#### Final

# Sampling and Analysis Plan/Quality Assurance Project Plan 2010 Sampling Events Standard Mine Site Gunnison County, Colorado

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# Signature Page Sampling and Analysis Plan/Quality Assurance Project Plan Standard Mine

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## Distribution List Sampling and Analysis Plan/Quality Assurance Project Plan Standard Mine

The following is a distribution list of personnel who will receive a copy of the Sampling and Analysis Plan/Quality Assurance Project Plan for the sampling events scheduled in 2010 at the Standard Mine. Agency and/or contractor affiliations are also listed for each individual.

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#### **Acronym List**

BERA Baseline Ecological Risk Assessment Celcius C Cd Cadmium **CETIS** Comprehensive Environmental Toxicity Information System Chemicals of Potential Concern COPC **Data Quality Objectives** DQO Environmental Services Assistance Team **ESAT** GPS Global Positioning System HHRA Human Health Risk Assessment **Hazard Quotient** HQ MHRW Moderately Hard Reconstituted Water **Principal Study Questions** PSQ Quality Assurance QA Quality Assurance Project Plan **QAPP Quality Control** QC RI/FS Remedial Investigation Feasibility Study SAP Sampling Analysis Plan SI Site Inspection SOP **Standard Operating Procedure** United States Environmental Protection Agency **USEPA** United States Forest Service USFS **USGS** United States Geological Survey Zn Zinc

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#### 1.0 Introduction

This document serves as the Sampling and Analysis Plan (SAP)/Quality Assurance Project Plan (QAPP) for the sampling events to be conducted in 2010 at the Standard Mine, located near the town of Crested Butte, Colorado. Sampling is being performed to support remedy implementation and establish baseline standards with water quality for seasonal variations. Activities proposed in this SAP/QAPP include the collection of surface water, sediment, and macro invertebrate (assemblage assessment) samples, as well as surface water toxicity testing. Data obtained from these investigations will be used in accordance with the provisions outlined in the Data Quality Objectives (DQOs).

## 2.0 Problem Definition and Background

The Standard Mine was a part of the Ruby Mining District located in Gunnison County, Colorado. Mining activity initially began at the Standard Mine around 1874, with the most significant operations beginning in 1931. Operations included the mining of lead, zinc, silver, and gold until 1966 when the mine was abandoned.

The mine consists of many open, unmarked adits and shafts giving access to 8,400 feet of mine workings on 6 levels. The site also has a dilapidated mill and railroad tracks running 50 feet above the ground with rotting wooden support poles. The former mine is near a popular hiking trail and has no access restrictions. There is evidence of human activity at the site. Wastes at this mining site are estimated to be 53,560 cubic yards of waste rock and 29,340 cubic yards of mill tailings, as well as seasonably variable amounts of water flowing out of the adits. Additionally, the site contains a non-engineered surface impoundment made entirely of highly mineralized waste rock. The unlined impoundment was built to collect metal-laden acid mine drainage containing cadmium, copper, lead, and zinc. There is evidence of overflow and seepage through the impoundment into Elk Creek, which runs directly adjacent to the mine. Elk Creek feeds into Coal Creek, which is a drinking water supply for the Town of Crested Butte, Colorado, four miles downstream from the former mine.

In 1999, a two-phase Site Inspection (SI) was conducted of the Ruby Mining District. Phase I was conducted in June 1999 to assess the environmental conditions during the high stream flow regime (spring runoff), and Phase II was conducted in September 1999 to assess the environmental conditions during the low stream flow regime. The 1999 SI was limited to surface water since, according to the United States Geological Survey (USGS), there is no extensive aquifer systems associated with the Ruby Mining District (USGS 1980).

SI results revealed elevated concentrations of the following metals during total metals analysis of the surface waters from Coal Creek and its tributaries: aluminum, antimony, arsenic, beryllium, cadmium, cobalt, copper, iron, lead, nickel, thallium, and zinc. In 2005 and 2006, several sampling events were conducted at the site in order to evaluate temporal and geospatial changes in stream contaminant concentrations (surface water, sediment, and pore water), evaluate previously unidentified watershed influences and biological tissue contaminant concentrations, evaluate the existing macro invertebrate assemblage, and evaluate toxicity to benthic and aquatic organisms. This data was utilized for the analysis of site conditions in the Human Health Risk Assessment (HHRA) and Baseline Ecological Risk Assessment (BERA), documents that were finalized in March of 2008 following the response to stakeholder comments on the external review draft.

The United States Environmental Protection Agency (USEPA) conducted non-time critical removal actions at the site in 2006 and 2007 that included construction of a mine waste repository

on United States Forest Service (USFS) land, removal of the tailings impoundment and waste rock from levels 1, 2, and 3 to the repository, and implementation of site stabilization and drainage control measures. In the fall of 2006, preliminary remediation activities took place at the site that included draining and covering the surface impoundment, removing a dilapidated mill, removing the remaining railroad infrastructure, and diverting Elk Creek to the western side of the site in an effort to reduced inputs from adit drainage. In 2007, the Remedial program installed a passive treatment bioreactor as part of a pilot study to determine the effectiveness of this technology at remediating acid mine drainage from the Level 1 Adit. Additionally, several re-vegetation test plots were installed on waste rock located at Level 98 to determine the ratio of soil amendments that is most effective for establishing plant growth on mine waste piles.

In 2008, additional sampling efforts were conducted in order to establish post-removal baseline site conditions, provide data for the development of a site wide biomonitoring program, and aid in evaluating the feasibility of passive and active treatment alternatives for adit discharges at the site.

Sampling was conducted in 2009 during the high flow and low flow regimes in support of the Remedial Investigation/Feasibility Study (RI/FS) of the Standard Mine Site. Data collected during 2009 followed similar protocols as those established from 2005 through 2008.

The purpose of this SAP/QAPP is to describe the sampling activities for 2010 in order to evaluate the effectives of cleanup efforts of the Standard Mine Site. Data collected in 2010 will follow similar protocols to the site investigation fieldwork conducted annually from 2005 through 2009. Sampling will occur at previously identified station locations for those parameters and requirements as detailed in the following sections of the SAP/QAPP in order to achieve the objectives identified in the DQOs. The data collected during the events planned for 2010 will be compared to data from previous years to establish current post-removal site conditions, provide data for the development of a site wide biomonitoring program, and aid in evaluating the feasibility of passive and active treatment alternatives for adit discharges at the site.

