# USGS Monitoring for
# Tributaries to the Clark Fork in the Anaconda Area
# SCOPE OF WORK
# April 1, 2016 through March 31, 2017

*Prepared by the U.S. Geological Survey*

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## Background

The U.S. Environmental Protection Agency funds the U.S. Geological Survey (USGS) to conduct monitoring activities at 10 data-collection stations in the Anaconda area under Interagency Agreement (IA) **DW1492388901**. The following are the proposed monitoring activities for the time period from April 1, 2016 through March 31, 2017 at the Anaconda area sites. The monitoring activities would be completed under an extension to the current IA.

Proposed activities 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 following are detailed descriptions of the proposed long-term monitoring activities for the time period from April 1, 2016 through March 31, 2017.

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

The continued routine water-quality monitoring at the 10 stations (table 1) will complement 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. Quality assurance of data collected during monitoring activities will be conducted following procedures outlined in the project Quality Assurance Project Plan (QAPP) approved on by the USEPA Region 8 QA Manager on April 29, 2014 (U.S. Geological Survey, 2014). QA procedures for specific monitoring activities also are described in the following sections.



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**Table 1. Surface-water sites currently administered under IA DW1492388901 and information on proposed data-collection activities in Anaconda area from April 1, 2016 through March 31, 2017.**

| Station | USGS Station number | Periodic water quality | 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 | X | X | -- | -- | -- |
| Willow Creek near Anaconda | 12323710 | X | X | -- | -- | -- | -- |
| Willow Creek at Opportunity | 12323720 | X | X | X | -- | -- | -- |
| Silver Bow Cr at Warm Springs | 12323750 | X | X | -- | -- | X | X |
| Warm Springs Cr near Anaconda | 12323760 | X[1] | X | -- | -- | -- | -- |
| Warm Springs Cr at Warm Springs | 12323770 | X | [3] | X | X | X | X |
| Lost Creek near Anaconda | 12323840 | X | 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 2015.
[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] Collection of continuous streamflow data is funded by another program.

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 all water, bed-sediment, and biota samples in the Anaconda area, Montana from April 1, 2016 through March 31, 2017.

| | Water | Bed sediment | Biota |
|---|---|---|---|
| **Property** | **Constituent** | **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) | | |



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

[Abbreviations: mg/L, milligrams per liter; µg/L, micrograms 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 | 0.022 mg/L | 20 | -- |
| Magnesium, filtered | .011 mg/L | 20 | -- |
| Arsenic, filtered | .10 µg/L | 20 | 25 |
| Arsenic, unfiltered recoverable | .28 µg/L | 20 | 25 |
| Cadmium, filtered | .03 µg/L | 20 | 25 |
| Cadmium, unfiltered recoverable | .03 µg/L | 20 | 25 |
| Copper, filtered | .80 µg/L | 20 | 25 |
| Copper, unfiltered recoverable | .80 µg/L | 20 | 25 |
| Iron, filtered | 4 µg/L | 20 | 25 |
| Iron, unfiltered recoverable | 4.6 µg/L | 20 | 25 |
| Lead, filtered | .04 µg/L | 20 | 25 |
| Lead, unfiltered recoverable | .04 µg/L | 20 | 25 |
| Manganese, filtered | .4 µg/L | 20 | 25 |
| Manganese, unfiltered recoverable | .4 µg/L | 20 | 25 |
| Zinc, filtered | 2.0 µg/L | 20 | 25 |
| Zinc, unfiltered recoverable | 2.0 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) | 0.02 mg/L | 20 | -- |
| Fluoride (filtered) | 0.01 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) | 0.02 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.

## Water-Quality Data



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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 (approximately April–September, 2016) at 4 sites near Anaconda (table 1) and will record turbidity values at 15-minutes intervals.

### *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, 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 suspendedsediment also will be collected from multiple



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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.

#### Replicates



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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):



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

where

| | |
|---|---|
| *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:

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

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



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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.

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).



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## *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 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



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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 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).



