
Stream Sediment Monitoring Sampling and Analysis Plan Green River Basin

August 17, 2012

Final



King County

Department of Natural Resources and Parks
Water and Land Resources Division

Science and Technical Support Section

King Street Center, KSC-NR-0600
201 South Jackson Street, Suite 600
Seattle, WA 98104
206-477-4800 TTY Relay: 711
www.kingcounty.gov/EnvironmentalScience

Alternate Formats Available

206-477-4800 TTY Relay: 711

THIS PAGE INTENTIONALLY LEFT BLANK

Stream Sediment Monitoring Sampling and Analysis Plan: Green River Basin Final

Dean Wilson, Project Manager
Streams Sediment Monitoring

Jean Power, Technical Coordinator
King County Environmental Laboratory

Fritz Grothkopp, Laboratory Project Manager
King County Environmental Laboratory

Colin Elliott, QA Officer
King County Environmental Laboratory

Table of Contents

1.0.	Project Background	1
1.1	Scope of Work.....	1
1.2	Project Questions	2
1.3	Sampling Strategy.....	2
1.3.1	Monitoring Program Streams	2
1.3.2	Stream Basin Analysis.....	2
1.4	Tools to be used in analyzing the data.....	4
1.5	Data Requirements.....	4
1.6	Chemical Testing.....	4
1.6.1	Data Quality Objectives	5
1.6.2	Precision, Accuracy, and Bias.....	7
1.6.3	Representativeness.....	7
1.6.4	Completeness.....	7
1.6.5	Comparability	8
2.0.	Sample Collection Methods and Techniques	9
2.1	Sampling Equipment.....	9
2.2	Sample Collection Location	9
2.3	Sample Collection and Processing.....	10
2.4	Sampler Decontamination	11
2.5	Sample Documentation	11
2.5.1	Sample Numbers and Labels.....	11
2.5.2	Field Notes	11
3.0.	Sample Handling Procedures	13
3.1	Sample Containers and Labels	13
3.2	Sample Preservation and Storage Requirements	14
3.3	Chain-of-Custody Procedures.....	15
4.0.	Laboratory Analytical Methods.....	16
4.1	Conventional Analyses and Detection Limits	17
4.2	Metal Analyses and Detection Limits	17

4.3	Organic Analyses and Detection Limits.....	18
4.4	Dioxin/Furan Analyses and Detection Limits	21
4.5	Quality Assurance/Quality Control (QA/QC) Practices.....	22
4.5.1	Analyses by KCEL.....	23
4.5.2	Dioxin/Furans	24
4.6	Data Qualifiers.....	25
5.0.	Data Review and Record Keeping.....	26
5.1	Data Review.....	26
5.2	Record Keeping.....	26
6.0.	Health and Safety Requirements.....	27
7.0.	References.....	28

Tables

Table 1.	Station Locations	3
Table 2.	Department of Ecology Proposed Freshwater Sediment Guidelines (2003)	5
Table 3.	Smith et al. Guidelines (1996).....	6
Table 4.	Sample Containers, Storage Conditions, Preservation and Analytical Hold Times.....	13
Table 5.	Conventional Methods and Detection Limits	17
Table 6.	Total Metals, Methods, and Detection Limits (mg/Kg wet weight).....	17
Table 7.	SEM Metals, Methods, and Detection Limits (mg/Kg wet weight).....	18
Table 8.	BNA Target Analytes and Detection Limits (µg/Kg wet weight).....	19
Table 9.	Chlorinated Pesticide/PCB Target Analytes and Detection Limits (µg/Kg wet weight)	20
Table 10.	EDC Target Analytes, Methods, and Detection Limits (µg/Kg wet weight)	21
Table 11.	Labeled Surrogates and Recovery Standards Used for EPA Method 1613b Dioxins/Furans Congener Analysis	21
Table 12.	Dioxin/furan solids sample detection limit goals in pg/g and lower calibration limit goals	22
Table 13.	Sediment Chemistry Quality Control Samples	23
Table 14.	QC Acceptance Criteria for Sediment Chemistry Samples.....	23

Table 15. Dioxins/furans QA/QC Frequency and Acceptance Criteria.....24
Table 16. KCEL Data Qualifier Flags and Conditions to Qualify.....25

Appendices

Appendix A. Metals Performance-Based QC Limits Tables
Appendix B. Organics Performance-Based QC Limits Tables
Appendix C. Laboratory Information Management System (Lims) Products and List Types

1.0. PROJECT BACKGROUND

This sampling and analysis plan (SAP) documents the project information and sampling and analytical methodologies for the Streams Sediment Monitoring Program. The SAP outlines the sample collection and analytical methods to evaluate bulk sediment chemical concentrations in four stream basins that drain to the Green River. Bulk sediment chemical concentrations will be monitored to better understand the potential sources of sediment-associated chemicals to the Green and Duwamish Rivers.

The methods and sampling strategies documented here were part of the King County Water and Land Resources Division (WLRD) 10-year stream sediment monitoring program, which was initiated in 2004. The program was developed using stream sediment data that had been collected between 1987 and 2002. The 10-year program was designed to collect data from the upper portions of stream basins to identify potential contaminant sources that may have contributed to concentrations found at the stream mouths in the earlier study. It was also designed to better characterize the variety of chemicals found in stream sediments by evaluating a broader range of chemicals including different categories of organic chemicals. In addition, the original stream sediment monitoring program included a limited number of sampling locations in the Green River watershed. The updated 10-year program added several Green River basin creeks to the program. For further information on the Streams Sediment Program design, see the Streams Sediment Monitoring Sampling and Analysis Plan (King County 2004).