### 3.0 Project/Task Description

Two sampling events will be conducted in 2010 to evaluate changes in the temporal and geospatial distribution of contaminants from previous sampling events and to support an annual site-wide biomonitoring program. The dates proposed for specific sampling activities include the following: June 2010 for the collection of field water quality parameters, stream flows, and surface water metals concentrations and September 2010 for the collection of field water quality parameters, stream flows, surface water and sediment metals concentrations, macro invertebrate assemblage, and toxicity testing of surface water. Data generated from these sampling events will be used in accordance with the provisions outlined in the DQOs. The following data will be collected during the two events:

- Real-time field water quality parameters pH, conductivity, dissolved oxygen, temperature, and Global Positioning System (GPS) locations (if needed)
- Stream flows using flow meters, flumes (where necessary), and stream flow measurement instrumentation already in place
- Surface water, including streams and adit discharges dissolved metals and total recoverable metals
- Sediment total recoverable metals and total mercury
- Macro invertebrates assemblage (species identification and count)

• Toxicity testing – surface water definitive test using moderately hard reconstituted water (MHRW) and Elk-29 water as the diluents

## 4.0 Data Quality Objectives

The DQO process is an iterative strategic planning approach designed to ensure that the type, quality, and quantity of environmental data used in decision making are appropriate for the intended application. Once established, the DQOs are used to develop a scientific and resource-effective data collection design.

The DQO process specifies project decisions, the data quality required to support those decisions, specific data types needed, data collection requirements, and analytical techniques necessary to generate the specified data quality. The process also ensures that the resources required to generate the data are justified. The DQO process consists of the following seven steps:

- 1. State the problem
- 2. Identify the decision
- 3. Identify the inputs to the decision
- 4. Define the study boundaries
- 5. Develop a decision rule
- 6. Specify tolerable limits on decision errors
- 7. Optimize the design

#### 4.1 State the Problem

Upstream release of metals from Standard Mine into Elk Creek and Coal Creek was identified through past investigations. These contaminants potentially pose a risk to ecological receptors, and further characterization of the watershed is warranted. A list of the Chemicals of Potential Concern (COPC) for the site was taken from the Baseline Ecological Risk Assessment (BERA) addendum (USEPA, 2010). COPCs were selected based on chemicals the BERA identified as needing further quantitative analysis. Note that in some cases, a chemical may have been retained as a COPC due to the absence of a benchmark/criterion for comparison. The primary COPCs identified for the site are aluminum, cadmium, calcium, copper, lead, manganese, nickel, silver, and zinc. However, the full suite of metals will be analyzed because additional contaminants may exist.

#### 4.2 Identify the Decision

Data collected from the sampling events will be incorporated into the decision making process for determining the extent of metals loading in the Elk Creek and Coal Creek watersheds. Additionally, the data will be used to determine if the contaminants pose a risk to human and/or ecological receptors. The principle study questions (PSQs) are as follows:

- PSQ 1 Do metals concentrations in Elk Creek and Coal Creek pose an unacceptable risk to ecological receptors?
- PSQ 2 To what degree have remedial efforts been effective at containing or reducing metals loading in Elk Creek?
- PSQ 3 What are the geospatial and temporal trends of contaminant concentrations in the Coal Creek watershed?

# 4.3 Planning Team and Stakeholders

The following sections list the members of the DQO planning team, primary decision makers, and parties who may be impacted by the results of this study or who may use this data generated as a result of the DQO process.

## 4.3.1 DQO Planning Team

The following table includes the DQO planning team members, respective organizations, and affiliation with that organization.

**Table 4.3-1 DQO Planning Team Members** 

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Name	Organization	Area of Technical Expertise					
Christina Progess	USEPA Region 8	Remedial Project Manager					
Dan Wall	USEPA Region 8	ESAT Task Order Project Officer					
Steve Auer	ESAT Region 8	ESAT Field Task Manager					
Jan Christner	START Region 8	RI/FS Implementation					

#### 4.3.2 Decision Makers

The decision-maker has the ultimate authority for making final decisions based on the recommendations of the DQO team. The decision maker for the events is Christina Progess, the USEPA Region 8 Remedial Project Manager for this site.

#### 4.3.3 Stakeholders

Stakeholders are parties who may be affected by the results of the study and/or persons who may later use the data resulting from the DQO process. Table 4.3-2 lists the impacted organizations/stakeholders and the individuals are representing those organizations.

OrganizationRepresented ByCoal Creek Watershed CoalitionSteve Glazer/Anthony PoponiTown of Crested ButteJohn HessUSEPA Region 8Christina ProgessUSFSLinda LanhamCDPHEJim Lewis

Table 4.3-2 Stakeholders

#### 4.4 Identify Inputs to the Decision

The purpose of this step is to identify the data required to answer to the PSQs listed in Section 4.2 and to determine which inputs require environmental measurements. The required data to answer the PSQs are as follows:

- Surface water collection for dissolved metals, total recoverable metals
- Sediment collection for total recoverable metals and mercury
- Collection of field water chemistry data (pH, dissolved oxygen, temperature, and conductivity)
- Collection of stream flow data
- Collection of macro invertebrate data
- Definitive toxicity testing using SM-00 adit water diluted with Elk-29 and MHRW
- Collection of sample locations using GPS (where applicable)

Tables 4.0-1 and 4.0-2 show the specific requirements for each of the sampling events to be conducted in 2010.

## 4.5 Define the Study Boundaries

The spatial boundaries identified for these investigations include the Standard Mine area, Coal Creek, and tributaries to Coal Creek (including Splains Gulch and Elk Creek). Additionally, potentially impacted media, including surface water, and sediment, will be collected. Temporal boundaries include high and low flow conditions in the associated watershed. Sampling locations will include some, but not all, of sites identified through past investigations.

### 4.6 Develop a Decision Rule

Risks to ecological receptors will be calculated using the standard risk assessment approaches developed by USEPA for use at Superfund sites (USEPA, 1997). The risks associated with the ecological receptors are based on the specific contaminants of concern determined from past investigations. Decisions regarding the risks associated with the ecological receptors from observed or calculated risks will be based on three lines of evidence, and include the following: hazard quotients (HQs), population or community observations, and site-specific toxicity tests. Each of these lines of evidence will be combined into a weight-of-evidence conclusion regarding risks to ecological receptors. These weight-of-evidence conclusions are semi-quantitative judgments which take many factors into account. Thus, no statistical or quantitative decision rule can be stated *a priori*. The following guidelines will be applied when interpreting risks to each ecological receptor of concern:

- If the calculated HQ does not exceed one for acute toxicity, and there is no ecologically significant effect observable in direct studies of community structure/function compared to reference, and site specific toxicity tests do not show significant mortality effects compared to reference and laboratory control, then remedial actions are not likely to be necessary.
- If the calculated HQ does not exceed one for acute toxicity, and there is evidence of an adverse impact to the community, structure or function observations, and site specific toxicity tests show mortality, then remedial actions may be necessary.
- If the results from each line of evidence are mixed, in which HQs exceed one but direct toxicity is not observed, a weight of evidence analysis will be performed. These observations will be used to determine if a decision can be reached.

