

LITTLE BLACKFOOT TMDL PLANNING AREA CHEMISTRY AND CHLOROPHYLL MONITORING

2009 Data Submittal and Quality Review Report
March 5, 2010

State of Montana Term Contract SPB05-894P-II, Contract 208052, T.O. -03

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1.0 INTRODUCTION

The enclosed submittal is the culmination of two chemistry (nutrients and metals) and chlorophyll monitoring events conducted by HydroSolutions Inc (HydroSolutions) of the Little Blackfoot Watershed Total Maximum Daily Load Planning Area (TPA) Phase II for the Montana Department of Environmental Quality (DEQ). The project was managed by Lisa Kusnierz of the DEQ Water Quality Planning Bureau. Work was completed under State of Montana Term Contract # SPB05-894P-II, DEQ contract number 208052, Task Order 03. HydroSolutions' project manager is Luke Osborne.

Tasks in the Scope of Work include: 1) Spring 2009 high flow metals monitoring and 2) Summer 2009 metals and nutrient monitoring. Work for these two tasks was completed by HydroSolutions staff. The sampling timeframe and the analytical suites collected for this project are summarized in Table 1. Energy Laboratories, in Helena, Montana provided laboratory analysis for the project.

TABLE 1 SUMMARY OF 2009 CHEMISTRY AND CHLOROPHYLL MONITORING IN THE LITTLE BLACKFOOT TPA

Monitoring Event	Nutrients	Chlorophyll-a	Metals	Sediment Metals
Spring 2009 (May 19-22)			X	
Summer 2009 (August 25- September 2)	X	X	X	X

The Sampling and Analysis Plan (SAP), final revision 1, t was completed by the DEQ Water Quality Planning Bureau and is dated May 19, 2009. The SAP is on file with the DEQ Water Quality Planning Bureau.

The purpose of this submittal is to fulfill the data review and reporting requirements for tasks one and two of this project. This submittal 1) transmits data collected and analyzed during the two monitoring events, 2) documents deviations to the SAP, and 3) provides results from the quality check completed on the laboratory data. Site visit forms, the results from the laboratory analysis and other supporting documents for this project are attached to this report. This submittal is being transmitted in paper (one copy) and digitally by compact disc. Included as separate files in the digital submittal are:

- MT-eWQX EDD file and user certificate (.zip)
- Laboratory electronic analytical data spreadsheets (Microsoft Excel)
- QA/QC calculation spreadsheet (Microsoft Excel)
- All Photo files: sample sites plus chlorophyll-a documentation (.JPG)
- Discharge and Cross-Section Calculations (Microsoft Excel)
- Shape file of sampling locations (.SHP)

2.0 DEVIATIONS TO THE SAMPLING AND ANALYSIS PLAN

Water quality sampling was conducted following the approved SAP dated May 19, 2009. Modifications or changes to the methods or processes defined in these plans are documented below.

Sampling Site Modifications:

The 2009 SAP identified 44 separate sampling site locations distributed throughout the Little Blackfoot River and its tributaries. Of these sample sites, metal samples were collected at 30 of the 44 sites and nutrient samples were collected at 23 of the 44 sites (during the Summer 2009 event only). Many of the sites were also sampled during phase I of this project in 2008, completed by HydroSolutions ((HydroSolutions, Inc 2009)). The 2009 SAP identified 11 additional sites and removed four other sites that were sampled in 2008. Sites were located at coordinates near those listed in the SAP, but may have been moved to a better nearby location to facilitate better access. Site locations that were moved significantly (more than about one quarter mile) are listed in Table 2. Actual sample site location coordinates were recorded using a hand-held global positioning system (GPS) unit during the initial monitoring event and are documented on the DEQ site visit forms and listed in the MT-eWQX database. Attachment A of this report summarizes all the sampling site locations as well as documents the data collected at each of the sampling sites. The sample site location map is also included in Attachment A and shows the spatial distribution of sample site locations in the watershed.

TABLE 2 SUMMARY OF SAMPLE SITE LOCATION MODIFICATIONS

Sample Site	Rationale for sample site deviation	Sampling Event	Sample site modification
TGH-2A	Inaccessible due to Snow	Spring 2009	Sampled new site TGH-2B above confluence with O’Keefe/Bryan Creek during Spring and Summer 2009 events
MCH-1	Inaccessible due to Snow	Spring 2009	Sampled new site MCH-3 Above confluence with Ontario Creek
MCH2-C01MONRC10	Inaccessible due to Snow	Spring 2009	Sampled new site MCH-3 Above confluence with Ontario Creek
ONT-0	Inaccessible due to Snow	Spring 2009	Did not sample in Spring, sampled in Summer 2009
ONT-1A	Inaccessible due to Snow	Spring 2009	Did not sample in Spring, sampled in Summer 2009
ONT-1	Inaccessible due to Snow	Spring 2009	Did not sample in Spring, sampled in Summer 2009

Sample site TGH-2A was not accessible during the Spring 2009 event. As a result a new site TGH-2B was selected in the field to replace TGH-2A. Site TGH-2B is located upstream of the confluence of O’Keefe and Bryan Creek and was also sampled during the Summer 2009 event.

Sample sites MCH-1 and MCH-2 were not accessible during the Spring 2009 event. As a result a new site MCH-3 was selected in the field to replace both MCH-1 and MCH-2. Site MCH-3 is located on Monarch Creek upstream of the confluence with Ontario Creek. Sites MCH-1 and MCH-2 were sampled during the Summer 2009 event, MCH-3 was not.

