samples to be run; remembering to make sure final volume is 5 mL example: Sample volume is 2 mL with 3 mL of DI water.
Mix the contents of each vial by gently rocking the vial back and forth. Try not to create any turbulence in the vials as this may cause zeroing problems for the instrument.

2.5 Place the Blank vial, clean the surface with a Kimwipe, and place it in the cell holder of the spectrophotometer with the Hach logo facing forward.

2.6 Press the Zero. The display will show – Zeroing.... And then 0.00 mg P/L, remove the vial.

2.7 Add the contents of one PhosVer3 Reagent (PV3R) powder pillow to the vial. Cap securely.

2.8 Use the Vortex Genie to mix the vial contents thoroughly. Please note that powder will not completely dissolve. This is normal.

2.9 Next press the CLOCK picture then OK a 2-minute reaction time will begin. The results in the mg P/L will be displayed. Continue to read each sample remembering to zero each vial.

3.0 HELPFUL HINTS

3.1 Remember to subtract the reading of the Blank from each sample reading before calculating your final result.

3.2 When using the PV3R powder pillows, always check that the contents of the pillows are white in color before adding it to the vial. Every now and then you can get a powder pillow that, when you open and look at it, is a yellowish color and/or has dark flecks in it. These powder pillows will not develop the color correctly. Discard and use a new one.

3.3 Check expiration dates on PV3R Powder Pillows.

4.0 SAFETY EQUIPMENT

4.1 Safety glasses
Latex/nitrile gloves
Lab coat
Safety shoes

Appendix L

2017 Field Sampling Plan

UPPER BLACKSTONE WATER POLLUTION ABATEMENT DISTRICT

Total Suspended Solids
and
Volatile Suspended Solids

Finalized Date: March 20, 2015

50 Route 20
Millbury, MA 01527

This procedure is performed as per USGS I-3765-85 and EPA 160.2

ID# 102 Revision Date: 3-20-2015 Revision# 2

STANDARD OPERATING PROCEDURES

Blackstone River Water Quality Monitoring Program

Total Suspended Solids And Volatile Suspended Solids
SOP-102

Prepared by: _____ Date: _____

Denise Prouty, UBWPAD Senior Laboratory Technician

Approved by: _____ Date: _____

Debra LaVergne, UBWPAD Lab/Pretreatment Manager

List of Revisions

Revision Date	Revision	Pages #s
2/20/2015	New Format	1,2,3,4,5
3/20/2015	New Format	1,4,5,6

1.0 PURPOSE

[1]The purpose of solids determinations is to measure the amount of solid material in wastes and process streams, generally to try to define the "strength" of those wastes. Total Suspended Solids (TSS) is defined as those solids which will not pass through a standard glass fiber filter. This includes both those solids that will settle or float in the clarifier and the lighter non-settleable (colloidal) solids.

2.0 EQUIPMENT AND SUPPLIES

- Filtration apparatus attached to vacuum system
- Filtering funnels
- Glass fiber filters (55 mm, 70 mm and 110 mm) Whatman 934-AH or similar
- Graduated cylinders (50 ml, 250 ml, 500 ml and 1000 ml)
- 5ml pipette and pipette bulb
- Deionized (DI) Water used for rinsing
- Aluminum pans and filter covers
- Drying oven (set to 103-105 degrees C)
- Furnace (set to 550 degrees C)
- Insulated gloves
- Tongs
- Marble slab for cooling of trays
- Analytical balance capable of weighing to 0.0001 g
- Desiccators with white and blue indicator stones
- Labels for each day to place on door of desiccators
- Tweezers

2.1 Worksheets:

- Aeration Solids
- Daily Composite Solids
- SSPS solids (Side Stream Pump Station)
- Recycles
- CSO (Combined Sewer Overflow)
- River
- Stormwater
- Bypass / blend

Table 1: Summary of Filter and Sample Preparation

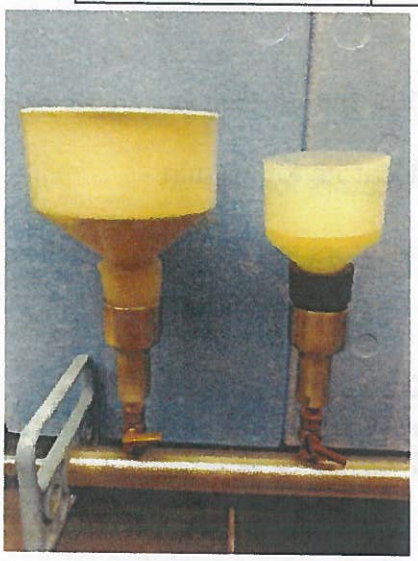
[1] Waste Water Laboratory Manual written by Pennsylvania DEP (chapter 2-3)

						TSS	TVSS
Process	**Filter size**	**Filter prep**	**Filter prep**	**Equipment**	**Sample prep**	**Sample prep**	**Sample prep**
		Weigh and record	Filters to be rinsed, volatized at 550 degrees C for 30 minutes *, weigh and record	Graduated cylinder or pipette size	Dry for at least one hour @ 104 degrees C *, weigh and record	Dry overnight @ 104 degrees C *, weigh and record	Volatized at 550 degrees C for 20 minutes *
Aeration Solids & RAS	55 mm	yes	no	5 ml pipette	yes	no	yes
Daily Composite Solids	110 mm	no	yes	Blank – 500 ml Raw, PE North and South – 250 ml Final -1000 ml	yes, only weigh and record Blank, Raw and Final	yes	yes, only Blank, Raw and Final
SSPS (sidestream pump station) solids grab	70 mm	yes	no	250 ml	no	yes	no
Recycles	70 mm	yes	no	250 ml each except filtrate 50 ml	yes, but can leave overnight	yes, ok to wait overnight	no
CSO	70 mm	no	yes	250 ml	no	yes	no
River	70 mm	no	yes	1000 ml	no	yes	no
Bypass	110 mm	no	yes	250 ml	no	yes	no
Bypass Blend	110 mm	no	yes	500 ml	no	yes	yes
Stormwater	70 mm	yes	no	100 ml – varies	no	yes	no

* Cooling times refer to 3.1.1

Table 2: Summary of Filter schedule

Composite tray filters	Weekdays	Weekends	Holidays
Blank	yes	yes	yes
Raw	yes	yes	yes
PE North & South	yes	yes	no
Final	yes	yes	yes
Sidestream	yes	no	no



3.0 PROCEDURE

3.1 Making Filters

3.1.1 Composite, bypass, bypass/blend and river filters

- Lay 6 110 mm filter blanks (with wrinkled surface up) into 6 filtering funnels. Use funnels that are slightly larger than filters to keep filters flat
- Wash 3 times with approximately 20 mL of deionized water (DI), turn on vacuum during first wash
- Turn off vacuum when removing filters and place on aluminum tray
- Place in muffle furnace for 30 minutes, cool in desiccators for 15 min, then weigh and record onto Daily Composite Solids worksheet. When removing filters from drying oven or furnace always place in desiccators to let temperature stabilize and the time should be consistent throughout the day, so if doing for 15 min always do for 15 min.
- Place into desiccators until use

3.1.2 Aeration, sidestream, recycles, CSO and stormwater filters

- Weigh & record 55 mm filters for each aeration train (i.e. 1A, 2A, 3A, 4A,1G, 2G, 3G, 4G), one 55 mm filter for RAS, and one 70 mm filter for sidestream grab. Record onto Aeration Solids worksheet
- Weigh & record one 70mm filter for sidestream grab. Filter goes on composite tray. Record onto SSPS worksheet
- Place into desiccators until use

3.2 Pouring Aliquot Samples on Filters

3.2.1 Aerations

- Place weighed aeration filters on the filtration funnels, center and press filter into place using the Gooch crucible, wet with DI, and smooth edges to seal against funnel wall with tweezers
- Mix sample. Rinse pipette with sample by pipetting 5 mls of sample, releasing the 5 mls of sample back into bottle then suction up another 5 mls to add to filter.
- Pipette 5 mls in sequence 1G-4G, 1A-4A, and RAS into filtration funnels turning on suction as the fluid hits the surface of the filter
- Wash filter once with DI
- Remove filters with tweezers, turning off the suction after the air seal is broken and place on labeled tray
- Place in drying oven for at least 1 hour then cool in desiccators for 15 min
- Weigh and record
- Place in muffle furnace for 20 minutes then cool in desiccators for 15 min
- Weigh and record