# 4.7 Specify Tolerable Limits on Decision Errors

The purpose of this step is to specify the tolerable limits on decision errors, which are used to establish performance goals for the data collection design. For this project, the number of samples and station locations are based largely on past investigations performed from 2005 through 2009. Some sampling locations have been eliminated based on evaluation of their contribution to the dataset as a whole. The locations selected, and the rationales for the selection, are included in Tables 4.0-1 and 4.0-2.

In order to mitigate the potential for false positive and/or false negative errors associated with field sampling, sampling collections activities will be consistent with established Standard Operating Procedures (SOPs). This includes the collection of duplicate samples (and subsequent analysis using relative percent difference statistics), implementing a decontamination procedure, and the use of field blanks.

For laboratory analysis of samples, quality assurance (QA)/quality control (QC) steps will be consistent with Environmental Services Assistance Team (ESAT) Region 8 laboratory requirements. Tables 7.0-1 through 7.0-4 show the specific analytical QC criteria. In addition,

performance evaluation samples may be included to evaluate laboratory analytical performance. This will be at the discretion of the decision maker.

## 4.8 Optimize the Design

The purpose of this step is to identify the most resource-effective data collection design for generating data that are expected to satisfy the DQOs specified in the preceding six steps. For this series of sampling events, sample locations were selected based on the results of previous sampling efforts at this site and existing data needs in order to maintain data comparability; assess surface water and sediment conditions; further determine the nature and extent of the contamination; evaluate the toxicological impacts of contamination; and effectively evaluate the biological condition of the study area. Site locations have historically been selected to generate a background or reference dataset, determine source contribution to COPC levels, and to evaluate potential COPC contributions from other sources (i.e., tributaries). Based on results and historical data from previous collection activities, the number of sampling locations is reduced for this event. Additional sites may be added in the field based on observed conditions.

# 5.0 Sampling Locations

The sampling plan follows a judgmental design, as described in USEPA Method QA/G-5S, Guidance for Choosing a Sampling Design for Environmental Data Collection (EPA, 2002). The specific parameters of interest and station locations are determined based on results from previous sampling events, as well as data that may be required to support the bio monitoring plan. Sampling locations, descriptions, and activities that will take place are listed in Tables 4.0-1 and 4.0-2 for the June and September sampling events, respectively. Existing sampling location maps will be used for the sampling events. Figure 5.0-1 shows the sampling locations and study area.

#### **6.0** Surface Water

The following sections describe the sampling methods to be used for surface water sample collection. Copies of the applicable SOPs outlining how field activities are performed (including critical documentation protocols) are located at the USEPA Region 8 laboratory (referred to as the Region 8 laboratory from this point forward) and are not included in this SAP/QAPP. The sampling checklist and field equipment checklist are shown in Tables 8.0-1 and 8.0-2.

#### 6.1 Surface Water Sampling Protocol

In order to address the objectives identified in the DQOs (Section 4), surface water quality will be evaluated based on data collected from field measurements, as well as laboratory analysis for the COPCs and additional chemicals identified in the DOOs.

Sampling protocols, sample containers, sample labeling/custody, and overall field management requirements for collecting surface water grab samples are described in the USEPA Region 8 SOP #720, Field Sampling Protocols. Precise sample locations not previously recorded will be documented following the USEPA Region 8 SOP, Global Positioning System, Project and Quality Assurance Considerations, and Standard Operating Procedure.

Collection of water for aquatic toxicity testing scheduled for September 2010 will require obtaining five 1-gallon cubitainer samples of surface water from each site indicated in Table 4.0-2. Surface water should be collected as specified in protocols for field sampling. For cases when minimal water is available, or water flow precludes submerging the cubitainers in the stream, the use of a peristaltic pump may be necessary. Water samples will be stored in coolers with ice and kept at or below 4°Celsius (C) until transport to the Region 8 Laboratory.

#### **6.2** Surface Water Field Measurements

During the June and September sampling events, the following water quality parameters will be measured on a real-time basis in the field:

- pH
- Conductivity
- Temperature
- Dissolved Oxygen

Field measurements will be taken at each surface water sampling location using a Hydrolab Multiprobe (or equivalent water quality probe) and recorded in a field notebook according to the provisions outlined in the USEPA Region 8 SOP, Setup, Calibration, Maintenance, and Use of the Hydrolab Probe. Field measurements will be recorded during the time of sample collection and in-situ when possible. In the event that measurements cannot be made real-time or in-situ, a sample will be collected and analyzed as soon as possible using the Multiprobe sample cup. In this situation, temperature and dissolved oxygen measurements will not be recorded since those parameters will not be representative of actual stream conditions.

# **6.3** Surface Water Analytical Measurements

Surface water samples collected during the June and September events will be submitted for analysis to the ESAT Analytical Chemistry department at the Region 8 Laboratory. Specific analysis for each event is presented in Tables 4.0-1 and 4.0-2. Samples will be collected, preserved, labeled, and stored in accordance with the USEPA Region 8 Field Sampling Protocols SOP, Section 11.1 – Grab Sample Collection (Table 6.0-1).

#### 6.4 Stream Flows

Stream flow measurements will be collected for each surface water sampling location during the June and September sampling events, provided conditions are deemed safe (based on observed stream conditions). Flows will be measured using a Marsh-McBirney meter or prefabricated flumes following the protocols outlined in the USEPA Region 8 Stream Flow Measurement SOP. Flow measurement data will be recorded on a Stream Discharge Form. Flumes may be necessary to establish flows for low discharge streams. In the event that an established stream flow gauge is present at the sampling location, stream flow data may be collected from the gauge rather than using the Marsh-McBirney meter. If stream flow data is collected from the gauge, the gauge type and stream depth will be recorded in the field notebook.