Sample sites ONT-0, ONT-1, and ONT-1A were not accessible during the Spring 2009 event. After conferring with the DEQ project manager no suitable replacements sites were able to be located. All three of these sites were sampled during the Summer 2009 event.

Data Collection & Sampling Method Modifications:

Stream Flow Measurement

Stream flow was measured or estimated at all sites during this project as prescribed in the SAP. In addition to using prescribed methods stream flow at site LBF10 was recorded using the United States Geological Survey (USGS) gauging station 12324590 (Little Blackfoot River near Garrison Montana), which is collocated at the site.

Chlorophyll-a Collection

Due to bank vegetation and difficulties laying measuring tape during the chlorophyll-a sampling event, transect spacing was delineated by pacing distances instead of stringing a tape measure.

Quality Control Samples

Field duplicates, field blanks, and filter blanks (quality control samples) were taken at a frequency specified in the SAP (10%) unless otherwise noted. As approved by the DEQ project manager the actual frequency of quality control samples collected may be reduced (10% of the total number of samples rounded to the nearest factor of 10). For instance there were 23 nutrient sites in the Summer 2009 event and only 2 quality control samples were collected.

Tables 5 and 6 in subsections D and E of section 4.0 (data quality assurance quality control summary), summarize the number and frequency of quality control samples taken for this project. Deviations from the quality control sample collection frequency specified in the SAP are described below:

- During the Spring 2009 event a field duplicate sample for dissolved iron, total recoverable mercury and total recoverable selenium was not collected or analyzed.
- During the Summer 2009 event a field duplicate sample for total recoverable beryllium, total recoverable and dissolved iron, total recoverable selenium, and total mercury (ultra low level) was not collected or analyzed.
- During the Summer 2009 event quality control samples were collected for the metals suite (specified in the SAP), and total suspended solids, but at a frequency less than specified in the SAP.

Data Analysis Modifications:

Ultra low level mercury analysis was not part of the original SAP, but was later included for Summer 2009 sampling only. As directed by the DEQ project manager, ultra low level mercury samples were collected and analyzed at mercury sites indicated in the SAP.

During the Summer 2009 event analysis of dissolved iron and total recoverable iron, beryllium, and selenium was added at sample site LBF-7. These analyses were not part of the SAP, and are included in the database and laboratory results. These results do

not contribute to measure the level of project completeness shown in Table 14 in section 4.0.

3.0 DATA AND SAMPLING SITE SUMMARY

A summary table describing each of the sample sites and data collected for each monitoring event is provided in Attachment A. The table lists each of the sample sites and their latitude and longitude coordinates and the day they were visited for each monitoring event. The table describes the analytical suite or parameter that was collected at each of the sites. Comments are listed for each visit describing quality control samples collected, flow measurement collection methods if other than flow meter, significant location changes, and any unusual site conditions.

During the Summer 2009 event, chlorophyll-a concentrations were visually evaluated at each of the nutrient sites shown in Attachment A. As described in the SAP, chlorophyll-a samples were only taken at sample sites where it was determined to have 'considerable' (>50 milligrams per square meter, mg/m²) algal growth. These sites are denoted with "chloro" in Attachment A. Other sites were estimated by visual assessment of the reach in comparison to algal density photographs provided by DEQ in the SAP. Sites determined to have considerable algal growth, where samples were collected and analyzed for chlorophyll-a and ash free dry weight (AFDW) include the following four sites: LBF-8, SIX-2, SPD-3, and THR-2.

Stream flow measurements were collected at all sample sites with a flow meter where the stream was accessible with chest waders and conditions were safe to wade as provided in the SAP. At sample sites where flow exceeded safe wading conditions, the float method (as described in the DEQ field procedures manual and in the SAP) was used to estimate flow. At sample sites where the float method was used, the water level was marked with a wooden stake and paint for cross-section measurement at the next sampling event. Measured and estimated flow rates are documented in the MT-eWQX database. Flow calculations are provided in the digital submittal of this report. During the spring 2009 event flow was estimated using the float method at the following sites: LBF4, LBF5, LBF7, LBF9, and LBF10.

4.0 DATA QUALITY ASSURANCE QUALITY CONTROL SUMMARY

Water quality sample results for this project have been reviewed for data quality following the DEQ quality control checklist. A copy of the checklist is provided in Attachment B. The following section details the data quality review.

A: Conditions of samples upon receipt

Samples were delivered to Energy Laboratories in Helena, Montana, following sample collection during each monitoring event. During the Spring 2009 event one sample delivery was made (batch H09050310). During the Summer 2009 event two sample deliveries were made (batches H09090064 and H09080356). Table 3 summarizes the conditions of the samples upon receipt to the lab for each monitoring event.

TABLE 2 RECORD OF SAMPLE RECEIPT

Sample Receipt Checklist	Spring 2009	Summer 2009	
Energy Laboratories Batch Number	H09050310	H09090064	H09080356
Samples in proper containers/bottles?	Y	Y	Y
Sample Containers Intact?	Y	Y	Y
Container temperature	4.0°C	1.0°C	5.1°C
Metals Bottles pH<2	Y	Y	Y
Nutrient bottles pH<2	NA	Y	Y

Notes:

NA Not analyzed

B: All field documentation complete

A Montana DEQ site visit form was completed for each monitoring station visited. Each site visit form along with all other appropriate field documentation for the monitoring event was completed in the field and subsequently reviewed for completeness.

