ROCK TMDL PLANNING AREA SAMPLING PROJECT - 2010:
NUTRIENTS & METALS

Sampling and Analysis Plan

Prepared for:

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1.0 Introduction and Background Information

This project is to support TMDL development in the Rock 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, 2010) and metals proposed assessment method (in development).

The Rock TPA is within Missoula and Granite Counties, Montana. The total extent of this TPA is 569,320 acres, or approximately 890 square miles, and it comprises the Rock River 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 Rock TPA are within the 4th code HUC 17010202, and they have been assigned a B-1 beneficial use classification (ARM 17.30.623).

The Water Quality Planning Bureau (WQPB) of the Montana Department of Environmental Quality (MDEQ) has identified 10 impaired (Category 5) streams within the Rock TPA; however only the streams identified in Table 1.1 will be sampled in 2010 for this project. Table 1.1 shows the waterbody segments to be sampled in 2010 with the pollutants of concern (nutrients/metals) within the Rock TPA. In addition, Basin Gulch (MT76E002_080) will be sampled for mercury as a source assessment for Eureka Gulch (Table 1.1).

Table 1.1 –Waterbody segments within the Rock TPA to be sampled in 2010 and 303(d) listings.

Waterbody Segment Name	Waterbody ID	Pollutant	
		Nutrients	Metals
East Fork Rock Creek	MT76E002_020	Nitrogen, Nitrate; Chlorophyll-a	-
West Fork Rock Creek	MT76E002_030	-	Mercury
Brewster Creek	MT76E002_050	Phosphorus (Total)	-
South Fork Antelope Creek	MT76E002_060	Nitrate/Nitrite (Nitrite + Nitrate as N); Phosphorus (Total)	-
Quartz Gulch	MT76E002_070	-	Mercury
Basin Gulch	MT76E002_080	-	-
Sluice Gulch	MT76E002_110	Nitrate/Nitrite (Nitrite + Nitrate as N)	Arsenic

2.0 Objectives and Design

2.1 Project Objectives

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

The goals for this project are as follows:

1. Measure physical parameters (temperature, DO, pH, and conductivity) *in situ*.
2. Collect metals (total recoverable, dissolved and sediment fractions) and total suspended solids (TSS) in those streams listed for metals, and collect nutrients, chlorophyll-a, and periphyton in those streams listed for nutrients.
3. Measure flow during each sampling event throughout spring and summer to assist in TMDL nutrients and metals load allocations.

2.2 Sampling Timeframe

For waterbodies listed for metals, the initial sampling event will occur once per site during high flow conditions (anticipated in early June). All subsequent sampling events for metals, nutrients, chlorophyll-a and periphyton will occur during the "growing season" for the Middle Rockies and Idaho Batholith Level III Ecoregions (July 1 – September 30, 2010) (Suplee and Sada, 2010).

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 *et al*. (2008) unless a specific location is to be sampled because a pollutant source was identified. These sites are proposed locations. 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 (MDEQ 2010).

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. Trip blanks will be made during each sampling run ("trip").

3.3.1 Chemistry Samples

Dissolved Metals: A 60 cm^3 syringe and a 0.45 um filter disposable filter are used. 100 ml of the filtrate will be placed in a 250 ml HDPE bottle 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 MDEQ (2010).

Nutrients, TSS and Metals: Summary information is shown in Table 3.1. TP and NO_{2+3} will be collected in a 250 ml HDPE bottle. 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 TR 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 HPDE bottle, no preservative, and held on ice. NOTE THE SHORT HOLDING TIME FOR TSS. Detailed methodology can be found in MDEQ (2010). Total recoverable mercury using the ultra-low level method follows a different procedure. A detailed explanation can be found in the MDEQ Ultra-low level mercury Standards Operating Procedure (2010).

3.4 Periphyton Samples

Periphyton samples will be collected only at some sites (Appendix A). The sample will be placed in a 50 ml centrifuge tube and preserved with formalin (see Table 3.1). Detailed methodology can be found in MDEQ (2010).

3.5 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 (MT DEQ 2010) (see Table 3.1). Ash-free dry weight (AFDW) will be calculated from the same samples of chlorophyll *a* (MDEQ 2010).

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)	30 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	500 ml	HDPE bottle	Nitric acid	Cool to <6 °C (on ice)	180 days
Dissolved Metals	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-a	N/A	Ziplock bag (hoop), Petri dish (template), or centrifuge tube (core)	None	Dry ice	45 days
Periphyton (species presence)	50 ml	Centrifuge Tube	Formalin	No ice	NA

3.6 Digital Photographs

Digital photographs will be taken at transect F of each site (metal sites). On the nutrient sites, 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.

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 periphyton samples will be sent to the Academy of Sciences.