#### 7.0 Sediment Sampling

Sediment samples will be collected during the September sampling event at the locations listed in Table 4.0-2 in order to determine contaminant loading in streambed sediments. Sediment samples will be collected using Teflon scoops in accordance with the protocols outlined in USEPA Environmental Response Team SOP #2016, Sediment Sampling. Samples will be stored and preserved as described in Table 6.0-1.

#### 8.0 Macro invertebrate Assemblage

Macro invertebrate samples will be collected using a semi-quantitative approach during the September sampling event at the locations identified in Table 4.0-2. Macro invertebrate sampling will be performed using a D-frame dip net (one foot base length). Samples will be collected from a 100 meter stretch (representative of the characteristics of the stream) at each sampling location. Samples will be collected by inserting the D-frame dip net into each identifiable stream

characteristic (riffle, run, and pool) and disturbing approximately one square foot of substrate (using the toe or heel of a boot) upstream from the net for a one minute time period. Large substrate particles may need to be picked up and rubbed by hand to dislodge attached organisms. This is repeated two additional times in each attribute for a total of three sub-samples. After each one minute interval, wash the debris/organisms from the net into a sieve using stream water, and then transfer to the sample container. Sub-samples collected at each attribute will be composited in the sample container (to obtain a single homogenous sample per location) and preserved with ethanol.

#### 9.0 Toxicity Testing

Toxicity testing will be performed according to USEPA Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, Fifth Edition (2002). Comprehensive Environmental Toxicity Information System (CETIS; 2007) will be used to calculate the statistical analysis. The purpose of this portion of the project is to evaluate the ecological impacts of contaminated surface water obtained from the investigation area on selected aquatic species. The following sections outline the tests to be performed and the representative species to be used. Mortality will be the endpoint for the surface water toxicity tests. Test results will ultimately be used to assess endpoint toxicity based on comparisons with the selected reference site, which has been determined to be Splain's Gulch-00 (SP-00) and Splain's Gulch-01 (SP-01).

96-hour static renewal tests on rainbow trout fry will be performed using undiluted water collected from locations identified in Table 4.0-2. Additionally, a definitive 96-hour acute toxicity test will be performed on the adit water. If significant toxic effects are shown to test organisms, then adit water will be diluted with reconstituted water following the serial dilution approach to determine what percentage of adit water is toxic to rainbow trout. Specific locations may change based on field observations. Due to the short hold time requirements from the time of test water collection until its use, adequate volumes of site water will be collected at the beginning of the September sampling event (during the first and second day of fieldwork) from applicable locations and immediately transported by vehicle to the Region 8 laboratory. Upon receipt at the laboratory, surface water toxicity tests will be initiated. Rainbow trout fry will be obtained from a commercial trout hatchery in the fry stage 15-30 days post yolk sac absorption (0.40-0.60 grams). Samples of water used for toxicity testing will be submitted to the Region 8 laboratory for analysis. Currently, it is anticipated that undiluted site water will be used for profile toxicity testing purposes. Two definitive toxicity tests will be performed on adit discharge water (SM-00) with the purpose of determining what percentage of adit concentration reduction is needed to support fish in Elk creek. Adit water will be diluted using a serial dilution approach and will be diluted with site water from Elk-29 and MHRW.

#### 10.0 References

Comprehensive Environmental Toxicity Information System (2001-2007). Tidepool Scientific Software, McKinleyville, CA 95519

United States Environmental Protection Agency. December 2002. Choosing a Sampling Design for Environmental Data Collection (EPA QA/G-5S).

United States Environmental Protection Agency. 2002. Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms. Fifth Edition.

United States Environmental Protection Agency. 2010. Baseline Ecological Risk Assessment for the Standard Mine Site, Gunnison County, Colorado. Addendum.

United States Geological Survey. 1980. Reconnaissance of Ground-Water Resources in the Vicinity of Gunnison and Crested Butte, West-Central, Colorado. United States Geological Survey Water-Resources Investigations, Open-File Report 80-12.

#### **Standard Operating Procedures:**

United States Environmental Protection Agency (2006) Region 8 – Field Flow Measurement

United States Environmental Protection Agency (2002) Region 8 – Field Sampling Protocols

Environmental Protection Agency (2003) Region 8 – Setup, Calibration, Maintenance and Use of the Hydrolab Surveyor 4a Multiprobe

United States Environmental Protection Agency Environmental Response Team (1994) – Sampling Equipment Decontamination

United States Environmental Protection Agency Environmental Response Team (1994) – Sediment Sampling

United States Environmental Protection Agency Environmental Response Team (1994) – Surface Water Sampling

