



Flathead-Stillwater TMDL Planning Area Sampling Project - 2012: Nutrients, Metals Sampling and Analysis Plan

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ACRONYM LIST

Acronym	Definition
AFDW	Ash Free Dry Weight
ARM	Administrative Rules of Montana
AUID	Waterbody Assessment Unit Identification Number
DEQ	Department of Environmental Quality (Montana)
DO	Dissolved Oxygen
EPA	Environmental Protection Agency (US)
ETOH	Ethanol
GIS	Geographic Information System
GPS	Global Positioning System
HDPE	High-Density Polyethylene
HUC	Hydrologic Unit Code
NAD	North American Datum
PCB	PolyChlorinated Biphenyls
PIBO	PACFISH/INFISH Biological Opinion
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
SAP	Sampling and Analysis Plan
TKN	Total Kjeldahl Nitrogen
TMDL	Total Maximum Daily Load
TN	Total Nitrogen
TP	Total Phosphorus
TPA	TMDL Planning Area
TPN	Total Persulfate Nitrogen
TSS	Total Suspended Solids
WQ	Water Quality
WQPB	Water Quality Planning Bureau (DEQ)

1.0 INTRODUCTION AND BACKGROUND INFORMATION

This project is to support TMDL development in the Flathead-Stillwater TMDL Planning Area (TPA) and 303(d) list assessments. The focus will be on nutrients and metals only. This Sampling and Analysis Plan (SAP) aims to meet requirements for the completion of source assessments and loading estimates for nutrients and metals listed streams in this TPA, and to have enough data to assess the streams based on the proposed nutrient criteria (Suplee and Sada de Suplee, 2011) and metals proposed assessment method (Montana Department of Environmental Quality, 2011a).

The Flathead-Stillwater TPA is within Flathead County, Montana. The total extent of this TPA is 948,436 acres, or approximately 1482 square miles, and it comprises part of the Flathead Lake watershed. Waterbodies in this TPA flow through both publicly-owned (United States Forest Service, State of Montana and Bureau of Land Management) and privately-owned land. The streams in the Flathead-Stillwater TPA are within the 4th code HUC 17010210. Fish Creek, Spring Creek, and Sheppard Creek have been assigned a B-1 beneficial use classification (ARM 17.30.623). The Whitefish River and Stillwater River are classified B2 (ARM 17.30.624). Haskill Creek is classified A-1 (ARM 17.30.622).

The Water Quality Planning Bureau (WQPB) of the Montana Department of Environmental Quality (DEQ) has identified twenty-five impaired (Category 5) streams within the Flathead-Stillwater TPA; however only the streams identified in **Table 1-1** will be sampled in 2012. **Table 1-1** shows the waterbody segments to be sampled in 2012 with the pollutants of concern (nutrients, metals) within the Flathead-Stillwater TPA.

Table 1-1. Waterbody segments within the Flathead-Stillwater TMDL planning area to be sampled in 2012 and 303(d) listings.

Waterbody Segment Name	AUID	Pollutant	
		Nutrients	Metals
Fish Creek	MT76O002_050	Phosphorus (Total)	
Spring Creek	MT76O002_040	Phosphorus (Total), Nitrate/Nitrite (Nitrite + Nitrate as N), Total Kjeldahl Nitrogen (TKN)	Arsenic
Whitefish River	MT76P003_010	Nitrogen (Total)	Copper, Lead
Stillwater River	MT76P001_010	Phosphorus (Total), Nitrates	Lead
Haskill Creek-upper	MT76P003_071	Not Assessed	
Haskill Creek-lower	MT76P003_070	Not Assessed	
Sheppard Creek	MT76P001_050	Phosphorus (Total), Nitrate/Nitrite (Nitrite + Nitrate as N)	

2.0 OBJECTIVES AND DESIGN

2.1 PROJECT OBJECTIVES

The main objective of this project is to provide monitoring and assessment support for the TMDL Program's schedule for development of nutrients and metals TMDLs in the Flathead-Stillwater TPA.

The goals for this project are as follows:

- Measure physical parameters (temperature, DO, pH, and conductivity) in situ.

- Collect metals (total recoverable and sediment fractions, only dissolved Aluminum, ultra low level mercury) and total suspended solids (TSS), and collect nutrients, ammonia, chlorophyll-*a* /Ash Free Dry Weight (AFDW), periphyton and macroinvertebrates samples.
- Measure stream flow during each sampling event, when practical, to assist in TMDL nutrients and metals load allocations.

