EC01TMDL03SAP-03 Rev.: final rev. 1 05/19/2009

# LITTLE BLACKFOOT TMDL PLANNING AREA CHEMISTRY AND CHLOROPHYLL MONITORING

# Sampling and Analysis Plan

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# Prepared by:

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# **TABLE OF CONTENTS**

1.0 Introduction and Background	1
2.0 Objectives and Design	2
3.0 Field Sampling Methods	7
4.0 Sample Handling and Laboratory Analytical Procedures	. 12
5.0 Quality Assurance and Quality Control Requirements	. 13
6.0 Data Analysis, Record Keeping, and Reporting Requirements	. 15
7.0 Schedule for Completion	. 16
8.0 Project Team and Responsibilities	. 17
9.0 References	. 17

IC01SAP-N02 Rev.: final rev. 1 05/19/2009 Page 1 of 17

This document constitutes the Sampling and Analysis Plan (SAP) for the completion of nutrient and metals source assessments and loading estimates for the listed streams in the Little Blackfoot TMDL planning area (TPA).

# 1.0 Introduction and Background

The majority of the Little Blackfoot TPA is within Powell County, with a minor area in Lewis and Clark County. The Little Blackfoot River originates in the Helena National Forest near Blackfoot Meadows and flows approximately 47 miles to its confluence with the Clark Fork River near Garrison. The total extent of the watershed is 264,124 acres, or approximately 413 square miles. The TPA is located within the Upper Clark Fork hydrologic unit (17010201), and is coincident with the combined 170102015 and 170102016 fifth-code watersheds. The TPA is bounded by the continental divide to the northeast and southeast, the Garnet Mountains to the northwest, and the divide between Spotted Dog Creek and the Clark Fork River to the southwest.

Under Montana law, an impaired water body is defined as a water body for which sufficient and credible data indicates non-compliance with applicable water quality standards (MCA 75-5-103). Section 303 of the Federal Clean Water Act requires states to submit a list of impaired water bodies or stream segments to the U.S. Environmental Protection Agency (EPA) every two years. Prior to 2004, the EPA and DEQ referred to this list as the 303(d) list. Since 2004, the EPA requested that states combine the 303(d) list with the 305(b) report containing an assessment of Montana's water quality and its water quality programs. This new combined 303(d)/305(b) report is referred to as the Integrated Water Quality Report. Section 303 of the Federal CWA and the Montana WQA (Section 75-5-703) require development of TMDLs for all water bodies appearing on the 303(d) list as impaired or threatened by "pollutants."

On Montana's 2006 303(d) list, four stream segments were listed for nutrient impairment, and six stream segments and one wetland were listed for metals impairment (**Table 1**). There are no point sources within the watershed and its population is just over 600, with more than half of residents residing near the towns of Elliston and Avon. The nutrient and metals listings are likely associated with a mix of current and historical land uses. Land use within the TPA is dominated by forest and agriculture, but mining was a prominent historical land use and waste rock and tailings are still present in many locations.

Table 1. Waterbody segments within the Little Blackfoot TPA listed for nutrient and metals impairments on the 2006 303(d) List.

<b>Nutrient Listed Stream Segments</b>	Metals Listed Stream Segments
Dog Creek (lower seg)	Dog Creek (upper seg): Pb, Zn, As
Little Blackfoot (lower seg)	Little BF (upper seg): As; cyanide
Snowshoe Creek	Little BF (lower seg): Cu, Pb
Spotted Dog Creek (lower seg)	Monarch Creek: As, Cu, Pb, Hg, Se; pH
	Ontario Mine Wetland: As, Cd, Cu, Pb, Hg, Zn; pH
	Telegraph Creek (upper seg): As, Be, Cd, Cu, Fe, Zn
	Telegraph Creek (lower seg): Pb, Hg

IC01SAP-N02 Rev.: final rev. 1 05/19/2009 Page 2 of 17

Excess nutrients can cause nuisance algae to proliferate and affect beneficial uses such as recreation and aquatic life. Numeric human health standards exist for nitrates but there are no statewide numeric aquatic life standards for nutrients. Montana DEQ is currently developing numeric nutrient criteria that will be considered as interim targets during TMDL development. However, nutrient targets currently exist for the Clark Fork River above the confluence with the Flathead River for total nitrogen (300 μg/L) and total phosphorus (20 μg/L upstream of the confluence with the Blackfoot River and 39 μg/L downstream of the confluence), as well as algal biomass measured as chlorophyll *a* (summer mean and maximum of 100 and 150 mg/m², respectively) established as part of a Voluntary Nutrient Reduction Plan (VNRP). Because the Little Blackfoot River flows into the Clark Fork River, the Clark Fork River targets will be considered during TMDL development. However, chlorophyll values will be used in conjunction with the interim nutrient targets (derived from the 90<sup>th</sup> percentile of DEQ ecoregional reference values) to verify nutrient impairment on the 303(d) listed water bodies within the TPA.

Elevated concentrations of heavy metals in streams and lakes can have a toxic, carcinogenic, or bioconcentrating effect on biota living in these environments. Threshold concentrations of these pollutants have been adopted by the State of Montana as standards. These standards were developed in compliance with Section 75-5-301, MCA of the Montana Water Quality Act and Section 303(c) of the Federal Clean Water Act (CWA). Montana's acute and chronic standards for aquatic life and human health as defined in Circular DEQ-7 will be applied in this study to assess the compliance of listed and potentially impaired water bodies with Montana surface water standards.

# 2.0 Objectives and Design

The objective of this sampling plan is to collect chemistry, physical, and chlorophyll data that will be used for the following:

- Verification of nutrient and metals impairment conditions on 303(d) listed tributaries in the Little Blackfoot TMDL Planning Area to aid in TMDL development decisions
- Quantification of nutrient and metals loads associated with specific land use categories in the Little Blackfoot TMDL Planning Area to assist in TMDL nutrient and metals load allocations

In situations where impairment cannot be verified, additional monitoring may be recommended in lieu of TMDL development.

