UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY
REGION VIII

IN THE MATTER OF: ATLANTIC RICHFIELD COMPANY, a Delaware corporation. Respondent. PROCEEDING UNDER SECTIONS 104(b), 122(a), AND 122(d)(3) OF THE COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION, AND LIABILITY ACT OF 1980, AS AMENDED, 42 U.S.C. SECTION 9601, et seq.	FOURTEENTH AMENDMENT TO ADMINISTRATIVE ORDER ON CONSENT Docket No. CERCLA-VIII-88-16

AMENDMENT TO ADMINISTRATIVE ORDER ON CONSENT REGARING PAYMENT OF COSTS FOR UNITED STATES GEOLOGICAL SURVEY MONITORING FOR TRIBUTORIES TO THE CLARK FORK RIVER IN THE ANACONDA AREA

In consultation with the State of Montana, represented by the Montana Department of Environmental Quality (DEQ), the U.S. Environmental Protection Agency (EPA) and the Atlantic Richfield Company (Respondent) hereby amend the Administrative Order on Consent, Docket No. CERCLA-VIII-88-16 (Consent Order) for the Anaconda Smelter Site as follows.

1. Respondent agrees to fund tasks associated with the surface water monitoring plan entitled *USGS Monitoring for Tributaries to the Clark Fork River in the Anaconda Area, New IA, Scope of Work - FY 2014* (2014 Scope of Work for Surface Water Monitoring), attached hereto as Exhibit A, for the time period beginning in October 2013 and ending September 30, 2014 by making a single payment to EPA in the amount of four hundred fifty eight thousand and five hundred dollars ($458,500.00).

2. The total amount to be paid by Respondent pursuant to this Amendment shall be deposited by EPA in the Anaconda Special Account within the EPA Hazardous Substance Superfund to be retained and used to finance response actions to be undertaken by the United

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States Geological Survey (USGS) necessary for implementing the 2014 Scope of Work Surface Water Monitoring. The total amount to be paid by Respondent shall be deposited in the Anaconda Special Account within the EPA Hazardous Substance Superfund to be retained and used to conduct or finance response actions at or in connection with the Anaconda Smelter Site, or to be transferred by EPA to the Hazardous Substance Superfund. EPA will direct USGS to provide to Respondent copies of it progress reports associated with such response actions at the same time such reports are provided to EPA.

3. The payment required by this Amendment shall be made by AR on or before sixty (60) days from the Effective Date of this Amendment. However, ARCO shall make best efforts to submit the payment required by the Amendment on August 15, 2013 or shortly thereafter. The payment shall be made by Electronic Fund Transfer online as follows:

www.pay.gov
Enter sfo 1.1 in the search field
Open form and complete required fields

4. To ensure that Respondent's payment is properly recorded by EPA, the following information must be included:

Site Name: Anaconda Smelter
Site #: 8-18
Type of Billing: FFY 2014 USGS Funding

5. Respondent will provide written notice that the funds transfer has occurred and payment made to: David Sturn, Cost Recovery Coordinator, U.S. EPA, Region 8, Montana Office, Federal Building, 10 West 15th Street, Suite 3200, Helena Montana 59626, (406) 457-5027, sturn.david@epa.gov.

6. All other provisions of the Consent Order as previously amended shall remain in effect. This Amendment shall be effective as of the date of signature by EPA.

It is so AGREED this _____ day of _____, 2013.

ATLANTIC RICHFIELD COMPANY

_____

Marcus R. Ferries, P.E., Vice President

It is so ORDERED AND AGREED:

BY:

_____ DATE:_____
Andrea Madigan, Supervisory Attorney
Legal Enforcement Program

BY:

_____ DATE:_____
Kelcey Land, Director
RCRA & CERCLA Technical Enforcement Program

BY:

_____ DATE:_____
Julie Dalsoglio, Director
EPA Montana Office

EFFECTIVE DATE: _____

USGS Monitoring for
Tributaries to the Clark Fork in the Anaconda Area
New IA
SCOPE OF WORK – FY 2014

Prepared by the U.S. Geological Survey

May 2013

Background

In FY2012, **IA DW1495784701** was created by the U.S. Environmental Protection Agency to fund U.S. Geological Survey (USGS) monitoring activities at 10 data-collection stations in the Anaconda area. The following are the FY2014 monitoring activities proposed at these sites under a new IA agreement.

FY 2014 activities covered under a **New IA** include:

- Routine water-quality data collection at the 10 surface-water sites located in the Anaconda area (upper Clark Fork basin) and routine monitoring of biota and bed sediment at 3 of the sites;
- Real-time monitoring of streamflow at 9 sites, turbidity at 4 sites, and water temperature at 1 site. Streamflow data-collection activities for the Warm Springs at Warm Springs gaging station (12323770) are funded by another program;
- Preparation of the annual data report as related to the Anaconda monitoring sites, and
- Project management activities as related to the Anaconda monitoring sites as part of Clark Fork Long-Term Monitoring Program.