3.2.2 Composites, bypass, bypass/blend, river, Recycles, CSO and Stormwater

- Place weighed composite filters on the filtration funnels, center and press filter into place using the plastic funnel, wet with DI, and smooth edges to seal against funnel wall with tweezers
- Mix sample and pour into graduated cylinder
- River samples come in bottles, pour into 1000 ml graduated cylinders, record total volume, add DI to bottle, shake bottle and pour onto filter three times to make sure all solids are removed from bottle
- Record volume of each sample. Pour samples onto filter with suction turned on
- Rinse the graduated cylinders with DI until no solids left in cylinder into the filtration device, usually three or less washes
- Remove filters with tweezers, turning off the suction after the air seal is broken and place on tray
- Place in drying oven for at least 1 hour then cool in desiccators for 15 min
- Weigh & record blank, raw and final
- Place blank, raw, p.e. north and south, final effluent and sidestream grab in drying oven overnight with labeled aluminum cover on top of each sample
- On the next day weigh and record, discard pe's and sidestream grab filter. Bypass, river, recycles, CSO and stormwater are complete at this point as well, no ashing needed.
- Place blank, raw and finals in muffle furnace for 20 minutes then cool in desiccators for 15 min. Bypass/blend also will be volatized
- Weigh and record

4.0 QUALITY CONTROL

4.1 Analytical Balance Check

- Check level bubble on analytical balance at beginning of day. Each time you sit to weigh something zero out scale by setting lower knob to zero and then adjusting upper knob until line is between the two arrows. If weighing a crucible and then go back to weighing filters zero out again since the weight difference is so great.
- Weekly check the analytical balance using the set of gram and milligram weights that are kept in the drawer under the furnace in a black box. Do not touch weights with hands, use the tweezers provided.
- Use weights bracketing the range you are working with..

4.2 Weight loss or gain

- Check the weight of blank filter
- If the weight loss or gain is more than 0.0005 g, make sure the balance was leveled and zeroed properly and reweigh filter in question

4.3 Duplicate Sample for Final Composite

- Pour duplicate of Final composite sample. Rinse and reuse Final sample 1000 ml graduate cylinder pouring final sample from composite final jug, then follow the same procedure as applied for the first Final sample.
- Compare the TSS and TVS results for each Final to make sure the results are close to each other.

4.4 Standard Sample

- ERA Hardness 507
- Standard will be run the 1st Monday of the month
- Analyze with other composites and follow the same procedure
- Log onto Daily Composite Solids worksheet

5.0 SAFETY WARNING/HEALTH ISSUES

- Be careful not to spill any sample on floor, slip or fall injury may occur
- Avoid open wounds. Keep cuts covered
- No eating i.e. chewing gum
- No drinking
- Avoid wearing contact lenses
- Caution hot!
- Don't open furnace during initial stages of burning to avoid smoke and fire escaping

6.0 HANDLING & PRESERVATION:

- Run samples as soon as possible after collection. If analysis cannot be accomplished immediately, refrigerate samples at or less than 6 degrees C to minimize microbiological decomposition of solids.
- Use tweezers when handling filters. Be careful not to rip or create holes in filters.
- Do not put filters and evaporating dishes in furnace at the same time to avoid ash from dishes falling onto filters thus altering weight
- Composite tray label system i.e.
  - On Tuesday's desiccant shelf you will have tray labeled Monday for composites and Tuesday on sidestream grab cover for Tuesday's work
  - On Tuesday pour Monday composites and Tuesday sidestream grab
  - Tray labeled Monday because that is day of composite sample
  - Sidestream grab cover labeled Tuesday because that is day of grab sample

7.0 TROUBLE SHOOTING

- Remove any large particles that fall onto filters that are non-representative such as leaves, sticks or big worms
- Filter time should be short, less than 10 minutes
- Rain events may affect the amount that will readily filter
- Desiccators indicator stone should be blue, if not replace
- Empty filtering flasks when getting full to avoid moisture getting into vacuum line
- Empty filtering flask at end of workday
- If Final blank filter weighs more than Final sample volatized filter the sample will need to be repoured. This will result in a higher than 100% 'EFF VSS % volatile %' (column in WIMS). This number must be 100% or less.
- If insufficient composite sample was taken for the day, can decrease volume for solids i.e. Final Effluent can be reduced to 250 mls from the usual 1000 mls
- If vacuum suction not strong;
  - check if other vacuum valves in lab are open and wait until they are not in use then close them.
  - Use vacuum grease on the small valves under each filter support to create a good seal, done periodically when drying out (every several weeks).
  - Check if stoppers are seated in filtering flasks tightly.

8.0 SAFETY EQUIPMENT

- Safety Glasses
- Latex+/or Nitrile Gloves
- Safety Shoes
- Insulated gloves
- Tongs

Sample Date _____

Computer entry Aeration Solids

Filter weight (mg)								
Zone G				Zone A				RAS
1	2	3	4	1	2	3	4	

Settleometers				dry weight (mg)								
Zone G				Zone G				Zone A				RAS
1	2	3	4	1	2	3	4	1	2	3	4	

volatilized weight (mg)								
Zone G				Zone A				RAS
1	2	3	4	1	2	3	4	

Sample Volume (all 5 mls unless noted)								
Zone G				Zone A				RAS
1	2	3	4	1	2	3	4	

Computer entry Daily Composite Solids

Sample Date _____

Filter weight (mg)						
Blank	Raw	ATIN	ATIS	Final	Final	Standard

Standard will be run 1st Monday of the month

Sample Volume (ml)						
Blank	Raw	ATIN	ATIS	Final	Final	Standard
500	250	250	250	1000	1000	

Correct volume here & computer if changed

1 hr. dry weight (mg)						
Blank	Raw	ATIN	ATIS	Final	Final	Standard

24 hr. dry weight (mg)						
Blank	Raw	ATIN	ATIS	Final	Final	Standard

volatilized weight (mg)						
Blank	Raw	ATIN	ATIS	Final	Final	Standard

Sample Date _____

WIMS Computer entry Recycles

	Incinerator # _____					Incinerator # 1				Incinerator # 3										
Underflow			Tray Scrubber							Venturi Scrubber							Filtrate			
TSS			TSS			TS				TSS			TS				TSS			
filter wt	sample mls	dry sample wt	filter wt	sample mls	dry sample wt	#__ dish wt	sample mls	dry sample wt	pH	filter wt	sample mls	dry sample wt	#__ dish wt	sample mls	dry sample wt	pH	filter wt	sample mls	dry sample wt	pH

Sample Date _____

	Incinerator # _____					Incinerator # 1				Incinerator # 3										
Underflow			Tray Scrubber							Venturi Scrubber							Filtrate			
TSS			TSS			TS				TSS			TS				TSS			
filter wt	sample mls	dry sample wt	filter wt	sample mls	dry sample wt	#__ dish wt	sample mls	dry sample wt	pH	filter wt	sample mls	dry sample wt	#__ dish wt	sample mls	dry sample wt	pH	filter wt	sample mls	dry sample wt	pH

Sample Date _____

	Incinerator # _____					Incinerator # 1				Incinerator # 3										
Underflow			Tray Scrubber							Venturi Scrubber							Filtrate			
TSS			TSS			TS				TSS			TS				TSS			
filter wt	sample mls	dry sample wt	filter wt	sample mls	dry sample wt	#__ dish wt	sample mls	dry sample wt	pH	filter wt	sample mls	dry sample wt	#__ dish wt	sample mls	dry sample wt	pH	filter wt	sample mls	dry sample wt	pH

Month _____

WIMS Computer entry SSPS solids

date	TSS		
	filter wt	sample mls	dry sample wt
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			
13			
14			
15			

date	TSS		
	filter wt	sample mls	dry sample wt
16			
17			
18			
19			
20			
21			
22			
23			
24			
25			
26			
27			
28			
29			
30			
31			

UBWPAD By-Pass and Final-By-Pass

Date of composite:

		By-Pass	Blend (Final-By-Pass Combined) (flow based)
		T.S.S.	T.S.S.
Date Analyzed (read):	wt.filter		
Bypass usually 250 Final-Bypass usually 500	sample volume	250	500
(24 hour dry)	wt.filter&sample		
Technician(s):	wt.sample	0	0
	s.s. mg/L	**0**	**0**