#### **Study Design**

In order to meet the above objectives, nutrient and metals conditions will be determined by extensive water quality sampling within the Little Blackfoot watershed. Synoptic surveys for nitrogen and phosphorus compounds in the water column will be performed at each of the selected sample sites during five sampling events: one in spring and two in summer of 2008 and one in summer of 2009 (**Table 2**). Chlorophyll *a* sampling will be done in conjunction with summer low flow nutrient sampling during 2008 and 2009. Synoptic surveys for key metals

IC01SAP-N02 Rev.: final rev. 1 05/19/2009 Page 3 of 17

concentrations in the water column will be performed at each of the selected sample sites during four sampling events: spring 2008 and 2009 and summer 2008 (event 1) and 2009 (**Table 2**). Sediment samples will be collected and analyzed for metals during the first summer 2008 sampling event. Sediment samples will be collected in summer 2009 for any sites not sampled in 2008 (**Table 6**). Total suspended solids (TSS) will be collected at all sites during all sampling events. Physical parameters (i.e. water temperature, dissolved oxygen, pH, and conductivity) will be collected with a field meter at all sites.

Sampling results from 2008 will be reviewed prior to 2009 sampling. For metals, the analysis constituents will be reduced to those with exceedances in 2008 of numeric criteria in DEQ-7 and to those metals on the 2006 303(d) List. Based on the results from 2008, sampling locations may be modified to help refine the source assessment.

Table 2. Sampling timeframe for nutrients and metals.

Sampling Event	Nutrients	Chlorophyll	Metals	<b>Sediment Metals</b>
May/June 2008	X		X	
Early-mid July 2008	X	X	X	X
Late August-early September 2008	X	X		
May/June 2009			X	
Mid August - Mid September 2009	X	X	X	X

# Nutrients and Chlorophyll

Sampling during spring runoff is anticipated to document diffuse non-point sources of nutrient loading, such as areas with riparian grazing and runoff from crop lands. Nutrient and chlorophyll *a* sampling during low flow in late summer is anticipated to measure nutrient concentrations when they are most likely to be negatively affecting beneficial uses, and measure chlorophyll *a* during peak algal growth.

Chlorophyll *a* sampling will occur at each site that is determined to have 'considerable' algal growth over the entire site. Algae will be collected for chlorophyll *a* analysis at each site where algal density is visually estimated to be close to or greater than 50 mg/m². The visual determination of algal growth will be made based on comparison to photos of sites with known concentrations (**Appendix A**, **Chlorophyll a Photo Packet**). The 50 mg/m² threshold is based on the results of a DEQ study that assessed the level of algal growth that negatively affects recreational use (Larix Systems, 2006). An algal density of 150 mg/m² was determined to negatively affect recreational use but 50 mg/m² will be used for this study to err on the conservative side during data collection and provide a margin of safety. Algal samples will be analyzed for ash-free dry weight (AFDW) in addition to chlorophyll *a* to help account for instances where algal biomass is high, but due to algal senescence, the chlorophyll values will not reflect the biomass. Instantaneous flow will be measured for each site so that nutrient loads can be calculated

IC01SAP-N02 Rev.: final rev. 1 05/19/2009 Page 4 of 17

## **Nutrient Export Model**

Data collected as part of this SAP will be used to supplement and further investigate nutrient concentrations from those streams listed for nutrient impairments in the Little Blackfoot TPA.

The DEQ is currently engaged in a watershed scale modeling effort in the Upper Clark Fork basin, including the Little Blackfoot watershed. It is anticipated to be completed within the next year. One goal of the Upper Clark Fork River Basin Modeling Project is to develop a planning model capable of simulating the concentration of dissolved and total nitrogen, phosphorus, and total suspended sediment contributed annually to the Little Blackfoot River from point and non-point source pollution.

#### <u>Metals</u>

Metals concentrations in surface waters are highly dependant upon the severity of the sources, spatial distribution of natural and human-caused sources, and the quantity of water to transport the toxics. Therefore, the sampling regime will account for two temporal timeframes; spring runoff/high flow conditions, and base flow conditions. Sampling during spring runoff is anticipated to document diffuse non-point sources of metals loading, such as metals contamination from runoff from historic mining practices and impacts and/or disturbance of metals laden in-stream sediment. Samples collected during base flow conditions will potentially isolate discrete sources, such as mine adit discharges and groundwater influence. Although state water quality standards are for total recoverable metals, with the exception of aluminum, the dissolved fraction will also be measured for a few metals in 2008 and at limited sites for iron in 2009 to aid in source identification. Instantaneous flow will be measured for each site so that metals loads can be calculated.

Although the goal of spring sampling is to target non-point sources and in-stream sediment that is only transported during high flows, depositional areas with fine-grained sediment will also be sampled for metals during the summer 2008 sampling event at each of the selected sample sites. Sediment samples will be collected and analyzed for metals during the summer 2009 sample event at any sites not sampled in 2008 (**Table 6**). This component of the metals monitoring will provide a direct measurement of in-stream metals deposition that can be entrained during higher flow conditions. Results from the sediment chemistry can also provide further information about how metals have moved from historical sources over time. Metals associated with stream sediments can also bioaccumulate via the food chain and cause toxicity to organisms that live in contact with it. Sediment metals screening values from the National Oceanographic and Atmospheric Administration (NOAA) will be used for data analysis. In some cases, monitoring will be completed above known sources to characterize natural conditions.

The field pH measurements may indicate if mining sources are altering ion balance via acid mine drainage and also the capacity of metals ions to either dissolve or precipitate. Water hardness will be collected along with metals samples because toxicity of seven common metals (Cd, Cr<sup>+3</sup>, Cu, Pb, Ni, Ag, and Zn) has been determined to be hardness-dependant. Montana's water quality criteria apply hardness in the determination of the allowable magnitude for these metals.