The proposed long-term monitoring for FY 2014 includes modifications to the monitoring activities as implemented in May 2013. The modifications included: the addition of dissolved organic carbon (DOC) and selected major ions to the previous list of water-quality analytical constituents, an increase in the frequency of discrete water-quality sample collection from 6 to 8 samples per year at the Warm Springs at Warm Springs station (12323770), and the relocation of 3 of the turbidity sondes.

Routine data collection in the Upper Clark Fork Basin (Anaconda area)

The continued routine water-quality monitoring at the 10 stations (table 1) will compliment the routine monitoring at other sites in the Clark Fork River network (funded by EPA and the State of Montana) and will provide continuity for long-term network operations. All data collected will be published in the Clark Fork annual data report. Historical streamflow and water-quality data, as well as provisional real-time streamflow and turbidity and discrete water-quality data, also may be accessed at the USGS website http://waterdata.usgs.gov/mt/nwis.

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Table 1.Surface-water sites administered under New IA and information on proposed data-collection activities in the Upper Clark Fork Basin (Anaconda area) during FY2014.

Station	USGS Station number	Periodic water quality[1]	Continuous streamflow	Continuous turbidity	Continuous water temperature	Periodic bed sediment[2]	Periodic biota[2]
Silver Bow Cr at Opportunity	12323600	X	X	--	--	X	X
Mill Creek near Anaconda	12323670	X	X	--	--	--	--
Mill Creek at Opportunity	12323700	X[3]	X	X[5]	--	--	--
Willow Creek near Anaconda	12323710	X	X	--	--	--	--
Willow Creek at Opportunity	12323720	X[3]	X	X[5]	--	--	--
Silver Bow Cr at Warm Springs	12323750	X	X	--	--	X	X
Warm Springs Cr near Anaconda	12323760	X	X	--	--	--	--
Warm Springs Cr at Warm Springs	12323770	X[3]	[4]	X[5]	X	X	X
Lost Creek near Anaconda	12323840	X[3]	X	X	--	--	--
Lost Creek near Galen	12323850	X	X	--	--	--	--

[1] Periodic water-quality samples will be collected 8 times per year, except for Warm Springs Creek near Anaconda (station number 12323760) which will be sampled 6 times in FY2014.

[2] Periodic bed-sediment and biota samples are collected 1 time per year (typically in August), except for Warm Springs at Warm Springs (station number 12323770) which is sampled once every 3 years.

[3] In addtion to filtered and unfiltered trace elements and filtered calcium and magnesium, water-quality samples from these sites will be analyzed for the following constituents: filtered silica, sodium, chloride, sulfate, potassium, fluoride, dissolved organic carbon, and alkalinity.

[4] Collection of continuous streamflow data is funded by another program.

[5] Three of the turbidity sondes were moved to new locations in FY2013. The sondes at the upstream sites on Mill Creek, Willow Creek, and Warm Springs Creekwere moved to the downstream sites on those creeks.

Properties that will be measured onsite and constituents for which water, bed-sediment, and biota samples will be analyzed are listed in table 2. Data-quality objectives for analyses of water samples are listed in table 3

Table 2. Properties and constituents measured onsite or analyzed in water, bed-sediment, and biota samples in the Anaconda area (Upper Clark Fork Basin), Montana.

Water		Bed sediment	Biota
Property	Constituent[1]	Constituent	Constituent
Streamflow	Hardness (calculated)	Arsenic	Arsenic
pH	Calcium (filtered)	Cadmium	Cadmium
Specific conductance	Magnesium (filtered)	Chromium	Chromium
Temperature	Suspended sediment	Copper	Copper
Turbidity	Alkalinity (laboratory)	Iron	Iron
	Chloride (filtered)	Lead	Lead
	Fluoride (filtered)	Manganese	Manganese
	Potassium (filtered)	Nickel	Nickel
	Silica (filtered)	Zinc	Zinc
	Sodium (filtered)		
	Sulfate (filtered)		
	Dissolved organic carbon		
	Arsenic (filtered and unfiltered)		
	Cadmium (filtered and unfiltered)		
	Copper (filtered and unfiltered)		
	Iron (filtered and unfiltered)		
	Lead (filtered and unfiltered)		
	Manganese (filtered and unfiltered)		
	Zinc (filtered and unfiltered)		

[1] In addtion to filtered and unfiltered trace elements and filtered calcium and magnesium, water-quality samples from selected sites will be analyzed for the following constituents: filtered silica, sodium, chloride, sulfate, potassium, fluoride, dissolved organic carbon, and alkalinity.