However, budget constraints resulted in the elimination of the 10-year monitoring program before it could be completed. Several streams that were slated to be sampled but were not, are located in the Green River basin. Interest in characterizing contaminants within tributaries to the Green River, as well as within upper and lower boundary locations along the mainstem of the Green River has resulted in new investigations focused on understanding the sources of contaminants to the Green/ Duwamish River system (e.g., King County 2011). The streams sediment sampling in the Green River Basin outlined in this SAP will support these characterization studies.

1.1 Scope of Work

This project will involve collection of sediment samples in wadeable streams in the Green River Basin including: Mill (Hill) Creek in Auburn, Mill Creek in Kent, Jenkins Creek, and Covington Creek. Samples will also be collected in the main stem Green River, both up- and downstream of where the streams listed above drain to the Green River. Where feasible, bulk sediment samples will be collected approximately every mile between the mouth and the headwaters of each stream. These samples will be analyzed for metals, semi-volatile organic compounds, polychlorinated biphenyls (PCBs), organochlorine pesticides and conventional parameters. A subset of samples collected from Mill (Auburn) and Mill (Kent) at the stations closest to the mouths of the streams, and from the Green River at the station farthest upstream (Flaming Geyser) and the farthest downstream (Foster Links golf course) will be analyzed for dioxins/furans. Samples were previously collected from Soos,

Newaukum, and Springbrook Creeks and analyzed for all of the parameters listed above except dioxins/furans. Therefore, composite samples will be collected at the mouths of these streams (Soos, Newaukum, and Springbrook) for the analysis of dioxins and furans.

1.2 Project Questions

Questions the streams sediment program was designed to answer are as follows:

- How does sediment quality in streams compare to available sediment guidelines or thresholds?
- Are there other chemicals present in stream sediments that do not have guidelines?
- Are there differences in sediment quality within a monitored stream basin?
- Are there differences in sediment quality between the creeks and the Green River?
- How is sediment quality different among monitored streams that have similar sampling strata?

1.3 Sampling Strategy

1.3.1 Monitoring Program Streams

A targeted stratified design was used to select sampling locations. Streams were selected for inclusion in the sampling program if they met certain criteria. This sampling design is based on existing data as well as the types of environments to be characterized. Streams in the monitoring area were screened using data on basin size, stream gradient, road density (as a measure of urbanization), elevation, existing sediment quality data, and whether salmonids had ever been present.

The list of screening criteria is as follows:

- Wadeable streams
- Basin size between 2000 and 36,000 acres
- Stations located in areas with a stream gradient from 0 to 2 percent
- Historic use by salmonids
- Elevation characteristic of Puget Sound lowland streams
- Urban development is dominant human activity in basin
- Existing sediment quality data suggest current conditions may be of concern to the aquatic community

1.3.2 Stream Basin Analysis

Stream basin analyses will yield a better understanding of the processes that affect sediment quality, and allow use of a statistical approach for the characterization of sediment quality in depositional areas in the Green River watershed stream basins.

Stations have been located in every stream mile that meets the criteria listed above. A reconnaissance of the four creek basins and the Green River was conducted and the following sediment sampling stations were established as shown in Table 1.

Table 1. Station Locations

Stream Sediment Sampling Stations				
	Locator	x plan	y plan	Notes
Mill Creek (Auburn)				
1	A315	1289725	137218	Existing Site
2	SD315	1289415	133275	
3	FR315	1290680	129960	
4	TS315	1290765	127160	
5	ED315	1290545	122530	
6	MS315	1288980	115860	
7	PR315	1287170	113555	
8	PC315	1281940	117340	
9	UH315	1281775	118130	
10	LD315	1280650	126365	
Mill Creek (Kent)				
1	IT318	1292010	163195	
2	DT318	1291450	158960	
3	FS318	1291205	155285	
4	CS318	1292480	150045	
5	AA3t18	1294800	146780	
6	EP318	1295940	142700	
7	EG318	1301075	135305	
8	SH318	1299685	137710	
Covington Creek				
1	AB320	1321350	119105	
2	CC320	1324280	116570	
3	C320	1327045	116490	
4	CD320	1329470	113590	
5	PT320	1338290	122575	
6	Z320	1339866	124875	Existing Site
7	S320	1346550	126070	
Jenkins Creek				
1	D320	1319039	126881	Existing Site
2	WX320	1322235	129990	
3	JK320	1325834	133151	Existing Site
4	FR320	1326790	137155	

Stream Sediment Sampling Stations				
	Locator	x plan	y plan	Notes
5	DT320	1331205	140380	
6	LW_20	1339395	140055	
Green River				
1	FL319	1288012	177997	Existing Site- Foster Links
2	0318	1294280	134927	Existing Site
3	A319	1307302	113108	Existing Site
4	FG319	1341097	104038	Existing Site-Flaming Geyser

1.4 Tools to be used in analyzing the data

- Freshwater sediment quality standards for the State of Washington are not available; therefore, chemical concentrations will be compared to Ecology's proposed freshwater sediment quality guidelines and other available thresholds and guidelines (i.e. Washington State Department of Ecology & Avocet Consulting, 2003, and Smith et al., 1996.)
- GIS will be used to map the spatial distribution of chemical concentrations and exceedances of sediment guidelines or thresholds.
- AVS/SEM ratios will be used to better understand the bioavailability of metals.