2.2 SAMPLING TIMEFRAME

All sampling events for nutrients, TSS, chlorophyll-*a*/AFDW, periphyton and macroinvertebrates will occur during the “growing season” for the Northern Rockies Level III Ecoregion (July 1 – September 30) (Suplee and Sada de Suplee, 2011). Samples collected at the same site will be taken at least 30 days apart (Suplee and Sada de Suplee, 2011).

For sites requiring metals sampling, the initial sampling events will occur during high flow conditions (anticipated in early June). All subsequent sampling events for metals, nutrients, chlorophyll-*a* and macroinvertebrates will occur during the “growing season” for the Northern Rockies Level III Ecoregion (July 1 – September 30, 2012) (Suplee and Sada de Suplee, 2011).

3.0 FIELD SAMPLING METHODS

3.1 SELECTION OF SITES

Specific site locations within those streams will be identified using GIS and topographic maps. The selected sites follow the guidelines and definitions found in Suplee and Sada (2011) unless a specific location is to be sampled because a pollutant source was identified. These sites are proposed locations. Eleven of the planned sampling sites are new for 2012. The new sites are identified in **Appendix A**. All other sites were established prior to this project. Changes might be made based on land access or other unforeseen problems. A complete list of the stream segments, sites, and the respective sampling needs at each site can be found in **Appendix A**.

3.2 PHYSICAL PARAMETERS

3.2.1 In Situ Measurements

During low flow sampling events (July – September), a YSI 85 meter will be used to measure temperature, dissolved oxygen, and specific conductance at each sampling site. These measurements will be collected prior to the collection of water samples or other physical disturbances to the water column or substrate. A portable pH meter will be used to measure pH at each site. See details about calibration in **Section 6.0**.

3.2.2. Flow Measurement

Flow will be measured at each sampling site during each sampling event. During high flow sampling events (June), flow will be measured using either the quantitative flow meter method or using the semi-quantitative float method when streams are not wadeable (Montana Department of Environmental Quality, 2011b).

3.3 WATER SAMPLE COLLECTION

Water samples will be collected at each site after completing the in situ YSI 85 measurements. All water samples from the stream will be placed in new high-density polyethylene (HDPE) bottles. Sample replicates will be randomly taken on 10% of the total samples for each parameter. Field blanks will be made during each sampling run ("trip").

3.3.1 Chemistry Samples

Dissolved Aluminum: A 60 cm³ syringe and a 0.45 um filter disposable filter are used. Fifty ml of the filtrate will be placed in a 250 ml HDPE bottle, preserved with HNO₃ and kept on ice until analyzed (**Table 3-1**). Filtration will be accomplished with a large syringe connected to a disposal filter capsule. A small amount of the sample will be wasted through the filter before the filtered sample is collected. Sample bottles and lids will be pre-rinsed with a small amount of the filtered sample before collecting the final filtered sample. Detailed methodology can be found in DEQ (Montana Department of Environmental Quality, 2011b).

Nutrients, Ammonia, TSS, and Metals: Summary information is shown in **Table 3-1**. TP, NO₂₊₃, and Ammonia will be collected in a 250 ml HDPE bottle. The sample bottles will be triple-rinsed with stream water before the water samples are collected. This sample will be preserved with sulfuric acid, and held on ice. TN will be collected in another 250 ml HDPE bottle, no preservative, and held on ice. Total recoverable metals will be collected in a 250 ml HDPE bottle, preserved with nitric acid, and held on ice. Hardness will be calculated from the total recoverable metals bottle. Sediment metals will be passed with a minimal amount of ambient stream water through a Teflon 60-micron sieve using a Buchner funnel into a 2000 ml HDPE bottle without preservative and held on ice (not frozen) until analyzed (see **Table 3-1**). TSS will be collected in a 500 ml HDPE bottle, no preservative, and held on ice. NOTE THE SHORT HOLDING TIME FOR TSS. Detailed methodology can be found in DEQ (Montana Department of Environmental Quality, 2011b).

