# ANNUAL BITTERROOT MAINSTEM LONG-TERM TRENDS MONITORING REPORT

2020

6/30/2021

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## Attachments

1. QA/QC Report for Clark Fork River Monitoring (MDEQ)

## **1.0** INTRODUCTION

This report presents 2020 nutrient and benthic algae monitoring results from the Bitterroot River Long-Term Trends Monitoring Project (BTMP) collected by the Bitterroot River Protection Association (BRPA), under guidance from the Montana Department of Environmental Quality (MDEQ), and in partnership with the Clark Fork Coalition (CFC), which assists with data management and reporting. This report also summarizes and presents results of quality assurance and quality control analysis by MDEQ. The purpose of the report is to present monitoring results and assess compliance with water quality targets.

2020 represented the second year of what is envision as a long-term monitoring effort on the Bitterroot River. Further analysis of annual results from this monitoring program will be accomplished on a five-year schedule with a statistical evaluation and trends analysis. The first 5-year trends report is anticipated in 2024 and will include data from 2019 through 2023.

### 2.0 HISTORY AND BACKGROUND

MDEQ completed Total Maximum Daily Loads (TMDLs) for the Bitterroot River watershed beginning with the 2003 Upper Lolo Creek TMDLs. The Bitterroot Headwaters TMDLs (the West and East Forks of the Bitterroot River) were completed in 2005. In 2011, DEQ completed the Bitterroot Temperature and Tributary Sediment TMDLs and in 2014 completed the remaining Bitterroot Watershed TMDLs.

In 2019, the Bitterroot watershed became the Water Quality Division's Nonpoint Source Program priority watershed for a 2-3 year timeframe (MDEQ 2019a). More detail about concurrent water quality improvement activities and objectives can be found within the Pilot Level I Priority: Bitterroot Watershed Protect Plan (MDEQ 2019b). A major focus of the priority project includes tracking nutrient trends on the mainstem Bitterroot River, which led to the creation of the BTMP.

## 3.0 MONITORING PROGRAM

The sampling design and primary objective of this monitoring effort is to detect long-term trends in nutrient and benthic algae chlorophyll concentrations in the Bitterroot River. Additional details on the project's objectives can be found in the Quality Assurance Project Plan (MDEQ 2020).

The objectives will be met by:

- 1. **Summer monitoring:** The BRPA collects nutrient samples, TSS, and field constituents in summer at six sites on the Bitterroot River on eight sampling occasions twice monthly, July through October.
- 2. **Benthic algae monitoring:** The BRPA, with assistance from the UM Watershed Health Clinic, collects summer benthic algae samples for chlorophyll-*a* and ash-free dry weight at six sites on the Bitterroot River in early August and September.

Specifically, the BTMP measures:

- Nutrients: total phosphorus (TP), total persulfate nitrogen (TPN), nitrate + nitrite nitrogen (NO<sub>2</sub>+NO<sub>3</sub>-N), ammonia nitrogen (NH<sub>3</sub>+NH<sub>4</sub>-N), and soluble reactive phosphorus (SRP).
- Total Suspended Solids (TSS).
- Field parameters: water temperature (°C), dissolved oxygen (mg/l), pH (standard units), redox potential (mv), specific conductance (μs/cm), total dissolved solids (mg/l), and turbidity (NTU).
- Benthic algae: chlorophyll-*a* (mg/m<sup>2</sup>) and ash-free dry weight (g/m<sup>2</sup>).

All nutrient samples were analyzed by Energy Laboratory in Helena, MT, and benthic algae samples were analyzed by the UM Watershed Health Clinic. Sampling, QA/QC and analytical methods are described in the QAPP (MDEQ, 2020). The **QA/QC Report for 2020 Bitterroot Mainstem Long-Term Nutrient Trends Monitoring** is attached to this report. Monitoring station locations are provided in **Table 1.** Rationale for sampling locations in explained in more detail in the QAPP (MDEQ, 2020).

All 2020 project data are available at the project website, hosted by the Clark Fork Coalition at <a href="https://clarkfork.org/our-work/what-we-do/monitor-watershed-health/nutrient-monitoring/">https://clarkfork.org/our-work/what-we-do/monitor-watershed-health/nutrient-monitoring/</a>.

Station	n Name/Location		Longitude
COMBITR02	Bitterroot River at Buckhouse Bridge	46.83194	-114.05306
COMBITR03	Bitterroot River at Florence Bridge	46.63309	-114.05096
BITR-C05BITRR24	Bitterroot River at Bell Crossing	46.4436	-114.12630
COMBITR04	Bitterroot River at Veterans Bridge, Hamilton*	46.2792	-114.1606
BITR-C05BITRR03	Bitterroot River at Main Street, Hamilton	46.2475	-114.17722
BITR-C05BITTR06	Bitterroot River at Hannon Memorial Bridge	45.9725	-114.1411

#### Table 1: BTMP Monitoring Locations, from upstream to downstream

\*Veterans Bridge is not formally part of the BTMP. The site is part of a separate BRPA monitoring program and data form the site are included in this report courtesy of BRPA. Note that sites in Table 1 are listed in downstream to upstream order starting at Buckhouse Bridge.