1.5 Data Requirements

The data requirements for both characterizations of the parameter concentrations and comparison with sediment quality guidelines require independent samples. For t-tests and calculation of means and standard deviations normally distributed data are required. If data are not normally distributed, appropriate statistics for use will be determined.

1.6 Chemical Testing

Sediment samples will be collected for chemical testing using standardized equipment and procedures.

Conventional parameters. Particle size distribution (PSD), pH, total solids, total organic carbon (TOC) and acid volatile sulfides (AVS) will be analyzed.

Metals. Simultaneously extractable metals (AVS/SEM for arsenic, cadmium, copper, lead, mercury, nickel, silver, and zinc). Total metals analysis to include arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc.

Organics. Base/neutral/acid extractable semivolatile compounds (BNAs), endocrine disrupting compounds (EDCs) (4-nonylphenol, bisphenol A, bis(2-ethylhexyl)adipate, coprostanol), chlorinated pesticides, and PCBs (as Aroclors).

Dioxin/Furan. 17 dioxin/furan (D/F) congeners.

1.6.1 Data Quality Objectives

It is the intent of this study to produce data of sufficient quality to be able to meet the following project goals:

- To evaluate sediment quality conditions in stream basins.
- To compare sediment data to available proposed sediment quality guidelines. For constituents that do not have proposed guidelines, literature values may be used to better understand the effects of the concentrations found.

The sediment quality guidelines chosen for comparison and interpretation of the streams sediment monitoring data are shown in Tables 2 and 3.

Table 2. Department of Ecology Proposed Freshwater Sediment Guidelines (2003)

Compound or Element	Guideline	Units (dry wt)
2-Methylnaphthalene	470	PPB
Acenaphthene	1060	PPB
Acenaphthylene	470	PPB
Anthracene	600	PPB
Antimony	0.4	PPM
Aroclor 1254	230	PPB
Arsenic	20	PPM
Benzo(a)anthracene	4260	PPB
Benzo(a)pyrene	3300	PPB
Benzo(g,h,i)perylene	4020	PPB
Bis(2-ethylhexyl) phthalate	230	PPB
Butyl benzyl phthalate	260	PPB
Cadmium	0.6	PPM
Chromium	95	PPM
Chrysene	5940	PPB
Copper	50	PPM
Dibenz(a,h)anthracene	300	PPB
Dibenzofuran	400	PPB
Dimethyl phthalate	46	PPB
Di-n-octyl phthalate	26	PPB
Fluoranthene	5000	PPB
Fluorene	200	PPB
Total HPAHs	3000	PPB
Indeno(1,2,3-c,d)pyrene	4120	PPB
Lead	335	PPM

Compound or Element	Guideline	Units (dry wt)
Total LPAHs	500	PPB
Mercury	0.5	PPM
Naphthalene	100	PPB
Nickel	55	PPM
Phenanthrene	6100	PPB
Pyrene	3000	PPB
Silver	0.55	PPM
Total Benzofluoranthenes (b,j,k)	450	PPB
Total PCBs	60	PPB
Zinc	140	PPM
Aroclor 1260	140	PPB

Notes:

HPAHs – High molecular weight PAHs

LPAHs – Low molecular weight PAHs

Total LPAHs is the sum of detected naphthalene, 2-methyl naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene.

Total HPAHs is the sum of detected fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene.

Total PCBs is the sum of the detected Aroclors

Table 3. Smith et al. Guidelines (1996)

Compound or Element	Guideline	Units (dry wt)
Arsenic	5.9	PPM
BAA (Benzo(a)anthracene)	31.7	PPB
BAP (Benzo(a)pyrene)	31.9	PPB
Cadmium	0.596	PPM
Chlordane	4.5	PPB
Chromium	37.3	PPM
Chrysene	57.1	PPB
Copper	35.7	PPM
Total DDT	7	PPB
Dieldrin	2.85	PPB
Endrin	2.67	PPB
Fluoranthene	111.3	PPB
HEPCL_EPOX (Heptachlor epoxide)	0.6	PPB
Lead	35	PPM
Lindane	0.94	PPB

Compound or Element	Guideline	Units (dry wt)
Mercury	0.174	PPM
Nickel	18	PPM
Total PCBs	34.1	PPB
Phenanthrene	41.9	PPB
4,4'-DDD	3.54	PPB
4,4'-DDE	1.42	PPB
Pyrene	53	PPB
Zinc	123.1	PPM

Project data will undergo rigorous quality assurance review, which will assess, among other things, precision and bias, representativeness, completeness, and comparability. Data will be reviewed according to Quality Assurance 1 (QA1) guidelines (PTI, 1989a).

1.6.2 Precision, Accuracy, and Bias

Precision is the agreement of a set of results among themselves and is a measure of the ability to reproduce a result. Accuracy is an estimate of the difference between the true value and the determined mean value. The accuracy of a result is affected by both systematic and random errors. Bias is a measure of the difference, due to a systematic factor, between an analytical result and the true value of an analyte. Precision, accuracy, and bias for analytical chemistry may be measured by the analysis of various laboratory QC samples such as method blanks, matrix spikes, certified reference materials, and laboratory duplicates or triplicates.

