

5.0 DATA COLLECTION METHODS

This section describes the standard procedures to be used during sample collection, field data generation, and laboratory analysis of samples collected under the monitoring programs described in Section 4 of this document. The methods described in this section were selected for the specific monitoring parameters to provide representative, reproducible data for environmental conditions in the Basin. The sample collection and analytical procedures were chosen to provide data that is comparable to previous (baseline) data. USFWS and USGS personnel will performed field data and sample collection. Table 5.1 describes the agencies responsible for sampling or monitoring each media or parameter.

Field and laboratory methods are included in Appendix E. The field data and sample collection methods identified herein are current as of the date that this document was developed. Given the 30-year time frame over which this monitoring program will be implemented, it is likely that the referenced methods will be updated or superceded. In the event that updated or new methods are recommended for implementation, the revised/new methods will be compared with methods described herein to ensure the appropriateness of the new method and comparability of results. Revisions to sampling or analytical methods will be reviewed by EPA, USGS, and USFWS, and will be documented via the corrective action form included with the Quality Assurance Project Plan (Appendix B). A review of sampling and analytical methods will be performed during the CERCLA-required 5-year reviews.

The following sections describe sample and field data collection procedures, laboratory analytical methods and data quality objectives for each monitoring parameter.

5.1 SURFACE WATER

This section describes the field and analytical methods identified for use during surface water sample collection, the agency responsible for performing the sampling, and the analytical methods and laboratories.

5.1.1 Surface Water Sample Collection

Surface water samples will be collected at the gauging stations identified in Section 4. The USGS will perform sampling in accordance with their standard procedures for sample collection, as described in the National Field Manual for the Collection of Water-Quality Data: U.S. Geological Survey Techniques of Water-Resources Investigations (TWRI), book 9, chaps. A1-A6 (USGS, variously dated). The TWRI manual describes the procedures for:

- Preparation for water sampling (Chapter A1)
- Selection of equipment for water sampling (Chapter A2)

- Cleaning of equipment for water sampling (Chapter A3)
- Collection of water samples (Chapter A4)
- Processing of water samples (Chapter A5)
- Field measurements (Chapter A6)

Appendix E includes TWRI chapters A1-A6. Additional details are provided in the Quality Assurance Project Plan (Appendix B). The recommended container sizes, container types, sample preservation, and holding times for each analysis are summarized on Table 5.1. Surface water samples will be collected using a depth-integrating sampler, as described in TWRI. Surface water samples collected for analysis of dissolved metals and dissolved nutrients will be field-filtered through a 0.45- μm filter prior to sample preservation.

During high-flow sampling events (such as rain-on-snow or peak spring runoff) when the suspended concentrations are elevated, water samples will be collected for analysis of total metals in the suspended sediment. Bulk (1-liter) water samples will be collected and processed through a 0.45- μm filter. The total metals analysis will be performed on the filter residue and requires one gram of sediment. If suspended sediment concentrations in surface water during high flows are found to be insufficient for the collection of one gram of sediment from 10 liters of water, then total metals analysis of suspended sediment will not be performed.

5.1.2 Surface Water Sample Analysis

Surface water samples will be analyzed at the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado in accordance with USGS analytical SOPs and/or EPA methods. Analytical methods for sample analyses are presented on Table 5-2. Surface water samples will be analyzed for:

- Dissolved metals (cadmium, lead, and zinc)
- Total metals (cadmium, lead, and zinc)
- Hardness
- Nutrients (total nitrogen, dissolved ammonia, dissolved nitrate/nitrite, total phosphorus, dissolved phosphorus)

Metals and hardness analyses will be performed by inductively-coupled plasma atomic emission spectrometry (ICP-AES) and inductively-coupled plasma mass spectrometry (ICP-MS) referencing USGS analytical SOPs. Nutrient analyses will be performed by conventional analyses, referencing USGS analytical SOPs and EPA methods presented on Table 5-2. Suspended sediment samples collected during high flows as part of the surface water monitoring program will be prepared and analyzed for total metals as described in Section 5.2.2. Suspended sediment samples will be prepared using a four-acid digestion capable of effecting nearly total

digestion of most minerals. As the four-acid digestion is not appropriate for mercury analysis, a split of the suspended sediment sample will be prepared for mercury analysis referencing EPA Method 7471B.