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Table 3. Data-quality objectives for analyses of water samples collected in the Anaconda Area (Upper Clark Fork Basin), Montana. (Sources: Dodge and others, 2010; USGS's National Water quality Laboratory website: http://wwwnwql.cr.usgs.gov/USGS/).

[Abbreviations: µg/L, micrograms per liter; mg/L, milligrams per liter; mm, millimeter. Symbol: --, not determined]

	Data-quality objectives		
	Detectability	Precision	Bias
Constituent	Laboratory reporting level	Maximum relative standard deviation of replicate analyses (percent)	Maximum deviation of spike recovery (percent)
Calcium, filtered	0.02 mg/L	20	--
Magnesium, filtered	.008 mg/L	20	--
Arsenic, filtered	.02 µg/L	20	25
Arsenic, unfiltered recoverable	.09 µg/L	20	25
Cadmium, filtered	.02 µg/L	20	25
Cadmium, unfiltered recoverable	.05 µg/L	20	25
Copper, filtered	.50 µg/L	20	25
Copper, unfiltered recoverable	.70 µg/L	20	25
Iron, filtered	3 µg/L	20	25
Iron, unfiltered recoverable	5 µg/L	20	25
Lead, filtered	.01 µg/L	20	25
Lead, unfiltered recoverable	.04 µg/L	20	25
Manganese, filtered	.1 µg/L	20	25
Manganese, unfiltered recoverable	.4 µg/L	20	25
Zinc, filtered	1.4 µg/L	20	25
Zinc, unfiltered recoverable	2.4 µg/L	20	25
Sediment, suspended, percent finer than 0.062 mm	1 percent	20	--
Sediment, suspended	1 mg/L	20	--
Alkalinity, laboratory	4.6 mg/L	20	--
Chloride (filtered)	0.06 mg/L	20	--
Fluoride (filtered)	0.04 mg/L	20	--
Potassium (filtered)	0.03 mg/L	20	--
Silica (filtered)	0.018 mg/L	20	--
Sodium (filtered)	0.06 mg/L	20	--
Sulfate (filtered)	0.09 mg/L	20	--
Dissolved organic carbon	0.23 mg/L	20	--

Quality assurance of data will be maintained through the use of documented procedures designed to provide environmentally representative data. Acceptable performance of the procedures will be verified with quality-control samples that will be collected systematically to provide a measure of the accuracy, precision, and bias of the environmental data, and to identify problems associated with sampling, processing, or analysis.

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Water-Quality Data

Water-quality data collection will consist of onsite measurements of selected stream properties and the analysis of concentrations of chemical constituents in stream samples. Routine water samples will be collected at the 10 sites in the Upper Clark Fork Basin 6 to 8 times per year (table 1) on a schedule designed to describe seasonal and hydrologic variability.

Continuous turbidity monitors will be operated seasonally (April–September, 2014) at 4 sites near Anaconda (table 1) and will record turbidity values at 15-minutes intervals. In FY2013, turbidity sondes deployed in Mill Creek, Willow Creek, and Warm Springs Creek were relocated from the upstream sites to the downstream sites to more accurately represent water-quality conditions downstream of on-going remediation activities. Turbidity monitoring will continue at these sites in FY2014.

Methods

Water samples will be collected and composited from vertical transits at multiple locations across each stream using depth- and width-integration methods described by Ward and Harr (1990), Edwards and Glysson (1999), and the U.S. Geological Survey (variously dated). These methods provide a vertically and laterally discharge-weighted composite sample that is intended to be representative of the cross section of a stream. Samplers consist of depth-integrating water-quality samplers (Davis, 2005) that are constructed of plastic or coated with a nonmetallic rubber-coating paint and equipped with nylon or tetrafluoroethylene (TFE) nozzles.

Instantaneous streamflow will be determined at the time of water sampling either by direct measurement or from stage-discharge rating tables (Rantz and others, 1982). Daily mean streamflow values during ice periods will be estimated if backwater affects the stage-discharge relation. Onsite measurements of pH, specific conductance, and water temperature will be made during collection of periodic water samples. Onsite sample processing, including filtration and preservation, will be performed according to procedures described by Ward and Harr (1990), Horowitz and others (1994), and the U.S. Geological Survey (variously dated).

Composite water samples will be analyzed for the constituents listed in table 2. The terms "filtered" and "unfiltered recoverable" replace the terms "dissolved" and "total recoverable". Filtered (0.45-micrometer (μm) pore size) and unfiltered constituents will be measured by the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado using the following methods. In addition, the concentrations of calcium and magnesium will be used to calculate water hardness.