1.6.3 Representativeness

Representativeness expresses the degree to which sample data accurately and precisely represent a characteristic of a population, parameter variations at the sampling point, or an environmental condition. Samples will be collected from stations with preselected coordinates to represent specific site locations. Following the guidelines described for sampler decontamination, sample acceptability criteria, and sample processing will help ensure that samples are representative.

1.6.4 Completeness

Completeness is defined as the total number of samples analyzed for which acceptable analytical data are generated, compared to the total number of samples to be analyzed. Sampling at stations with known position coordinates in favorable conditions, along with adherence to standardized sampling and testing protocols will aid in providing a complete set of data for this project. The goal for completeness is 100 percent. If 100 percent completeness is not achieved, the study project manager will evaluate if the data quality objectives can still be met or if additional samples may need to be collected and analyzed.

1.6.5 Comparability

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another. This goal is achieved through using standard techniques to collect and analyze representative samples, along with standardized data validation and reporting procedures. By following the guidance of this SAP, the goal of comparability will be achieved.

2.0. SAMPLE COLLECTION METHODS AND TECHNIQUES

This section describes sample collection procedures that will be followed to help ensure that program data quality objectives are met. Included in this section are health and safety requirements, station positioning, sample collection and processing procedures, and field documentation.

2.1 Sampling Equipment

- Pre-cleaned PVC core tubes. King County Environmental Laboratory (KCEL) uses 2 ¾" x 3' tubes with one end filed to tapered edges to form a penetrating edge.
- Petite Ponar sediment sampler
- Set of pre-labeled sampling containers. For current King County routine streams project, this includes containers for metals, organics, conventionals, and subcontracted parameters. See Section 3.1 for container type, preparation, and sample volumes.
- Stainless steel spoon for collecting sample if core tube is not appropriate
- Stainless steel spatula, spoons, and bowl for compositing and splitting sample
- Sturdy nitrile or PVC gloves for sample collection from stream
- Lab quality nitrile gloves for compositing and splitting samples
- Field sheets with a clipboard and waterproof pens
- Scientific collection permit if appropriate
- Field clothes and safety gear, including orange traffic vest
- Digital camera
- Handheld GPS
- Several plastic 5 gallon carboys of laboratory RO water for equipment cleaning
- Detergent 8 and scrub brush
- Coolers with ice and plastic barrier

2.2 Sample Collection Location

As outlined in the EPA method for sampling streams sediments (EPA, 1999), "contaminants are more likely to be concentrated in sediments typified by fine particle size and high organic matter content. This type of sediment is most likely to be collected from depositional zones." For this reason, KCEL personnel will attempt to select a sampling location where fines are present. If no such location can be found, a location with the

smallest grain size observed will be sampled, and this will be noted on the field sheet. If appropriate, a handheld GPS will be used to acquire and record NAD83 coordinates for latitude and longitude of the location.

2.3 Sample Collection and Processing

Samples from the tributary streams are collected from beneath a shallow aqueous layer (<2 ft) using a pre-cleaned PVC core tube to penetrate the bottom sediment of the stream to a depth of 5 to 10 centimeters. A stainless steel spatula or gloved hand is inserted under the core tube mouth to trap the sediment inside, and the tube is removed from the stream. The tube can be slowly angled to the side to allow excess water to drain off, but care should be taken not to allow any fines to escape. The sediment in the tube is then transferred into the stainless steel compositing container. This process is repeated a minimum of five times to acquire an appropriate amount of material to fill all sample containers after compositing. If core tube penetration is poor, or streambed is rocky or gravelly, or if additional sediment volume is needed to fill all sample containers, additional core tubes may be collected.

If there is excess water in the compositing container after material is collected, it will be decanted off once fines have been allowed to settle. A stainless steel spoon or spatula is used to homogenize the sample by stirring. Rocks or other debris a half inch in diameter or larger can be removed and discarded.

If fine sediments at the sampling site are present but are confined to areas smaller than approximately 3"x 3", a pre-cleaned stainless steel spoon will be used to acquire the subsamples. This method works well in areas that are out of the main flow of the stream, which is where depositional areas are located. Care will be taken to insure that fine material will not be lost during subsample collection.

At the Foster Links site on the Green River mainstem, sediment will be collected using a Petite Ponar device lowered from the golf cart bridge over the river. A minimum of three casts will be collected from the top 5 to 10 centimeters and composited before homogenization of the sediment in a stainless steel bowl. Once sufficient sediment has been collected in the stainless steel bowl, it will be thoroughly mixed. Any particles greater than 2 centimeters in size will be removed from the sample and returned to the river. After mixing, samples will be placed into pre-cleaned sample containers provided by KCEL.

It is possible that not all stations will yield sufficient sample volume to allow completion of all requested analyses. Analyses have been ranked in order of decreasing priority, as follows:

- Total PCBs (as Aroclors)
- Metals and mercury
- Conventional analyses (PSD, total solids, TOC, and pH)
- BNA and selected other organic compounds
- Dioxin/Furan
- Organochlorine pesticides

- AVS/SEM

Note: The exception to the sediment compositing regime is the collection of a sample aliquot for analysis of AVS/SEM. This aliquot should be collected from the first acceptable grab and placed immediately into the appropriate container (no headspace).

2.4 Sampler Decontamination

Prior to arriving on site, core tubes are cleaned in the lab with detergent 8, soaking in a 5 % acid solution, and finally rinsed with deionized water. After air drying, both ends of the tubes are covered with foil.