3.4 BENTHIC CHLOROPHYLL-A AND ASH-FREE-DRY WEIGHT

Benthic chlorophyll-*a* will be collected at 11 transects only at some sites (**Appendix A**). Samples will be collected either using the template, hoop, or core methods, depending on the dominant substrate and/or algae type present. These samples will be composited in the lab according to the collection method (i.e., hoops, cores, templates). Hoop chlorophyll-*a* samples will be stored in zip-lock bags wrapped in aluminum foil, template samples on filters in Petri dishes and wrapped in foil, and cores in centrifuge tubes wrapped in aluminum foil. All samples will be frozen (Montana Department of Environmental Quality, 2011b) (see **Table 3-1**). Ash-free dry weight (AFDW) will be calculated from the same samples of chlorophyll-*a* (Montana Department of Environmental Quality, 2011b).

3.5 MACROINVERTEBRATES

Macroinvertebrate samples will be collected only at some sites (**Appendix A**). Macroinvertebrate samples will be stored in 1 L bottles and preserved with ethanol (ETOH) (see **Table 3-1**). A detailed explanation can be found in DEQ 2011.

3.6 PERIPHYTON SAMPLES

Periphyton will be collected at some nutrient monitoring sites (**Appendix A**). The samples will be placed in a 50 ml centrifuge tube and preserved with formalin (see **Table 3-1**). Detailed methodology can be found in DEQ (Montana Department of Environmental Quality, 2011b).

Table 3-1. Sampling Volumes, Containers, Preservation, and Holding Times

Analyte	Bottle Size	Container	Preservation	Storage	Holding time
TN	250 ml	HDPE bottle	None	Cool to <6 °C (on ice)	28 Days
TP, NO ₂ +NO ₃	250 ml	HDPE bottle	Sulfuric acid	Cool to <6 °C (on ice)	28 days
Total Suspended Solids	500 ml	HDPE bottle	None	Cool to <6 °C (on ice)	7 days
Total Recoverable Metals	250 ml	HDPE bottle	Nitric acid	Cool to <6 °C (on ice)	180 days
Dissolved Aluminum	250 ml	HDPE bottle	0.45 um field filtered, nitric acid	Cool to <6 °C (on ice)	180 days
Ultra Low Level Hg	100 ml	Glass	0.5 ml 12N HCl	Cool to <6 °C (on ice)	28 days
Sediment Metals	2000 ml	HDPE bottle	None	Cool to <6 °C (on ice)	180 days
Chlorophyll- <i>a</i>	N/A	Ziplock bag (hoop), centrifuge tube (template), or centrifuge tube (core)	None	Dry ice	45 days
Periphyton	50 ml	Centrifuge tube	Formaline	No Ice	NA
Macroinvertebrates (species presence)	1000 ml	HDPE bottle	Ethanol	No ice	NA

3.7 DIGITAL PHOTOGRAPHS

Digital photographs will be taken at transect F of each site (metal sites). On the nutrient sites (chlorophyll-*a* sampling), photographs will be taken at each transect (A-K). The objective of the photos is to document visible changes in the stream flora as time passes, and as such photos may be a mix of close-ups and stream panoramas. The photo number will be recorded along with the transect identification.

3.8 AQUATIC PLANT VISUAL ASSESSMENT FORM

Form will be completed when chlorophyll-*a* is collected according to the procedure found in MT DEQ 2012

3.9 AQUATIC PLANT TRACKING FORM

Form will be completed when either chlorophyll-*a* or periphyton is collected according to the procedure found in MT DEQ 2011.

4.0 SAMPLE HANDLING PROCEDURES

This project follows the WQPB “internal process”. Appropriate storage times for water quality samples discussed in **Sections 3.3 to 3.6** are shown in **Table 3-1** above. Water quality samples will be delivered to Energy Laboratory and macroinvertebrate samples will be delivered to Rhithron, Inc.

5.0 LABORATORY ANALYTICAL MEASUREMENTS

Table 5-1 summarizes the analytical methods and required laboratory detection and reporting limits to be used for this project.

Table 5-1. Analytical Methods and Required Reporting Values.