IC01SAP-N02 Rev.: final rev. 1 05/19/2009 Page 5 of 17

# **Sampling Sites**

#### 2008

There are 37 sample sites spatially distributed throughout the Little Blackfoot River and its tributaries. Of the sample sites, 26 are metals sites and 22 are nutrient sites (see **Table 4** and **Appendix B**, **Watershed Map**). One of the metals sites, Ontario Mine Wetland (ONT-1-3629ON03), is a remote wetland site and will not be sampled during the spring sampling trip because access will likely be difficult during the spring and metals are most likely to be highest in the summer when the water level is lower. Sampling sites were chosen to represent the range of landscape characteristics and land use/ land cover influences existing in the watershed, as well as the contribution of major tributaries. Sampling sites were identified by both assessment of aerial images and field surveying to capture the variability in land use and watershed characteristics potentially contributing to metals concentrations in streams including: land use/land cover (e.g. known mined areas, forest, grass, riparian area, geology, and soils), watershed residence times, and stream order. Monitoring locations are spatially located to aid in determining the contribution of known sources and the location of and contribution from other sources.

#### 2009

Based on the results of 2008 sampling, 44 sites will be sampled throughout the Little Blackfoot River and its tributaries. Of the sample sites, 30 are metals sites and 23 are nutrient sites (see **Table 4** and Appendix B). Sites ONT-0, ONT-1, and ONT-1A may not be accessible during high flow sampling due to snow and accessibility. Sites LBF-1, SIX-1, and SPD-1 were sampled for background metals concentrations in 2008 but will not be sampled in 2009. Additional sites for 2009 are shown below in **Table 3**.

If site inaccessibility or other limitations preclude collecting samples at the locations identified in this SAP, field personnel and/or the HydroSolutions Project Manager must contact the DEQ Project Manager to discuss alternatives and agree on a resolution prior to relocating the sample location.

Table 3. New sites for 2009 sampling events.

Site Name	Site Type	Rationale for Additional Site
CAR-2	Nutrient	Nutrient site as close as possible to the mouth
ONT-0	Metal	Background concentration in Ontario Creek
ONT-1A	Metal	To capture loading from the Ontario Mine adit
ONT-2A	Metal	To assess metals loading u/s of Monarch Cr confluence
OPH-1	Nutrient	To capture metals loading from Ophir Cr to Carpenter Cr
SIX-2	Nutrient	To capture nutrient loading from Sixmile Creek
SPD-1A	Nutrient	Intended location of SPD-1 in 2008; To capture loading from
		headwaters
TGH-0	Metal	Background concentration in Telegraph Creek
TGH-2A	Metal	To capture loading from Lily/Orphan Boy priority mine
TGH-3A	Metal	Intended location of TGH-3 in 2008; To capture loading
		from Moose Gulch
THR-2	Nutrient	To capture nutrient loading from Threemile Creek

IC01SAP-N02 Rev.: final rev. 1 05/19/2009 Page 6 of 17

Table 4. Sample locations for nutrients and metals sampling. Shaded sites were sampled in

2008 but will not be sampled in 2009.

<b>2000</b> D	ut will not be s	ampicu m		_	<u>.                                      </u>	1			
Water Body	Waterbody ID	Site Name	2 0 0 8	2 0 0 9	Metals	Nutrients/ Chlorophyll/ AFDW	TSS	Latitude	Longitude
Carpenter Creek	MT76G004_092	CAR-1	Х	Х	Х		Х	46.63151	-112.54308
Carpenter Creek	MT76G004_092	CAR-2		Х		Х	Х	46.60403	-112.55115
Dog Creek	MT76G004_071	DOG-1	Х	Χ	Χ		Х	46.71944	-112.35498
Dog Creek	MT76G004_071	DOG-2	Х	Χ	X		Х	46.69793	-112.35215
Dog Creek	MT76G004_071	DOG-3	Х	Х	Х		Х	46.69667	-112.35231
Dog Creek	MT76G004_071	DOG-4- 3629DO01	Х	Х		Х	Х	46.69078	-112.35708
Dog Creek	MT76G004_072	DOG-5	Х	Χ	Χ	X	Х	46.67536	-112.38199
Dog Creek	MT76G004_072	DOG-6	Х	Χ		Х	Х	46.61551	-112.34269
Dog Creek	MT76G004_072	DOG-7	Х	Х		Х	Х	46.61650	-112.33807
Dog Creek	MT76G004_072	DOG-8	Х	Х	Х	Х	X	46.56071	-112.38686
Little	W1700004_072	2000	<u> </u>			A	Λ	40.30071	112.30000
Blackfoot									
River Little	MT76G004_020	LBF-1 LBF2-	Х		Χ		Х	46.39328	-112.47294
Blackfoot River	MT76G004_020	C01LTBLR 02	X	X	X		X	46.45729	-112.41854
Little Blackfoot River	MT76G004 020	LBF-3	X	X	Х		x	46.48520	-112.42915
Little Blackfoot River	MT76G004_020	LBF-4	X	X	Х	х	x	46.50443	-112.40382
Little Blackfoot River	MT76G004 020	LBF-5	x		Х	х	x	46.55673	-112.40946
Little Blackfoot River	MT76G004_010	LBF6- C01LTBLR 04	×	X		х	x	46.56531	-112.43281
Little Blackfoot River	MT76G004_010	LBF-7	Х	X	Х	х	x	46.57767	-112.51064
Little Blackfoot River	MT76G004_010	LBF-8	X	X		х	x	46.59650	-112.59167
Little Blackfoot River	MT76G004_010	LBF-9	X	X	Х	х	х	46.54842	-112.67853
Little Blackfoot River	MT76G004_010	LBF-10- 3725Ll01	Х			Х	Х	46.51949	-112.79343
Monarch Creek	MT76G004_060	MCH-1	Х		Х		Х	46.40935	-112.40897
Monarch Creek	MT76G004_060	MCH2- C01MONR C10	Х	X	Х		Х	46.42699	-112.39420
Ontario Creek	Not listed	ONT-0		Х	Х		Х	46.42365	-112.32684
Ontario Creek	Not listed	ONT-1A		Х	X		Х	46.42918	-112.34044