C: Holding times

A review of the laboratory results indicate that sample holding times were met, except for the samples summarized in Table 4. The results for samples exceeding analytical holding times have been qualified with an “H” value in the analytical reports and the database. Based on discussions with Energy Laboratories assistant manager, Jon Hager, the samples exceeded holding times due to re-analysis. The samples were originally run within the Environmental Protection Agency (EPA) holding time, but did not pass laboratory quality control review so they were re-analyzed. Re-analysis of these samples occurred after the sample holding time. The re-analyzed sample results passed quality control and have been incorporated into the final laboratory report.

TABLE 4 SUMMARY OF SAMPLE HOLDING TIME EXCEEDENCES

Site Name	Lab ID	Analyses	Collection Date	Analysis Date	Qualifier
DOG-8	H09080356-038	Nutrient Nitrogen (Total)	8/26/2009	10/15/2009	H
DOG-8FB	H09080356-030	Nitrate+Nitrite, N	8/26/2009	10/19/2009	H
DOG-8FB	H09080356-030	Nutrient Nitrogen (Total)	8/26/2009	10/15/2009	H
DOG-8DUP	H09080356-013	Nutrient Nitrogen (Total)	8/26/2009	10/15/2009	H

Note: All results of the above samples were non-detect

D: Field duplicates collected at the proper frequency as specified in the SAP

Field duplicates were collected at the frequency listed in Table 5. As discussed above in section 2.0 and shown in Table 5 field duplicates for some analytes were collected at a frequency less than that specified in the SAP.

TABLE 5 NUMBER & FREQUENCY OF FIELD DUPLICATES COLLECTED

	Spring 2009			Summer 2009		
	Dup	Total	%	Dup	Total	%
Metals Suite ¹	3	26	12%	2	30	7%
Beryllium	1	6	17%	0	6	0%
Iron (TR)	1	7	14%	0	11	0%
Iron (Dis)	0	2	0%	0	2	0%
Selenium	0	1	0%	0	2	0%
Mercury	0	3	0%	NA	NA	NA
Mercury, ultra low	NA	NA	NA	0	5	0%
Cyanide	1	2	50%	1	2	50%
Total Suspended Solids	3	26	12%	2	44	5%
Nutrients Suite ²	NA	NA	NA	2	23	9%

1 Metals suite includes: Aluminum (dissolved), Arsenic, Cadmium, Lead, Zinc,

2 Nutrients suite includes: Total Phosphorus, Nutrient Nitrogen (total), Nitrate plus Nitrite

Dup = Field Duplicate; TR = Total Recoverable; Dis = Dissolved; NA = Not Analyzed;

Total is the total number of samples collected

E: Field blanks collected at the proper frequency as specified in the SAP

Field blanks were collected at the frequency listed in Table 6. As discussed above in section 2.0 and shown in Table 6 field blanks for some analytes were collected at a frequency less than that specified in the SAP.

TABLE 6 NUMBER & FREQUENCY OF FIELD BLANKS COLLECTED

	Spring 2009			Summer 2009		
	FB	Total	%	FB	Total	%
Metals Suite ¹	3	26	12%	2	30	7%
Beryllium	1	6	17%	2	6	33%
Iron (TR)	1	7	14%	2	11	18%
Iron (Dis)	3	2	150%	2	2	100%
Selenium	3	1	300%	2	2	100%
Mercury	3	3	100%	NA	NA	NA
Mercury, ultra low ²	NA	NA	NA	2	5	40%
Cyanide	1	2	50%	1	2	50%
Total Suspended Solids	3	26	12%	2	44	5%
Nutrients Suite ³	NA	NA	NA	2	23	9%

1 Metals suite includes: Aluminum (dissolved), Arsenic (TR), Cadmium (TR), Lead (TR), Zinc (TR)

2 One method blank and one trip blank were analyzed during the Summer 2009 event, a field blank was not collected

3 Nutrients suite includes: Total Phosphorus, Nutrient Nitrogen (total), Nitrate plus Nitrite

FB = Field Blank; TR = Total Recoverable; Dis = Dissolved; NA = Not Analyzed;

Total is the total number of samples collected

F: Sample IDs match those provided in the SAP. Field Duplicates are clearly marked on all samples and noted as such in lab results.

All sample IDs match those provided in the SAP. Field duplicates are clearly marked on sample and noted as such in lab results. The duplicate sample IDs were labeled with "site name-Dup" on the field sheet, on the sample bottle, and in the lab report.

G: Analyses carried out as described within the SAP

Analytical methods were completed by the laboratory as described in the SAP or approved by the DEQ project manager. Table 7 lists the analytical methods described in the SAP and the laboratory methods used in this project. Project deviations to the SAP are presented in section 2.0 of this report.