Filtered concentrations of arsenic, cadmium, copper, lead, manganese, and zinc will be measured using inductively coupled plasma-mass spectrometry (ICP–MS) (Faires, 1993; Garbarino and others, 2006). Filtered concentrations of calcium, magnesium, iron, silica, and sodium will be measured using inductively coupled plasma-atomic emission spectrometry (ICP–AES) (Fishman, 1993). Samples will be analyzed for dissolved organic carbon (DOC) by UV-promoted persulfate oxidation and infrared spectrometry (Brenton and Arnett, 1993); filtered potassium by ICP-AES as described in the Standard methods for the Examination of Water and Wastewater (20th edition) (1998); and filtered fluoride by ASF, Ion-selective Electrode, as described by Fishman and Friedman (1989). Analyses for filtered chloride and sulfate will be done by ion chromatography (IC) (Fishman and Friedman, 1989).

Unfiltered recoverable concentrations of trace elements will be measured in unfiltered samples that will be first digested with dilute hydrochloric acid (Hoffman and others, 1996). For cadmium, iron,

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lead, and manganese, the digested samples will be analyzed by ICP–MS as described by Garbarino and Struzeski (1998). For arsenic, copper, and zinc, the digested samples will be analyzed by ICP–MS as described by Garbarino and others (2006).

Water samples for analysis of suspended-sediment also will be collected from multiple vertical transits concurrent to the collection of discrete water-quality samples. These samples will be analyzed for suspended-sediment concentration and the percentage of suspended-sediment mass finer than 0.062-millimeter (mm) diameter (silt size and smaller) by the USGS Montana Water Science Center sediment laboratory (hereinafter referred to as the Montana Sediment Laboratory) in Helena, Mont., according to methods described by Guy (1969) and Dodge and Lambing (2006).

Turbidity data will be measured using continuous turbidity monitors (Yellow Springs Instruments Company (YSI) 6136 turbidity sensor) at four tributary sites in the upper Clark Fork basin near Anaconda (table 1). The monitors will be operated seasonally, generally from early spring (after ice breakup) to early winter (before stream freeze-up). Turbidity values will be recorded at 15-minute intervals and can be viewed in real-time at http://waterdata.usgs.gov/mt/nwis. Continuous recordings enable the determination of the minimum and maximum values for each day as well as a daily mean turbidity, which is based on the average of all values in a 24-hour period. Procedures for the operation of continuous turbidity monitors and for daily record computations are described by Wagner and others (2006).

Quality Assurance

Quality-assurance procedures used for the collection and field processing of water samples are described by Ward and Harr (1990), Horowitz and others (1994), Edwards and Glysson (1999), Lambing (2006), and the U.S. Geological Survey (variously dated). Standard procedures used by the NWQL for internal sample handling and quality assurance are described by Friedman and Erdmann (1982), Jones (1987), and Pritt and Raese (1995). Quality-assurance procedures used by the Montana Sediment Laboratory are described by Dodge and Lambing (2006). Standard procedures used for the calibration, measurement, and quality assurance of turbidity monitors are described by Anderson (2005).

The quality of analytical results reported for water samples will be evaluated using quality-control samples that will be submitted from the field and analyzed concurrently in the laboratory with routine samples. These quality-control samples consist of replicates, spikes, and blanks that provide quantitative information on the precision and bias of the overall field and laboratory process. Each type of quality-control sample will be submitted at a proportion equivalent to about 5 percent of the total number of water samples. Therefore, the total number of quality-control samples represents about 15 percent of the total number of water samples.

In addition to the use of quality-control samples submitted from the field, internal quality-assurance practices are performed systematically by the NWQL to provide quality control of analytical procedures (D.L. Stevenson, U.S. Geological Survey, written commun., 2012). These internal practices include analyses of quality-control samples such as calibration standard samples, standard reference water samples, replicate samples, deionized-water blank samples, or spiked samples at a proportion equivalent to at least 10 percent of the sample load. The NWQL participates in a blind-sample program in which standard reference water samples prepared by the USGS Branch of Quality Systems are routinely inserted into the sample line for each analytical method at a frequency proportional to the sample load (*http://bqs.usgs.gov*). The laboratory also participates in external evaluation studies and audits with the National Environmental Laboratory Accreditation Program, the U.S. Environmental Protection Agency, Environment Canada, and the USGS Branch of Quality Systems, to assess analytical performance.

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Replicates

Replicate data can be collected in different ways to provide an assessment of precision (reproducibility) of analytical results. Replicate samples are two or more samples considered to be essentially identical in composition. Replicate samples can be collected in the field (field replicate) either by repeating the collection process to obtain two or more independent composite samples or by splitting a single composite sample into two or more subsamples. The individual replicate samples are then analyzed separately. Likewise, a single sample can be analyzed two or more times in the laboratory to obtain a measure of analytical precision (laboratory replicate).