## 4.0 DATA QA/QC SUMMARY

All laboratory and field data were reviewed and validated per guidance in the QAPP (MDEQ, 2021). Montana DEQ analyzes and flags the monitoring data each year for quality assurance/quality control and provides the **QA/QC Report for 2020 Bitterroot Mainstem Long-Term Nutrient Trends Monitoring** that is attached to this report. This section briefly summarizes the results.

The overall project data had:

- 18 results H flagged for exceeding method holding time
- 51 results J flagged for result value between the MDL and LRL
- 7 Ammonia results were B flagged for field blank contamination
- 7 results J flagged for MS/MSD failed low, expect low bias

The BRPA, UM, CFC, and DEQ discussed ways to improve data quality and QA/QC reporting at their annual meeting, and the QAPP and SAPs were updated accordingly prior to the start of the 2021 field season.

### 5.0 NUTRIENT TARGETS

The Total Maximum Daily Load (DEQ, USEPA 2014) established the following nutrient targets for the mainstem of the Bitterroot River:

- Total phosphorus as P: 30 μg/L
- Total Nitrogen as N: 300 μg/L

DEQ also uses 100 ug/L nitrate + nitrite as a benchmark for assessment purposes on the Bitterroot River. When concentrations are equal or greater than 100 ug/L during the growing season it can be assumed that the stream is saturated for nitrate and detrimental eutrophication impacts may ensure (Suplee 2013).

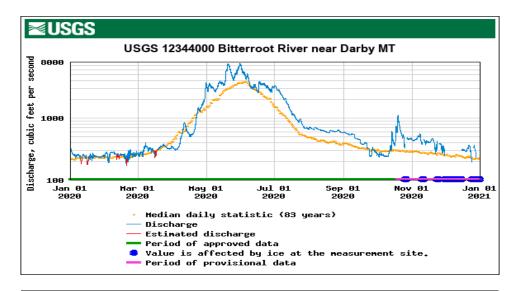
Although no targets currently exist for algal growth in the Bitterroot River, targets developed for the Clark Fork River as part of the Voluntary Nutrient Reduction Program may be useful to provide context for interpretation of chlorophyll a results and are included here for that purpose:

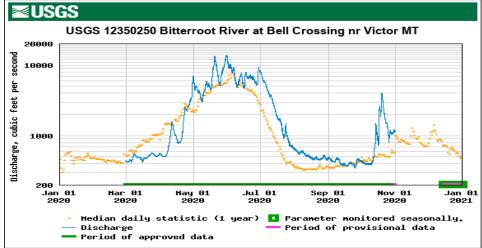
- (Summer mean) Benthic 100 mg/square meter algal chlorophyll a
- (Maximum) Benthic 150 mg/square meter algal chlorophyll a

### 6.0 NUTRIENT RESULTS

Streamflow conditions during spring runoff and summer months influence nutrient concentrations and algal densities. Years with less-than-average peak flows and early summer low flows typically see higher algal densities, and conversely, years with higher peak flows tend to produce less algal density. **Figure 1** presents three 2020 annual hydrographs (including the median daily flow for the period of record at each site) from stations in the study area, arranged upstream to downstream, to provide context for interpreting nutrient and algae results (USGS, 2021).

In general, discharge in the Bitterroot River during 2020 closely tracked with the historical average, though the rising limb of all three hydrographs included several mini-peak flow events on the way to the actual annual peak, which at all three locations was slightly higher than average. Early fall also saw higher than average discharge at all three locations, most noticeably at the gauge near Missoula (**Figure 1**).





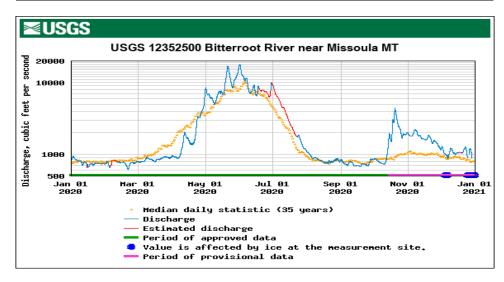
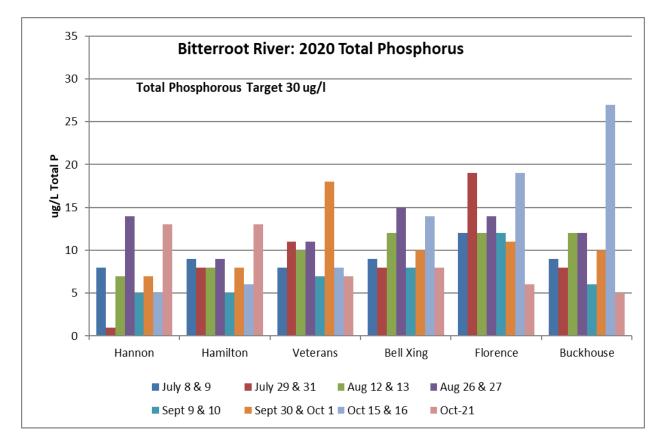


Figure 1: 2020 Hydrographs from USGS continuous monitoring stations (USGS, 2021).