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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 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 the time period from April 1, 2016 through March 31, 2017 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,



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etc.). The costs associated with the report and project management are split between the Clark Fork monitoring programs (Anaconda/upper Clark Fork monitoring program (currently **IA DW1492388901)** 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 proposed USGS monitoring activities in the Anaconda area from April 1, 2016 through March 31, 2017.**

| Program Activity | Cost |
|---|---|
| Total Data Collection Costs | **$448,745** |
| Annual Data Report | **$25,682** |
| Project management | **$16,971** |
| **Total** | **$491,398** |

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 are shown in Table 6. Only actual expenses will be charged to the program.

**Table 5. Costs by budget category for proposed USGS monitoring activities in the Anaconda area from April 1, 2016 through March 31, 2017.**

| Budget Category | Cost |
|---|---|
| Personnel | $200,730 |
| Fringe | $23,320 |
| Travel | $10,770 |
| Equipment | $0 |
| Supplies | $11,566 |
| Procurement/Assistance | $0 |
| Construction | $0 |
| Other (laboratory analyses, equipment and vehicle rental; report preparation and publication) | $76,861 |
| Indirect costs | $168,151 |
| **Total** | **$491,398** |



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**Table 6. Estimated costs for USGS monitoring activities in the Anaconda area from April 1, 2016 through March 31, 2017.**

| 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 | $17,780 | -- | $17,250 | -- | $11,245 | $4,000 | $50,275 |
| 2 | Mill Creek near Anaconda | 12323670 | $17,780 | --- | $17,250 | -- | | | $35,030 |
| 3 | Mill Creek at Opportunity | 12323700 | $17,780 | $20,450 | $17,250 | -- | | | $55,480 |
| 4 | Willow Creek near Anaconda | 12323710 | $17,780 | --- | $17,250 | -- | | | $35,030 |
| 5 | Willow Creek at Opportunity | 12323720 | $17,780 | $20,450 | $17,250 | -- | | | $55,480 |
| 6 | Silver Bow Cr at Warm Springs | 12323750 | $17,780 | --- | $17,250 | -- | $11,245 | $4,000 | $50,275 |
| 7 | Warm Springs Cr nr Anaconda | 12323760 | $13,340 | -- | $17,250 | -- | | | $30,590 |
| 8 | Warm Springs Cr at Warm Spr. | 12323770 | $17,780 | $20,450 | –[4] | $2,770 | $3,745 | $1,330 | $46,075 |
| 9 | Lost Creek near Anaconda | 12323840 | $17,780 | $20,450 | $17,250 | -- | | | $55,480 |
| 10 | Lost Creek near Galen | 12323850 | $17,780 | --- | $17,250 | -- | | | $35,030 |
| **TOTAL DATA COLLECTION COST** | | | **$173,360** | **$81,800** | **$155,250** | **$2,770** | **$26,235** | **$9,330** | **$448,745** |

[1]Sampled 8/year, except Warm Springs Creek nr Anaconda, which is sampled 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 funded by another program.



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## References Cited


Anderson, C.W., 2005, Turbidity (version 2.1): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6, section 6.7, 64 p. (Also available at http://pubs.water.usgs.gov/twri9A6/.)

Axtmann, E.V., and Luoma, S.N., 1991, Large scale distribution of metal contamination in the fine-grained sediment of the Clark Fork River, Montana: Applied Geochemistry, v. 6, no. 1, p. 75–88.

Brenton, R.W., and Arnett, T.L., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of dissolved organic carbon by uv-promoted persulfate oxidation and infrared spectrometry: U.S. Geological Survey Open-File Report 92-480, 12 p.

Cain, D.J., Luoma, S.N., Carter, J.L., and Ferd, S.V., 1992, Aquatic insects as bioindicators of trace element contamination in cobble-bottom rivers and streams: Canadian Journal of Fisheries and Aquatic Sciences, v. 49, no. 10, p. 2141–2154.

Davis, B.E., 2005, A guide to the proper selection and use of federally approved sediment and water-quality samplers: U.S. Geological Survey Open-File Report 2005–1087, 26 p. (Also available at *http://pubs.usgs.gov/of/2005/1087*.)

Dodge, K.A., and Lambing, J.H., 2006, Quality-assurance plan for the analysis of suspended sediment by the U.S. Geological Survey in Montana: U.S. Geological Survey Open-File Report 2006–1242, 35 p. (Also available at *http://pubs.usgs.gov/of/2006/1242*.)