Precision of analytical results for field replicates can be affected by numerous sources of variability within the field and laboratory environments, including sample collection, sample processing, and sample analysis. To provide data on overall precision for samples exposed to both field and laboratory sources of variability, replicate stream samples for chemical analysis will be obtained in the field by splitting a composite stream sample. Replicate stream samples for suspended-sediment analysis will be obtained in the field by collecting two independent cross-sectional samples.

Precision of analytical results for laboratory replicates, which exclude field sources of variability, will be determined using two independent chemical analyses of aliquots from a single sample selected from the group of samples constituting each analytical run. A separate analysis of the sample will be made at the beginning and end of each analytical run to provide information on the reproducibility of laboratory analytical results independent of possible variability caused by field sample collection and processing. Laboratory replicates are not obtainable for suspended-sediment samples because the samples are consumed during the analysis.

The precision of analytical results for a constituent can be determined by estimating a standard deviation of the differences in concentrations between replicate analyses for several sets of samples. These replicate analyses may consist either of individual analyses of a pair of samples considered to be essentially identical (field replicates) or of multiple analyses of an individual sample (laboratory replicates). The differences in concentration between replicate analyses can be used to estimate a standard deviation according to the following equation (Taylor, 1987):

$$S = \sqrt{\frac{\sum d^2}{2k}}$$

where

S	is the standard deviation of the difference in concentration between replicate analyses,
d	is the difference in concentration between each pair of replicate analyses, and
k	is the number of pairs of replicate analyses.

Precision also can be expressed as a relative standard deviation (*RSD*), in percent, which is computed from the standard deviation and the mean concentration for all the replicate analyses. Expressing precision relative to a mean concentration standardizes the comparison of precision among individual constituents. The *RSD* is calculated according to the following equation (Taylor, 1987):

$$RSD = \frac{S}{\bar{x}} \times 100,$$

where

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RSD	is the relative standard deviation;
S	is the standard deviation; and
$\bar{x}$	is the mean concentration for all replicate analyses.

Spikes

Spiked samples are used to evaluate bias, which measures the ability of an analytical method to accurately quantify a known amount of analyte added to a sample. Because some constituents in stream water can potentially interfere with the analysis of a sample for a targeted analyte, it is important to determine whether such effects are causing biased (consistently high or low) results. Deionized-water blank samples and aliquots of stream samples will be spiked in the laboratory with known amounts of the same trace elements for which water samples will be being analyzed. Analyses of spiked blanks indicate if the spiking procedure and analytical method are within control for a water matrix that is presumably free of chemical interference. Analyses of spiked aliquots of stream samples indicate if the chemical matrix of the stream water interferes with the analytical measurement and whether these interferences could contribute substantial bias to reported trace-element concentrations for stream samples.

Recovery efficiency for analyses of constituents is determined by comparison of a sample and a spiked aliquot of the same sample. The data-quality objective for acceptable spike recovery of trace elements in water samples will be a maximum deviation of 25 percent from a theoretical 100-percent recovery of added constituent (table 3). At the laboratory, a spiked deionized-water blank sample and a spiked aliquot of a stream sample will be prepared and analyzed along with the original unspiked sample. The differences between the spiked and unspiked sample concentrations will be determined and used to compute recovery, in percent, according to the following equation:

$$R = \frac{D}{C} \times 100 \ ,$$

where

R	is the spike recovery, in percent;
D	is the difference between the spiked and unspiked sample concentrations; and
C	is the concentration of material used to spike the sample.

If the spike recovery of a trace element is outside a range of 75 to 125 percent, the instrument will be recalibrated and the entire sample set and all spiked samples will be reanalyzed for that particular trace element until recoveries are improved to the extent possible. High or low bias is indicated if the 95-percent confidence interval does not include 100-percent recovery, thereby indicating a consistent deviation or bias, either high or low.

Blanks

Deionized-water blank samples will be submitted for every field trip and analyzed to identify the presence and magnitude of contamination that could potentially bias analytical results. The type of blank sample routinely tested will be a field blank. Field blanks are aliquots of deionized water that are certified as trace-element free and are processed in the field through the sampling equipment used to collect stream samples. These blanks then are subjected to the same processing (sample splitting, filtration, preservation, transportation, and laboratory handling) as stream samples. Blank samples are analyzed for the same constituents as stream samples in order to identify whether any detectable concentrations exist.