TABLE 7 ANALYTICAL METHODS AND REPORTING LIMITS

Parameter	SAP		Laboratory	
	Analytical Method	Project Required Reporting Limit (mg/l)	Laboratory Method	Reporting limit (mg/l)
Total Suspended Solids	EPA 160.0	4	A2540D	4
Total Hardness as CaCO ₃	Calculation	1	A2340 B	1
Nutrient Nitrogen (Total)	SM45010-N-C	0.5	A4500 N-C	0.05
Total Phosphorus as P	EPA 365.1	0.005	E365.1	0.005
Nitrate+Nitrite as N	EPA 350.1	0.01	E353.2	0.01
Cyanide	EPA 335.4 R1	0.005	KELDA-01MT	0.005
Aluminum (Dis)	EPA 200.7	0.03	E200.7	0.03
Iron (Dis)	EPA 200.7	0.05	E200.7	0.03
Arsenic (TR)	EPA 200.8	0.003	E200.8	0.003
Cadmium (TR)	EPA 200.8	0.00008	E200.8	0.00008
Copper (TR)	EPA 200.8	0.001	E200.8	0.001
Iron (TR)	EPA 200.7	0.05	E200.7	0.03
Lead (TR)	EPA 200.8	0.0005	E200.8	0.0005
Selenium (TR)	EPA 200.8	0.001	E200.8	0.001
Zinc (TR)	EPA 200.7	0.01	E200.7	0.01
Beryllium (TR)	EPA 200.7	0.01	EPA200.8	0.001
Mercury (TR)	EPA 245.1	0.00005	E245.7	0.000005 ¹
Mercury, ultra low (total)	EPA 245.1	0.000005	E245.7	0.000005
Chlorophyll-a	SM 10200 H	*	EPA 447.0	0.04 (mg/m ²)
Ash Free Dry Weight	SM10300C-5	*	SM10300C-5	0.1 g/m ²
Arsenic (sediment)	EPA 200.8	1 (mg/kg)	EPA 200.8	1 (mg/kg)
Cadmium (sediment)	EPA 200.8	0.2 (mg/kg)	EPA200.8	0.2 (mg/kg)
Copper (sediment)	EPA 200.8	15 (mg/kg)	EPA 200.8	5 (mg/kg)
Lead (sediment)	EPA 200.8	5 (mg/kg)	EPA 200.8	5 (mg/kg)
Zinc (sediment)	EPA 200.7	20 (mg/kg)	EPA 200.8	5 (mg/kg)
Mercury (sediment)	EPA 7471B	0.05 (mg/kg)	SW7471A	0.05 (mg/kg)

Notes: * Not Specified in SAP; Dis = Dissolved, TR = Total Recoverable; mg/l = milligrams per liter; mg/kg = milligrams per kilogram; mg/m² = milligrams per square meter; g = grams
 1 Field Blank samples DOG-8FB and LBF-10FB during the Summer 2009 event were analyzed by method E200.8 at reporting limit of 0.001 mg/l.

H: Reporting detection limit met the project-required detection limit

The project required detection limits and analytical reporting limits are summarized in Table 7. The project required detection limits were met on all analysis except field blank samples DOG-8FB and LBF-10FB. During the Summer 2009 event these were analyzed by method E200.8 at reporting limit of 0.001 mg/l.

I: All blanks were less than the project-required detection limit

Tables 8 and 9 include all field blank results from the Spring and Summer 2009 events. Blanks that were detected to have equaled to or exceeded the project required detection limits are shown in **bold** in Tables 8 and 9. The corrective action for dealing with the field blank hits is described in the SAP. It says that if the results of field blanks equal or exceed the project required reporting limit all associated project data with results less than ten times the detected field blank value will be qualified. In this case all data collected the same day as the field blank is assumed to be the associated data. The corresponding data in the MT-eWQX database has been qualified with a "B" flag.

TABLE 8 SUMMARY OF FIELD BLANK DETECTIONS SPRING 2009

Sample-ID_Date Collected	Analyte	Detected Value (mg/l)	Reporting Limit (mg/l)
Dog-5 FB_05222009	Hardness, Ca, Mg	ND	1
Dog-5 FB_05222009	Total suspended solids (Total)	ND	4
Dog-5 FB_05222009	Aluminum (Dissolved)	ND	0.03
Dog-5 FB_05222009	Arsenic (Total Recoverable)	ND	0.003
Dog-5 FB_05222009	Cadmium (Total Recoverable)	0.00089	0.00008
Dog-5 FB_05222009	Copper (Total Recoverable)	ND	0.001
Dog-5 FB_05222009	Lead (Total Recoverable)	ND	0.0005
Dog-5 FB_05222009	Zinc (Total Recoverable)	ND	0.01
Dog-5 FB_05222009	Iron (Dissolved)	ND	0.03
Dog-5 FB_05222009	Mercury (Total Recoverable)	ND	0.00005
Dog-5 FB_05222009	Selenium (Total Recoverable)	ND	0.001
ONT-2 FB_05212009	Total suspended solids (Total)	ND	4
ONT-2 FB_05212009	Aluminum (Dissolved)	ND	0.03
ONT-2 FB_05212009	Arsenic (Total Recoverable)	ND	0.003
ONT-2 FB_05212009	Cadmium (Total Recoverable)	0.00101	0.00008
ONT-2 FB_05212009	Copper (Total Recoverable)	ND	0.001
ONT-2 FB_05212009	Lead (Total Recoverable)	ND	0.0005
ONT-2 FB_05212009	Zinc (Total Recoverable)	ND	0.01
ONT-2 FB_05212009	Hardness, Ca, Mg	ND	1
ONT-2 FB_05212009	Iron (Dissolved)	ND	0.03
ONT-2 FB_05212009	Mercury (Total Recoverable)	ND	0.00005
ONT-2 FB_05212009	Selenium (Total Recoverable)	0.001	0.001
TGH-2 FB-05202009	Total suspended solids (Total)	ND	4
TGH-2 FB-05202009	Aluminum (Dissolved)	ND	0.03
TGH-2 FB-05202009	Arsenic (Total Recoverable)	ND	0.003
TGH-2 FB-05202009	Beryllium (Total Recoverable)	ND	0.001
TGH-2 FB-05202009	Cadmium (Total Recoverable)	0.00086	0.00008
TGH-2 FB-05202009	Copper (Total Recoverable)	ND	0.001
TGH-2 FB-05202009	Iron (Total Recoverable)	ND	0.03