Once in the field, both the Ponar sampler and the core tubes will be decontaminated between sampling stations by scrubbing with a brush to remove excess sediment, and a thorough *in situ* rinsing. The use of a phosphate-free detergent solution will be optional. Solvent or acid decontamination of samplers in the field is not recommended to prevent the introduction of these chemicals into the sampling environment. A pre-cleaned stainless steel spoon and bowl (compositing container) will be used at each location as necessary. Spoons and bowls used at one location will be transported back to the laboratory for cleaning before any additional field use.

2.5 Sample Documentation

This section provides guidance for documenting sampling and data gathering activities. The documentation of field activities provides important project information and data that can support data generated by laboratory analyses.

2.5.1 Sample Numbers and Labels

Sample locations will be identified using a unique locator name. The locator name, the date of collection and the unique sample identification number generated by KCEL will identify individual samples collected at each location. Sample numbers will be assigned prior to the sampling event and waterproof labels generated for each sample container.

2.5.2 Field Notes

Field notes will be maintained for all field activities, both the collection of samples and the gathering of environmental data. Field notes will be kept on water-resistant paper and all field documentation will be recorded in indelible, black or blue ink. Field notes will be recorded on pre-printed field sheets, prepared specifically for this project. Information recorded on field notes will include, but not be limited to:

- name of recorder
- sample or station number
- sample station locator information
- date and time of sample collection

- physical characteristics of sediment such as color, gross grain size distribution, debris, and odor
- GPS coordinates, if collected
- # of individual grabs collected

Additional information that may be recorded on the field sheets includes sampling methodology and any deviations from established sampling protocols. Additional anecdotal information pertaining to observations of unusual sampling events or circumstances may also be recorded on the field sheets.

3.0. SAMPLE HANDLING PROCEDURES

Consistent sample handling procedures are necessary to maintain sample integrity and provide high-quality defensible data. This section provides requirements for proper sample containers, labeling, preservation and storage, and chain-of-custody.

3.1 Sample Containers and Labels

All samples will be collected into pre-cleaned, laboratory-supplied containers affixed with computer-generated labels. Sample containers will be selected based on Puget Sound Protocol guidelines (PSEP, 1996). Information contained on sample labels will include: a unique sample number; information about the sampling location; the collection date; the requested analyses; and information about any chemical used in sample preservation. Sample containers are summarized in Table 4.

Table 4. Sample Containers, Storage Conditions, Preservation and Analytical Hold Times

Analyte	Container	Preferred Storage Conditions	Hold Time	Acceptable Storage Conditions	Hold Time
Particle Size Distribution	16-oz. CWM PP or glass (collect one extra 16-oz container per 20 samples for QC)	refrigerate at 4°C	6 months to analyze	N/A	N/A
Total Organic Carbon (TOC)	4-oz. CWM PP or glass	freeze at -18°C	6 months to analyze	refrigerate at 4°C	14 days to analyze
Total Solids (collect w/ TOC)	4-oz. CWM PP or glass	freeze at -18°C	6 months to analyze	refrigerate at 4°C	14 days to analyze
pH	4-oz. CWM PP or glass	refrigerate at 4°C	1 day	N/A	N/A
Acid Volatile Sulfide (AVS)	4-oz. CWM PP or glass	refrigerate at 4°C No headspace	14 days to analyze	N/A	N/A
Mercury (Hg) (collect with other metals)	4-oz. CWM PP	freeze at -18°C	28 days to analyze	N/A	N/A
SEM Mercury (collect w/AVS; distill w/other SEM metals)	500-ml acid washed HDPE	room temperature	14 days to analyze	N/A	N/A

Analyte	Container	Preferred Storage Conditions	Hold Time	Acceptable Storage Conditions	Hold Time
Other Metals (collect w/Mercury)	4-oz. CWM PP	freeze at -18°C	2 years to analyze	refrigerate at 4°C	6 months to analyze
SEM Metals (collect w/AVS; distill w/SEM Mercury)	500-ml acid washed HDPE	room temperature	14 days to analyze	N/A	N/A
BNAs, including PAHs, phthalates, EDCs and other compounds	16-oz. glass	freeze at -18°C	1 year to extract 40 days to analyze	refrigerate at 4°C	14 days to extract 40 days to analyze
Organochlorine pesticides/PCBs	16-oz. glass	freeze at -18°C	1 year to extract 40 days to analyze	refrigerate at 4°C	14 days to extract 40 days to analyze
Dioxins/furans	8-oz. glass	freeze at -10°C	1 year to extract 1 year to analyze	N/A	N/A

Notes:

BNAs – base/neutral/acid extractable semivolatile organic compounds

PP - polypropylene

CWM PP – Clear, wide-mouth polypropylene

3.2 Sample Preservation and Storage Requirements

All samples will be kept in ice-filled coolers until delivery to KCEL on the day of collection. No additional preservative is required for solids samples. Sediment samples will be stored under chain of custody at the KCEL and maintained as such throughout the analytical process. Depending on the type of analysis, samples will be stored either refrigerated at a temperature of approximately 4° C or frozen at approximately -18° C. Sample preservation requirements and storage conditions as well as analytical holding times are summarized in the table above.

Dioxin/furan samples will be wrapped in individual Ziploc bags and shipped frozen in coolers with ice or frozen gel packs to AXYS Analytical Services (AXYS) via overnight delivery within four to eight weeks of sample collection. The temperature inside the cooler(s) containing dioxin/furan samples will be checked upon receipt at AXYS. AXYS will also assign each dioxin/furan sample with a unique laboratory number for tracking within their system.