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A field blank with constituent concentrations equal to or less than the LRL for the analytical method indicates that the entire process of sample collection, field processing, and laboratory analysis is presumably free of contamination. If detectable concentrations of trace elements in field blanks are equal to or greater than twice the LRL, the concentrations will be noted during data review. Analytical results from the field blank collected as part of the subsequent sample set will be evaluated for evidence of a consistent trend that could indicate systematic contamination. Sporadic, infrequent exceedances of twice the LRL probably represented random contamination or instrument calibration error that will be not persistent in the process and will be not likely to cause positive bias in a long-term record of analytical results. However, if concentrations for a particular constituent exceeded twice the LRL in field blanks from two consecutive field trips, additional blank samples will be collected from individual components of the processing sequence and will be submitted for analysis to identify the source of contamination.

Quality-Assurance Sample Processing and Data Analysis

All water samples will be handled in accordance with chain-of-custody procedures that provide documentation of sample identity, shipment, receipt, and laboratory handling. All routine and quality-control samples submitted from a sampling episode will be stored in a secure area of the NWQL and analyzed as a discrete sample group, independent of other samples submitted to the NWQL. Therefore, the quality-control data will apply solely to the analytical results for stream samples collected for this program and provide a direct measure of the data quality.

Data-quality objectives (table 3) were established for water-quality data as part of the study plan for the expanded long-term monitoring program initiated in 1993. The objectives identify the analytical requirements of detectability and serve as a guide for identifying questionable data by establishing acceptable limits for precision and bias of laboratory results. Comparisons of quality-control data to data-quality objectives will be used to evaluate whether sampling and analytical procedures will be producing environmentally representative data in a consistent manner. Data that do not meet the objectives will be evaluated for acceptability. If necessary, additional quality-control samples will be submitted and corrective action will be taken.

Bed-Sediment Data

Bed-sediment data for the long-term monitoring program in the Clark Fork basin consist of trace-element concentrations in the fine-grained (less than 0.063 mm) fraction of bed-sediment samples. Bed-sediment samples are collected once annually at 2 sites (table 1) during low, stable flow, typically in August, to facilitate data comparisons among years. Warm Springs Creek at Warm Springs is sampled once every 3 years rather than once annually (table 1).

Methods

Fine-grained bed-sediment samples will be collected using protocols described by Axtmann and Luoma (1991). Samples will be collected from the surfaces of streambed deposits in areas near the edge of the stream using an acid-rinsed polypropylene scoop. Whenever possible, samples will be collected from both sides of the stream.

Individual samples of bed sediment will be collected by scooping material from the surfaces of three to five randomly selected deposits along pools or low-velocity areas. The three to five individual samples will be combined to form a single composite sample. This collection process will be repeated

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three times to obtain three composite samples. Each composite sample will be wet-sieved onsite through a 0.063-mm polyester-mesh sieve using ambient stream water. The fraction of bed sediment in each composite sample that will be finer than 0.063 mm will be collected in an acid-rinsed 500-milliliter (mL) polyethylene bottle and transported to the laboratory on ice.

Bed-sediment samples will be processed and analyzed at the USGS National Research Program Ecology and Contaminants Project laboratory in Menlo Park, California. Bed-sediment samples will be oven-dried at 60°C and ground into smaller particle sizes using an acid-rinsed, ceramic mortar and pestle. Single aliquots of approximately 0.5–0.6 grams (g) of sediment from each of the three composite bed-sediment samples will be digested using a hot, concentrated, nitric acid reflux according to methods described by Luoma and Bryan (1981). Lab replicates will be analyzed by taking an aliquot from one of the three sieved replicate samples at each station. After a 2-week digestion period, the aliquots will be evaporated to dryness on a hot plate. The dry residue will be reconstituted in 10 mL of 0.6N (normal) hydrochloric acid. The reconstituted aliquots will be then will be filtered through a 0.45-µm pore-size filter by using a syringe and in-line disposable filter cartridge. The filtrate will be diluted to a 1:10 ratio with 0.6N hydrochloric acid. These final solutions will be analyzed for arsenic, cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc by using ICP–AES. The smallest concentration of a constituent that can be reliably reported for analyses of bed sediment is termed the minimum reporting level (MRL). Because the conversion from liquid-phase to solid-phase concentration is dependent on both the dilution ratio and the dry weight of the sample, MRLs for some trace elements might differ among stations and among years.