Blend (Final-By-Pass Combined) Filter and Ash Wt	

updated 9/11

WIMS Computer entry CSO TSS

Sample Date _____

Filter wt.		start		sample volume (mls)		Finish		Filter wt. dry (24hrs)	
Raw	Final	test date	initials	Raw	Final	test date	initials	Raw	Final

Sample Date _____

Filter wt.		start		sample volume (mls)		Finish		Filter wt. dry (24hrs)	
Raw	Final	test date	initials	Raw	Final	test date	initials	Raw	Final

Sample Date _____

Filter wt.		start		sample volume (mls)		Finish		Filter wt. dry (24hrs)	
Raw	Final	test date	initials	Raw	Final	test date	initials	Raw	Final

Sample Date _____

Filter wt.		start		sample volume (mls)		Finish		Filter wt. dry (24hrs)	
Raw	Final	test date	initials	Raw	Final	test date	initials	Raw	Final

RIVER STUDY T.S.S. ANALYSIS

date sampled
date poured

Sample ID:	RMSDG	BLANK	R116G	RMSLG	W1023G
	NBC Slater Mill Dam		NBC Bike Path	State Line	Canal St
filter #	1	2	3	4	5
sample volume					
wt.filter&sample					
wt.filter					
wt.sample	0	0	0	0	0
t.s.s. mg/L	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!

Sample ID:	W1779G	W1779B	W1764G	W0767G	W1242G
	Hartford St	Rice City Pond	Riverdale St	US Gage	Rt 122A
filter #	6	7	8	9	10
sample volume					
wt.filter&sample					
wt.filter					
wt.sample	0	0	0	0	0
t.s.s. mg/L	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!

Sample ID:	W1242D	W1017G	BLANK	W1763G	W1763D
	Rt 122A	Singing Dam		Riverlin St	Riverlin St
filter #	11	12	13	14	15
sample volume					
wt.filter&sample					
wt.filter					
wt.sample	0	0	0	0	0
t.s.s. mg/L	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!

Sample ID:	W1258G	W0505G	UBWPADG	W0680G	BLANK
	Central Cemetery	McCraken Rd		New Millbury St	
filter #	16	17	18	19	20
sample volume					
wt.filter&sample					
wt.filter					
wt.sample	0	0	0	0	0
t.s.s. mg/L	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!

Volatize 70mm filters before use.
Rinse containers into filters.
24 hour dry.

UBWPAD Stormwater Quarterly Results

Year _____

		Sector T			Sector L
Sample Date:		**Outfall #1**	**Outfall #2**	**Outfall #3**	**Outfall #4**
		T.S.S.			
Dates Tested :	wt.filter				
	sample volume				
(24 hour dry)	wt.filter&sample				
Technician(s):	wt.sample	0	0	0	0
	s.s. mg/L	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**

		Sector T			Sector L
Sample Date:		**Outfall #1**	**Outfall #2**	**Outfall #3**	**Outfall #4**
		T.S.S.			
Dates Tested :	wt.filter				
	sample volume				
(24 hour dry)	wt.filter&sample				
Technician(s):	wt.sample	0	0	0	0
	s.s. mg/L	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**

		Sector T			Sector L
Sample Date:		**Outfall #1**	**Outfall #2**	**Outfall #3**	**Outfall #4**
		T.S.S.			
Dates Tested :	wt.filter				
	sample volume				
(24 hour dry)	wt.filter&sample				
Technician(s):	wt.sample	0	0	0	0
	s.s. mg/L	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**

		Sector T			Sector L
Sample Date:		**Outfall #1**	**Outfall #2**	**Outfall #3**	**Outfall #4**
		T.S.S.			
Dates Tested :	wt.filter				
	sample volume				
(24 hour dry)	wt.filter&sample				
Technician(s):	wt.sample	0	0	0	0
	s.s. mg/L	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**	**#DIV/0!**

BLACKSTONE RIVER WATER QUALITY MONITORING PROGRAM FIELD 2020 SAMPLING PLAN

Presented To:
Karla Sangrey, Director

Upper Blackstone Clean Water
50 Route 20
Millbury, MA 01527-2199

Submitted By:
Marie-Françoise Hatte Massachusetts

Water Resources Research Center
209 Agricultural Engineering Bldg.
250 Natural Resources Way
University of Massachusetts
Amherst, MA 01003

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Note that all forms, SOPs, and instructions can be found in the Blackstone River Assessment of Water Quality, Ecological Health, and Ecological Risk through Data Collection and Modeling Quality Assurance Project Plan 2020 – 2022

2020 Sampling Season
Scope of Work
Blackstone River, Massachusetts

1.0 Historical Overview

The Blackstone River Watershed Assessment Study began in 2003 with the goal of conducting a watershed management study of the Blackstone River Basin in Massachusetts and Rhode Island. Objectives included evaluation of trends in river quality as well as flow management opportunities with existing hydraulic structures so that water quality and aquatic habitat can be improved throughout the basin.

In 2004 through 2006, a monitoring program was conducted to collect water quality, streamflow, and sediment data sufficient for the calibration and validation of computer models to simulate pollutant loading, transport, and in-stream fate and distribution along the main stem and tributaries of the Blackstone River. From 2006 – 2012, a water quality model of the Blackstone River was developed, calibrated, and validated using Hydrological Simulation Program – Fortran (HSPF). This model was based on an existing water quantity model of the Blackstone River watershed, which was developed by the United States Geological Survey (USGS) (Barbaro and Zariello, 2006). The HSPF model currently represents conditions through 2011 and has been used to evaluate and model dynamic water quality conditions incorporating daily, monthly, seasonal and inter-annual variability. Both point source (e.g., waste water treatment plants) and non-point source (e.g., stormwater runoff) loads to the river are incorporated explicitly into the modeling analysis.

Upper Blackstone Clean Water (Upper Blackstone or UB) plant upgrades designed to meet the 2001 permit limits have been online since Fall 2009. In late 2009 and early 2010, slight adjustments to the system were made to optimize performance. As of August 2010, the Upper Blackstone Wastewater Treatment Facility 2001 permit upgrades were fully operational. A new monitoring program was initiated in Spring 2011 and expanded in 2012 to help assess response of the river to the reduced nutrient concentrations in the effluent. Water quality monitoring of the main stem river will continue in 2019, as described in this Scope of Work. Sampling in 2020 will continue the 2019 program and include routine (monthly) sampling for nutrients and chlorophyll-a, measurement of water temperature, dissolved oxygen, pH and conductivity, and deployment of four dissolved oxygen data loggers.

2.0 Objectives for 2020 Monitoring

The Blackstone River is formed by the confluence of the Middle River and Mill Brook in Worcester, Massachusetts. From there, the River flows approximately 48 miles south into Rhode Island where it becomes the Pawtucket River at the Main Street Dam in Pawtucket, Rhode Island. The main stem Blackstone River is joined by many small tributaries, as well as six major rivers: the Quinsigamond River, the Mumford River, the West River, the Mill River, the Peters River, and the Branch River. The

watershed consists of over 1,300 acres of lakes and ponds; the largest is Lake Quinsigamond in Shrewsbury and Grafton.

The scope of the 2020 monitoring program is outlined in this document. The 2019 water quality monitoring program is designed to:

- Build upon work conducted by Upper Blackstone, Massachusetts Department of Environmental Protection (MassDEP), the U.S. Geological Survey (USGS) and others;
- Support future analysis, if needed, of river surface water flow and quality;
- Collect data to assess changes in riverine nutrient and chlorophyll-a concentrations and fluxes through comparison against historical data; and
- Collect data to describe riverine water temperature, dissolved oxygen, pH, and conductivity.

These objectives were used to select sampling locations as well as suitable sampling methods, analytes, measurement techniques, and analytical protocols with the appropriate quality assurance and quality control guidelines. This Scope of Work falls under the Blackstone River 2020 – 2022 Quality Assurance Project Plan (QAPP) and associated Standard Operating Procedures (SOPs), submitted to MassDEP in March, 2020. The 2020 – 2022 QAPP is a revision of the 2017 – 2019 QAPP last approved by MassDEP in December, 2019. The QAPP is designed to cover the range of sampling activities anticipated under the Blackstone River Watershed Assessment Study and serves as an umbrella document for specific Field Sampling Plans, such as this Scope of Work, that will be conducted as part of the study.