## 6.1 TOTAL PHOSPHORUS

Results of total phosphorus (TP) monitoring are presented in **Figure 2**. TP concentrations were below the target of 30 ug/l on all occasions at all sampling locations in 2020. Concentrations were generally below 20 ug/l, except in early October at Buckhouse where they reached 27 ug/l.

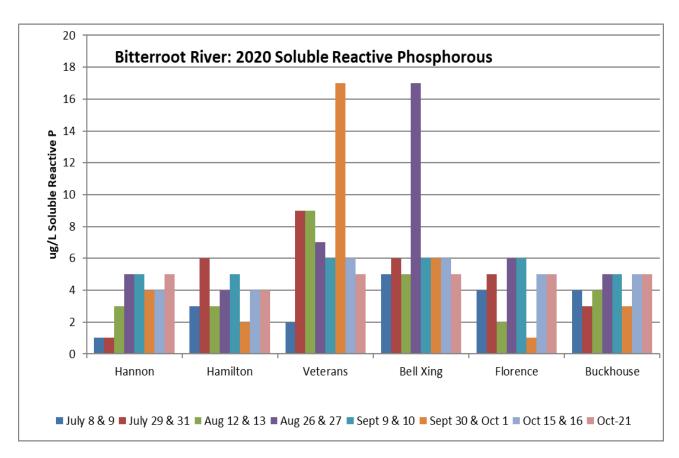


#### Figure 2: Bitterroot River: 2020 Total Phosphorous

Samples below detection are shown at  $\frac{1}{2}$  the lower reporting limit of 2  $\mu$ g/L. Sites appear in upstream to downstream order from Hannon to Buckhouse.

## 6.2 SOLUBLE REACTIVE PHOSPHORUS

Soluble Reactive phosphorous (SRP) results are presented in **Figure 3**. SRP concentrations were generally 9 ug/l or less, except in late August at Bell Crossing and late September at Veterans Bridge, where concentrations reached 17 ug/l on both occasions.

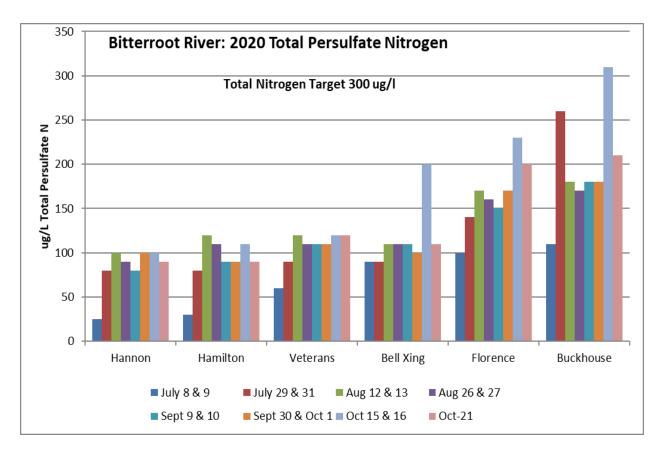


#### Figure 3: Bitterroot River: 2020 Soluble Reactive Phosphorous

Samples below detection are shown at  $\frac{1}{2}$  the lower reporting limit of 2  $\mu$ g/L. Sites appear in upstream to downstream order from Hannon to Buckhouse.

### 6.3 TOTAL NITROGEN

Results of total persulfate nitrogen (TPN) monitoring are presented in **Figure 4**. TPN concentrations were below the target of 300 ug/l at all sites and on all occasions, except for a slight exceedance at Buckhouse in early October. TPN was noticeably higher at the two downstream sites, Florence and Buckhouse, than it was at the four upper sites.



#### Figure 4: Bitterroot River: 2020 Total Persulfate Nitrogen

Samples below detection are shown at  $\frac{1}{2}$  the lower reporting limit of 50 µg/L. Sites appear in upstream to downstream order from Hannon to Buckhouse.

### 6.4 NITRATE + NITRITE

Results of nitrate + nitrite monitoring are presented in **Figure 5**. There are no numeric standards for nitrate + nitrite, but as discussed in Section 5.0, MDEQ uses 100 ug/L as a benchmark for assessment purposes. Nitrate + nitrite concentrations were at or below this benchmark on all sampling occasions in 2019. As with TPN, concentrations of nitrate+nitrite were highest at the two downstream sites, Florence and Buckhouse Bridge, where nitrate+nitrite generally ranged from 30 to 60 ug/l, except during the mid-July sampling event, when an unusually high concentration of 100 ug/l was measured at Buckhouse. At the four upstream sites, concentrations were generally near 20 ug/l or below, except for an unusual spike to 48 ug/l, also during the mid-July monitoring event. Nitrate + nitrite as a percentage of total nitrogen is shown in **Table 2**.