3.3 Chain-of-Custody Procedures

Field chain-of-custody (COC) procedures will be followed from the time a sample is collected until it is relinquished to the analytical laboratory. COC documentation will be initiated when the first sample is collected and updated continuously throughout the sampling event. Documentation will be completed for each day of field sampling. Information to be included on the documentation is sample number, date and time of sampling, names of all sampling personnel and requested analyses. A sample will be considered to be “in custody” when in the possession of sampling personnel or in a secured sampling area such as locked in a field vehicle. Samples will not be considered in custody when left unattended in the field or in an unlocked field vehicle. Custody seals will be placed on the sample cooler when it is not in the custody of a member of the sampling team.

COC will be maintained throughout the analytical phase of the project according to standard KCEL protocols and any subcontracting laboratory standard operating protocols. Copies of COC forms will accompany dioxin/furan samples being shipped to AXYS. Once completed, original COC forms will be archived in the project file at KCEL.

4.0. LABORATORY ANALYTICAL METHODS

This section presents the chemical analytical methodologies that will be employed during this project, along with associated detection limits where appropriate. Adherence to standardized analytical protocols and associated quality assurance/quality control (QA/QC) guidelines for chemical testing will help produce data able to undergo the rigors of QA1 data analysis and meet the project goals and objectives. KCEL will conduct all chemical and conventional analyses except dioxin/furans. Dioxin/furans will be analyzed by AXYS Analytical Services.

For chemical analyses, the KCEL distinguishes between a *method* detection limit (MDL) and a *reporting* detection limit (RDL).

- The MDL is defined as the minimum concentration of a chemical constituent that can be detected.
- The RDL is defined as the minimum concentration of a chemical constituent that can be reliably quantified. The RDL can be considered equivalent to a Practical Quantitation Limit (PQL).

Actual KCEL MDLs and RDLs may differ from the target detection limit goals as a result of necessary analytical dilutions or a reduction of extracted sample amounts based on a preliminary examination of the sample (including total solid values). When sample extracts are diluted because the concentrations for one or more target analytes exceed the upper end of the calibration curve or parameter specific interferences, MDLs and RDLs from the original, undiluted extract will be reported for parameters other than the target analytes that required dilution. Every effort will be made to meet the MDL/RDL goals listed in the SAP. However there may be times when the MDL/RDL values rise because the sample must be run at a greater dilution. This may be due to the concentration of some target analytes exceeding the calibration range, interfering target or non-target compounds, or run QC not passing (e.g., internal standard failures). Non-detected target analytes will be reported from the lowest dilution possible (no interferences and the run QC must pass). Target analytes that are detected must be reported from an appropriate dilution. The dilution chosen must have no interferences, the run QC must pass, and wherever possible the value that is greater than the RDL will be chosen.

For dioxin/furan high resolution isotopic dilution based methods, the MDL and RDL terms are less applicable because limits of quantitation are derived from calibration capabilities and ubiquitous but typically low level equipment and laboratory blank contamination. Additional reporting limit terms used for dioxin/furan congener analyses are: sample specific detection limit (SDL), and lowest method calibration limits (LMCL). The SDL is determined by converting the area equivalent to 2.5 times the estimated chromatographic noise height to a concentration. SDLs are determined individually for every congener of each sample analysis run and accounts for any effect of matrix on the detection system and

for recovery achieved through the analytical work-up. LMCLs are based on calibration points from standard solutions. They are prorated by sample size and are supported by statistically derived method reporting limit (MRL) values. The dioxin/furan congener data will be reported to LMCL and flagged as estimates down to the SDL value. In many cases the SDL may be below the LMCL.

4.1 Conventional Analyses and Detection Limits

Conventional analyses, analytical methods and associated detection limits are summarized in Table 5. All conventional analyses will be performed at the KCEL.

Table 5. Conventional Methods and Detection Limits

Parameter	LIMS Product	LIMS Listtype	Method	MDL	RDL	Units
PSD (gravel and sand)	PSD	CVPSD	ASTM D422	0.1	1	percent dry wt.
PSD (silt and clay)	PSD	CVPSD	ASTM D422	0.5	1	percent dry wt.
Total Organic Carbon	TOC	CVTOC	EPA 9060, PSEP 1996	500	1,000	mg/Kg wet wt.
pH	PH	CVPH	SW846 9045D	N/A	N/A	pH
Total Solids	TOTS	CVTOTS	SM 2540-G	0.005	0.01	percent wet wt.
Acid Volatile Sulfide	AVS	CVAVS	EPA, Dec 1991	0.25	1	mg/Kg wet wt.

PSD: particle size distribution

ATSTM - American Society for Testing and Materials

SM - Standard Methods

4.2 Metal Analyses and Detection Limits

All metals analyses will be performed by the KCEL. Target elements, analytical methods, and associated detection limits are summarized in Table 6. With the exception of mercury, all metals will be analyzed by inductively coupled plasma mass spectroscopy (ICP-MS).