Target reporting limits and quality control criteria (precision, accuracy, and completeness) are summarized for each analysis on Table 5-2.

5.2 SOIL AND SEDIMENT

USGS personnel will perform soil and sediment sampling, and samples will be analyzed at the NWQL in Denver, Colorado. The methods for sample collection and analysis are summarized on Tables 5-1 and 5-2.

5.2.1 Soil and Sediment Sample Collection

Soil and sediment samples will be collected at the locations and frequencies described in Section 4-2. The schedule for soil/sediment sample collection is summarized on Table 4-5. Samples will be collected in accordance with the USGS standard procedures for sample collection, as described in TWRI, book 9, chapter A8. TWRI chapter A8 describes the field procedures for collection of bottom-material samples.

Annual and 10-year sampling of depositional areas will be performed as described in USGS' TWRI chapter A8. However, the samples will be collected in the subaerial portion of the high water channel or floodplain rather than in the submerged channel. A plastic or Teflon scoop or spatula will be used to sample the upper 2 cm of sediment. Because of the variations in boulder/cobbles and the distribution of the finer sampled material (<250 μm) along the channel, sample collection details such as the number of subsamples to be composited per sampling location, the size of the sampling area, and the method of selecting subsample points (evenly spaced grid, random selection of grid points, quasi-random opportunistic sampling, etc.) are expected to vary by site. A sampling approach suitable for each specific sampling location will be documented during the first sampling event so that subsequent events are completed the same way.

5.2.2 Soil and Sediment Sample Analysis

Soil/sediment samples will be analyzed at the NWQL in Denver, Colorado. Soil/sediment samples will be analyzed for the COECs arsenic, cadmium, copper, lead, mercury, silver and zinc. Samples will be prepared using a four-acid digestion method capable of nearly digesting most minerals. The four-acid total digestion was selected to minimize variability associated with sample preparation method. Sample digestion methods such "total-extractable" microwave digestions introduce variability to analytical results by partially digesting the solid samples. A total digestion of soil/sediment samples will therefore promote comparable sample preparation

results by reducing variability of the extent of extraction. Soil/sediment metals concentrations by the four-acid digestion method may or may not be higher than by the USEPA strong acid digestion procedures typically used for comparison of analytical results to risk-based screening or cleanup levels. As the four-acid digestion method is not appropriate for mercury analysis, a split of each sample will be prepared for mercury analysis referencing EPA Method 7471B.

Digested samples will be analyzed for total arsenic, cadmium, copper, lead, silver, and zinc by ICP-AES referencing USGS method OFR 02-223-G. Mercury analysis will be performed by cold vapor atomic absorption, referencing EPA Method 7471B. Analytical methods, target reporting limits, and quality control criteria (precision, accuracy, and completeness) are presented on Table 5-2.

5.3 BIOLOGICAL RESOURCES

USFWS personnel will perform biological resources monitoring. Biological resources monitoring program includes both analytical (e.g., blood lead levels) and observational data (e.g., waterfowl population). Sample and data collection methods for biological resource monitoring are shown on Table 5-1 and analytical methods, when applicable, are shown on Table 5-2.

Biological resources monitoring data will be collected in accordance with SOPs developed specifically for the Basin by the Upper Columbia Fish and Wildlife Office. Data collection will be performed and reviewed by USFWS personnel. Fish, macroinvertebrate, and blood samples collected for metals analysis will be prepared and analyzed by the EPA Region 10 laboratory at Manchester, Washington. Songbird blood analysis for δ -aminolevulinic acid dehydrates will be performed by the USGS laboratory at Patuxent, Maryland.