Site	Mean Percentage Nitrate+Nitrite of Total Nitrogen
Hannon	15%
Hamilton Main Street	10%
Veterans Bridge	11%
Bell Crossing	7%
Florence	14%
Buckhouse Bridge	18%

#### Table 2: Nitrate + nitrite as a percentage of total nitrogen

(Note: below detect values calculated at ½ detection limit)

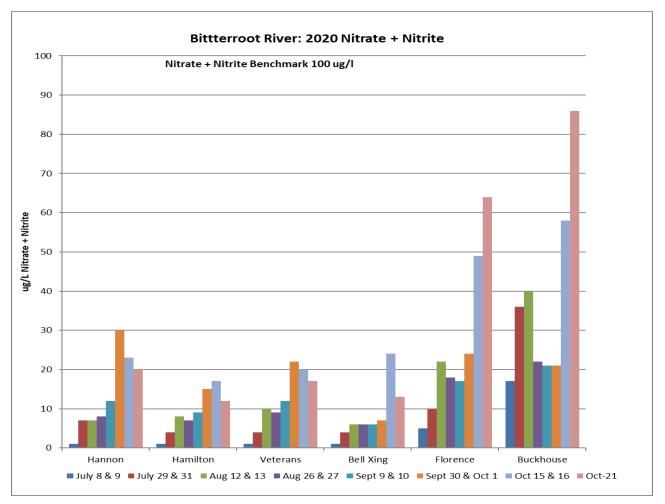
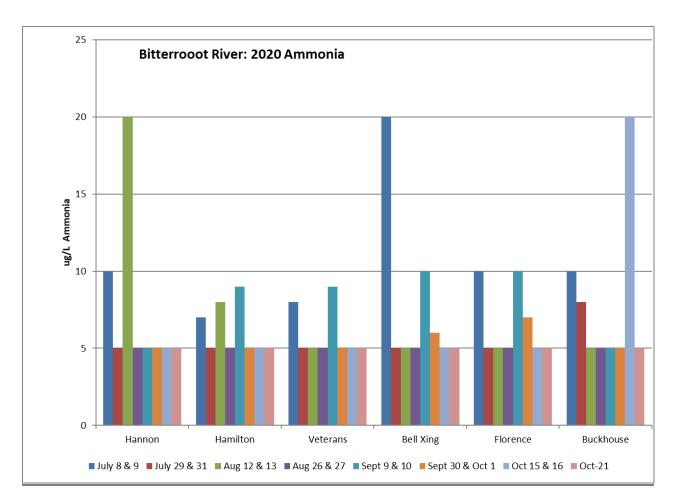


Figure 5: Bitterroot River: 2020 Nitrate + Nitrite

Samples below detection are shown at  $\frac{1}{2}$  the lower reporting limit of 2  $\mu$ g/L. Sites appear in upstream to downstream order from Hannon to Buckhouse.

### 6.5 AMMONIA

Results of ammonia monitoring are presented in **Figure 6**. Concentrations were generally 10 ug/L or lower except for a single increase to 20 ug/l on different occasions at Hannon, Bell Crossing, and Buckhouse.



#### Figure 6: Bitterroot River: 2020 Ammonia

Samples below detection are shown at  $\frac{1}{2}$  the lower reporting limit of 10  $\mu$ g/L. Sites appear in upstream to downstream order from Hannon to Buckhouse.

## 7.0 NITROGEN – PHOSPHORUS RATIOS

Since the observation of Redfield (1934 and 1958) that marine phytoplankton contains a molecular C:N:P ratio of 106:16:1 (40:7:1 by mass), the relative concentrations of N and P have been used to estimate which of these nutrients might be limiting, preventing additional primary production (algae growth) in aquatic ecosystems. Redfield also recognized that the ratio is an average with considerable variation by species, season, and environment. A departure from this ratio is assumed to imply nutrient deficiency such that by identifying which nutrient is responsible for enhanced algae growth, management actions can be directed toward the nutrient with the highest impact.

It is important to note that the C:N:P ratios in the above literature for benthic algae are for the internal contents of the algal matrix (cellular C:N:P concentration), not water column concentrations. The C:N:P of the benthic algal material is a much better estimator of nutrient limitation than water column TN:TP ratio. This is especially true for benthic algae; while water column total nutrients can be good estimators of optimal stoichiometry for phytoplankton (where suspended algal biomass is a large fraction of the total nutrients in the water column) benthic algae are more loosely coupled with the water column and respond only to bioavailable nutrients.

Total nitrogen-phosphorus ratios (by mass) were calculated for 2020 results and are shown below in **Table 3**. The N:P Redfield ratio (by mass) is 7:1, and the color-coded thresholds in Table 4 are based on the following from Suplee and Watson (2013): *"Studies of benthic algae show that it is necessary to move some distance above or below the Redfield ratio in order to be strongly convinced that a lotic waterbody is P or N limited (Dodds, 2003). When a benthic algal Redfield ratio (by mass) is <6, N limitation is suggested, and when it is >10 P limitation is indicated (Hillebrand and Sommer, 1999). Thus, there is a range of N:P values between about 6 and 10 where one can state, for practical purposes, that algal growth is co-limited by N and P."* 

We also include dissolved N: P ratios (by mass) in Table 4 with caveats: the Redfield ratio is based on total N: P, but dissolved concentrations may better reflect nutrient limitation if total concentrations are dominated by particulates (including sediment particles and terrestrial material) which are not necessarily reflective of the condition of the benthic algae. The dissolved N:P ratios are simply presented for comparison.