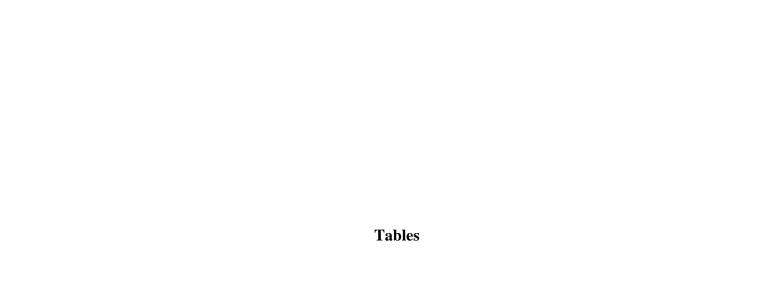


Table 4.0-1 Sampling Locations and Activities - June 2010

			Field Para	meters	Surface V	Water
	Station Name	Site Description/Access Information	Temperature, Dissolved Oxygen, pH, Conductivity	Stream Flows (or gage reading)	Total Recoverable Metals (Nitric)	Dissolved Metals (Nitric) <sup>1</sup>
	Coal-10	Coal Creek approximately 50 yards upstream of Keystone Mine WWTP outfall. Access site in the same way as Coal-05. Look for two yellow-colored poles with blue tops that mark the drinking water intake.	✓	✓	1	1
*	Coal-Opp1	Coal Creek upstream of Fen outfall.	✓	✓	1	1
Coal Creek	Coal-15 <sup>2</sup>	Coal Creek 100+ meters downstream of Elk Creek confluence. Sample where water is well-mixed.	✓	✓	2	2
Coa	Coal-20	Coal Creek approximately 50 yds upstream of Elk Creek confluence.	<b>√</b>	✓	1	1
	Coal-25	Coal Creek downstream from Independence and Anthracite/Ruby confluence. Access site before right-hand turn to Irwin Lake. Look for a short road that ends at a dirt mound that heads toward Coal Creek from CO-12. Sample downstream of culverts.	<b>√</b>	✓	1	1
Reference Location	SP-00	Splain's Gulch at mouth of Coal Creek.	<b>√</b>	✓	1	1
Refer	SP-01	Upper Splain's Gulch above road crossing (reference).	✓	✓	1	1
	Elk-00	Elk Creek at CO-12 crossing approximately 100 yds upstream of confluence with Coal Creek. There is an old flume in an old channel at this location. No water is going through flume.	<b>√</b>	✓	1	1
*	Elk-05	Elk Creek approximately 130 feet downstream of confluence of several seeps that feed Elk Creek from the eastern bank. There are rock outcrops located on the forest service road just upstream of the sampling location. Access on foot via forest service road that follows Elk Creek.	<b>√</b>	✓	1	1
Elk Creek	Elk-6 <sup>2</sup>	Elk Creek upstream of sampling location Seep-01. Access on foot via forest service road that follows Elk Creek.	✓	✓	2	2
图图	Elk-08	Elk Creek downstream of Copley Lake outfall. Access on foot via forest service road that follows Elk Creek.	✓	✓	1	1
	Elk-10	Elk Creek approximately 30 meters below tailings impoundment. Sample further downstream if site is not well-mixed. Access via forest service road or Keystone Mine road.	✓	✓	1	1
	Elk -29	Elk Creek downstream of confluence of individual Elk Creek flows (tributaries near the headwaters).	✓	✓	1	1
Standard Mine	SM-00	Standard Mine adit as it passes through the flume.	<b>✓</b>	✓	1	1
		Total Number	14	14	16	16
	Location of Analyses:	Field ESAT Laboratory EPA Laboratory	✓	✓	✓	✓
		Contracted Laboratory				

<sup>&</sup>lt;sup>1</sup> Samples will be filtered in field.

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<sup>&</sup>lt;sup>2</sup> Two Duplicates are required during this event. .

Note: preservation requirements are in parentheses next to analytes.

			Field Parameters		Surface Water Sediment			Pore Water	Macros	Toxicity
	Station Name	Site Description/Access Information	Temperature, Dissolved Oxygen, pH, Conductivity	Stream Flows (or gage reading)	Total Recoverable Metals (Nitric)	Dissolved Metals (Nitric) <sup>1</sup>	Metals and Mercury	Dissolved Metals (Nitric) <sup>1</sup>	Assemblage	Surface Water
	Coal-10	Coal Creek approximately 50 yards upstream of Keystone Mine WWTP outfall. Access site in the same way as Coal-05. Look for two yellow-colored poles with blue tops that mark the drinking water intake.	✓	<b>√</b>	1	1	1	1		
şk	Coal-Opp1	Coal Creek upstream of Fen outfall.	✓	<b>√</b>	1	1	1	1	1	1
Coal Creek	Coal-15 <sup>2</sup>	Coal Creek 100+ meters downstream of Elk Creek confluence. Sample where water is well-mixed.	✓	✓	2	2	2	2	1	1
	Coal-20	Coal Creek approximately 50 yds upstream of Elk Creek confluence.	<b>√</b>	<b>√</b>	1	1	1	1	1	1
	Coal-25	Coal Creek downstream from Independence and Anthracite/Ruby confluence. Access site before right-hand turn to Irwin Lake. Look for short road that ends at a dirt mound that heads toward Coal Creek from CO-12. Sample downstream of culverts.	a 🗸	<b>✓</b>	1	1	1	1	1	
Reference Location	SP-00	Splain's Gulch at mouth of Coal Creek.	✓	<b>√</b>	1	1	1	1	1	1
Refe	Refer Loca	Upper Splain's Gulch above road crossing (reference).	✓	✓	1	1	1	1	1	1
	Elk-00	Elk Creek at CO-12 crossing approximately 100 yds upstream of confluence with Coal Creek. There is an old flume in an old channel at this location. No water is going through flume.	<b>✓</b>	<b>√</b>	1	1	1	1	1	1
	Elk-05	Elk Creek approximately 130 feet downstream of confluence of several seeps that feed Elk Creek from the eastern bank. There are rock outcrops located on the forest service road just upstream of the sampling location. Access on foot via forest service road that follows Elk Creek.	<b>√</b>	<b>✓</b>	1	1	1	1	1	1
sk	Elk-6 <sup>2</sup>	Elk Creek upstream of sampling location Seep-01. Access on foot via forest service road that follows Elk Creek.	<b>√</b>	<b>√</b>	2	2	2	2	1	2
Elk Creek	Elk-08	Elk Creek downstream of Copley Lake outfall. Access on foot via forest service road that follows Elk Creek.	<b>√</b>	<b>√</b>	1	1	1	1	1	1
	Elk-10	Elk Creek approximately 30 meters below tailings impoundment. Sample further downstream if site is not well-mixed. Access via forest service road or Keystone Mine road.	<b>√</b>	<b>√</b>	1	1	1	1	1	1
	SM-00	Standard Mine adit as it passes through the flume.	✓	<b>√</b>	1	1				2*
	Elk -29	Elk Creek downstream of confluence of individual Elk Creek flows (tributaries near the headwaters).	<b>√</b>	<b>√</b>	1	1	1	1	1	1
	Location of A1-	Total Number	14	14	16	16	15	15	12	14
	Location of Analyses:	Field ESAT Laboratory EPA Laboratory Contracted Laboratory	✓	<b>✓</b>	<b>√</b>	✓	✓		<b>√</b>	✓

<sup>&</sup>lt;sup>1</sup> Samples will be filtered in field.

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 $<sup>^2\,\</sup>mathrm{Two}$  duplicates will be collected during this event. .

Note: preservation requirements are in parentheses next to analytes.