Table 5-1
Sample and Field Data Collection Methods

Monitoring Component	Responsible Agency	Data / Sample Collection Method ^(c)	Analysis	Container Size	Container Type	Preservation	Holding Time	Analytical Laboratory
Surface Water	USGS	USGS - TWRI, Book 9, 1998 ^(d) Chapters A1-A6	Ammonia, diss. ^(a)	125 mL	Polyethylene bottle	Cool to 4 C	28 days	USGS
			Total nitrogen	125 mL	Polyethylene bottle	H2SO4 to pH<2, cool to 4 C	28 days	
			Nitrate + nitrite, diss. ^(a)	125 mL	Polyethylene bottle	Cool to 4 C	28 days	
			Total phosphorus	125 mL	Polyethylene bottle	H2SO4 to pH<2, cool to 4 C	28 days	
			Phosphorus, diss. ^(a)	125 mL	Polyethylene bottle	H2SO4 to pH<2, cool to 4 C	28 days	
			Total metals	250 mL	Polyethylene bottle, acid rinsed	Nitric acid to pH<2	6 months	
			Dissolved metals ^(a)	250 mL	Polyethylene bottle, acid rinsed	Nitric acid to pH<2	6 months	
		Total metals in suspended sediment ^(b)	1 g	Polypropylene bottle	None	6 months (28 days for Hg)		
Surface Sediment	USGS	USGS - TWRI, Book 9, 1998 ^(d) Chapter A8	Total metals	40 g	Polypropylene bottle	None	6 months (28 days for Hg)	USGS
Sediment Coring	USGS	USGS - TWRI, Book 9, 1998 ^(d) Chapter A8	Total metals	40 g	Polypropylene bottle	None	6 months (28 days for Hg)	USGS
Fish diversity/ abundance	USFWS	UCFWO 1020.1001 (Procedures for sampling fish to determine diversity and abundance)	NA	NA	NA	NA	NA	NA
Fish Tissue Metal Levels (Upper Basin and Spokane River) Whole-body trout only.	USFWS	UCFWO 1020.1002 (Collection of individual fish samples for analysis of whole body metal residues)	Total metals	Field: Plastic bags; Lab: 4 ounce glass jars with Teflon-lined lids. Sufficient headspace must be left in jars such that expansion during freezing does not		Freeze	1 year	EPA Manchester
Bull Trout Habitat/ Temp. and Other Aquatic Resources Assessment	USFWS	UCFWO 1020.1003 (Bull trout habitat and water temperature)	NA	NA	NA	NA	NA	NA
Bull Trout Population Survey and Assessment of Other Aquatic Resources	USFWS	UCFWO 1020.1004 (Bull trout and native species survey in temperature refuge areas)	NA	NA	NA	NA	NA	NA
Macroinvertebrate diversity/abundance	USFWS	UCFWO 1020.1005 (Procedures for determining macroinvertebrate diversity and abundance)	NA	NA	NA	NA	NA	NA
Macroinvertebrate tissue metal levels	USFWS	UCFWO 1020.1006 (Procedures for the collection of benthic macroinvertebrate samples for the analysis of metal residues)	Total metals, percent solids	Field: Plastic bags or 4 ounce polypropylene jars; Lab: 4 ounce glass jars with Teflon-lined lids. Sufficient headspace must be left in jars such that		Freeze	1 year	EPA Manchester
Aquatic habitat quality	USFWS	UCFWO 1020.1007 (Procedures for assessing aquatic habitat quality)	NA	NA	NA	NA	NA	NA
Waterfowl population	USFWS	UCFWO 1020.1013 (Waterfowl Survey in the Coeur d'Alene River Basin)	NA	NA	NA	NA	NA	NA
Waterfowl mortality	USFWS	UCFWO 1020.1008 (Procedures for waterfowl mortality searches)	NA	NA	NA	NA	NA	NA
Waterfowl blood collection	USFWS	UCFWO 1019.3742 (Techniques for capturing mallards and redhead ducks); UCFWO 1020.1009 (Procedures for the collection of waterfowl blood samples for the analysis of blood-lead only)	Lead	5 ml	Cryogenic tube	Frozen	1-year	EPA Manchester
Riparian vegetation / invertebrates	USFWS	UCFWO 1020.1010 (Procedures for evaluating plant communities in riparian areas of the Coeur d'Alene River Basin); UCFWO 1020.1011 (Procedures for monitoring invertebrates in riparian areas of the Coeur d'Alene River Basin)	NA	NA	NA	NA	NA	NA
Songbird diversity/abundance	USFWS	UCFWO 1020.1012 (Procedures for conducting MAPS songbird studies)	NA	NA	NA	NA	NA	NA
Songbird blood collection	USFWS	UCFWO 1019.3757 (Use of mist nets for capturing passerines); UCFWO 1019.3765 (Collection and preservation of blood from small birds for laboratory analysis)	Lead	1-2 ml	Cryogenic tube	Frozen	1-year	EPA Manchester
			ALAD enzyme assay	1-2 ml	Cryogenic tube	Snap frozen in liquid nitrogen	1-year	USGS-Patuxent
			Hematocrit		Hematocrit tubes, sealed with hematocrit tube sealant	Heparin-treated fresh blood	8-hours	UCFWO field crew