For total N:P ratios, phosphorous limitation was far more common than nitrogen limitation, which was evident in only 2 of 48 samples, both in early July in the upper river. In contrast, 32 samples suggested phosphorous limitation and another 14 were indeterminate. Dissolved N:P ratios were more suggestive of nitrogen limitation, particularly at the four upstream sites, where no phosphorous limitation was apparent. At the two downstream sites, Florence and Buckhouse, estimated nutrient limitation was more mixed between nitrogen and phosphorous.

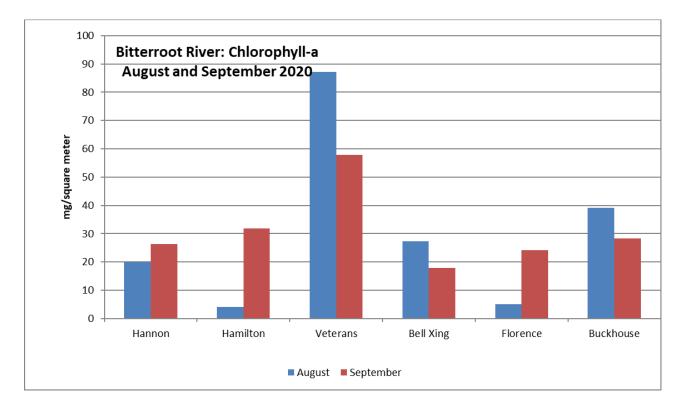
#### Table 3: 2019 Mass-based N:P ratios for Total N:P (upper) and Dissolved N:P (lower)

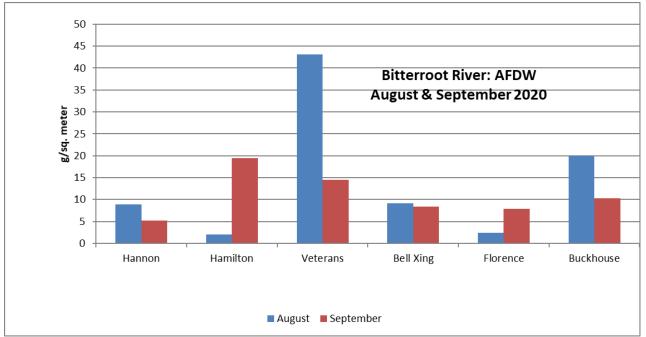
Total N:	Р				
Hannon	Hamilton	Veterans	Bell Xing	Florence	Buckhouse
3.1	3.3	7.5	10.0	8.3	12.2
80.0	10.0	8.2	11.3	7.4	32.5
14.3	15.0	12.0	9.2	14.2	15.0
6.4	12.2	10.0	7.3	11.4	14.2
16.0	18.0	17.1	13.8	12.5	30.0
14.3	11.3	6.1	10.0	15.5	18.0
20.0	18.3	13.8	14.3	12.1	11.5
6.9	6.9	15.7	13.8	33.3	42.0
	<6 indicate	es N-limite	d		
		tes P-limite			
	6 - 10 indi	cates eithe	r N or P ma	ay be limiti	ng
Dissolve	ed N:P				
1.0	0.3	0.5	0.2	1.3	4.3
7.0	0.7	0.4	0.7	2.0	12.0
2.3	2.7	1.1	1.2	11.0	10.0
1.6	1.8	1.3	0.4	3.0	4.4
2.4	1.8	2.0	1.0	2.8	4.2
7.5	7.5	1.3	1.2	24.0	7.0
5.8	4.3	3.3	4.0	9.8	11.6
4.0	3.0	3.4	2.6	12.8	17.2
		es N-limite			
		tes P-limite			
	6 - 10 indi	ay be limiti	ng		

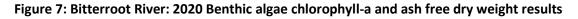
### 8.0 BENTHIC ALGAE RESULTS

Benthic algae were sampled according to the QAPP at all sites in August and September. Averages for chlorophyll-a and ash free dry weight from each sample date are shown in **Figure 7**. Although no numeric standards for benthic algae chlorophyll-a are established for the Bitterroot River, the targets developed for upper Clark Fork River include a summer maximum of 150 mg/m<sup>2</sup>and a summer mean of

100 mg/m<sup>2</sup>. These standards are included here to provide context for interpreting the Bitterroot results. Chlorophyll a concentrations in the Bitterroot were below both Clark Fork targets at all sites, though much higher at Veterans Bridge than at surrounding sites. AFWD concentrations followed a similar pattern.







Sites appear in upstream to downstream order from Hannon to Buckhouse.