IC01SAP-N02 Rev.: final rev. 1 05/19/2009 Page 7 of 17

			2	2					
Water			0	0		Nutrients/			
Water Body	Waterbody ID	Site Name	0 8	9	Metals	Chlorophyll/ AFDW	TSS	Latitude	Longitude
Ontario	Waterbody ID	ONT-2-	Ū	-	Motais	AIDW	100	Latitudo	Longitude
Creek	Not listed	3628ON01	Х	Х	Χ		Х	46.45528	-112.41389
Ontario									
Creek	Not listed	ONT-2A		Х	Χ		Х	46.43141	-112.38577
Ontario Mine		ONT-1-							
Wetland	MT76G006_010	3629ON03	Х	Х	Χ		X	46.42720	-112.34130
Ophir Creek	Not Listed	OPH-1		X	X		X	46.63173	-112.54315
Sixmile	NOT LISTEU	OI II-I		^			^	40.03173	-112.04313
Creek	Not listed	SIX-1	Х	-	Χ		Х	46.64763	-112.63704
Sixmile									
Creek	Not listed	SIX-2		Χ		Χ	Χ	46.60972	-112.62658
0		SNO1-							
Snowshoe Creek	MT76G004 080	C01SNOW C10	Х	Х		x	Х	46.68395	-112.46645
Snowshoe	1011700004_000	010	^	^		, <u>, , , , , , , , , , , , , , , , , , </u>	^	40.00393	-112.40043
Creek	MT76G004_080	SNO-2	Х	Х		X	Х	46.65471	-112.47956
Snowshoe									
Creek	MT76G004_080	SNO-3	Х	Х		X	Х	46.64331	-112.48840
Snowshoe	MT700004 000	CNO 4	V	V	V	V	V	40 50770	440 50575
Creek Spotted	MT76G004_080	SNO-4	Х	Х	X	X	Х	46.59772	-112.53575
Dog Creek	MT76G004 031	SPD-1	Х	-		X	X	46.46437	-112.52214
Spotted								1 101 10 101	
Dog Creek	MT76G004_031	SPD-1A		Χ		Χ	Χ	46.46497	-112.52482
Spotted							l		
Dog Creek	MT76G004_032	SPD-2	Х	Χ		Х	Х	46.50263	-112.55833
Spotted Dog Creek	MT76G004_032	SPD-3	Х	Х		x	Х	46.56861	-112.60246
Spotted	W11700004_032	01 0 3				X		40.30001	112.00240
Dog Creek	MT76G004_032	SPD-4	Х	Х	Χ	Х	Х	46.58864	-112.60262
Telegraph									
Creek	MT76G004_051	TGH-0		Х	X		Χ	46.46291	-112.32799
Telegraph Creek	MT76G004_051	TGH-1	Х	Х	X		Х	46.45929	-112.34053
Telegraph	W1170G004_031	1011-1	^	^	^		^	40.45929	-112.34033
Creek	MT76G004_051	TGH-2	Х	Х	Χ		Х	46.45964	-112.33707
Telegraph									
Creek	MT76G004_051	TGH-2A		Χ	X		Х	46.44437	-112.34398
Telegraph	MT76C004 054	TCH 2	V		V		_	46 40040	112 27020
Creek Telegraph	MT76G004_051	TGH-3	X		Χ		X	46.48848	-112.37032
Creek	MT76G004_051	TGH-3A		Х	Χ		Х	46.49299	-112.37487
Telegraph									
Creek	MT76G004_052	TGH-4	Χ	Χ	Χ		Χ	46.51041	-112.38012
Threemile	MT700004 446	TUD 1		.,	V		\ \ \	40.00470	440.0070:
Creek	MT76G004_112	THR-1	Х	Х	Х		Х	46.60170	-112.62791
Threemile Creek	MT76G004 112	THR-2		Х		X	Х	46.60992	-112.62608
CIECK	WIT / 00004_112	IIIN*Z		^		Λ	^	+0.00332	-112.02000

# **3.0 Field Sampling Methods**

Monitoring will be done in accordance with the MDEQ's Field Procedures Manual which is available on the internet at:

http://www.deq.state.mt.us/wqinfo/QAProgram/SOP%20WQPBWQM-020.pdf (DEQ, 2005a). Grab samples will be collected and analyzed for nutrients and/or metals as identified in

IC01SAP-N02 Rev.: final rev. 1 05/19/2009 Page 8 of 17

**Table 4.** The nutrient and metals monitoring suite for 2008 and 2009 is contained in **Table 5a** and **Table 5b**, respectively. Because the metals suite is smaller in 2009 and several additional sites will have sediment samples collected and/or water samples analyzed for iron, selenium, cyanide, and/or mercury, they are identified in **Table 6**.

Water samples will be collected directly in acid washed, polyethylene bottles. Bottles shall be rinsed three times with native water prior to sampling. For dissolved constituents, field filtering will be performed with a  $0.45~\mu m$  syringe filter and the sample rinses will be done with the filtrate. Samples will be collected in a well-mixed portion of each stream, or, if the stream has ceased flowing (intermittent), the sample will be collected at the surface in a pool without disturbing the sediments. During sampling, the sample bottle opening should face upstream and should be drawn through the water column once, carefully avoiding disturbance of bottom sediments.