<sup>\*</sup> Definitive acute toxicity test using Elk-29 and laboratory water as diluent

# Table 6.0-1 Water QC Criteria

Target Analytes	EPA Method <sup>1</sup>	Instrument	Fraction Evaluated	Sample Volume Req'd (ml)	Preservation	Holding Time	Laboratory MDL, ug/L	Laboratory PQL, ug/L	CDPHE Surface Water Regulations <sup>3</sup>	MCL <sup>4</sup>
Aluminum (Al)	200.7	ICP-OE	TR & Diss				20	50	750	-
Beryllium (Be)	200.7	ICP-OE	TR & Diss				2	5	-	4
Calcium (Ca)	200.7	ICP-OE	TR & Diss				100	250	NA	NA
Iron (Fe)	200.7	ICP-OE	TR & Diss				100	250	300 (WS)	300 (Diss only)
Chromium (Cr)	200.7	ICP-OE	TR & Diss	Diss - 250ml			2	5	50 (TR)	100
Magnesium (Mg)	200.7	ICP-OE	TR & Diss	TR - 500ml		180 days	100	250	NA	NA
Manganese (Mn)	200.7	ICP-OE	TR & Diss				2	5	50 (WS)	50
Strontium (Sr)	200.7	ICP-OE	TR & Diss				2	10	NA	NA
Silica (SiO <sub>2</sub> )	200.7	ICP-OE	TR & Diss				250	1000	NA	NA
Zinc (Zn)	200.7	ICP-OE	TR & Diss				10	20	65	5000
Calculated Hardness	2340B <sup>2</sup>	Calculated from 200.7, Ca & Mg	TR & Diss	-	HNO <sub>3</sub> to pH <2		-	-	(50)	-
Antimony (Sb)	200.8	ICP-MS	TR & Diss				0.5	1	-	6
Arsenic (As)	200.8	ICP-MS	TR & Diss				0.5	2	50	50
Cadmium (Cd)	200.8	ICP-MS	TR & Diss				0.1	0.2	3.5	5
Copper (Cu)	200.8	ICP-MS	TR & Diss				0.5	1	7	1000
Lead (Pb)	200.8	ICP-MS	TR & Diss	Diss - 250ml TR - 500ml		180 days	0.1	0.2	1.2	50
Nickel (Ni)	200.8	ICP-MS	TR & Diss				0.5	1	29	100
Selenium (Se)	200.8	ICP-MS	TR & Diss				0.5	1	4.6	50
Silver (Ag)	200.8	ICP-MS	TR & Diss				0.2	0.5	0.1	100
Thallium (Tl)	200.8	ICP-MS	TR & Diss				0.1	0.2	15	500
Dissolved Organic Carbon	415.3	Combustion/Non- dispersive IR	Diss	250 ml	Phosphoric acid, pH<2	28 days	1 mg/L	1 mg/L	-	-
Alkalinity	160.1	Mettler AT	Total	250 ml	Cooled to 4°C +/- 2	14 days	5	5	NA	NA
Chloride	300.0 <sup>6</sup>		Diss				1.0 mg/L	2.0 mg/L	250 mg/L	250 mg/L
Fluoride	300.0 <sup>6</sup>	Ion Chromatography	Diss	250 ml	Cooled to 4°C +/- 2	28 days	0.1 mg/L	0.2 mg/L	2 mg/L	4 mgL
Sulfate	300.0 <sup>6</sup>		Diss				2 mg/L	5 mg/L	250 mg/L	250 mg/L

Diss = Dissolved metals fraction, i.e. source water filtered through 0.45 um filter prior to preservation (acidified).

MDL: Method Detection Limit, statistically determined from the deviation in a series of seven low level (3-5x the anticipated MDL) analyses, treated exactly as unknown samples for analysis. 40 CFR Chapter 1, Part 136, Appendix B

PQL: Practical Quantitation Level. Target analyte concentrations between PQL and MDL qualified as estimated, T, due to potential high variability. 40 CFR Parts 9, 141 and 142 [WH-FRL-6934-9]

TR = Total recoverable metals, source water, acidified (preserved).

 $<sup>^{1}</sup>EPA's \textit{ Methods for the Determination of Metals in Environmental Samples} \ \ , Supplement I, May 1994 (Series 200 Methods)$ 

<sup>&</sup>lt;sup>2</sup>Standard Methods for the Examination of Water and Wastewater , 18th Edition, 1992

<sup>&</sup>lt;sup>3</sup> Colorado Department of Public Health and Environment Water Quality Control Commission, Regulation 31, The Basic Standards and Methodologgies for Surface Water (5 CCR 1002-31), Effective March 22, 2005. Three different standards apply to the waters in th

<sup>&</sup>lt;sup>4</sup> MCL: Maximum Contaminant Level, a concentration set by the above CDPHE publication, Table III, "Drinking Water Supply".

<sup>&</sup>lt;sup>5</sup>EPA's Test Methods for Determining Solid Waste, SW-846

 $<sup>^6\</sup>mathrm{EPA}$  's Methods for Chemical Analysis of Water and Wastes , June 2003

<sup>&</sup>lt;sup>7</sup>Water supply limits for organic chemicals taken from CDPHE EWQCC, Reg. 31. Lower value of given range is reported.