3.0 Nutrient Sampling

3.1 Nutrient Sampling Locations & Rationale

The number and location of sampling sites are described in this section. Nutrient sampling will be conducted at 9 main stem run-of-river locations deemed to be the most relevant for understanding potential impacts of the Upper Blackstone's wastewater effluent on downstream water quality. The main stem sampling locations included in the 2020 FSP have been selected in order to provide:

1. Data on changes in concentration and load along the river, particularly downstream of the confluence with the Upper Blackstone effluent and upstream of the confluences with the Mumford and West Rivers,
2. Information on nutrient loads crossing the MA/RI state line, and
3. Information to help understand the impact of the impoundments and nutrients on productivity within RI reaches.

Starting in April 2020, UMass, with the assistance of Upper Blackstone staff, will collect samples for nutrient and chlorophyll-a analysis and collect hand-held meter measurements monthly (e.g., roughly every 4 weeks) at nine locations, including three Rhode Island sites along the main stem of the Blackstone River that will be co-sampled with the Narragansett Bay Commission (NBC). Sampling will continue through November. Samples will be collected routinely each month for nutrients, including

phosphorus, nitrogen, and chlorophyll-a, regardless of weather conditions, as described in Section 4.0. Information on sampling frequency, sampling program logistics, schedule, and sampling methods is provided in subsequent subsections.

The sampling sites are provided in Table 1 and are consistent with the sites sampled in 2017 – 2019. The sampling location at RMSD will be changed to be from the bridge on Exchange Street rather than from the bank to better measure water quality at the center of the channel. Samples will be collected at both locations a few times in 2020 to document any difference between results from the two sites. Detailed text descriptions, driving directions, and maps of the locations are provided in Appendix A. Figure 1 shows the location of the sampling sites relative to each other and the basin.

Table 1: 2020 Sampling Sites (all sites located on the main stem)

Site ID#	Site Name	Lat	Lon	River Mile[2]
RMSDh[1,5] RMSDn[1,6]	Slater Mill Dam, Pawtucket, RI	41.876909[5] 41.879836[6]	-71.381940[5] -71.381556[6]	0.0
R116[1]	Rte 116 Bikepath Bridge, Pawtucket, RI	41.938066	-71.433769	6.3
RMSL[1]	State Line, RI	42.009974	-71.529313	15.5
W1779	Below Rice City Pond Sluice Gates, Hartford St., Uxbridge, MA	42.097270	-71.62241	27.8
W0767	Sutton St. Bridge, Northbridge, MA	42.153922	-71.652521	33.4
W1242	Route 122A, Grafton, MA	42.177153	-71.687964	36.3
W1258	Central Cemetery, Millbury, MA	42.19373	-71.76603	42.7
UBWPAD2	New Confluence site, downstream of effluent canal	42.20702	-71.78154	44.6
W0680[3]	New Millbury St Bridge, Worcester, MA	42.22784	-71.78762	45.9

[1] Locations of co-sampling with NBC
[2] Corresponding river mile
[3] W0680 is located between the Worcester CSO discharge and UBWPAD2. The Worcester CSO enters the river downstream of the confluence of Mill Brook and the Middle River at approximately river mile 46.4.
[5] Historical RMSD site
[6] New RMSD site

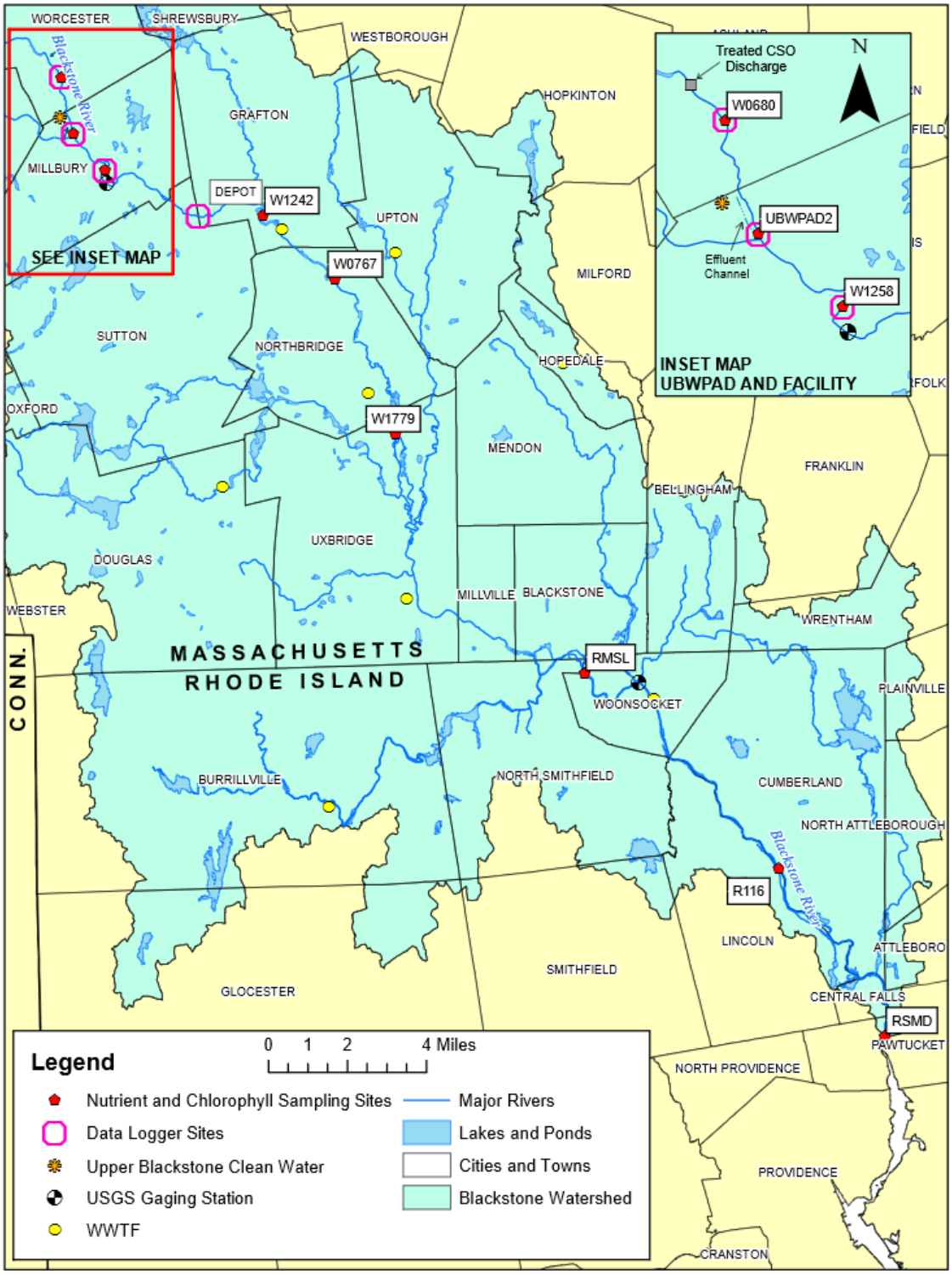

Figure 1: 2020 Blackstone River water quality monitoring locations

3.2 Nutrient Parameters, Methods, and Detection Limits

Aliquots prepared from the surface water grab samples will be analyzed at the Upper Blackstone laboratory, UMass Dartmouth (UMD) laboratory, or the UMass Environmental Analysis Laboratory (EAL), depending on the parameter. Samples collected from the sites co-sampled with NBC will also be analyzed at the NBC laboratory. Laboratory analysis methods and detection limits are summarized in Table 2.

Method Detection Limits (MDLs) are the lowest values at which a parameter can be measured using the reference method. The MDL is defined as the constituent concentration that, when processed through the complete method, produces a signal with 99 percent probability that it is different from the blank. Lab specific MDLs are developed for each particular analyte of interest and are established as targets for ensuring that the data quality obtained is adequate for interpreting the data; these MDLs are the minimum to be achieved by the laboratories.

The reporting limit (RL) is defined as the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions and can vary by sampling date. For this project, laboratories will be responsible for calculating the RL for each analysis batch, and will report out values below their RL as "non-detect."