Sample-ID_Date Collected	Analyte	Detected Value (mg/l)	Reporting Limit (mg/l)
TGH-2 FB-05202009	Lead (Total Recoverable)	ND	0.0005
TGH-2 FB-05202009	Zinc (Total Recoverable)	ND	0.01
TGH-2 FB-05202009	Hardness, Ca, Mg	ND	1
TGH-2 FB-05202009	Iron (Dissolved)	ND	0.03
TGH-2 FB-05202009	Mercury (Total Recoverable)	ND	0.00005
TGH-2 FB-05202009	Selenium (Total Recoverable)	ND	0.001
LBF-3 FB_05212009	Cyanide, Total	ND	0.005
Notes: mg/l = milligrams per liter; ND = Non-Detect			

The cadmium field blank detections in the Spring 2009 monitoring event were reviewed and discussed with Energy Laboratories. Initially, the detection of the cadmium in the field blanks was thought to be due to possible contamination in the acid preservative, but this could not be positively identified. Energy Laboratories re-digested, re-extracted, and re-analyzed the samples as documented in the case narrative in Attachment F. Due to this uncertainty all cadmium results collected during the Spring 2009 event have been qualified with a "B" flag. Selenium was detected in ONT-2FB at the reporting limit. The associated result for MCH-3 was qualified with a "B" flag.

TABLE 9 SUMMARY OF FIELD BLANK DETECTIONS SUMMER 2009

Site ID_Date Collected	Analyte	Detected Value (mg/L)	Reporting Limit (mg/L)
DOG8FB_08262009	Aluminum (Dissolved)	ND	0.03
DOG8FB_08262009	Arsenic (Total Recoverable)	ND	0.003
DOG8FB_08262009	Cadmium (Total Recoverable)	ND	0.00008
DOG8FB_08262009	Copper (Total Recoverable)	ND	0.001
DOG8FB_08262009	Hardness, Ca, Mg	ND	1
DOG8FB_08262009	Nitrate+nitrite, N	ND	0.01
DOG8FB_08262009	Lead (Total Recoverable)	ND	0.0005
DOG8FB_08262009	Nutrient Nitrogen (Total)	ND	0.05
DOG8FB_08262009	Phosphorus (Total)	ND	0.005
DOG8FB_08262009	Total suspended solids	ND	4
DOG8FB_08262009	Zinc (Total Recoverable)	ND	0.01
DOG8FB_08262009	Iron (Dissolved)	ND	0.03
DOG8FB_08262009	Beryllium (Total Recoverable)	ND	0.001
DOG8FB_08262009	Iron (Total Recoverable)	ND	0.03
DOG8FB_08262009	Mercury (Total Recoverable)	ND	0.001
DOG8FB_08262009	Selenium (Total Recoverable)	ND	0.001
LBF10FB_09012009	Aluminum (Dissolved)	ND	0.03
LBF10FB_09012009	Arsenic (Total Recoverable)	ND	0.003
LBF10FB_09012009	Cadmium (Total Recoverable)	ND	0.00008
LBF10FB_09012009	Copper (Total Recoverable)	ND	0.001
LBF10FB_09012009	Hardness, Ca, Mg	ND	1
LBF10FB_09012009	Nitrate+nitrite, N	0.05	0.01
LBF10FB_09012009	Lead (Total Recoverable)	ND	0.0005

Site ID Date Collected	Analyte	Detected Value (mg/L)	Reporting Limit (mg/L)
LBF10FB_09012009	Nutrient Nitrogen (Total)	0.08	0.05
LBF10FB_09012009	Phosphorus (Total)	0.006	0.005
LBF10FB_09012009	Zinc (TR)	ND	0.01
LBF10FB_09012009	Iron (Dissolved)	ND	0.03
LBF10FB_09012009	Beryllium (Total Recoverable)	ND	0.001
LBF10FB_09012009	Iron (Total Recoverable)	ND	0.03
LBF10FB_09012009	Mercury (Total Recoverable)	ND	0.001
LBF10FB_09012009	Selenium (Total Recoverable)	ND	0.001
LBF4FB_09012009	Cyanide (Total)	ND	0.005
SPD4FB_09022009	Total suspended solids	ND	4
Notes: mg/l = milligrams per liter; ND = Non-Detect			

Based on the correction action criteria in the SAP, the following results were qualified for the Summer 2009 event with a “B” flag:

- Total Phosphorus: SPD-1A, SPD-2, LBF-7, LBF-8, LBF-9, LBF-10, and LBF-4.
- Nitrate plus Nitrite as N: SPD-1A, SPD-2, LBF-7, LBF-8, LBF-9, LBF-10, and LBF-4.
- Nutrient Nitrogen (total): SPD-1A, SPD-2, LBF-7, LBF-8, LBF-9, LBF-10, and LBF-4.

J: Laboratory blanks/duplicates/matrix spikes/lab control samples were analyzed at a 10% frequency.

Laboratory quality control water samples were analyzed at a frequency listed in Tables 10, 11, and 12. Laboratory quality control samples were analyzed at a frequency which is consistent with standard laboratory practices.