Table 5a. 2008 analyte suite for nutrients and metals. TR = total recoverable

	Water Column		Sediment			
<u>Nutrients</u>	<u>Metals</u>	Non-Metals	<u>Metals</u>			
Total P	Aluminum (dissolved)	Hardness	Arsenic			
Total N	*Mercury (TR) (ONT1, ONT2, TGH1-TGH4, MCH1, MCH2)	TSS	Cadmium			
Nitrate + Nitrite	Arsenic (TR)	*Cyanide (at LBF3 & LBF4)	Chromium			
TSS	Cadmium (TR)		Copper			
	Chromium (TR)		Iron			
	Copper (TR and dissolved)	Lead				
	Iron (TR)	Nickel				
	Lead (TR and dissolved)	Selenium				
	Manganese (TR)		Silver			
	Nickel (TR)		Zinc			
	Selenium (TR)					
	Silver (TR)					
	Zinc (TR and dissolved)					

<sup>\*</sup>Only measured at limited sites as indicated.

Table 5b. 2009 analyte suite for nutrients and metals. TR = total recoverable

	Water Column						
<u>Nutrients</u>	<u>Metals</u>	Non-Metals	<u>Metals</u>				
Total P	Aluminum (dissolved)	Hardness	Arsenic				
Total N	Arsenic (TR)	TSS	Cadmium				
Nitrate + Nitrite	Cadmium (TR)	*Cyanide	Copper				
TSS	Copper (TR)		Lead				
	Lead (TR) Zinc						
	Zinc (TR) Mercury*						
	*Beryllium (TR) only)						
	*Iron (TR and dissolved)						
	*Selenium (TR)						
	*Mercury (Total)						

<sup>\*</sup>Only measured at limited sites as indicated in Table 6.

IC01SAP-N02 Rev.: final rev. 1 05/19/2009

Page 9 of 17

Table 6. 2009 metals sites with sediment samples and/or additional metals constituents in the water column. Cells with an "X" indicate that constituent needs to be analyzed.

Water Body	Site	Sediment	Sediment	Hg	CN	Be	Fe (TR)	Fe	Se
•	Name		Hg					(diss)	
Little Blackfoot River	LBF-3				X				
Little Blackfoot River	LBF-4				X				
Monarch Creek	MCH-1						X		X
Monarch Creek	MCH-2			X			X	X	X
Ontario Creek	ONT-1A			X			X	X	
Ontario Creek	ONT-1			X			X		
Ontario Creek	ONT-0	X					X		
Ontario Creek	ONT-2A	X							
Ontario Creek	ONT-2						X		
Telegraph Creek	TGH-0	X				X	X		
Telegraph Creek	TGH-1					X	X		
Telegraph Creek	TGH-2					X	X		
Telegraph Creek	TGH-2A	X				X	X		
Telegraph Creek	TGH-3A	X	X	X		X	X		
Telegraph Creek	TGH-4			X		X	X	X	

## **Nutrients**

As shown in **Tables 5a** and **5b**, the suite of nutrients that will be measured for each sampling event and site include nitrate + nitrite (NO<sub>2+3</sub>), total nitrogen (TN), and total phosphorus (TP). TSS will also be collected at all sites. Three bottles will be needed for the identified nutrient analytes:

TP, NO<sub>2+3</sub>, NH<sub>3+4</sub>: preserved with sulfuric acid (to a pH<2);  $\leq 6^{\circ}$ C

TN: no preservative;  $\leq 6^{\circ}$ C TSS: no preservative;  $\leq 6^{\circ}$ C

All samples will be properly labeled, stored in coolers and chilled to 6°C or less for transport to the lab. Additional details regarding the analytes, collection bottles, and preservation methods are contained in **Appendix C**, **Analyte Checklist**. The site names on the sample labels must correspond to the site names provided in this SAP (**Table 4**).

# Chlorophyll

Chlorophyll *a* will be collected using the method described in *Sample Collection and Laboratory Analysis of Chlorophyll-a SOP* (available at

http://deq.mt.gov/wqinfo/QAProgram/SOP%20WQPBWQM-011v4\_final.pdf). Template samples must be field-filtered using a 47 mm glass fiber filter with a nominal pore size of 0.7

IC01SAP-N02 Rev.: final rev. 1 05/19/2009 Page 10 of 17

μm; filtrate volume does not need to be recorded. The site visit form must be filled out in its entirety, including the collection method for each transect. For any transects that are not sampled, an "X" will be put on the site visit form. "Composite" must be specified on the chain of custody forms so the laboratory will properly process the samples. Note: samples will <u>not</u> be composited in the field.

For each sampling site that chlorophyll *a* is collected, one or two reach pictures must be taken that provide an overview of chlorophyll growth within the sampled section of stream. Preferably, the first reach picture will be taken between transects A and F, and the second will be taken between transects F and K. Additionally, a substrate photo must be taken at <u>each</u> transect. The transect letter must be recorded in the photo log with the picture documentation. Compositing algal samples eliminates the ability to discern variability among transects and taking reach and transect substrate photos will aid in result interpretation, particularly if there are any data quality issues. Photos must be taken for each sampling event and should be taken in the same manner as those contained in **Appendix A, Chlorophyll a Photo Packet**. A polarized lens should be used where necessary to reduce glare. If substrate visibility is low due to factors including, but not limited to, low light, turbidity, and glare, the cause of low visibility should be noted on the field form. Additionally, if visibility is low and substrate is poorly visible in template substrates photos, collect 5 representative rocks from the site and photograph at close range if substrate permits (i.e. small boulders, cobble or gravel).