In the database for the project, these data points will be flagged with the code "LT" (less than) and the detection limit value from Table 2 listed as the result. This value will be used in plotting; half of the MDL will be utilized for calculations. The analyses and responsible laboratories for the 2020 sampling season are as follows:

- Samples will be analyzed at Upper Blackstone for total suspended solids (TSS), conductivity (Specific Conductance or SC), and total orthophosphate (TOP).
- The NBC lab[1] will analyze samples collected at the three Rhode Island sites for dissolved nutrients, including dissolved nitrate/nitrite (dNO_{23}), dissolved ammonium (dNH_4), total dissolved nitrogen (TDN), dissolved orthophosphate (DOP), total nitrogen (TN), and total suspended solids (TSS). These three sites are co-sampled by UMass and NBC. A single large volume bulk environmental sample is collected, and aliquots for analysis at each lab are then split from this volume.
- Samples will be sent to the UMD laboratory for analysis of total dissolved nitrogen (TDN), dissolved nitrite/nitrate nitrogen (dNO_{23}), and dissolved ammonium (dNH_4). These samples will be filtered in the field utilizing a 0.22-micron filter.
- UMD will also analyze samples for particulate organic nitrogen (PON) and calculate total nitrogen (TN) for each sampling location/date based on the results of these analyses, Table 3.
- Samples will be analyzed for chlorophyll-a (chl-a) and total phosphorus (TP) at EAL.

Table 3 provides a summary of the data calculated by each lab.

[1] SOPs and the QAPP for the NBC were not included under cover of the QAPP for this project, as these data are part of their sampling program and considered external to the UMass sampling program. Details of their analysis methods, however, are provided herein.

Table 2: 2020 Analyses, Laboratories, Methods, and Limits

Upper Blackstone Clean Water		
Parameter	Method	Minimum Detection Limit
TOP	Hach 8048	20 ppb[4]
TSS	USGS I-3765-85	2 ppm
Conductivity	STD Method 2510B	0.0 µS/cm
UMass EAL		
Parameter	Method	Minimum Detection Limit/Minimum Reporting Limit
TP	STD Method 20th ed., 4500P	2 ppb/8 ppb
Chl-a[1c]	STD Method 20th ed., 10200 H	1 ppb
UMass Dartmouth		
Parameter	Method	Minimum Detection Limit/Minimum Reporting Limit
dNH_4[1d]	STD Method 20th ed, 4500-NH3-F	1.4 ppb/2.8 ppb
dNO_{23}[1d]	STD Method 19th ed, 4500-NO3-F	3.5 ppb/7 ppb
TDN[1d]	STD Method 19h ed, 4500-Norg	5.3 ppb/10.3 ppb
PON	EPA 440.0	10 ppb

[1] Filtration for dissolved nutrients varies by lab as detailed below.

[a] Starting in 2015, NBC moved to lab filtration for their dissolved constituents utilizing 0.45 micron filters.

[c] Filtered in the lab within 4-hours of sample collection with Whatman GF/F 47 mm, 0.70 micron filter.

[d] Field filtered utilizing Millipore (SLGP033RS), Millex-GP Syringe 0.22-micron filter units.

[3] Laboratories will be responsible for calculating the RL for each analysis batch, and will report out values below their RL as "BRL.". In the database for the project, these data points will be flagged with the code "LT" (less than) and the detection limit value listed as the result. This value will be use in plotting; half of the MDL will be utilized for calculations.

[4] The Upper Blackstone lab has worked to achieve the lowest detection limit possible with their existing equipment and methodologies, however the labs primary focus is analysis of WWTF effluent. It is acknowledged that these DLs are high for riverine analysis.

Table 3: Parameters Calculated Based on Lab Results

Lab	Parameter	Calculation[1]
NBC	Dissolved Inorganic Nitrogen	$DIN = dNO_{23} + dTAM$
	Dissolved Organic Nitrogen	$dON = TDN - DIN$
	Dissolved Kjeldahl Nitrogen	$dTKN = TDN - dNO_{23}$
UMD	Total Nitrogen	$TN = TDN + PON$

Note: [1] Half the detection limit will be utilized in the calculation when laboratories report results for constituent parameters below the reporting limit.

3.3 Sampling Collection Details

This section describes the procedures for collecting and analyzing samples. It identifies the sampling equipment, performance requirements, and decontamination procedures utilized. The procedures for identifying sampling or measurement system failures and for implementing corrective actions are also summarized.

General Sample Collection

The field program will be conducted based on the Standard Operating Procedures (SOPs) on file as part of the 2020-2022 Quality Assurance Project Plan (QAPP) prepared for the Blackstone River Watershed Assessment Study. The QAPP is designed to serve as an umbrella document for any field sampling conducted as part of the project. Utilizing standard procedures and sampling techniques helps ensure the collection of accurate, precise, and representative samples, as well as helping to ensure data comparability and usability.

The SOPs on file that will be utilized during this field monitoring program include SOP-FLD-001: Collection and Handling of Water Samples for Water Quality Analysis, SOP-FLD-009: Calibration and maintenance of measuring and test equipment, and SOP-FLD-010: Field Sampling of Chlorophyll-a. All were submitted in the "SOP Compendium" as part of the QAPP prepared for the project. These relevant project SOPs are listed in Table 4. Note that the original numbering of the SOPs from an earlier QAPP has been retained although several field SOPs have been removed from the study. SOP-FLD-013 was added in 2019 for the field measurement of temperature, dissolved oxygen and pH.

Table 4: Summary of SOPs for Sample Collection of Nutrients and Field Measurements

Document Name	Title
SOP-FLD-001	Collection and Handling of Water Samples for Water Quality Analyses
SOP-FLD-009	Calibration and Maintenance of Measuring and Test Equipment
SOP-FLD-010	Field Sampling of Chlorophyll-a
SOP-FLD-013	Field Measurement of Temperature, Dissolved Oxygen, and pH
SOP-FLD-014	Data Logger Measurement of Temperature and Dissolved Oxygen

Samples collected during the 2020 sampling season will be surface water samples collected from locations believed to be generally representative of net water quality within the river. Routine monthly samples will be collected regardless of precipitation and antecedent conditions.

Field data sheets will be used to document daily site activities and sample collection. Any variations from established procedure will be documented on the project Field Change Request and submitted to the Project Manager for review and archival.

Prior to collecting samples, the sampling location will be visually inspected and a Rivers and Streams Field Sheet completed. Any sampling issues will either noted on an Equipment Problem Report Sheet or a Field Change Request Form. At each sampling location, the collection date, time, and additional collection details will be noted on the Bulk Sample Collection Data Sheet for the sampling event. Sampling data sheets will be transferred to UMass and retained as part of the monitoring record. Project field sheets and checklists are provided in Appendix B. Any observation that is not appropriate to note on individual field sheets will be recorded in the sampling crew's Field Notes Log Book.

Sample collection and bulk storage bottles will be cleaned with non-phosphate containing detergent between each sampling event as per the project SOPs, summarized in Table 5. The bottles will be filled

with DI water after washing and the conductivity tested after 24-hours. Bottles with conductivity results above 2 microsiemens/centimeter will be rejected. Bottles that pass will be emptied, allowed to air dry, then capped and stored for the next event. All aliquot bottles, with the exception of those received from UMD, will be similarly washed, tested, and dried. At least two spare bottles will be available each sampling trip in case of mishap.

Table 5: Sampling Container Decontamination Procedures

Sample type	Container	Decontamination	Staff
Sampling container	4 L, plastic	Phosphate-free soap, DI rinse	UMass
Bulk sample container	4 L and 6 L, plastic	Phosphate-free soap, DI rinse	UMass
Chl-a	500 mL and 1 L, amber plastic	Phosphate-free soap and acid wash, DI rinse	UMass
TP	125 mL, amber plastic	Phosphate-free soap and acid wash, DI rinse	UMass
TOP	237 mL, plastic	New, DI rinse	UMass
TSS, SC	1 L, plastic	New, DI rinse	UMass
dNH_4, dNO_{23}, TDN	60 mL, plastic	Acid wash, DI rinse	UMD
PON	1 L, plastic	Acid wash, DI rinse	UMD

Nitrile gloves will be worn by all sampling personnel, and will be changed between sampling sites.