TABLE 10 FREQUENCY OF QUALITY CONTROL SAMPLES ANALYZED FOR WATER

	Spring 2009 H09050310	Summer 2009 H09080356	Summer 2009 H09090064
Lab Duplicates	9%	18%	10%
Matrix Spikes	79%	79%	81%
Method Blanks	47%	45%	52%
Lab Control Samples	21%	42%	43%

TABLE 11 FREQUENCY OF QUALITY CONTROL SAMPLES ANALYZED FOR SEDIMENT

	Summer 2009
Lab Duplicates	NA
Matrix Spikes	80%
Method Blanks	80%
Lab Control Samples	NA

TABLE 12 FREQUENCY OF QUALITY CONTROL SAMPLES ANALYZED FOR CHLOROPHYLL-A SUMMER 2009

Summer 2009	
Lab Duplicates	50%
Matrix Spikes	50%
Method Blanks	50%
Lab Control Samples	50%

K: Laboratory blanks/duplicates/matrix spikes/lab control samples were all within the required control limits defined in the SAP

Table 13 summarizes the laboratory quality control samples that did not meet required control limits. Based on discussion with Energy Laboratories matrix spike samples like those in Table 13 do not always meet recommended control limits as they may be biased due to sample matrix interference. Laboratory control samples (LCS), which determine method performance, are within recommended control limits. No corrective action is needed.

TABLE 13 SUMMARY OF QUALITY CONTROL SAMPLES THAT DID NOT MEET CONTROL LIMITS

Sampling Event	Sample Name	Analyte	Spike Recovery (%)	Control Limit (%)
Summer 2009	Matrix Spike of H09100030-009AMS	Nutrient Nitrogen (Total)	88%	90-110
Summer 2009	Matrix Spike of H09080356-033A	Zinc (sediment)	172%	70-130
Spring 2009	Matrix Spike of B09052547-002AMS	Copper	182%	70-130
Spring 2009	Matrix Spike of 09060093-002EMS	Cyanide	66%	90-110

L: Project Data Quality Objectives

Data Quality Objectives established in the SAP for this project include representativeness (spatial and temporal), comparability, and completeness. An assessment of DQOs is summarized below.

- Representativeness** refers to the extent to which measurements represent an environmental condition in time and space. Design of the study ensured that this objective was met. Sampling sites were chosen to represent the potential of landscape characteristics and land use/land cover influences existing in the watershed to influence the analyte concentrations in the listed waters. Sampling sites were identified by assessment of aerial and topographic maps 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. This study was designed to be conducted over two temporal periods during spring runoff and base flow conditions in 2009.
- 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** is a measure of the amount of data prescribed for assessment activities and the usable data actually collected and expressed as a percentage. The overall project goal is 90% completeness; the overall project goals were met. Table 14 summarizes the completeness for this project, comparing individual completed components to the total number prescribed in the SAP.

TABLE 14 PROJECT COMPLETENESS

Component	Spring 2009			Summer 2009			Overall %
	No.	Total	%	No.	Total	%	
Sites Visited	26	30	87%	44	44	100%	95%
Flow	26	30	87%	42	44	95%	92%
Physical Parameters	26	30	87%	44	44	100%	95%
Total Suspended Solids	26	30	87%	44	44	100%	95%
Nutrient Sites	0	0	NA	23	23	100%	100%
Metals Sites	26	30	87%	30	30	100%	93%
Beryllium	6	6	100%	6	6	100%	100%
Iron (TR)	8	12	67%	12	12	100%	83%
Iron (Dis)	2	3	67%	3	3	100%	83%
Selenium	1	2	50%	2	2	100%	75%
Mercury	3	5	60%	5	5	100%	80%
Cyanide Sites	2	2	100%	2	2	100%	100%
Sediment Metals	0	0	NA	5	5	100%	100%
Sediment (Mercury)	0	0	NA	1	1	100%	100%

Notes:

No. is the number of sites visited, flow and physical parameters measured, and samples collected for that project component

Total is the total number of prescribed samples per the SAP for that component

During the Spring 2009 event, five sites: ONT-0, ONT-1, ONT-1A, MCH-1, and MCH-2, were inaccessible due to snow and were not sampled. Site MCH-3 was selected as an alternate site and was sampled in place of MCH-1 and MCH-2. Because of site inaccessibility, completeness for this event was reduced below the project goal of 90%. Overall completeness for the Spring 2009 event is 84%, calculated by tallying the total number of sites visited, flow and physical parameters measured, and samples collected for all of the components divided by the total number prescribed for all of the components shown in Table 14.

During the Summer 2009 event the project completeness goal of 90% was met for all components. Stream flow at sites ONT-1 and ONT-1A could not be measured or estimated using the float method because the sites are in a wetlands area and flow is not channelized. Overall completeness for the Summer 2009 event is 99%, calculated by tallying the total number of sites visited, flow and physical parameters measured, and samples collected for all of the components divided by the total number prescribed for all of the components shown in Table 14.

Overall completeness for both events met the project's 90% goal for all components except for total recoverable and dissolved iron, selenium, and mercury. The reason completeness was not met for these project components was due to site inaccessibility during the Spring 2009 event. Overall completeness for the project is 93%, calculated

by tallying the total number of sites visited, flow and physical parameters measured, and samples collected for all of the components divided by the total number prescribed for all of the components shown in Table 14.

As described in section 3.0, chlorophyll-a and AFDW samples were collected at nutrient sites where algal growth was determined to be considerable during the Summer 2009 event. These four sites include: LBF-8, SIX-2, SPD-3, and THR-2. At the other 19 nutrient sites during the Summer 2009 event, algal concentrations were evaluated and recorded to be less than the threshold criteria specified in the SAP. Project completion for chlorophyll-a and AFDW sample collection was met.