Water Sample – Nutrients		
Analyte	Method	Req. Report Limit (ug/L)
Total Nitrogen (TN)	A 4500-N-C	40
Total Phosphorus as P	EPA 365.1	3
Nitrate-Nitrite as N	EPA 353.2	10
Water Sample - Suspended Solids		
Analyte	Method	Req. Report Limit (ug/L)
TSS	EPA 2540D	4000
Water Sample - Dissolved Metals		
Aluminum	EPA 200.7	30
Water Sample - Total Recoverable Metals		
Metal	Method	Req. Report Limit (ug/L)
Arsenic	EPA 200.8	3
Cadmium	EPA 200.8	0.08
Chromium	EPA 200.8	1
Copper	EPA 200.8	1
Iron	EPA 200.7	50
Lead	EPA 200.8	0.5
Mercury (Ultra-low level)	EPA 245.7	0.005
Selenium	EPA 200.8	1
Silver	EPA 200.8	0.5
Zinc	EPA 200.7	10
Total Hardness	A2340B (calculated)	1000
Total Recoverable Metals Digestion	EPA 200.2	N/A
Sediment Sample - Metals		
Metal	Method	Req. Report Limit (mg/kg - dry weight)
Arsenic	EPA 200.8	N/A
Cadmium	EPA 200.8	N/A
Chromium	EPA 200.8	N/A
Copper	EPA 200.8	N/A
Iron	EPA 200.7	N/A
Lead	EPA 200.8	N/A
Mercury	EPA 7471B	N/A
Uranium	EPA 200.8	N/A
Zinc	EPA 200.7	N/A
Total Recoverable Metals Digestion	EPA 200.2	N/A

Table 5-1. Analytical Methods and Required Reporting Values.

Parameter	Others	
	Method	Req. Report Limit
Chlorophyll -a	A 10200H	N/A
Ash Free Dry Weight	A 10300 (C5)	N/A

6.0 QUALITY ASSURANCE AND QUALITY CONTROL REQUIREMENTS

This project will follow the WQPB “internal process”. All QA/QC requirements followed by MT DEQ will be instituted for this project. The QA/QC requirements are described in MT DEQ (Montana Department of Environmental Quality, 2005).

6.1 INSTRUMENT CALIBRATION

YSI 85 meter

Pre-calibration of the YSI 85 meter will be undertaken in the laboratory. The YSI meter will also be calibrated just prior to measuring dissolved oxygen for site-specific altitude at each site following the instructions indicated in the YSI 85 manual.

Hand-held pH meter

The pH meter will be pre-calibrated in the laboratory using the two-point method (pH 4.0 and 7.0 standards), and checked against a 4.0 and 7.0 standard prior to each measurement in the field.

7.0 DATA ANALYSIS, RECORD KEEPING, AND REPORTING REQUIREMENTS

This project will follow the WQPB “internal process”. Site Visit/Chain of Custody forms, field forms digital photos, and lab will be processed by WQPB staff following QA/QC procedures as indicated in **Section 6.0**. The GPS coordinate system datum used will be NAD 1983 State Plane Montana, in decimal degrees, to at least the third decimal.

8.0 SCHEDULE

The Water Quality Monitoring and Assessment staff will sample 7 streams within the Flathead-Stillwater TPA at 31 proposed sites (**Appendix A**). The high flow sampling events will occur in June 2012 whereas the low flow sampling event will begin in July 2012. Data collection should be completed no later than September 30, 2011 (Suplee and Sada de Suplee, 2011).

9.0 PROJECT TEAM AND RESPONSIBILITIES

The Water Quality Monitoring and Assessment Section will lead the monitoring component. Darrin Kron will oversee the overall Monitoring and Assessment component. Alan Nixon will lead the monitoring project with support and assistance from the monitoring and assessment section staff. Dean Yashan will oversee and lead the overall TMDL component.

10.0 REFERENCES

- Montana Department of Environmental Quality. 2005. Quality Assurance Project Plan (QAPP): Sampling and Water Quality Assessment of Streams and Rivers in Montana, 2005. Report WQPBOAP-02, Rev. 03.
- , 2011a. Assessment Methodology for Metals Assessments. Helena, MT: Montana Department of Environmental Quality.
- , 2011b. Field Procedures Manual for Water Quality Assessment Monitoring, Draft. Helena, MT: Montana Department of Environmental Quality. Report WQPBWQM-020.v.3.
- Suplee, Michael W. and Rosie Sada de Suplee. 2011. Assessment Methodology for Determining Wadeable Stream Impairment Due to Excess Nitrogen and Phosphorus Levels. Helena, MT: Montana Department of Environmental Quality.

APPENDIX A

Flathead-Stillwater TPA proposed 2011 Sampling Site locations and proposed number of samples to be collected per parameter per site. New sites for 2012 are: 1F, 1G, 2A, 3B, 3D, 6B, 6C, 6D, 7A, 7B, and 7C. All other sites were stations established prior to this project. Site 3B on Sheppard Creek is a PIBO station using the PIBO Station Name PIBO_0166.