For sites that are determined not to have 'considerable' algal growth, take one or two reach photos to provide an overview of chlorophyll growth in the sampling frame. Preferably, the first reach picture will be taken between transects A and F, and the second will be taken between transects F and K. Also, take a substrate photo at the approximate location of the downstream transect (A), center transect (F), and upstream transect (K). The algae condition in the photos should be clearly visible in the foreground. If visibility is low and substrate is poorly visible in the substrates photos, collect 5 representative rocks from the site and photograph at close range if substrate permits (i.e. small boulders, cobble or gravel). This will provide additional documentation of low chlorophyll a density at the site and the rationale for not sampling. Sites that are visually assessed to have  $<50 \text{mg/m}^2$  algal growth will be included in the chlorophyll data entry process as estimated values  $<50 \text{mg/m}^2$ .

All photographs will be recorded with picture number, date/time, stream name, site ID, and transect number or "reach photo".

#### Metals

The water column and sediment metals suites are shown in **Tables 5a** and **5b**. TSS will be collected at all sites. Additional constituents will be analyzed at a limited number of sites in 2008 (**Table 5a**) and in 2009 (**Tables 5a** and **6**).

◆ Total recoverable samples will be acidified to a pH of less than 2 by adding concentrated nitric acid (HNO<sub>3</sub>). Samples for dissolved metals constituents will be field-filtered with a

IC01SAP-N02 Rev.: final rev. 1 05/19/2009 Page 11 of 17

0.45 um syringe filter (membrane filter), then preserved to a pH of less than 2 by adding concentrated HNO<sub>3</sub>). The typical volume of HNO<sub>3</sub> needed is 5mL.

♦ Sediment samples are a composite sample made by collecting equivalent proportions of sediment from at least five wadeable deposition zones at each site. The sediment composite is wet sieved to a nominal particle size of < 60 um. Collect enough material to cover the bottom of the sample container (at least 1.0 gram).

All samples will be properly labeled, stored in coolers and chilled to 6°C or less for transport to the lab. Additional details regarding the analytes, collection bottles, and preservation methods are contained in **Appendix C**, **Analyte Checklist**. The site names on the sample labels must correspond to the site names provided in this SAP (**Table 4**).

#### Other Data

Stream discharge data will be collected at all water quality monitoring sites using a *Marsh McBirney Flo-Mate 2000*<sup>TM</sup> current velocity meter in accordance with MDEQ's Field Procedures Manual (DEQ, 2005a). Additional precautions may be necessary to obtain discharge during high flow sampling. If high flow sampling necessitates the use of a bridge crane or the float method if there is no bridge nearby, this must be indicated on the site form and documented with a photograph of the measurement location. For bridge sampling, the orientation of the bridge to the channel must be apparent in the photograph. As the sample collection method from a bridge may differ slightly from the standard collection method, the sampling equipment and collection method must also be documented on the site form (i.e. grab vs. depth and/or width integrated).

#### Discharge via the Float Method

Find a reach of stream that is linear/straight, as well as uniform in width and depth. This will assure that laminar flow is achieved to the greatest extent possible. Determine mean wetted width by visual estimation of three transects. Measure or pace off the distance twice the mean wetted width (in feet) along the bank and mark each end by driving a stake or piece of rebar into the ground at the high water line. The high water line should be marked so the cross sectional area can be calculated during the first low flow sampling trip. A photograph should be taken of the wooden stake/rebar location to help document the water line and aid in finding the location again during low flow (particularly if the water line marker is no longer there). If there is not a linear/straight reach near the sampling location that is long enough to mark off twice the wetted width, measure the distance of the mean wetted width instead. Record the measured distance on the discharge form.

Toss an orange into the middle of the stream above the upstream marker of the measured reach. Begin timing when the orange passes the upstream marker. Count (with a watch or stopwatch) the seconds it takes the orange to reach the downstream marker. The orange must stay in the main current. If it does not, repeat the measurement. Complete three measurable floats. Record the data on the site visit form and the discharge form.

#### Calculations:

IC01SAP-N02 Rev.: final rev. 1 05/19/2009 Page 12 of 17

Mean width x mean depth = cross-sectional area ( $ft^2$ ) Convert stick float time to ft/second (i.e., 26 ft/15 sec = 1.7 ft/sec) Determine CFS (a x b)

#### Other Data

A site form will be completed for each site that includes the site coordinates, time, weather, and any other observations (e.g. beaver dams, cattle, or excessive macrophyte growth). Separate site visit forms will be completed for each set of duplicate and blank samples, with unique site visit IDs and location IDs applied to both, indicating the sample is either a duplicate or a blank.

Physical parameters (i.e. water temperature, dissolved oxygen, pH, and conductivity) will be collected in the field with a YSI 85 or equivalent meter in accordance with MDEQ's Field Procedures Manual (DEQ, 2005a). The field meter and velocity meter will be calibrated prior to each use according to their respective operation manuals. The GPS coordinate system datum will be NAD 1983 State Plane Montana, in decimal degrees to at least the fifth decimal. All data and information for this project must meet other data reporting requirements identified in the Contract for work. Data formats identified in the contract will be used for TMDL related data analysis.

Pictures will be taken at each sampling location during the first sampling event in spring 2008 to document the general sample location. Pictures that document the sample site location do not need to be retaken for each sampling event, unless the sample location changes or an additional site is added. All pictures will be documented on field forms with the following information recorded:

Picture number, if taken on a digital camera
Date/time
Stream name
Sample site ID
Directional reference (facing upstream or downstream and N, S, E, W)