^(a) Samples will be field filtered through a 0.45 um filter.

^(b) Suspended sediment analyses will be performed on residue from 0.45 um filtration of surface water collected during high-flow sampling events

^(c) SOPs will be reviewed prior to sample/data collection. Modifications to SOPs will be reviewed and approved by USFWS or USGS and EPA prior to use.

^(d) USGS, 1998, National Field Manual for Collection of Water-Quality Data, Techniques of Water-Resources Investigations, Book 9, numerous chapters.

Field measurements for pH, temperature, and specific conductivity will be collected at surface water sampling locations at the time of sampling.

**Table 5-2
 Analytical Methods and Data Quality Objectives (DQOs)**

Analysis	Matrix	Laboratory	Prep Method	Analytical Method	Target Reporting Limit	Sample Container		Sample Preservation	Holding Time	Precision	Accuracy	Completeness	
						Size	Type						
Conventionals													
Total nitrogen	Water	USGS	NA	USGS I-4650-03	0.03 mg/L	125 mL	Polyethylene bottle	H2SO4 to pH<2, cool to 4 C	28 days	+/- 25%	+/- 25%	95%	
Nitrate + nitrite, diss. ^(a)			NA	USGS I-2546-91	0.016 mg/L	125 mL	Polyethylene bottle	Cool to 4 C	28 days				
Ammonia, diss. ^(a)			NA	USGS I-4515-91	0.01 mg/L	125 mL	Polyethylene bottle	Cool to 4 C	28 days				
Phosphorus, total			EPA 365.1 USGS I-2525-89	0.004 mg/L	125 mL	Polyethylene bottle	H2SO4 to pH<2, cool to 4 C	28 days					
Phosphorus, diss. ^(a)			EPA 365.1	0.004 mg/L	125 mL	Polyethylene bottle	H2SO4 to pH<2, cool to 4 C	28 days					
Total metals													
Cadmium	Water	USGS	USGS I-3486-95	USGS I-4471-97	0.00004 mg/L	250 mL	Polyethylene bottle, acid rinsed	Nitric acid to pH<2	6 months	+/- 25%	+/- 25%	95%	
Lead			USGS I-4471-97		0.00006 mg/L								
Zinc			USGS I-4471-97		0.002 mg/L								
Dissolved metals ^(a)													
Cadmium	Water	USGS	USGS I-3486-95 USGS I-4471-97	USGS I-2477-92	0.00004 mg/L	250 mL	Polyethylene bottle, acid rinsed	Nitric acid to pH<2	6 months	+/- 25%	+/- 25%	95%	
Lead					0.00008 mg/L								
Zinc					0.00006 mg/L								
Calcium					USGS I-1472-87								0.01 mg/L
Magnesium													0.008 mg/L
Total metals (suspended sediment) ^(b)													
Cadmium	Soil / Sediment	USGS	NAWQA Size Fractionation Sieving Protocol; USGS OFR 02-223-G	USGS OFR 02-223-G	2 mg/kg	1 L	Polypropylene bottle	Cool to 4 C	6 months	+/- 35%	+/- 25%	95%	
Copper					2 mg/kg								
Silver					2 mg/kg								
Zinc					2 mg/kg								