Edwards, T.K., and Glysson, G.D., 1999, Field methods for measurement of fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. C2, 89 p. (Also available at *http://pubs.usgs.gov/twri/twri3-c2/*.)

Faires, L.M., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of metals in water by inductively coupled plasma-mass spectrometry: U.S. Geological Survey Open-File Report 92–634, 28 p.

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93–125, 217 p.

Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.

Friedman, L.C., and Erdmann, D.E., 1982, Quality assurance practices for the chemical and biological analyses of water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A6, 181 p. (Also available at http://*pubs.usgs.gov/twri/twri5a6/*.)

Garbarino, J.R., and Struzeski, T.M., 1998, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of elements in whole-water digests using inductively coupled plasma-optical emission spectrometry and inductively coupled plasma-mass spectrometry: U.S. Geological Survey Open-File Report 98–165, 101 p.

Garbarino, J.R., Kanagy, L.K., and Cree, M.E., 2006, Determination of elements in natural-water, biota, sediment, and soil samples using collision/reaction cell inductively coupled plasma-mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, sec. B, chap. 1, 88 p.

Guy, H.P., 1969, Laboratory theory and methods for sediment analysis: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. C1, 58 p. (Also available at *http://pubs.usgs.gov/twri/twri5c1/*.)

Hoffman, G.L., Fishman, M.J., and Garbarino, J.R., 1996, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—In-bottle acid digestion of whole-water samples: U.S. Geological Survey Open-File Report 96–225, 28 p.




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Hornberger, M.I., Lambing, J.H., Luoma, S.N., and Axtmann, E.V., 1997, Spatial and temporal trends of trace metals in surface water, bed sediment, and biota of the upper Clark Fork basin, Montana, 1985–95: U.S. Geological Survey Open-File Report 97–669, 127 p.

Horowitz, A.J., Demas, C.R., Fitzgerald, K.K., Miller, T.L., and Rickert, D.A., 1994, U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94–539, 57 p.

Jones, B.E., 1987, Quality control manual of the U.S. Geological Survey's National Water Quality Laboratory: U.S. Geological Survey Open-File Report 87–457, 17 p.

Lambing, J.H., comp., 2006, Quality-assurance plan for water-quality activities of the U.S. Geological Survey Montana Water Science Center: U.S. Geological Survey Open-File Report 2006–1275, 39 p. (Available online only at *http://pubs.usgs.gov/of/2006/1275/*.)

Luoma, S.N., and Bryan, G.W., 1981, A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants: Science of the Total Environment, v. 17, no. 2, p. 165–196.

Pritt, J.W., and Raese, J.W., eds., 1995, Quality assurance/quality control manual—National Water Quality Laboratory: U.S. Geological Survey Open-File Report 95–443, 35 p.

Rantz, S.E., and others, 1982, Measurement and computation of streamflow: U.S. Geological Survey Water-Supply Paper 2175, Volumes 1 and 2, 631 p.

Standard methods for the examination of water and wastewater (20th edition), 1998; Washington, D.C., American Public Health Association, American Water Works Association, and Water Environment Federation, 3120, p3-37 to 3-43.

Taylor, J.K., 1987, Quality assurance of chemical measurements: Chelsea, Mich., Lewis Publishers, 328 p.

U.S. Geological Survey, 2014, U.S. Geological Survey monitoring of water-quality, bed sediment, and biota in the Clark Fork Basin, Butte to Missoula, Montana: Quality Assurance Project Plan, approved April 29, 2014, 50 p.

U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A9. (Also available at http://pubs.usgs.gov/twri/.)

Wagner, R.J., Boulger, R.W., Oblinger, C.J., and Smith, B.A., 2006, Guidelines and standard procedures for continuous water-quality monitors—Station operation, record computation, and data reporting: U.S. Geological Survey Techniques and Methods 1–D3, 51 p., 8 attachments. (Also available at *http://pubs.usgs.gov/tm/2006/tm1D3/*.)

Ward, J.R., and Harr, C.A., eds., 1990, Methods for collection and processing of surface-water and bed-material samples for physical and chemical analyses: U.S. Geological Survey Open-File Report 90–140, 71 p.



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