# 4.0 Sample Handling and Laboratory Analytical Procedures

Immediately following grab-sample collection, samples will be put on ice. Sample handling procedures will follow DEQ standard operating procedures as defined in DEQ guidance, *Sampling and Water Quality Assessment of Streams and Rivers in Montana, 2005: Quality Assurance Project Plan* (DEQ, 2005b). ). See **Appendix C, Analyte Checklist**, for chlorophyll a samples preservation methods. As indicated in **Appendix C, Analyte Checklist**, algal samples will be analyzed for ash-free dry weight in addition to chlorophyll. Algal samples from each transect should be stored in separate containers but grouped together by site for shipping. Caution should be used with algal samples during shipping. Refer to the DEQ *Sample Collection and Laboratory Analysis of Chlorophyll-a SOP* (DEQ, 2008) for specific guidance. **Chlorophyll a samples from waters with a pH less than 7 require faster processing than other samples to prevent degradation. If the sample water has a pH less than 7, this should be indicated on the Chain of Custody form so the lab will expedite sample processing. Standard DEQ** 

IC01SAP-N02 Rev.: final rev. 1 05/19/2009 Page 13 of 17

Water Quality Planning Bureau site visit/chain of custody forms will be used to document and track all samples collected in the project. Samples will be delivered to a state approved lab for analysis. **Appendix C, Analyte Checklist,** contains a table with the collection container, preservative, analytical method, required reporting limit, and holding time for each analyte. The lab must use "J value" reporting. The lab will retain samples in a manner consistent with lab policy.

# **5.0 Quality Assurance and Quality Control Requirements**

During each sampling trip, field duplicates will be collected randomly for 10% of all samples and field blanks will be prepared for 10% of all samples. Field blanks must use deionized water. Filter blanks will be completed for 10% of filtered samples to address bias due to filter contamination. If the number of samples is greater than 10 but less than midway between the next multiple of 10, round down for the number of blanks and duplicates (e.g. 23 samples = 2 duplicates and 2 blanks). Conversely, if the number of samples is greater than 10 and more than midway between the next multiple of 10, round up for the number of blanks and duplicates (e.g. 27 samples = 3 duplicates and blanks). No blanks are necessary for chlorophyll and sediment samples.

Data quality objectives (DQOs) are the quantitative and qualitative criteria established for a sampling design in order to meet the project's objectives. Data quality indicators (DQIs) are quantitative criteria established for the data acquired within this design to assure it is of sufficient quality for its intended use. Descriptions of data qualifiers and common QC terms and acronyms are included in **Appendix D, QA/QC Checklist**.

#### Representativeness

Representativeness refers to the extent to which measurements represent an environmental condition in time and space. This is a judgmental sampling design using the following rationale:

## Spatial representation:

Sampling sites were chosen to represent the potential of landscape characteristics and land use/land cover influences existing in the watershed to influence the nutrient and metals concentrations in the listed waters, as well as the contribution of major tributaries. Sampling sites were identified by both assessment of aerial images and field surveying to capture the variability in land use and watershed characteristics potentially contributing to pollutant concentrations in streams including: land use/land cover (e.g. known mined areas, forest, grass, riparian area, geology, and soils), watershed residence times, and stream order.

# Temporal representation:

Two time periods are used to spatially represent the potential for flows, which increase during runoff to influence the nutrient and metals concentration in the listed waters. These are the spring runoff and summer base flow of 2008/2009 for metals and the spring runoff and summer base flow of 2008/2009 for nutrients.

IC01SAP-N02 Rev.: final rev. 1 05/19/2009 Page 14 of 17

# **Comparability**

Comparability is the applicability of the project's data to the project's decision rule. The decision rules used for this project are the acute and chronic aquatic life criteria listed in Department Circular DEQ-7. All methods selected conform to the requirement listed in footnotes 3, 4, 9, 12, 19, and 29 of DEQ-7.

#### **Completeness**

Completeness is a measure of the amount of data prescribed for assessment activities and the usable data actually collected, expressed as a percentage. Prior to leaving a sampling site each field person will be required to fill out a data sheet, which will later be reviewed and initialed by the project manager. These checks will reduce the occurrence of empty data fields. The overall project goal is 90% completeness. Sites lost due to inaccessibility will reduce the total number of sites in the equation above but not the completeness goal. If any listed stream has less than 50% of its planned sites sampled due to accessibility issues, the project conclusions will note this fact and account for the increased uncertainty in the TMDLs margin of safety.

#### **Sensitivity**

Sensitivity refers to the limit of a measurement to reliably detect a characteristic of a sample. For analytical methods, sensitivity is expressed as the method detection limit (MDL). Laboratories must determine their MDL's annually and routinely check each method's ability to achieve this level of sensitivity using negative controls (e.g., Method Blanks, Continuing Calibration Blanks, and Laboratory Reagent Blanks).

Sensitivity quality controls for all laboratory methods will follow the frequency and criteria specified in the analytical method or as described in the Laboratory's Quality Assurance Plan (LQAP). The criteria used to assess field method sensitivity for water and sediment samples shall be:

• Field method controls (Field Blank) < Reporting Limit in **Appendix C** 

<u>Corrective Action</u>: If analytical method controls fail the specified limit, check with the laboratory to see how they addressed the non-conformance and qualify data as necessary. If Field Blanks fail, qualify all associated project data < 10x the detected value.

#### **Precision**

Precision refers to the degree of agreement among repeated measurements of the same characteristic. This project will rely on analytical and field duplicates to assess precision based on their relative percent difference (RPD).

RPD as 
$$\% = ((D1 - D2)/((D1 + D2)/2)) \times 100$$

Where:

R1 is first replicate result R2 is second replicate result

IC01SAP-N02 Rev.: final rev. 1 05/19/2009 Page 15 of 17

#### Lab precision (laboratory duplicates)

Precision quality control for all laboratory methods will follow the frequency specified in the analytical method or as described in the LQAP. The criteria used to assess analytical method precision shall be:

- Water samples: 20 % RPD for duplicate results > 5 times the reporting limit
- Sediment samples: 35% RPD for duplicate results > 5 times the reporting limit

## **Overall precision (field duplicates)**

Frequency of field co-located duplicates will be 10% of samples collected in the field. The criteria used to assess overall precision shall be:

- Water samples: 25 % RPD for duplicate results > 5 times the reporting limit
- Sediment samples: 40% RPD for duplicate results > 5 times the reporting limit

<u>Corrective Action</u>: If laboratory duplicates fail this limit, check with the laboratory to see how they addressed or qualified the data and add additional qualifiers and notes as needed. If the field duplicates fail this limit, qualify all associated results with a "J". Associated results may be considered by collection period (e.g. day or time of day) or water body; results that need to be qualified should be verified by the DEQ project manager.