#### 9.0 **R**EFERENCES

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## QA/QC REPORT FOR 2020 BITTERROOT MAINSTEM LONG-TERM NUTRIENT TRENDS MONITORING

## **QAPP ID: BRMMASQAPP-19**

May 2021

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## **ACRONYM LIST**

Acronym	Definition
AFDW	Ash-free Dry Weight
BRPA	Bitterroot River Protection Association
CFC	Clark Fork Coalition
COC	Chain-of-Custody
DEQ	Department of Environmental Quality
DQI	Data Quality Indicators
DQO	Data Quality Objectives
EDD	Electronic Data Deliverable
FB	Field Blank
FD	Field Duplicate
LRL	Lower Reporting Limit
MDL	Method Detection Limit
MS/MSD	Matrix Spike/Matrix Spike Duplicate
MT-eWQX	Montana EQuIS Water Quality Exchange
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPD	Relative Percent Difference
SAP	Sampling and Analysis Plan
SRP	Soluble Reactive Phosphorus (Orthophosphate)
ТР	Total Phosphorus
TPN	Total Persulfate Nitrogen
TSS	Total Suspended Solids

## **1.0 INTRODUCTION**

A data quality control (QC) review has been completed on all data collected and submitted to DEQ in 2020 for the Bitterroot Mainstem Nutrient Monitoring Program. Monitoring activities were performed by the Clark Fork Coalition (CFC), Bitterroot River Protection Association (BRPA) and DEQ personnel in accordance with the *"Bitterroot Mainstem Long-term Nutrient Trends Monitoring-Quality Assurance Project Plan (QAPP)"* (QAPP ID: BRMMASQAPP-19) and associated SAP. The scope of the QC evaluation was to evaluate documentation associated with sampling and measurement (i.e., field logbooks and site visit forms) and laboratory analytical results to verify data quality. The QC evaluation included a review of the data quality objectives (DQOs) and data quality indicators (DQIs) as outlined in the QAPP and an assessment of compliance with the DEQ QA/QC process. The review also included:

- Review of field data sheets to verify calibration and to identify field notes that explain any deviations from the QAPP.
- Review of field notes and field data sheets for a data logic check and to identify any notes indicating deviations from the QAPP.
- Review of the sample delivery group to evaluate the overall quality of the data including reporting errors, data omissions, and suspect or anomalous values.

The QC review applies to the nutrient monitoring for the months of July through October conducted by the BRPA and CFC, and the benthic algae monitoring in August and September, conducted by DEQ.

## **2.0 FIELD COMPONENTS**

#### FIELD DOCUMENTATION

The BRPA and CFC submitted monthly nutrient and algae field forms as part of their data deliverable. There was one detailed field meter calibration log provided. All the field forms were a consistent format and contained all of the relevant field metadata including station IDs, site coordinates, collection date, and personnel.

### **CHAIN OF CUSTODY FORMS**

The BRPA and CFC submitted COC forms for each monthly nutrient sampling date that included a relinquished signature by field personnel and lab signatures. The writing on two of the COC's was very light and hard to read. The monthly nutrient samples were relinquished by field personnel the same day to two days after the samples were collected.

The algae field forms acted as the COC, and were signed and dated by field personnel and lab manager. They were all submitted in a timely manner.

#### **SAMPLE SITES**

The monthly nutrient field forms included site name, descriptions, station IDs, and coordinates that matched locations specified in the QAPP. The site COMBITR04 was added to the SAP for 2020; this is the only site in the SAP where lab analysis is funded by the BRPA and not DEQ. The algae field forms included all the above information including site name.

### **FREQUENCY OF FIELD BLANKS AND FIELD DUPLICATES**

At least one field blank sample and one duplicate sample were collected for each nutrient monitoring event. This frequency met the frequency outlined in the requirements as described in the QAPP.

## **3.0 SAMPLE HANDLING**

#### PRESERVATION

Preservation methods were reviewed for all sampling using the SAP, field forms, and lab reports. Table 3.1 summaries the planned preservation methods.

Characteristic	SAP Preservation	Preservation from Field Forms	
Total Nitrogen	Cool on ice in field (freeze if need be)	Cool on ice (<6 deg C)	
Total Phosphorus			
Nitrate + Nitrite	H <sub>2</sub> SO <sub>4</sub> , cool on ice in field	H <sub>2</sub> SO <sub>4</sub> , cool on ice (<6 deg C)	
Ammonia			
Orthophosphate	Filter, cool on ice in field, then freeze solid*	Filter, freeze	
Total Suspended Solids	Cool on ice in field	Cool on ice (<6 deg C)	
	Prevent light exposure; cool on ice in field,	[roozo	
Chlorophyll a	freeze in lab	Freeze	
Ash-free Dry Weight	Cool on ice in field; freeze in lab	Freeze	

#### Table 3.1: Sample Preservation Summary

\*SAP indicates: "If samples are to be shipped the day following data collection activities, freeze applicable samples in a freezer overnight upon completion of field work. If samples are to be shipped immediately after data collection activities (on the same day), ship on ice."

### **HOLDING TIMES**

Analytical holding times were reviewed for Bitterroot River monthly and summer nutrient monitoring. Two batches of results exceeded the holding time from the SAP (Table 3.2).