Table 6. Total Metals, Methods, and Detection Limits (mg/Kg wet weight)

Analyte	LIMS Product	LIMS listtype	Method	MDL	RDL
Silver	Ag-ICPMS	MTICPMS-SED, 6-SED	SW846 3050B*SW846 6020A	0.10	0.50
Arsenic	As-ICPMS	MTICPMS-SED, 6-SED	SW846 3050B*SW846 6020A	0.025	0.125
Cadmium	Cd-ICPMS	MTICPMS-SED, 6-SED	SW846 3050B*SW846 6020A	0.0125	0.0625
Chromium	Cr-ICPMS	MTICPMS-SED, 6-SED	SW846 3050B*SW846 6020A	0.050	0.25
Copper	Cu-ICPMS	MTICPMS-SED, 6-SED	SW846 3050B*SW846 6020A	0.10	0.50
Lead	Pb-ICPMS	MTICPMS-SED, 6-SED	SW846 3050B*SW846 6020A	0.025	0.125
Mercury	HG-CVAA-M	MTHG-MIDS, 6-SED	EPA 7471B	0.04	0.4
Nickel	Ni-ICPMS	MTICPMS-SED, 6-SED	SW846 3050B*SW846 6020A	0.025	0.125
Zinc	Zn-ICP	MTICPMS-SED, 6-SED	SW846 3050B*SW846 6020A	0.125	0.625

The MDLs and RDLs are presented on a wet-weight basis. The Total Metals MDL/RDLs are based on an initial analytical sample weight of 1 (± 0.05 g) and a final volume of 100 mL for mercury and 50 mL for all other metals. Sample weights will be increased if the total solids are low enough that, when dry-weight normalized, the sample-specific RDL will not meet the freshwater sediment quality reference values.

SEM-extract metals, with the exception of mercury, will be analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-OES). SEM-extract mercury will be analyzed by cold vapor atomic absorption (CVAA). Target SEM metals, methods and associated detection limits are summarized in Table 7. The SEM Metals MDL/RDLs are based on an initial analytical sample weight of 10 g and a final volume of 200 mL. The SEM Metals are extracted by the Conventional unit.

Table 7. SEM Metals, Methods, and Detection Limits (mg/Kg wet weight)

Analyte	LIMS Product	LIMS listtype	Method	MDL	RDL
Silver	Ag-SEM, EXT	MTICP-SEM, 6-SEM	EPA 821 1991/200.7*SW846 6010C	0.08	0.40
Arsenic	As-SEM, EXT	MTICP-SEM, 6-SEM	EPA 821 1991/200.7*SW846 6010C	0.5	2.5
Cadmium	Cd-SEM, EXT	MTICP-SEM, 6-SEM	EPA 821 1991/200.7*SW846 6010C	0.04	0.20
Chromium	Cr-SEM, EXT	MTICP-SEM, 6-SEM	EPA 821 1991/200.7*SW846 6010C	0.06	0.30
Copper	Cu-SEM, EXT	MTICP-SEM, 6-SEM	EPA 821 1991/200.7*SW846 6010C	0.08	0.40
Lead	Pb-SEM, EXT	MTICP-SEM, 6-SEM	EPA 821 1991/200.7*SW846 6010C	0.4	2.0
Mercury	Hg-SEM, EXT	MTHG-SEM, 6-SEM	EPA 821 1991/200.7*SW846 6010C	0.001	0.003
Nickel	Ni-SEM, EXT	MTICP-SEM, 6-SEM	EPA 821 1991/200.7*SW846 6010C	0.1	0.5
Zinc	Zn-SEM, EXT	MTICP-SEM, 6-SEM	EPA 821 1991/200.7*SW846 6010C	0.1	0.5

4.3 Organic Analyses and Detection Limits

All organic analyses except dioxins/furans will be performed by the KCEL. Organic parameters will include BNAs, EDCs, organochlorine pesticides and PCBs (as Aroclors). The analytical methods and detection limits for the target organic compounds are summarized on a wet-weight basis below.

The detection limits for the target BNASMS compounds are summarized in Table 8. BNASMS analysis is performed according to EPA methods 3550C/8270D (SW 846), which employs solvent extraction with sonication and analysis by gas chromatography/mass spectroscopy (GC/MS). The LIMS product for reporting these analytical parameters is BNASMS, and the corresponding listtype is ORBNASMS.

Table 8. BNA Target Analytes and Detection Limits ($\mu\text{g}/\text{Kg}$ wet weight)

Analyte	MDL	RDL	Analyte	MDL	RDL
1,2,4-Trichlorobenzene	0.53	1.07	Dibenzofuran	5.3	10.7
1,2-Dichlorobenzene	5.33	5.33	Diethyl phthalate	11	21.3
1,4-Dichlorobenzene	8.00	8.00	Dimethyl phthalate	10.7	10.7
2,4-Dimethylphenol	5.3	10.7	Di-n-butyl phthalate	11	21.3
2-Methylnaphthalene	5.3	10.7	Di-n-octyl phthalate	10.7	10.7
2-Methylphenol	5.3	10.7	Fluoranthene	5.3	10.7
3-,4-Methylphenol	27	53.3	Fluorene	5.3	10.7
Acenaphthene	5.3	10.7	Hexachlorobenzene	0.53	1.07
Acenaphthylene	5.3	10.7	Hexachlorobutadiene	2.7	5.33
Anthracene	5.3	10.7	Indeno(1,2,3-cd)pyrene	5.3	10.7
Benzo(a)anthracene	5.3	10.7	Naphthalene	5.3	10.7
Benzo(a)pyrene	5.3	10.7	N-Nitrosodiphenylamine	13.3	13.3
Benzo(b,j,k)fluoranthene	5.3	10.7	Pentachlorophenol	80.0	80.0
Benzo(g,h,i)perylene	5.3	10.7	Phenanthrene	5.3	10.7
Benzoic acid	107	107	Phenol	27	80.0
Benzyl alcohol	13.3	13.3	Pyrene	5.3	10.7
Benzyl butyl phthalate	8.00	8.00	Total LPAHs	5.3	10.7
Bis(2-ethylhexyl) phthalate	11	21.3	Total HPAHs	5.3	10.7
Chrysene	5.3	10.7	Total 4-nonylphenol	53	107
Dibenzo(a,h)anthracene	5.3	10.7	Carbazole***	5.3	10.7