Project Data Quality Indicators

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. The DQIs established in the SAP for this project include sensitivity, precision, bias, and accuracy.

- **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). 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 was the analytical result of the field blank less than that of the project reporting limit. Field blanks that fail this criteria were qualified for all associated project data if the result is less than 10 times the detected value in the field blank. Table 8 lists field blanks that exceeded project reporting limits. The associated results that are qualified with result qualifier "B" are assumed to be all of the data collected on the same day as the field blank that failed criteria above for that analyte. The appropriate associated data is qualified in the MT-EWQX database. Result qualifier "B" is defined as, "detection in the field and/or trip blank."

Section I above summarizes the corrective action taken for the field blanks that did not pass the sensitivity criteria.

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

Laboratory precision quality control for all laboratory methods follows the frequency specified in the analytical method or as described in the Laboratory's Quality Assurance Plan (LQAP). The criteria used to assess analytical method precision was:

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

Laboratory duplicates did not exceed the above criteria.

Overall precision evaluates field duplicates. The criteria used to assess overall precision was:

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

Laboratory results were reviewed and evaluated for overall precision. Field duplicate results for the Spring and Summer 2009 event are presented Tables 15 and 16 respectively. Duplicate results that equaled or exceeded RDP of 25% and have results greater than 5 times the reporting limit are in shown in **bold** in Tables 15, of which there are two, both for cadmium. No duplicate results exceeded precision criteria in Table 16.

The corrective action in assessing overall precision is to qualify all associated results of those field duplicates that fail the precision criteria with a "J" flag. The associated results are assumed to be all of the data collected on the same day as the field duplicate that failed criteria for that analyte. The appropriate associated data is qualified in the MT-eWQX database. Result qualifier "J" is defined as estimated: the analyte was positively identified and the associated numerical value is the approximate concentration of the analyte in the sample.

TABLE 15 SUMMARY OF FIELD DUPLICATE SAMPLE RESULTS SPRING 2009

Site ID _Date Collected	Analyte	Reported Result mg/L	Duplicate Result mg/L	RPD (%)	5xRL*
TGH2FD_05202009	Total suspended solids	<4	5	22	
TGH2FD_05202009	Aluminum (Dissolved)	0.07	0.09	25	
TGH2FD_05202009	Arsenic (Total Recoverable)	0.003	0.003	0	
TGH2FD_05202009	Beryllium (Total Recoverable)	ND	ND	0	
TGH2FD_05202009	Cadmium (Total Recoverable)	0.00293	0.00163	57	0.0004
TGH2FD_05202009	Calcium (Total Recoverable)	3	3	0	
TGH2FD_05202009	Copper (Total Recoverable)	0.005	0.005	0	
TGH2FD_05202009	Hardness, Ca, Mg	10	10	0	
TGH2FD_05202009	Iron (Total Recoverable)	0.42	0.42	0	
TGH2FD_05202009	Lead (Total Recoverable)	0.0017	0.0016	6	
TGH2FD_05202009	Magnesium (Total Recoverable)	ND	ND	0	
TGH2FD_05202009	Zinc	0.07	0.07	0	
ONT2FD_05212009	Hardness, Ca, Mg	9	9	0	
ONT2FD_05212009	Total suspended solids	10	11	10	
ONT2FD_05212009	Aluminum (Dissolved)	0.13	0.14	7	
ONT2FD_05212009	Arsenic (Total Recoverable)	0.010	0.010	0	
ONT2FD_05212009	Cadmium (Total Recoverable)	0.00123	0.00110	11	
ONT2FD_05212009	Calcium (Total Recoverable)	3	3	0	
ONT2FD_05212009	Copper (Total Recoverable)	0.004	0.004	0	
ONT2FD_05212009	Lead (Total Recoverable)	0.0049	0.0046	6	
ONT2FD_05212009	Magnesium (Total Recoverable)	ND	ND	0	

Site ID _Date Collected	Analyte	Reported Result mg/L	Duplicate Result mg/L	RPD (%)	5xRL*
ONT2FD_05212009	Zinc (Total Recoverable)	0.02	0.02	0	
DOG5FD_05282009	Total suspended solids	6	5	18	
DOG5FD_05282009	Aluminum (Dissolved)	0.11	0.09	20	
DOG5FD_05282009	Arsenic (Total Recoverable)	ND	ND	0	
DOG5FD_05282009	Cadmium (Total Recoverable)	0.00102	0.00276	92	0.0004
DOG5FD_05282009	Calcium (Total Recoverable)	28	27	4	
DOG5FD_05282009	Copper (Total Recoverable)	0.002	0.002	0	
DOG5FD_05282009	Lead (Total Recoverable)	0.0005	0.0005	0	
DOG5FD_05282009	Magnesium (Total Recoverable)	6	6	0	
DOG5FD_05282009	Zinc (Total Recoverable)	ND	ND	0	
DOG5FD_05282009	Hardness, Ca, Mg	94	91	3	
LBF3FD_05202009	Cyanide	0.023	<.005	129	0.025

Note:

* The value for 5x the reporting limit is listed only for relative percent differences greater than 25%.
 ND Not detected; RPD Relative percent difference
 RL Reporting limit
 Mg/L Milligram per liter

The following cadmium results from the Spring 2009 event have been qualified with a "J" flag: TGH-0, TGH-1 TGH-2, LBF-4, LBF-10, LBF-9, LBF-7, LBF-4, and DOG-5.