For orthophosphate, the holding time is 45 days if received frozen, or two days if not frozen. The orthophosphate samples in lab batch H20070313 were collected 8/12/20 and 8/13/20, and the comment on COC is that the sample was refrigerated, not frozen, until shipped on 8/15/20. These results were H flagged for being over the holding time of 2 days.

For total suspended solids (TSS), the holding time is seven days. Two lab batches exceeded the hold time by just a few hours. For lab batch H20090465 collected on 9/9/20, hold time was approximately 3 hours past hold. For lab batch H20100196 collected on 9/30/20, hold time was approximately 6 hours past hold. It appears that these two batches were shipped and/or analyzed at a different time as the rest of the samples from those dates.

Activity ID	Characteristic Name	Lab Method	Sample Date	Analysis Date	Holding Time (days)
BITR-C05BITRR24-					
09102020-S	Orthophosphate	365.1	9/10/2020	9/17/2020	7
BITR-C05BITTR03-					
09092020-QC-FB	Orthophosphate	365.1	9/9/2020	9/17/2020	8
BITR-C05BITTR03-					
09092020-QC-FD	Orthophosphate	365.1	9/9/2020	9/17/2020	8
BITR-C05BITTR03-					
09092020-S	Orthophosphate	365.1	9/9/2020	9/17/2020	8
BITR-C05BITTR06-					
09092020-S	Orthophosphate	365.1	9/9/2020	9/17/2020	8
COMBITR02-09102020-S	Orthophosphate	365.1	9/10/2020	9/17/2020	7
COMBITR03-09102020-S	Orthophosphate	365.1	9/10/2020	9/17/2020	7
COMBITR04-09092020-S	Orthophosphate	365.1	9/10/2020	9/17/2020	7
BITR-C05BITTR03-					
09092020-QC-FB	Total suspended solids	2540-D	9/9/2020	9/16/2020	7
BITR-C05BITTR03-					7
09092020-QC-FD	Total suspended solids	2540-D	9/9/2020	9/16/2020	
BITR-C05BITTR03-					7
09092020-S	Total suspended solids	2540-D	9/9/2020	9/16/2020	
BITR-C05BITTR06-					7
09092020-S	Total suspended solids	2540-D	9/9/2020	9/16/2020	
COMBITR04-09092020-S	Total suspended solids	2540-D	9/9/2020	9/16/2020	7
BITR-C05BITTR03-					7
09302020-S	Total suspended solids	2540-D	9/30/2020	10/7/2020	
BITR-C05BITTR06-		2540-D			7
09302020-QC-FB	Total suspended solids		9/30/2020	10/7/2020	
BITR-C05BITTR06-		2540-D			7
09302020-QC-FD	Total suspended solids		9/30/2020	10/7/2020	
BITR-C05BITTR06-					7
09302020-S	Total suspended solids	2540-D	9/30/2020	10/7/2020	
COMBITR04-09302020-S	Total suspended solids	2540-D	9/30/2020	10/7/2020	7

Table 3.2: Results H flagged for exceeding method holding time

## 4.0 ANALYSIS

#### **REQUIRED ANALYTICAL METHODS**

All requested parameters specified in the SAP were reported. All analyses were performed in accordance with the primary method as defined in the QAPP and SAP.

#### Table 4.1: Analytical Methods

Parameter	Method Reported	Method in QAPP/SAP
Total Phosphorus (TP)	EPA 365.1	EPA 365.1
Total Persulfate Nitrogen (TPN)	4500-N-C	4500-N-B or C
Nitrate + Nitrite-Nitrogen (NO2+NO3-N)	EPA 353.2	EPA 353.2
Total Ammonia-Nitrogen (NH3+NH4-N)	EPA 350.1	EPA 350.1
Orthophosphate (SRP)	EPA 365.1	EPA 365.1
Solids, Total Suspended (TSS) @ 105 C	A2540-D	A2540-D

#### **REQUIRED DETECTION LIMITS**

The laboratory lower reporting limits (LRL) met the project-required detection limits defined in the QAPP and SAP for all parameters except Ash-free Dry Weight (AFDW). Although AFDW's LRL did not meet the SAP and QAPP requirements, the method detection limit (MDL) did.

#### **Table 4.2: Detection Limit Variations**

Parameter	Lab Lower Reporting Limit	Lab Method Detection Limit	Project Limit in SAP	Project Limit in QAPP
Ash Free Dry Weight	Template – 2 g/m2	Template – 0.2 g/m2	Template – 0.5 g/m2	0.5 g/m2

#### FIELD BLANKS

#### B – Flags:

If an analyte is detected in a field blank at or above the lower reporting limit (LRL), all result values for samples associated with the blank that are less than or equal to 10 times the value detected in the blank are qualified with a B flag. Samples are considered associated with a field blank if they are the same analyte and collected during the same sampling trip as the blank.

Table 4.3 shows the blanks with detections at or above the LRL, and Table 4.4 shows the associated sample result values that were B flagged.