Liquid-phase concentrations, in micrograms per milliliter (µg/mL) (which is equivalent to parts per million; ppm), that will be analyzed in the reconstituted aliquots of digested bed sediment will be converted to solid-phase concentrations, in micrograms per gram (µg/g), by using the following equation:

$$\mu g / g = \frac{(\mu g / mL)(volume\ of\ digested\ sample, in\ mL)}{(dry\ weight\ of\ sample, in\ g)(dilution\ ratio)} .$$

Quality Assurance

The USGS protocols for field collection and processing of bed-sediment samples are designed to prevent contamination from metal sources. Non-metallic sampling and processing equipment (white plastic scoop, funnel-frame apparatus, and 500-mL sample bottles) will be acid-rinsed with deionized water prior to the collection of the first sample. Polyester-mesh sieves will be cleaned in laboratory-grade detergent and rinsed with deionized water. All equipment will receive a final rinse onsite with native stream water. Sampling equipment used at more than one site will be rinsed thoroughly between sites with native stream water. Separate sieves will be used at each site and, therefore, will not require between-site cleaning. Bed-sediment samples will be collected sequentially at sites along an increasing concentration gradient to minimize effects from potential site-to-site carryover contamination.

Quality assurance of analytical results for bed-sediment samples included laboratory instrument calibration with standard solutions and analysis of quality-control samples designed to identify the presence and magnitude of bias (Ellen V. Axtmann, U.S. Geological Survey, written commun., 1994). Quality-control samples consisted of standard reference materials (SRMs) and procedural blanks.

SRMs are commercially prepared materials that have certified concentrations of trace elements. Analyses of SRMs are used to indicate the ability of the method to accurately measure a known quantity of a constituent. Multiple analyses of SRMs are made to derive a mean and 95-percent confidence interval

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for recovery. The digestion process used to analyze bed-sediment samples is not a "total" digestion (does not liberate elements associated with crystalline lattices); therefore, 100-percent recovery may not be achieved for elements strongly bound to the sediment. The percent recovery of trace elements for SRM analyses that use less than a total digestion is useful to indicate which trace elements display strong sediment-binding characteristics in the SRM and whether analytical recovery is consistent between multiple sets of analyses.

Procedural blanks for bed-sediment samples consist of the same reagents used for sample digestion and reconstitution. Concentrated nitric acid used for sample digestion will be heated and evaporated to dryness. After evaporation, 0.6N hydrochloric acid will be added to reconstitute the dry residue. Procedural blanks, therefore, represent the same chemical matrix and exposure to analytical materials and handling as the reagents used to digest and reconstitute bed-sediment samples. A procedural blank will be prepared and analyzed concurrently with bed-sediment samples for each site.

Biological Data

Biological data for the long-term monitoring program in the Clark Fork basin consist of analyses of trace-element concentrations in the whole-body tissue of aquatic benthic insects. Insect samples are collected once annually at the two Upper Clark Fork Basin sites on the same dates as bed-sediment samples (table 1), allowing for a direct comparison of biological data with bed-sediment data among the years. Warm Springs Creek at Warm Springs is sampled once every 3 years rather than once annually (table 1).

Methods

Insect samples will be collected using protocols described in Hornberger and others (1997). Benthic insects at immature stages will be collected with a large nylon-mesh kick net. A single riffle at each site will be sampled repeatedly until an adequate number of individual insects are collected to provide sufficient mass for analysis. Sampling is conducted during base flow conditions, typically in August, such that the benthic community sampled in generally at the same life-stage from year to year allowing for temporal annual comparisons. Targeted taxa for collection will be the order Trichoptera (caddisflies) and the order Plecoptera (stoneflies).

Two caddisfly species of the genus *Hydropsyche* (*Hydropsyche cockerelli* and *Hydropsyche occidentalis)* will be targeted for collection in this study because of their occurrence at most sites. On the rare and unlikely chance that *Hydropsyche* cannot be found, other caddisfly taxa, i.e. *Rhyacophila* spp. or *Brachycentrus* spp., will be collected instead. The caddisfly *Arctopsyche grandis* and the stoneflies *Claassenia sabulosa* and *Hesperoperla* spp. also will be collected where available to represent additional insect taxa that are commonly distributed in the Clark Fork basin. While multiple species may be collected during a sampling event, spatial comparisons of data to track changes over the contamination gradient is limited to targeted taxa within the same genus.

Samples of each taxon will be sorted by genus in the field and placed in acid-rinsed plastic containers. Samples will be frozen in a small amount of ambient stream water on dry ice within 30 minutes of collection. Insect samples will be processed and analyzed at the USGS National Research Program Ecology and Contaminants Project laboratory in Menlo Park, Calif. Insects will be thawed and rinsed with ultrapure deionized water to remove particulate matter and then sorted to their lowest possible taxonomic level, usually to species. If large numbers of specimens will be collected at a site, similar-sized individuals will be composited into replicate subsamples. Subsamples will be placed in tared scintillation vials and oven-dried at 70°C. Subsamples will be weighed to obtain a final dry weight and digested by

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reflux using concentrated nitric acid (Cain and others, 1992). After digestion, insect samples will be evaporated to dryness on a hot plate. The dry residue will be reconstituted in 0.6N hydrochloric acid, filtered through a 0.45-μm pore-size filter, and analyzed undiluted by ICP–AES for arsenic, cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc. The smallest concentration of a constituent that can be reliably reported for analyses of biota is termed the MRL.