#### **Bias and Accuracy**

Bias is directional error from the true value. In this context, it is an extension of the representativeness concept applied to an individual sample. Bias can occur either at sample collection or during measurement.

Accuracy is the combination of high precision and low bias. Accuracy of individual measurements will be assessed by reviewing the analytical method controls (i.e. Laboratory Control Sample, Continuing Calibration Verification, Laboratory Fortified Blank, Standard Reference Material) and the analytical batch controls (i.e. Matrix Spike and Matrix Spike Duplicate). The criteria used for this assessment will be the limits that the laboratory has developed through control charting of each method's performance or based on individual method requirements. Method QC descriptions are contained in Table D-2 in **Appendix D, QA/QC Checklist**.

<u>Corrective Action</u>: For any QC value outside of the recovery range, check with the laboratory to see how they addressed the non-conformance and qualify data as necessary.

# 6.0 Data Analysis, Record Keeping, and Reporting Requirements

#### **QC Review and Documentation**

A review of field and analytical data will be conducted following receipt of the laboratory data package that includes all items on the QC Checklist in **Appendix D**. All water quality data collected as part of this SAP will be evaluated against the criteria listed in section 5.0. Data

IC01SAP-N02 Rev.: final rev. 1 05/19/2009 Page 16 of 17

qualifiers provided in **Appendix D** (**Table D-1**) will be assigned to data in both hardcopy and electronic form that does not meet these target quality control criteria.

A written summary of data quality will be prepared following review of field documentation and data received from the laboratory. The data quality analysis will summarize the QA/QC information from the field event and laboratory analysis (including QC sample results), audit information, corrective actions taken (if any), and the overall results of sampling and analytical activities with respect to compliance with the provisions of this SAP. Any modifications to this SAP must be approved by the DEQ Project Manager and noted in the data quality summary. The primary focus of the data quality analysis will be to ensure the data has sufficient quality to minimize errors in decision making.

### **Record Keeping**

Data generated during this project will be stored on field forms and in laboratory reports obtained from the laboratories. Site Visit/Chain of Custody forms will be properly completed for all samples and are located online at

http://www.deq.mt.gov/wqinfo/datamgmt/2008 SiteVisitForm.pdf. Written field notes, field forms, and digital photos will be processed by field staff following QA/QC procedures and Scope of Work requirements to screen for data entry errors. Field sheets should be used to create an electronic photo log in MS Excel. The photo log may be organized with a tab for each sampling event or a separate tab or file for each site. Photograph file names should reflect the sampling data and site name. All associated field forms will be submitted to the project manager upon the completion of this project. After DEQ approval of the data quality summary, data from all sampling events and all known fields for site visits will be uploaded to STORET or the most current upload process. Direction concerning the upload process can be accessed at the Bureau's Data Management's web pages: <a href="http://www.deq.mt.gov/wqinfo/datamgmt/index.asp">http://www.deq.mt.gov/wqinfo/datamgmt/index.asp</a> or by contacting the Bureau's Data Management Section <a href="http://www.deq/staffdir.asp#ppa">Water Quality Metric Database Manager</a> (contact information is available at: <a href="http://svc.mt.gov/deq/staffdir.asp#ppa">http://svc.mt.gov/deq/staffdir.asp#ppa</a>). Station IDs for the data upload must be the project code, "LBF-" followed by the <a href="https://site.Name">Site Name</a> listed in Table 4.

# 7.0 Schedule for Completion

Exact dates for sampling collection to be finalized between DEQ and contractor. Sampling events to occur as follows:

One sampling event at peak of 2008 spring high flow May/June 2008

Two sampling events to occur in Summer 2008
Early-mid July 2008 and Late August-early September 2008

One sampling event at peak of 2009 spring high flow May/June 2009

One sampling event to occur in Summer 2009

IC01SAP-N02 Rev.: final rev. 1 05/19/2009 Page 17 of 17

Mid August to Mid September 2009

# 8.0 Project Team and Responsibilities

Table 5. Project staff and responsibility.

Name	Responsibility
Lisa Kusnierz	DEQ Project Manager
Luke Osborne	HydroSolutions Project Manager
David Donohue	HydroSolutions, senior review and QC
Rye Svingen	HydroSolutions, Field crew
Mark Bostrom	DEQ QA Officer – SAP review

## 9.0 References

DEQ. 2008. Little Blackfoot TMDL Planning Area Project Plan.

- DEQ 2005a. Water Quality Planning Bureau Field Procedures Manual for Water Quality Assessment Monitoring. Montana Dept. of Environmental Quality, WQPBWQM-020, revision 2. April 21, 2005. *Available at* http://www.deq.state.mt.us/wqinfo/QAProgram/SOP%20WQPBWQM-020.pdf
- DEQ. 2005b. Quality Assurance Project Plan (QAPP) Sampling and Water Quality Assessment of Streams and Rivers in Montana, 2005. *Available at* http://www.deq.state.mt.us/wqinfo/QAProgram/WQPBQAP-02.pdf.
- DEQ. 2008. Sample Collection and Laboratory Analysis of Chlorophyll-a Standard Operating Procedure. Montana Dept. of Environmental Quality, WQPBWQM-011, revision 4. June 5, 2008. *Available at* http://deq.mt.gov/wqinfo/QAProgram/SOP%20WQPBWQM-011v4 final.pdf