Bulk water samples for nutrient analysis will typically be collected from either a bridge, utilizing a Nalgene 4-L wide-mouth HDPE bottle attached to a rope and reel or a peristaltic pump, or from the stream bank directly using the bulk sampling bottle attached to a sampling pole. The sampling rope and reel are technically considered to be non-dedicated sampling apparatus, as they contact surface water samples from more than one monitoring location. However, because they come into contact with the outside of the bottle only, this will not cause cross-contamination. The associated sampling container, however, is also utilized at more than one location. To minimize potential cross-contamination, the sampling container will be rinsed three times with river water prior to collecting the final sample. The sampling container is filled twice after rinsing with river water. The first time, the water is poured from the sampling container to the chlorophyll sample bottle to rinse it three times, then to fill it. The second fill is transferred into a clean 4-L wide-mouth HDPE bottle (the bulk collection bottle), which will also be rinsed three times with the sample water previous to final sample collection. An equipment blank will be collected at one site from the sampling container at the start of the sampling season, mid-season, and at the end of the season.

To collect samples from the stream bank, the sample bottle will be attached to the sampling pole. At W1779, the sample bottle used is the 4-L bulk sample bottle. At W0680 and UBWPAD2, the sample bottle used is the 1-L brown Nalgene bottle. The sample bottle is uncapped and dipped upside down in the water, rinsed and emptied downstream three times. The sample bottle is then dipped upside down in the water until fully submerged. The bottle is then turned right-side up and held in place until no more air bubbles come out and brought back to the stream bank. This bottle is used to rinse three times the other bottle at the stream bank (whether the other bottle is a 1-L brown Nalgene bottle or a 4-L bulk sample bottle), and is refilled as many times necessary to fill the other sample bottle at the stream bank. It is then filled and capped.

At the RI sites, a 6-L Nalgene carboy bottle with spigot will be utilized as the collection bottle to enable collection of a bulk sample large enough to provide splits for both NBC and UMass. At these three locations, the sample will be collected utilizing NBC's peristaltic pump. This pump is designed to have minimal effect on water quality. Cross-contamination will be minimized by fully flushing the pump tubing prior to rinsing the collection bottles and caps three times with river water. Rinse water will be emptied away from the sampling location.

The bulk sample bottles will be labeled and put into a cooler packed with ice until they can be transferred to the lab for splitting into sub-sample bottles and preserved for subsequent laboratory analysis. Labels for the bulk sample bottles will be printed prior to the event (see Appendix C).

Chlorophyll-a Sample Collection

As per the chlorophyll-a SOP, samples for chl-a analysis are collected in amber containers, protected from sunlight, and filtered as soon as possible through a 47 mm diameter Whatman GF/F 0.7-micron pore size glass microfiber filter. Amber bottles will be put into a cooler packed with ice until they can be transferred to the Upper Blackstone lab where they will be filtered. Filtering will typically occur within four hours of sample collection.

Field Filtering for Dissolved Nutrients

NBC analyzes samples collected at their three Blackstone River sampling locations for dissolved nutrients. NBC filters samples in the field with a 45 µm filter. UMass began field filtration in 2015 per MassDEP guidance, both with a 45 µm filter and with a 22µm filter. UMass will filter only with 22 µm filters in 2020, for analysis of dissolved nutrients at UMD as part of the project. Table 6 provides an overview of the preparation of filtered samples.

Table 6: Summary of Sample Filtration

Parameter	Filter	Sites	Filtering location	Staff filtering
dNO_{23}	0.22 µm	All	Field	UMass (5 sites), Upper Blackstone (4 sites)
dNH_4	0.22 µm	All	Field	UMass (5 sites), Upper Blackstone (4 sites)
TDN	0.22 µm	All	Field	UMass (5 sites), Upper Blackstone (4 sites)
Chl-a[1]	0.7 µm	All	Upper Blackstone Lab	UMass

[1] Sample analyzed is filter residue, not the filtrate.

At all sites, aliquots for dissolved analysis will be field filtered with Millipore (SLGP033RS) 0.22-micron filter units attached to a Millex-GP syringe for analysis of the nitrogen series at UMD. A new syringe and filter unit will be utilized at each site. The syringe will be rinsed three times with water from the bulk collection bottle by removing the plunger, pouring into the barrel, and then replacing the plunger to shake and then dispose of the rinse water. After the final rinse, the Millipore filter unit will be attached,

and the syringe filled with water from the bulk collection bottle. Next, 20 mL of sample will be filtered through the disposable 0.22-micron filter housing and discarded. Then, 20 mL of sample will be filtered into the sample bottle to rinse and discard. The remaining 20 mL water in the syringe will be filtered into the 60 mL sample bottle. After removing the plunger, the filter will be removed from the syringe and discarded, then a new 0.22-micron filter will be attached. The syringe will be refilled with sample water, 20 mL wasted through the filter, and the remaining 40 mL of sample in the syringe then utilized to fill the 60 mL bottle containing 20 mL of sample from the first 0.22-micron filter. It should be noted that aliquot bottles provided by UMD will not be washed at UMass.

Field Blanks

Field blanks will consist of water that is transferred from one bulk collection bottle that was filled with DI water from the EAL lab the day before sampling, to a "field blank" collection bottle at the sampling site. A field blank will be collected for all parameters at a frequency of at least ten percent, or one field blank per ten samples. Sampling crews will be given specific instructions as to the sampling location where field blanks should be processed, transferring the DI water from the lab bottle to the bulk sample bottle. Processing of the field blank to aliquots, including the field filtration step, will occur in the same manner as for regular grab samples. Field blanks will provide an indication of whether atmospheric conditions or field procedures have the potential to lead to sample contamination.

Equipment Blanks

To ensure that samples collected with the 4-L sampling container are not contaminated from water collected at previous sites, an equipment blank will be collected the first sampling day in 2020 at a randomly selected bridge site. Two one-gallon jugs of Upper Blackstone DI will be transported to the field and used to rinse the sampling container three times and fill the sampling container. A bulk sample bottle labeled 'Equipment Blank' will then be filled from the sampling container. Processing of the equipment blank to aliquots, including the field filtration step, will occur in the same manner as for regular grab samples. An equipment blank will be also run mid-season at another bridge site.

Field Duplicates

Field duplicates will consist of a second bulk sample collected at approximately the same time. Field duplicates will be collected for all parameters at a frequency of at least ten percent, or one duplicate per ten samples. Processing of the field duplicates, including the field filtration step, will occur in the same manner as for regular grab samples. Field duplicates will provide an indication of the inherent variability of nutrients in the water column over short spatial and temporal differences

Field Splits

Field splits will consist of a second set of aliquots processed from the bulk collection bottle. Field splits will be collected for all parameters at a frequency of at least ten percent, or one split per ten samples. Field splits will provide an indication of the inherent variability within a sample, independent of replicates run by the laboratories. Enough water will be collected to allow splitting into all the aliquots at the UB lab. An extra 2-L bottle will be given to the crew collecting the field split in order to have enough sample water for 2 TSS/SC samples.

Performance Tests

A performance test (PT) will be provided to each laboratory per sampling event for dissolved phosphorus, dissolved orthophosphate, dissolved nitrite-nitrate, and dissolved ammonia, depending on the parameters analyzed for in their laboratory. The PT aliquots will be prepared each day before sampling by EAL staff from standards of a known concentration.

Sample Processing

The remainder, after field filtration, of the bulk samples will be transported back to the Upper Blackstone building, where they will be split into smaller volume bottles for subsequent analysis. Labels for the aliquot splits will be printed prior to the event (see Appendix C). In general, when the coolers are brought inside for sample processing, the amber bottles for Chl-a analysis will be separated so that one crew member can begin filtering. The second crew member will begin to process the aliquots from the bulk samples.

All lab personnel will wear nitrile gloves, and will change gloves when switching to processing a new site. Working from downstream to upstream, the order in which sites were sampled, the bulk sample for each site will be found in the cooler and processed. Sets of bottles (a 1-L jug, a 243 mL squat bottle, etc.) will be set out for the given sampling location. Based on a sampling QAQC table provided to the sampling crew identifying sites where field splits are to be analyzed, additional bottles will be added to the site sets. Labels for the bulk and aliquot bottles will be compared; the sample collection time will be added to the aliquot bottle labels. After loosening the aliquot bottle caps, the bulk sample bottle will be fully mixed by inverting 10 times and the aliquot bottles rinsed three times. The bulk sample bottle will then again be fully mixed and the aliquot bottles filled with sample. Both the aliquot and bulk sample bottles will be re-capped as soon as possible and the bulk sample returned to its cooler. After completing the appropriate line on the chain of custody forms for the aliquots, the aliquots will be placed in separate coolers, one for each bottle type. If called for, bulk sample field blanks and duplicates will be processed after the bulk grab sample for the same site is processed.