Quality Assurance

The protocols for field collection and processing of biota samples are designed to prevent contamination from metal sources. Nonmetallic nets, sampling equipment, and processing equipment will be used in all sample collection. Equipment will be acid-rinsed, then rinsed in ultrapure deionized water prior to the first sample collection. Nets and equipment will be thoroughly rinsed in ambient stream water at each main-stem site. New nets will be used for all tributary sites. Biota samples will be collected sequentially at sites along an increasing concentration gradient to minimize effects from potential site-to-site carryover contamination (Hornberger and others, 1997).

Quality assurance of analytical results for biota samples included laboratory-instrument calibration with standard solutions and analyses of quality-control samples designed to quantify precision and to identify the presence and magnitude of bias. Quality-control samples consist of replicates of the tissue SRM (lobster hepatopancreas) and procedural blanks (one at each site). Quality-control samples will be analyzed in a proportion equivalent to about 20 percent of the total number of biota samples.

Budget summary

A general summary of estimated costs by program activity for FY 2014 is presented in table 4. The budget includes costs of routine data-collection operations; costs associated with the preparation of data from the Anaconda sites for inclusion in the annual data report; and project management expenses (including technical oversight, meetings, quarterly reports, data requests, quality assurance, administration, training, etc.). The costs associated with the report and project management are split between the Clark Fork monitoring programs (Anaconda/upper Clark Fork monitoring program (**new IA**) and the Milltown/lower Clark Fork monitoring (**IA DW1495804001**)) based on the number of sites included in each program.

Table 4. Costs by program activity for FY 2014 activities administered under New IA

Program Activity	FY2014 Cost
Total Data Collection Costs	**$416,955**
Annual Data Report	**$24,840**
Project management	**$16,705**
Total	**$458,500**

A breakdown of costs by budget category is shown in Table 5, with a detailed breakdown of estimated data collection costs by station and data type in FY 2014 shown in Table 6. Only actual expenses will be charged to the program.

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Table 5. Costs by budget category for FY 2014 activities administered under New IA

Budget Category	FY2014 Cost
Personnel	$181,655
Fringe	$28,265
Travel	$10,155
Equipment	$0
Supplies	$13,975
Procurement/Assistance	$0
Construction	$0
Other (laboratory analyses, equipment and vehicle rental; report preparation and publication)	$65,945
Indirect costs	$158,505
Total	**$458,500**

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Table 6. Estimated FY2014 USGS data collection costs in the Upper Clark Fork basin under the New IA.

Station number	USGS station name	USGS station identification	Periodic water quality[1]	Continuous turbidity[2]	Continuous streamflow	Continuous water temperature	Periodic biota[3]	Periodic bed sediment[3]	COST PER STATION
1	Silver Bow Cr at Opportunity	12323600	$14,510	--	$16,500	--	$10,865	$3,865	$45,740
2	Mill Creek near Anaconda	12323670	$14,510	---	$16,500	--			$31,010
3	Mill Creek at Opportunity	12323700	$16,275	$20,645	$16,500	--			$53,420
4	Willow Creek near Anaconda	12323710	$14,510		$16,500	--			$31,010
5	Willow Creek at Opportunity	12323720	$16,275	$20,645	$16,500	--			$53,420
6	Silver Bow Cr at Warm Springs	12323750	$14,510	--	$16,500	--	$10,865	$3,865	$45,740
7	Warm Springs Cr nr Anaconda	12323760	$11,160	--	$16,500	--			$27,660
8	Warm Springs Cr at Warm Spr.	12323770	$16,275	$20,645		$2,700	$3,620	$1,285	$44,525
9	Lost Creek near Anaconda	12323840	$16,275	$20,645	$16,500	--			$53,420
10	Lost Creek near Galen	12323850	$14,510	--	$16,500	--			$31,010
TOTAL DATA COLLECTION COST			**$148,810**	**$82,580**	**$148,500**	**$2,700**	**$25,350**	**$9,015**	**$416,955**

[1]Sampled 8/year, except Warm Springs Creek nr Anaconda, which is 6/year.
[2]Continuous turbidity monitor operated seasonally (March/April-September).
[3]Sampled 1/year, except for Warm Springs Creek at Warm Springs, which is sampled once every three years (annual cost prorated).
[4] Daily streamflow currently (2014) funded by another program.

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