Arsenic					10 mg/kg								
Lead					4 mg/kg								
Mercury					USEPA 7471B USEPA 7471B				0.1 mg/kg				28 days
Total metals (soil / sediment)													
Cadmium	Soil / Sediment	USGS	NAWQA Size Fractionation Sieving Protocol; USGS OFR 02-223-G	USGS OFR 02-223-G	2 mg/kg	40 g	Polypropylene bottle	Cool to 4 C	6 months	+/- 35%	+/- 25%	95%	
Copper					2 mg/kg								
Silver					2 mg/kg								
Zinc					2 mg/kg								
Arsenic					10 mg/kg								
Lead					4 mg/kg								
Mercury					USEPA 7471B USEPA 7471B				0.1 mg/kg				28 days
Fish Tissue Metal Levels													
Arsenic	Tissue	EPA Manchester	Manchester SOP INOR-006	EPA 206.2	0.25 mg/kg	Field: Plastic bags; Lab: 4 ounce glass jars with Teflon-lined lids. Sufficient headspace must be left in jars such that expansion during freezing does not cause the jar to break.	Freeze	1 year	+/- 20%	+/- 25%	95%		
Cadmium				EPA 200.7/200.8	0.05 mg/kg								
Lead				0.05 mg/kg									
Zinc				1.0 mg/kg									
Macroinvertebrate Tissue Metal Levels													
Arsenic	Tissue	EPA Manchester	Manchester SOP INOR-006	EPA 206.2	0.25 mg/kg	Field: Plastic bags or 4-ounce polypropylene jars; Lab: 4 ounce glass jars with Teflon-lined lids. Sufficient headspace must be left in jars such that expansion during freezing does not cause the jar to break.	Freeze	1 year	+/- 20%	+/- 25%	95%		
Cadmium				EPA 200.8/200.9	0.05 mg/kg								
Lead				0.05 mg/kg									
Zinc				1.0 mg/kg									
Waterfowl / Songbird Blood Lead (ALAD and Hematocrit on songbird only)													
Lead (songbird)	Blood	EPA Manchester	Manchester SOP INOR-006	EPA 200.9	0.1 mg/kg	Cryogenic tube	Frozen	1 year	+/- 20%	+/- 25%	95%		
Lead (waterfowl)		Manchester SOP INOR-006	EPA 200.9	0.05 mg/kg	5 mL								
ALAD enzyme assay (songbird only)		USGS-Patuxent	Inclusive of UCFWO 1019.3801	UCFWO 1019.3801 (ALAD determination)	Per method	1-2 mL	Cryogenic tube	Snap frozen in liquid nitrogen	1 year	Per method		95%	
Hematocrit (songbird only)		UCFWO field personnel	NA	Hematocrit procedures in UCFWO 1019.3765 (Collection and Preservation of Blood form Small Birds for Laboratory Analysis)	5 %		Hematocrit tubes sealed with hematocrit tube sealant	Fresh blood pre-treated with sodium heparin	8 hours	NA	NA	95%	

^(a) Samples will be field filtered through a 0.45 um for dissolved analyses.

^(b) Suspended sediment analyses will be performed on residue from 0.45 um filtration of surface water collected during high-flow sampling events.