At least one split duplicate (e.g., two aliquots taken from the same bulk sample bottle) and one field duplicate (a second bulk sample co-collected in the field) will be collected, processed, and analyzed for each parameter and sampling event to meet our QAQC objectives.

Table 7 summarizes the container, handling and preservation, and hold time for each analyte. At least two spare bottles for each aliquot type and blank labels will be available in case of mishap. Step-by-step directions utilized by the aliquot splitter have been developed and are available upon request.

Table 7: Sample Container Codes, Types, Volumes, Preparation, Special Handling, Preservation, Holding Times

Analysis	Cont. Code	Container	Handling & Preservation	Holding Time
TOP	A - Upper Blackstone	237 mL, plastic	Store ≤6°C	48 hours
TSS, SC	C - Upper Blackstone	1 L, plastic	Store <=6°C	7 days
Chl-a[1, 2]	D – EAL (filter retained only[1])	1 L, amber plastic	0.7-micron pore size glass microfiber filter, dry filter and freeze, store in dark, discard filtrate	21 days
TP	E - EAL	125 mL, amber plastic acid washed	Freeze	1 year
PON[1]	H – UMass Dartmouth	1 L, Plastic	Store 4±2°C. Transport to UMD (lab filtered by UMD; filter analyzed, filtrate discarded)	48 hours
dNH_4, dNO_{23}, TDN	I – UMass Dartmouth	60 mL, Plastic	0.22 µm filter[3]. Store filtrate 4±2°C. Transport to UMD.	48 hours

Notes:

[1] Sample analyzed is filter residue, not the filtrate

[2] Filtration occurs within 4 hours of sample collection.

[3] Filters are analyzed within 21 days according to the EAL QAPP

Preparation of Lab Blanks

The day prior to sampling, lab blanks will be prepared by filling aliquot bottles directly from the EAL source of DI water. The lab blank aliquot bottles will travel with the samplers from site-to-site and then be added to the appropriate cooler based on analyte type and lab at the end of the day. Lab blanks will provide an indication of whether DI source water, transportation steps, or laboratory analysis procedures have the potential to lead to sample contamination. In the event that positive blanks or duplicates are outside the acceptable precision range, additional blanks and/or duplicates will be added in subsequent sampling events to try and determine the source of contamination if it is not readily identifiable from existing data and documentation.

Sample Preservation

Once all aliquots are split, the 243 mL (TOP), 1 L (TSS/SC) for analysis at the Upper Blackstone will be moved from coolers to the walk-in refrigerator, unpreserved. Samples for delivery to UMD will be placed in a dedicated cooler with fresh ice and shipped via FedEx overnight. Samples for delivery to EAL will be moved from the Upper Blackstone freezer to a cooler, transported, and immediately placed in the EAL freezer. No acidification is necessary for sample preservation this season, except for RI samples on one summer sampling date, if pertinent.

Filtering for Chlorophyll-a

Following SOP protocols, water samples collected in amber bottles for chlorophyll-a analysis will be filtered in the Upper Blackstone lab through a 47 mm diameter Whatman GF/F 0.7-micron pore size glass microfiber filter as soon as possible but no later than within 4 hours. Prior to filtering, all filtering equipment and containers will be rinsed three times with deionized (DI) water and then once with sample water. The filtering process will be set up with vacuum flask, filter holder, glass fiber filter, and filling funnel. After placing the filter rough side up on the filter holder, an exact sample volume will be measured out using a graduated cylinder, filtered, and the volume filtered recorded. Each sample will be filtered until the filter is visibly green or greenish brown. This coloration indicates enough chlorophyll has been collected for the chlorophyll-a analysis. For the Blackstone River, 250 mL of water will be typically filtered during the growing season, but during early spring and late fall, when productivity in the river is less, larger volumes will likely be filtered. During July and August, peak seasons for growth, smaller volumes may be filtered. When the entire measured sample has been filtered, the filling funnel will be removed and the filter carefully transferred from the filter holder with forceps, folded in half (green side in), and placed in an air-drying box. When all samples have been filtered, the drying box will be plugged in and the sample filters completely air-dried for approximately 25 minutes. The filters will then be removed with forceps, placed in aluminum foil, and labeled with the site name, date, time of sampling, and volume of water filtered. Filters will be frozen as soon as possible for preservation prior to chlorophyll-a analysis.

Chain of Custody

Chain of custody will be maintained in accordance with standard procedures. Chains of custody will be pre-filled out with the expected samples and analyses, including a line for each aliquot. At the time bulk samples are split into aliquots for preservation and subsequent analysis, chain of custody forms will be checked against the aliquot bottles and the collection times will be added. One chain of custody form will be prepared for each lab (Upper Blackstone, EAL, UMD), plus one for the NBC lab to accompany the PT sample given to the NBC sampling crew. Copies of the chain of custody forms are provided in Appendix D. Once the chain of custody forms are checked and signed by UMass staff, they will be transferred to the respective laboratories for their staff to sign.

Sample ID Nomenclature

Sample IDs will follow a set nomenclature consisting in general of four parts: sampling site ID, sample type, filtration code, and date. Unique sampling site identifications for each site are listed in the first column of Table 1. Sample types include both the sample itself, designated as a grab sample, as well as the quality assurance quality control (QAQC) samples such as splits, duplicates, blanks, and performance evaluation samples, Table 8. Each sample ID will also include a filtration code, as indicated in Table 9. The last field will be the sample collection date as MMDDYY.

Table 8: Sample Type Codes

Code	Description
G	Grab sample
FS	Field split
FD	Field duplicate
LB	EAL DI water lab blank
FB	EAL DI water field blank
EB	UB DI water equipment blank
P	Performance evaluation sample
TC	Temperature Check bottle

Table 9: Filtration Codes

Code	Description
UF	Unfiltered
FF22	22-micron field filtered
NA	Not applicable (e.g., for lab blanks)
FR	Filter residue (e.g., analysis done on a filter, such as for PON)

4.0 Field Water Quality Measurements

In 2020, field water quality measurements (water temperature, dissolved oxygen [DO], and pH will be collected at all sites. Field parameters will be collected with a hand-held Hach HQ 40 D multimeter equipped with two probes. Temperature, DO, and pH will be measured in situ by each field crew.

Each meter will be calibrated by UB staff at the UB lab on the morning of each sampling day, prior to sampling. Both DO and pH probes will be attached to the meter. Calibration forms are found in Appendix E, along with measurement instructions from the meter manual.

At the sampling site, measurements will be taken with the meter before or at the same time as the collection of river samples. The probe comes with a 25-foot cable. If the river surface cannot be reached, measurements will be taken from a sampling container. Measurements will be taken from both the river and a sampling container a few times during the season to compare the two sets of measurements. If sampling container measurements are not acceptable, no further measurements will be made from those containers. At each site:

1. Rinse the probes with DI water, then lower the probes into the river where water chemistry samples are collected, just below the water surface.
2. Press the READ key. When the screen shows that the measurements have stabilized, record the readings for water temperature (%), DO saturation, DO concentration in mg/L, and pH on the field sheet.
3. Rinse the probes with DI water, and place the probes in their respective sleeves/flasks. Place the meter and probes in the travel bucket.

An SOP was created in 2019 and submitted as an addendum to the QAPP: SOP-FLD-013: Handheld Multimeter Field Measurements (see SOP-013 in Appendix F).

At the RI sites, the field parameters recorded by NBC should also be recorded on the field sheet.

Upon return to the UB lab, the pH probe will be placed in each of the buffers and readings recorded on the calibration form. The DO probe will be placed in the air-saturated water flask and the reading will be recorded on the calibration form. A photocopy of the calibration form for the sampling day will be given to the UMass team.

Conductivity will be measured with the Hach meter and a conductivity probe in the UB lab from the same samples used for TSS analysis. The lab SOP for conductivity measurement is included in Appendix F.

5.0 Schedule

The nutrient sampling program will follow the sampling schedule NBC has in place for their Blackstone River sampling. Because NBC sometimes needs to adjust their schedule, sampling dates will be confirmed with NBC and the labs one-week prior to each planned event. Samples will be collected routinely for nutrients once every 4th Wednesday, regardless of weather conditions, starting in April. See Table 9 for sampling dates in 2019.