TABLE 16 SUMMARY OF FIELD DUPLICATE SAMPLE RESULTS SUMMER 2009

Site ID _Date Collected	Analyte	Reported Result mg/L	Duplicate Result mg/L	RDP %	5xRL*
Dog-8FD_08262009	Hardness, Ca, Mg	134	136	1	
Dog-8FD_08262009	Nutrient Nitrogen (Total)	<0.05	<0.05	0	
Dog-8FD_08262009	Total suspended solids (Total)	6	6	0	
Dog-8FD_08262009	Aluminum (Dissolved)	<0.03	<0.03	0	
Dog-8FD_08262009	Arsenic (Total Recoverable)	0.008	0.007	13	
Dog-8FD_08262009	Cadmium (Total Recoverable)	<0.00008	<0.00008	0	
Dog-8FD_08262009	Calcium (Total Recoverable)	39	40	3	
Dog-8FD_08262009	Copper (Total Recoverable)	0.003	0.003	0	
Dog-8FD_08262009	Lead (Total Recoverable)	0.0017	0.0018	6	
Dog-8FD_08262009	Magnesium (Total Recoverable)	9	9	0	
Dog-8FD_08262009	Zinc (Total Recoverable)	<0.01	<0.01	0	
Dog-8FD_08262009	Nitrate+nitrite, N	<0.01	<0.01	0	
Dog-8FD_08262009	Phosphorus (Total)	0.023	0.02	14	
LBF-10FD_09012009	Nutrient Nitrogen (Total)	0.15	0.17	13	
LBF-10FD_09012009	Aluminum (Dissolved)	<0.03	<0.03	0	
LBF-10FD_09012009	Arsenic (Total Recoverable)	0.005	0.006	18	
LBF-10FD_09012009	Cadmium (Total Recoverable)	<0.00008	<0.00008	0	
LBF-10FD_09012009	Calcium (Total Recoverable)	40	42	5	
LBF-10FD_09012009	Copper (Total Recoverable)	0.001	0.001	0	
LBF-10FD_09012009	Lead (Total Recoverable)	<0.0005	<0.0005	0	

Site ID _Date Collected	Analyte	Reported Result mg/L	Duplicate Result mg/L	RDP %	5xRL*
LBF-10FD_09012009	Magnesium (Total Recoverable)	9	9	0	
LBF-10FD_09012009	Zinc (Total Recoverable)	<0.01	<0.01	0	
LBF-10FD_09012009	Nitrate+nitrite, N	<0.01	<0.01	0	
LBF-10FD_09012009	Phosphorus (Total)	0.031	0.036	15	
LBF-10FD_09012009	Hardness, Ca, Mg	138	142	3	
SPD-4FD_09022009	Total suspended solids (Total)	<4	<4	0	
LBF-3FD_09012009	Cyanide (Total)	<0.005	<0.005	0	

Note:

- * The value for 5x the reporting limit is listed only for relative percent differences greater than 25%.
- ND Not detected
- RL Reporting limit
- Mg/L Milligram per liter
- RPD Relative percent difference

- **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 was assessed by reviewing the Laboratory Control Samples (LCS) and Matrix Spike results. The criteria used for this assessment were the limits that the laboratory has developed through control charting of each method's performance.

M: Summary of results of QC analysis, issues encountered, and how issues were addressed

The following summarizes results of the data quality control analysis, the issues that were encountered and how they were addressed.

- The analytical holding time was exceeded for the analysis of four samples due to laboratory re-analysis. These results were non-detect and have been qualified with an "H" flag. See part C above.
- Field duplicate samples were not collected at the frequency specified in the SAP for some metals analytes. See part D above.
- Field blank results detected concentrations of cadmium above the reporting limit in the Spring 2009 event. The laboratory re-digested, re-extracted, and re-analyzed the samples to verify the results. All cadmium results for the Spring event have been qualified with a "B" flag. See part I above.
- Field blank results detected concentrations of nitrate plus nitrite as N, nutrient nitrogen (total), and total phosphorus at or above the reporting limit in the Summer 2009 event. Associated results have been qualified with a "B" flag. See part I above.
- Overall project completeness was calculated to be 93% meeting the project goal. Some individual components were calculated to be less than the project 90% completeness goal. See part L above.
- Overall precision was evaluated in reviewing precision criteria for field duplicates. Two field duplicate results exceeded precision criteria and associated data have been qualified in the database. See part L above.
- A field audit was conducted by the DEQ project manager and DEQ Quality Assurance Officer, Chris Shirley, on September 1, 2009. The issues that were discussed and resolved during and following the audit include: maintaining fresh

- ice in coolers or using dry ice for chlorophyll-a samples, collecting grab samples in the stream prior to creating any disturbances in the stream, and transmitting a copy of the field meter calibration log.
- DEQ draft standard operating procedures for the collection of ultra low level mercury were received on August 24, 2009 from DEQ Environmental Scientist Specialist Patrick Lizon. The document was incorporated into this project for the collection of mercury samples during the Summer 2009 event. The DEQ project manager and Patrick Lizon, under the direction from DEQ Monitoring and Assessment Supervisor, Rosie Sada, presented and reviewed these procedures with HydroSolutions project manager in a short training session on August 12, 2009.

N: Completed QC checklist before MT-eWQX upload

The quality control checklist was completed and data was reviewed prior to upload to the MT-eWQX database.

5.0 REFERENCES

HydroSolutions, Inc. "Little Blackfoot TMDL Planning Area Chemistry and Chlorophyll Monitoring, Data Submittal Quality Review Report Revision 1." Helena, Montana, 2009.