Table 7.0-1 ESAT Region 8 - Metals QC Criteria

QC Check / Symbol	Explanation	Run Frequency	Acceptance Criteria	Corrective Action
Initial Calibration Verification (ICV)	Certified standard or standard from a different lot/source than calibration standards	Beginning of run to verify calibration	90-110% recovery (%R) of "true value"	Terminate analysis, restandardize
Continuing Calibration Verification (CCV)	Approximate mid-range standard made from working standards stock	Every 10 unknowns and at end of run	90-110%R "True" value	Re-analyze immediately (once). Then: Restandardize and rerun all samples following last "acceptable" CCV. If recovery >110% and <120% and all associated samples (same analyte) show non-detected, no action required.
Spectral/Mass Interference Check for ICP-OE & ICP- MS (ICSA / ICSAB)	Analyze spectral interferents at high concentrations alone (ICSA) and with other target analytes (ICSAB) to evaluate the effect on analyte recovery	Once per analytical run, prior to sample analyses	ICSAB: ±20%R 'true value' ICSA: ±20%R 'true value' or <±PQL whichever is greater	Evaluate the sample analyte levels. Rerun ICSA/AB or use an alternate wavelength. If interferent levels in the samples don't approach ICSA interferent levels, no action is required. If necessary, recalculate IECs & rerun associated samples
Calibration Blanks, Initial & Continuing (ICB & CCB)	Blank with same reagents as working standards; i.e. zero point on curve	Beginning, end, and after each ICV/CCV during analytical run	$\leq \pm PQL$ $(PQL = 5x MDL)$	Re-analyze immediately once. If still unacceptable, terminate analysis & restandardize.  Rerun all samples analyzed after last "acceptable" blank. Evaluate interferent level(s)  vs samples, use prof judgement for addit'l required sample reruns.
Preparation Blank (PB)	Digested or prepared blank processed identical to samples. Aliquot of clean water prepared using same reagents/volumes as unknown samples.	Once per preparation batch/per matrix, or at 5% frequency, whichever is greatest	$\leq \pm PQL$ $(PQL = 5x MDL)$	PB > PQL: Redigest all samples >MDL and <10x PB value PB < -PQL: Re-calibrate and re-analyze all associated samples
Matrix Spike & Matrix Spike Duplicate (MS & MSD)	Unknown sample (NOT a field blank) fortified at approximately 10-100x MDL for each target analyte. High concentration samples (spike <25% sample target analyte concentration), no calculation is required	1 per 20 unknowns per matrix, whichever is greatest (One PB Spike per PB)	Spike recovered at: 80-120% (ICP& MS) - waters 65-135% (all) - solids	Compose 1 post-digest spike (PS) and retest, note in the narrative. (Analyze original sample with PS) Evaluate duplicate reproducibility. Compare results to LFB/PBS for similar trends. If no similar trends observed, assume a matrix effect. Qualify corresponding analyte data as estimated 'J' for similar matrix samples in set.
Lab Fortified Blank (LFB or PBS)	Spike of reagent blank at same level as MS (analyze/prep identical to samples)	Recommend: once/run	85-115%R of expected (for target analytes)	Used for comparison to Matrix Spike.  If MS/MSD in-control no corrective action necessary.
Lab Control Sample (LCS)	For solid & liquid digested samples. A known of similar matrix prepared the same as unknown samples.	1 per prep batch or one per matrix, whichever is greater.	Aq: 80-120%R of "true" Solids: 70-130%R of "true" or published limits	Recalibrate & reanalyze. If still unacceptable, check for corresponding high or low results in pre-digest spikes, if similar, redigest all associated samples
Serial Dilution (L)	Sample analyzed at 5x the reported analysis. (for matrix effect evaluation) Applies to analytes >50x MDL (in the original analyzed solution)	1 per 20 unknown	Diluted value 90-110% of original analysis.	Concentrations compared/reported from the analyzed solution only. Check IECs and re-analyze. May re-analyze both sample and 'L' at a higher dilution. Use professional judgement, and discuss outliers in the narrative.
Detection Limit Standard (CRI/CRA)	Low level standard ≈3-5x MDL concentration.  Applies to all target analytes except Al, Ca, Fe, Mg,  Na, & K	Once per analytical batch prior to unknowns	50-150%R for Sb, Pb, and Tl. 70-130%R for other target analytes*.	Rerun 2. If all associated samples ≥CCV for outlier analyte, no action required 3.  Correct instrument's sens. problem or else need to redetermine and raise reporting limits  *[Al, Ca, Fe, Mg, Na, & K are monitored without corrective actions]
ICP-MS Internal Standard (IS)	IS standard solution added to all samples, blanks, and standards.	All samples and standards corrected for IS response.	60% - 125%R of IS associated with target analyte(s)	[IS recovery determined versus calibration blank response.] Dilute sample by 2, re-analyze. Continue to dilute until IS %R acceptable.

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Table 7.0-2 ESAT Region 8 - Anions QC Criteria

QC Check (Symbol)	Explanation	Run Frequency	Acceptance Criteria	Corrective Action
Laboratory Control Standard (LCS) / Initial Calibration Verification (ICV)	Known value standard from a source other than the calibration standards. Second source calibration verification.	Beginning of each run to verify calibration	90 -110 % True Value	Terminate analysis and recalibrate IC (Ion Chromatograph)
Continuing Calibration Verification (CCV)	Mid range calibration standard	Every 10 samples, and at the end of each analytical set.	80 -120 % Recovery. Prepared monthly.	Re-analyze immediately. If still unacceptable: terminate analysis and recalibrate IC, rerun all samples following last acceptable CCV
Calibration Blanks, Initial & Continuing (ICB & CCB)	DI water carried through the same method as all samples	Prior to sample analysis, following every 10 samples, and at the end of the analytical set.	≤ PQL (Practical Quantition Limit = 5x MDL)	Re-analyze immediately. If still unacceptable: terminate analysis and recalibrate IC, rerun all samples following last acceptable CCB
Duplicate Sample ("D" following sample ID)	Second aliquot from sample, Note: may not be a field or equipment blank	One per every 10 samples or per sample set, whichever is greater.	≤ 20 % RSD, for samples greater than PQL	Re-prepare & re-analyze sample and duplicate once. Visually check sample for homogeneity. Discuss in narrative.
Matrix Spike & Spike Duplicate ("S" or "SD" following sample ID)	Unknown sample (not field blank) fortified at 10-100 times the PQL for each target analyte	One per 10 samples or per sample set, whichever is greater.	80 -120 % Recovery	If MSD same as MS recovery, and LFB is acceptable, assume matrix effect and record in narrative. If LFB also unacceptable, re-prepare and reanalyze LFB and QC sample set.
Laboratory Fortified Blank (LFB)	DI water fortified with same solution as MS/MSD	Recommended one for each day's analytical set	90 -110 % Recovery. Prepare fresh daily	Identify source of problem and correct.

Note: IC calibration performed every 6 month, or as required by QC criteria. Correlation coefficient must be  $\geq$  0.995 for all analytes of interest. All reported values must fall between lowest and highest calibration standards. Criteria specified on QC chart based on EPA Method 300.0.

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Table 7.0-3 EPA Region 8 QC Parameters for Anion, and DOC/TOC Samples

QC Check (Symbol)	Explanation	Run Frequency	Acceptance Criteria	Corrective Action
Initial Calibration Verification (ICV)	Preferably out-of-house, critiqued standard, or a standard from different lot than calibration standards	Beginning of run to verify calibration	Published limits or 90-110% of "true"	Re-standardize and rerun ICV
Continuing Calibration Verification (CCV)	Approximate mid-range standard made from working standards stock	Every 10 samples and at end of run	90-110% of expected	Re-standardize and rerun all samples from last "acceptable" QC or check sample
Preparation Blank (PB)	Digested or extracted blank with same reagents as prepared unknowns	Once per run or once per 20 samples - whichever is greatest	# RL	Rerun all samples <10 times PB value
Matrix Spike ( <b>SPK</b> )	Unknown sample fortified at 5-25x RL for each analyte	Every 20th unknown sample	80-120% of expected, for high conc. samples (> 4x spike conc.), no acceptance criteria	Check for instrument drift, respike and re-analyze, or dilute, respike and re-analyze.
Duplicate Sample ( <b>DUP</b> )	A lab aliquot of previous unknown sample	1 per 10 unknown samples	#20% RSD for samples \$5x RL, for samples < 5x RL) difference <rl, (#35%)<="" matrices="" solid="" td=""><td>Check for instrument drift, noise, non-homogenous sample, or contamination prior to re- preparation</td></rl,>	Check for instrument drift, noise, non-homogenous sample, or contamination prior to re- preparation
Laboratory Control Standard (LCS)	An aliquot of a standard reference material similar to sample matrix. Verifies correct sample preparation.	1 per 20	70-130% recovery or within acceptance criteria of standard reference material.	Check for corresponding high or low results in matrix spikes, if similar, re-prepare all samples.
Detection Limit Standard (CRA)		1 per batch prior to unknowns	50-150% of expected concentration	Correct instruments sensitivity problem or redetermine and raise RL.