#### Table 4.3: Field blanks with detects at or above the LRL

Activity ID	Characteristic Name	ristic Name Result Value (mg/l)		MDL (mg/l)
BITR-C05BITRR24-10152020-QC-FB	Ammonia	0.01	0.01	0.006

#### Table 4.4: Associated results B flagged

Activity ID	Characteristic Name	Result Value (mg/l)	LRL (mg/l)	MDL (mg/l)
BITR-C05BITRR24-10152020-FD	Ammonia	0.02	0.01	0.006

Activity ID	Characteristic Name	Result Value (mg/l)	LRL (mg/l)	MDL (mg/l)
BITR-C05BITRR24-10152020-S	Ammonia	0.02	0.01	0.006
BITR-C05BITRR03-10162020-S	Ammonia	0.02	0.01	0.006
BITR-C05BITRR06-10162020-S	Ammonia	0.02	0.01	0.006
COMBITR02-10152020-S	Ammonia	0.02	0.01	0.006
COMBITR03-10152020-S	Ammonia	0.02	0.01	0.006
COMBITR04-10162020-S	Ammonia	0.02	0.01	0.006

#### **FIELD DUPLICATES**

#### J – Flags:

As specified in the QAPP, field duplicate relative percent difference (RPD) should be less than 25% for duplicate results that are greater than 5 times the lower reporting limit (LRL). When RPD is exceeded, the field duplicate along with any associated results are J flagged. No results were J flagged for exceeding the RPD.

#### REJECTED

No results were rejected.

### **GENERAL QUALITY CHECKS**

The results were reviewed to make sure the individual components were not more than the total. Total Phosphorus was compared to Orthophosphate, and Total Nitrogen was compared to Nitrate+Nitrite plus Ammonia. Total Phosphorus results were all greater than Orthophosphate values. Total Nitrogen results were greater than the combined individual Nitrogen values. No results were flagged for either comparison.

### LABORATORY QC

**Percent Recovery:** The percent recovery for all lab samples, particularly the matrix spike and matrix spike duplicate (MS/MSD), should be within the low and high limits established by the lab. If result is outside the limits (90% or 120%), the associated results are J flagged and include the comment "MS/MSD failed [high/low] (xx/xx%), expect [high/low] bias." A result is considered associated if it is the same parameter and analyzed in the same lab batch as the MS/MSD.

Activity ID	Characteristic Name	Result Value (mg/l)	Matrix Spike (%)	Matrix Spike Duplicate (%)
BITR-C05BITRR24-08272020-S	Nitrate + Nitrite	0.006	88	89
BITR-C05BITTR03-08262020-S	Nitrate + Nitrite	0.007	88	89
BITR-C05BITTR06-08262020-S	Nitrate + Nitrite	0.008	88	89
COMBITR04-08262020-QC-FD	Nitrate + Nitrite	0.010	88	89
COMBITR04-08262020-S	Nitrate + Nitrite	0.009	88	89
COMBITR02-08272020-S	Nitrate + Nitrite	0.022	88	89
COMBITR03-08272020-S	Nitrate + Nitrite	0.018	88	89

Table 4.5: Results J flagged for low MS/MSD, expect low bias

### 5.0 QC SUMMARY

#### FLAGGED DATA

The overall project data had:

- 18 results H flagged for exceeding method holding time (Table 3.2)
- 51 results J flagged for result value between the MDL and LRL, meaning they are estimated values
- 7 Ammonia results were B flagged for field blank contamination (Table 4.4)
- 7 results J flagged for MS/MSD failed low, expect low bias (Table 4.5)

#### **COMPLETENESS**

The overall project sample completeness rate for sites included in the QAPP is 97.5%, well over the required 90% in the SAP. If any sample collection is missed, rationale should be documented and clearly communicated in a report to DEQ at the time of EDD submission.

### **6.0 CORRECTIVE ACTIONS**

As a result of the QA review, the following are corrective actions items for 2021:

- ISSUE: There were five trips where the time on the COC and bottles didn't match.
  - ACTION: Each COC will be reviewed by the field team leader to ensure that the time recorded on the COC and sample bottles match
- ISSUE: Two BRPA field forms were very light and hard to read.
  - ACTION: Field forms will be reviewed by the field team leader for legibility, and field personnel will ensure that they are writing with sufficient pressure to ensure adequate carbon copy transfer.
- ISSUE: Only one COC was not signed when relinquished.
  - ACTION: COC forms will be reviewed by the field team leader just prior to sample shipping to ensure that all "relinquished by" signatures and other required information is complete.
- ISSUE: Only orthophosphate samples from one cooler were at an unacceptable temperature when it reached the lab (4.5 C from the first 07/08 and 07/09/20 sampling, when the samples should have been frozen, or 0 C).
  - ACTION: Additional measures will be taken to ensure that frozen SRP samples remain frozen until delivery at the lab (including freezing samples solid before shipping, using adequate ice packed around the sample bottles; adding adequate insulating material to fill in large air gaps, and using expedited shipping practices as needed. Alternately, if samples are not frozen, samples will be shipped same day or overnight to ensure arrival within the 48 hour hold time and similar measures stated above will be taken to ensure cooler temperatures remain below the required temperature.