Table 9: 2020 proposed sampling dates

22 April
20 May
17 June
15 July
12 August
9 September
7 October
4 November

6.0 Quality Assurance

Prior to the first sampling event, sampling staff from UMass and Upper Blackstone will read through the Field Sampling Plan, sampling SOPs, and review field data sheets. UMass and Upper Blackstone sampling staff will then participate in a conference call or meeting which will act as a refresher on sampling protocols and will also enable staff to discuss any questions or concerns related to sampling. To ensure sampling procedures are followed and QAQC objectives are being met, Marie-Françoise Hatte will conduct a field audit during at least one sampling event to observe sampling crews and document any deviations from the sampling SOPs. Field audit results will be made available to all sampling staff and any issues will be corrected.

Measurement performance criteria, including the precision, accuracy, completeness, comparability, and representativeness of the data will be used to assess the quality of all environmental measurements in relation to the objectives of this Scope of Work. The criteria for this project are presented in Appendix E. To meet these objectives, field duplicates, laboratory replicates, and blanks will be run. QAQC samples will at a minimum consist of 1 field duplicate (rate of 1:9) and one blank each sampling run (rate of 1:9). Additional blanks and duplicates will be added if positive blanks or duplicates outside of the acceptable precision range are noted.

In addition, a limited number of Performance Test (PT) samples will be used as a double-blind evaluation on the respective laboratory's performances for the following parameters: total dissolved phosphorus (TDP), dissolved orthophosphate (DOP), dissolved nitrate/nitrite (dNO_{23}), and dissolved total ammonia (dNH_4). The PT samples will be purchased from an outside PT manufacturer, diluted to concentrations representative of riverine conditions, and will be provided with a known quantity of analyte. Typically, one set of PT samples will be incorporated within the batch of river samples and submitted blindly to the laboratories. The laboratory's analytical results will be compared to the known analyte concentrations provided based on the PT manufacturer and known dilutions.

To ensure proper temperature storage of samples on sampling day, a 500 mL bottle filled with tap water will be added to each cooler before setting out to sample. The temperature of the water in this bottle will be measured when the cooler arrives at the UB laboratory.

7.0 Team Organization and Contact Information

Key team members participating on the Blackstone River Watershed Assessment Study include the following:

- Upper Blackstone Clean Water (Upper Blackstone)
- University of Massachusetts at Amherst (UMass)
- University of Massachusetts at Dartmouth (UMD)
- CDM Smith
- Narragansett Bay Commission (NBC)

The following section provides a brief discussion of the team member roles and responsibilities. Table 10 provides contact information for these team members and others that will assist with the sample collection.

Program Management and Technical Oversight. Ms. Karla Sangrey, P.E., Upper Blackstone Director, shall serve as the primary point of contact for the UB on the river sampling. Ms. Kristina Masterson, P.E., CDM Smith, will serve as the primary point of contact for CDM Smith on the river sampling. They will provide program management guidance and technical oversight, including review of the proposed Scope of Work and data reporting.

Upper Blackstone Laboratory Coordinator. Mr. Timothy Loftus will be the primary contact for the UB laboratory. He will coordinate with UMass to ensure the UB can assist with sampling and analysis on sampling week, reserve the Upper Blackstone vehicle, and coordinate with the Upper Blackstone staff in terms of meeting times and duties. In addition, he will assist UMass to ensure the sample volumes and plans for filtering/preserving meet the UB needs.

EAL Laboratory Coordinator. Mr. Cameron Richards will be the primary contact for the EAL laboratory. He will ensure that all necessary supplies are available. He will also run Chl-a and TP samples sent to EAL.

NBC Laboratory Coordinator. Ms. Karen Cortes will be the primary contact for NBC. She will assist in coordinating sampling dates and co-sampling timing.

UMD Laboratory Coordinator. Ms. Sara Sampieri Horvet will be the primary contact for UMD. She will assist with coordinating aliquot bottle and filter delivery to UMass prior to each sampling event, and be the interface for data delivery and questions.

Principal Investigator. UMass will be responsible for field sampling and associated activities performed under this Scope of Work under the direction of Ms. Marie-Françoise Hatte, who will serve as principal investigator. Ms. Hatte will ensure that the work completed by the Project Team meets the prescribed scope of work; she will be the primary point of contact between UMass and the Upper Blackstone. Ms. Hatte will work closely with the Upper Blackstone, CDM Smith and NBC to make any necessary adjustments to the sampling plan and solicit feedback regarding the effort. Ms. Hatte and staff will also be responsible for coordinating the specific details of the data collection and review efforts, including:

- Oversight/assistance of the field program
- Oversight of identifying and resolving problems at the field team level
- Identifying, implementing, and documenting corrective action
- Oversight of documentation
- Data review and reporting.

Field Program Coordinator. Mr. Cameron Richards will serve as the Field Program Coordinator. He will be responsible for mobilizing, coordinating and managing sampling events, as well as, gathering and analyzing data in the field. Ms. Hatte will provide assistance where necessary.

Document and Data Custodian. Mr. Cameron Richards will serve as the document custodian, assisted by Ms. Hatte. The Document Custodian will be responsible for maintaining project files and filing project documents, project correspondence, sample integrity data sheets, chain of custody forms, field report forms, field and equipment notebooks, generated data and other associated and pertinent project information. The Document Custodian will:

- Review documents for quality control when submitted, ensuring that data recording procedures have been carried out as per this SOP
- Maintain hardcopy and electronic records, converted paper files to an electronic database as needed
- Maintain and backup the master database for the project
- Assist in data analysis and visualization

- Assist in the interface between the monitoring and modeling portions of the project
- Be responsible for transferring data to Project PI
- Complete the required QAQC calculations based on duplicate and blank sample data returned from the labs
- Perform data review, verification, and validation, as described in Section 4

QAQC Officer. Ms. Hatte will serve as the QAQC Officer. She will review the QAQC data and suggest modifications to the sampling plan to address any concerns. She will also conduct a field sampling audit once during the 2019 sampling season.

Table 10: Team Contact Information

Name/Organization	Role	Contact
UMass: Marie-Françoise Hatte Cameron Richards	Principal Investigator Field Sampling Assistance QAQC Review EAL Lab Coordinator Field Program Coordinator Document & Data Custodian Primary Field Sampler	mfhatte@umass.edu 413.545.5531 (w) 413.768.8402 (c) cameronr@umass.edu 413.545.5979 (w) 978.732.4007 (c)
CDM Smith: Kristina Masterson Zach Eichenwald	Program Management & Technical Oversight "	MastersonKK@cdmsmith.com 617.452.6284 (w) 978.618.6646 (c) eichenwaldzt@cdmsmith 508.654.2866 (c)
Upper Blackstone: Timothy Loftus Sharon Lawson Denise Prouty Cindy D'Alessandro Rick Vaudry Ornela Piluri Devon Avery	 Upper Blackstone Lab Manager Upper Blackstone Sampling and Lab Assistance " " " " "	TLoftus@ubcleanwater.org (774.312.3956) slawson@ubcleanwater.org (774.696.8423 Sharon) dprouty@ubcleanwater.org (508.523.9538 Denise) CD'Alessandro@ubcleanwater.org (508.769.4125 Cindy) RVaudry@ubcleanwater.org (401.580.7175 Rick) opiluri@ubcleanwater.org (508.981.5540 Ornela) davery@ubcleanwater.org (774.482.0568 Devon)
UMD: Sara Sampieri Horvet Dr. David Schlezinger Brian Howes	 UMD Lab Coordinator UMD Lab Director UMD Lab QA Officer	508.910.6325 ssampieri@umassd.edu dschlezinger@umassd.edu bhowes@umassd.edu
NBC: Karen Cortes Eliza Moore John Motta Luis Cruz Molly Welsh Sara Nadeau Bekki Songolo Jeff Tortorella	 Asst Mgr, Environmental. Monitoring Sr. Environmental Scientist Manager, Environmental Monitoring Environmental Scientist Environmental Scientist Field Supervisor	 Karen.cortes@narrabay.com 401.461.8848 ext. 274 eliza.moore@narrabay.com 401.461-8848, ext. 267 401.641.2709 401.641.1635 401.641.3274 401.461.3274 401.461.2709 401.461.1635

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