5.0 Laboratory Analytical Measurements

TABLE 5.1 Analytical Methods and Required Reporting Values.		
Water Sample – Nutrients		
Analyte	**Method**	**Req. Report Limit (ug/L)**
Total Persulfate Nitrogen (TPN)	A 4500-N-C	50
Total Phosphorus as P	EPA 365.1	5
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
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
Silver	EPA 200.8	0.5
Zinc	EPA 200.7	10
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	1
Cadmium	EPA 200.8	0.2
Chromium	EPA 200.8	9
Copper	EPA 200.8	15
Iron	EPA 200.7	10
Lead	EPA 200.8	5
Mercury	EPA 7471B	0.05
Zinc	EPA 200.7	20
Mercury	EPA 7471B	0.05
Total Recoverable Metals Digestion	EPA 200.2	N/A
Others		
Parameter	**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 (2005b).

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 seven streams within the Rock TPA at 25 proposed sites (Appendix A). The high flow sampling events will occur most likely in June 2010 whereas the low flow sampling event will begin in July 2010. Data collection should be completed no later than September 30, 2010 (Suplee, 2008).

9.0 Project Team and Responsibilities

The Water Quality Monitoring and Assessment Section will lead the monitoring component. Rosie Sada will oversee the overall Monitoring and Assessment component. Jonathan Drygas will lead the monitoring project. Al Nixon, Steven Reistroffer, Steve Fernandes and/or Katie Makarowski will assist with the field data collection. Lisa Kusnierz (Watershed Management Section) will lead the TMDL component.

10.0 References

MT DEQ (Montana Department of Environmental Quality), 2010. Water Quality Planning Bureau Field Procedures Manual for Water Quality Assessment Monitoring. In progress.

MT DEQ (Montana Department of Environmental Quality), 2010. Ultra-low level mercury Standard Operating Procedure. Draft. Montana Department of Environmental Quality, Water Quality Planning Bureau.

MT DEQ (Montana Department of Environmental Quality), 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.

Suplee, M., and R. Sada de Suplee. 2010. Guidance Document: Assessment Methodology for Determining Wadeable Stream Impairment due to Excess Nutrients (Nitrogen and Phosphorus). Draft. Montana Department of Environmental Quality, Water Quality Planning Bureau.

Appendix A

Rock TPA proposed 2010 Sampling Site locations

and

proposed number of samples to be collected per parameter per site

Site No.	Water Body Name	LAT (DD)	LONG (DD)	Metals (TR and Dissolv.)*	Low Level Hg	Metals (Sediment)	TSS#	Nutrients	Chlorophyll *a* / AFDW	Periphyton
EFROCRK01	East Fork Rock Creek	46.1311	-113.3821	-	-	-	3	3	1	1
EFROCRK02	East Fork Rock Creek	46.1559	-113.4368	-	-	-	3	3	1	1
EFROCRK03	East Fork Rock Creek	46.1832	-113.4661	-	-	-	3	3	1	1
EFROCRK04	East Fork Rock Creek	46.1508	-113.4092	-	-	-	3	3	1	1
New Site, Lower Segment	East Fork Rock Creek	46.1706	-113.4530	-	-	-	3	3	1	1
New Site, Upper Segment	East Fork Rock Creek	46.1505	-113.4095	-	-	-	3	3	1	1
New 2010, Mid Site	West Fork Rock Creek	46.2411	-113.6502	2	2	1	2	-	-	-
New 2010, Upper Site	West Fork Rock Creek	46.1563	-113.7669	2	2	1	2	-	-	-
WFKRCRK01	West Fork Rock Creek	46.1957	-113.7437	2	2	1	2	-	-	-
WFKRCRK02	West Fork Rock Creek	46.2028	-113.7037	2	2	1	2	-	-	-
WFKRCRK03	West Fork Rock Creek	46.2437	-113.5907	2	2	1	2	-	-	-
WFKRCRK04	West Fork Rock Creek	46.2239	-113.5242	2	2	1	2	-	-	-
BREWCRK01	Brewster Creek	46.6210	-113.5802	-	-	-	3	3	1	1
BREWCRK02	Brewster Creek	46.6198	-113.6004	-	-	-	3	3	1	1
BREWCRK03	Brewster Creek	46.6149	-113.6205	-	-	-	3	3	1	1
BREWCRK04	Brewster Creek	46.6111	-113.6475	-	-	-	3	3	1	1
SFANCRK01	South Fork Antelope Creek	46.2334	-113.4476	-	-	-	3	3	1	1
SFANCRK02	South Fork Antelope Creek	46.2479	-113.4574	-	-	-	3	3	1	1
SFANCRK03	South Fork Antelope Creek	46.2620	-113.4619	-	-	-	3	3	1	1
QUARTGUL01	Quartz Gulch	46.3162	-113.6098	4	4	1	4	-	-	-
BASINGUL01	Basin Gulch	46.3188	-113.5839	4	4	1	4	-	-	-
SLUIGUL01	Sluice Gulch	46.3045	-113.4450	2	-	1	4	3	1	1
SLUIGUL02	Sluice Gulch	46.3040	-113.4802	2	-	1	4	3	1	1
SLUIGUL03	Sluice Gulch	46.3025	-113.4957	2	-	1	4	3	1	1
SLUIGUL04	Sluice Gulch	46.3051	-113.5087	2	-	1	4	3	1	1

* Total Recoverable Metals (TR), Dissolved Metals (Dissolv.)

Total Suspended Solids (TSS)