Site No.	Water Body Name	LAT (DD)	LONG (DD)	Nutrients	Ammonia	TSS*	TR* Metals	Dissolved Aluminum	Metals - Sediment	Chlorophyll- <i>a</i> /AFDW	Macroinvertebrates	Periphyton
1A	Whitefish River	48.2188	-114.2859	2	2	3	2	2	1	1	1	1
1B	Whitefish River	48.2911	-114.2892	2	2	3	2	2	1	1	1	1
1C	Whitefish River	48.3206	-114.2786	2	2	3	1	1	0	1	1	1
1D	Whitefish River	48.3712	-114.3026	2	2	3	2	2	0	1	1	1
1E	Whitefish River	48.3856	-114.3295	2	2	3	2	2	1	1	1	1
1F	Whitefish River	48.3890	-114.3300	6	6	6	0	0	0	1	0	0
1G	Whitefish River	48.4155	-114.3539	2	2	3	1	1	0	1	1	1
2A	Stillwater River	48.1740	-114.2780	2	0	3	2	2	1	1	1	1
2B	Stillwater River	48.2039	-114.2808	2	0	3	2	2	1	1	1	1
2C	Stillwater River	48.2175	-114.3122	2	0	3	1	1	0	1	1	1
2D	Stillwater River	48.2828	-114.3528	2	0	3	2	2	1	1	1	1
2E	Stillwater River	48.3189	-114.3864	2	0	3	1	1	0	1	1	1
2F	Stillwater River	48.4489	-114.4842	2	0	2	0	0	0	1	1	1

Site No.	Water Body Name	LAT (DD)	LONG (DD)	Nutrients	Ammonia	TSS*	TR* Metals	Dissolved Aluminum	Metals - Sediment	Chlorophyll- <i>a</i> /AFDW	Macroinvertebrates	Periphyton
2G	Stillwater River	48.4658	-114.5092	2	0	3	1	1	0	1	1	1
5A	Fish Creek	48.1920	-114.6484	3	0	3	0	0	0	1	1	1
5B	Fish Creek	48.1943	-114.6681	3	0	3	0	0	0	1	1	1
5C	Fish Creek	48.2041	-114.6841	3	0	3	0	0	0	1	1	1
3A	Sheppard Creek	48.3717	-114.6812	3	0	3	0	0	0	1	0	1
3B	Sheppard Creek	48.3798	-114.7098	3	0	3	0	0	0	1	0	1
3C	Sheppard Creek	48.3810	-114.7499	3	0	3	0	0	0	1	0	1
3D	Sheppard Creek	48.3700	-114.8190	3	0	3	0	0	0	1	0	1
4A	Spring Creek	48.1964	-114.3340	2	0	3	2	2	1	1	0	1
4B	Spring Creek	48.2003	-114.3347	2	0	3	2	2	1	1	0	1
4C	Spring Creek	48.2061	-114.3514	2	0	3	2	2	0	1	0	1
4D	Spring Creek	48.2198	-114.3731	2	0	3	2	2	0	1	0	1
4E	Spring Creek	48.2252	-114.3834	2	0	3	1	1	0	1	0	1
6A	Haskill Creek-lower	48.3889	-114.3096	3	0	3	0	0	0	1	1	1
6B	Haskill Creek-lower	48.4000	-114.2880	3	0	3	0	0	0	1	1	1
6C	Haskill Creek-lower	48.4230	-114.2830	3	0	3	0	0	0	1	1	1

Site No.	Water Body Name	LAT (DD)	LONG (DD)	Nutrients	Ammonia	TSS*	TR* Metals	Dissolved Aluminum	Metals - Sediment	Chlorophyll- <i>a</i> /AFDW	Macroinvertebrates	Periphyton
6D	Haskill Creek-lower	48.4650	-114.3210	3	0	3	0	0	0	1	1	1
7A	Haskill Creek-upper	48.4640	-114.3320	3	0	3	0	0	0	1	1	1
7B	Haskill Creek-upper	48.4760	-114.3470	3	0	3	0	0	0	1	1	1
7C	Haskill Creek-upper	48.4880	-114.3460	3	0	3	0	0	0	1	1	1

* Total Suspended Solids (TSS), Total Recoverable Metals (TR)