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# Table 7.0-4 QA/QC Calculation Algorithms

Statistical QC Parameter Evaluated  Acronym		Analyses Applied to	Calculation Algorithm
Percent Recovery	%R	Spike recovery determinations	$%R = ((C_s - S_a) \div (S_a)) \times 100$
Percent Recovery	%R	ICV/CCV, ICSAB, LCS	$\%R = (A_T \div T) \times 100$
Relative Percent Difference	RPD	Variance between duplicates	$RPD = ((C - C_D) / ((C + C_D) \div 2)) \times 100$
Percent Difference	%D	Serial dilution variance	$%D = ((C - C_L) / C) \times 100$

Notes:

C = Sample extract concentration

 $C_s$  = Sample extract, spiked concentration

 $S_a$  = Spike amount added

T = True (possibly certified) amount in standard solution

Hardness = (Ca, mg/L)\*2.497 + (Mg, mg/L)\*4.118

 $C_D$  = Duplicate sample concentration

 $C_L$  = Sample extract concentration, dilution factor corrected.

AT = Analyzed concentration for the known standard.

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#### Table 8.0-1 Sampling Checklist

- 1. Make sure the necessary paperwork is in place for a field event: Approved LSR, SAP, and QAPP.
- 2. Coordinate sampling dates and times with members of the field team and talk with chemists involved in the project to see if your plans work for them. Coordinate sample delivery with outside laboratories.
- 3. Fill out the necessary paperwork: Comp Time forms and TAs if travel will be more than 50 miles from the laboratory. Be sure to have reservations made for airlines and hotels if necessary.
- 4. Make necessary arrangements with people outside of the Region VIII laboratory that are involved with the project. Arrange meeting times and places, vehicle needs, sampling teams, additional equipment needs, etc.
- 5. Inform any volunteers outside of the EPA laboratory group what will be involved with sampling physical stressors, equipment to bring, lunch, water, etc.
- 6. Calibrate meters needed for fieldwork well-before leaving. Make sure:
  - a. pH probes are filled.
  - b. DO membranes are intact.
  - c. Spare batteries, calibration logs, and pens are available for each meter.
  - d. Replace pH and conductivity calibration standards with fresh solution.
  - e. Condition new probes and replace damaged ones as needed. Buy new equipment from a scientific vendor if necessary.
- 7. Lay out needed sampling equipment in the field room (see attached list).
- 8. Check vehicles: fill with gas, top off windshield wiper fluid, equip with cell phones, walkie-talkies, and chargers.
- 9. Charge batteries for needed sampling equipment one or two nights before leaving: digital camera, hydrolab, GPS units, walkie-talkies, etc.
- 10. Pack vehicles the night before leaving. In the event of hot or cold weather, leave meters and deionized water in the field room and pack the day you leave.
- 11. In the event of a day-trip, calibrate meters the morning you leave.

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#### Table 8.0-2 Field Equipment List

Sonde

**Sample Containers:** Logbook Summer Field Gear: 250 ml HDPE containers Cables - long/short Backpacks **Hiking Boots** Gallon cubitainers VOA vials Misc: Hat Battery charger GorTex Waders Glass Amber (BNA, pest) Wading Boots pH test strips 1 oz plastic (sed. metals) Latex gloves Rain Parka Neoprene gloves Filter Apparatus: Wool Socks 250 or 500 ml filters Safety glasses Layered Clothing Filter Stands **Kimwipes** Sunscreen Vacuum pump with spare Trash bags Chapstick **Prefilters** Plastic Bags Bug Spray Sun Glasses **Teflon Tweezers** Tape Bucket Water/Food Coolers Pocket Knife **Preservatives:** HNO<sub>3</sub> - metals DI rinse bottles H<sub>2</sub>SO<sub>4</sub> - nutrients Cell Phones w/ charger Winter Field Gear: Shovel/Ice Breaker Phosphoric - TOC/DOC Walkie-Talkies w/batteries HCl - VOAs (pipet) Shovel Backpacks CaCO<sub>3</sub> Acid Waste Snowshoes Spare car keys Container Vehicle log & credit card Hiking Poles Ice/Snow Govt. purchase card **Insulated Water Gloves** DI water for blanks Hat DI rinse bottles Gloves Paperwork: Flow forms with clipboard Balaclava SAP / HSP **Macroinvertebrate Samples:** Neoprene Waders Maps/Gazeteer Sample containers Wading Boots D-Frame Dip Net Wool Socks Chains Surber Sampler Layered Clothing **Tags** Field Notebook(s) Sieve Sunscreen FedX Forms White Tray Chapstick Pens Rinse bottle Sunglasses Picking forceps/brush Water/Food Markers 95% Ethanol preservative **Custody Seals** Pocket Knife Bucket Meters (w/logs): Orange water gloves Field Meters (when not using Flow metermultimeters): Tape measure Wading rod **Well Sampling:** logbooks Solinst depth meter w/battery D batteries pHbuffers Grundfos well pump-Rebar probe solutions batteries Control unit Spare membranes filling **Forms** DO-Calculator Stopwatch, Hose reel w/ pump solution bucket Discharge tube Barometer Cooling sleeve Calibration equip: Flumes- bubble level, Screw driver shovel Winkler Bottle Wrenches GPS Units (charged)-Starch Compass Metric hex keys 0.035N Na Thio DI water Buret/Pipet Distance meter 3 to 2 prong electrical Digital Camera w/batteries Buret Holder Multimeters (charged)converter Flask w/ stir bar Generator- gas, ext. chord Cal standards Powder Pillows: Cap & cal. cup Well Bailors MnSO4 Membranes String or chord Alk Iodide-Azide Fill solutions Long multimeter cable Sulfamic Acid Control unit Conductivitycalibration stds

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