*** Carbazole will be added to the ORBNASMS list type for the purposes of this project only.

Note: MDL and RDLs based upon a standard 30 g to 1 ml final volume with GPC clean up

Prior to BNA preparation and analysis, the total solid results will be used to verify that the standard 30 g to 1 ml extraction will allow analyte LIMS RDLs to meet the proposed freshwater sediment guidelines (see Table 2 and Table 3). If necessary, the extraction sample amount and final volumes will be adjusted accordingly to ensure that the LIMS RDL is at or below the appropriate criteria value.

The MDL and RDL for specific analytes requiring dilution (e.g., exceedance of analyte calibration range) will be increased to reflect the dilution. In cases where a dilution is necessitated by a matrix interference or other sample issue, and the resulting LIMS RDL for a specific analyte exceeds the specified criteria and the analyte is not detected, the LIMS RDL exceedance of the criteria will be discussed with the project manager and noted in the appropriate analytical case narrative.

The detection limits for the target chlorinated pesticide/PCB compounds are summarized in Table 9. Chlorinated pesticide/PCB analysis is performed according to EPA methods 3550C/8081B/8082A (SW 846), which employs solvent extraction with sonication and analysis by gas chromatography/electron capture detector (GC/ECD) with dual column confirmation. The LIMS products for this analysis CLPEST and PCB and listtypes are ORCLPEST and ORPCB.

Table 9. Chlorinated Pesticide/PCB Target Analytes and Detection Limits (µg/Kg wet weight)

Analyte	MDL	RDL	Analyte	MDL	RDL
Aroclor 1016	1.3	5.33	Delta-BHC	0.53	1.07
Aroclor 1221	2.7	5.33	Dieldrin	0.53	1.07
Aroclor 1232	2.7	5.33	Endosulfan I	0.53	1.07
Aroclor 1242	1.3	5.33	Endosulfan II	0.53	1.07
Aroclor 1248	1.3	5.33	Endosulfan Sulfate	0.53	1.07
Aroclor 1254	1.3	5.33	Endrin	0.53	1.07
Aroclor 1260	1.3	5.33	Endrin Aldehyde	0.53	1.07
4,4'-DDD	0.53	1.07	Gamma-BHC (Lindane)	0.53	1.07
4,4'-DDE	0.53	1.07	trans-Chlordane	0.53	1.07
4,4'-DDT	0.53	1.07	Heptachlor	0.53	1.07
Aldrin	0.53	1.07	Heptachlor Epoxide	0.53	1.07
Alpha-BHC	0.53	1.07	Methoxychlor	2.7	5.33
Alpha-Chlordane	0.53	1.07	Toxaphene	11	53.3
Beta-BHC	0.53	1.07			

Note: MDLs and RDLs based upon a split 30 g extraction to a final volume of 2 mls for pesticides and 1 ml for PCBs with GPC clean up.

Prior to pesticide/PCB preparation and analysis, the total solid results will be used to verify that the planned extraction regime will allow analyte LIMS RDLs to meet the proposed freshwater sediment guidelines (see Table 2 and Table 3). If necessary, the extraction sample amount and final volumes will be adjusted accordingly to ensure that the LIMS RDL is at or below the appropriate criteria value.

The MDL and RDL for specific analytes requiring dilution (e.g., exceedance of analyte calibration range) will be increased to reflect the dilution. In cases where a dilution is necessitated by a matrix interference or other sample issue, and the resulting LIMS RDL for a specific analyte exceeds the specified criteria and the analyte is not detected, the LIMS RDL exceedance of the criteria will be discussed with the project manager and noted in the appropriate analytical case narrative.

The target list for the EDC organic compounds and associated MDLs and RDLs are listed below in Table 10. The LIMS product is EDC and the corresponding list type is OREDC.

Table 10. EDC Target Analytes, Methods, and Detection Limits (µg/Kg wet weight)

Analyte	LIMS Product	LIMS listtype	Method	MDL	RDL
Bis(2-ethylhexyl)adipate	EDC	OREDC	SW846 3550B*SW846 8270D	110 *	533
Bisphenol A	EDC	OREDC	SW846 3550B*SW846 8270D	110 *	533
Total 4-nonylphenols	EDC	OREDC	SW846 3550B*SW846 8270D	110 *	533
Coprostanol	EDC	OREDC	SW846 3550B*SW846 8270D	530 *	1070

* There are no listed criteria for any of the EDC compounds. These wet weight detection limits may change based upon any required changes to the BNASMS extraction noted above.

Note: MDLs and RDLs based upon a typical 30 g to 1 ml final volume with GPC clean up.

4.4 Dioxin/Furan Analyses and Detection Limits

Dioxin/furan congener analysis will be performed according to EPA Method 1613B (EPA 1994), which is a high-resolution gas chromatography/high-resolution mass spectroscopy (HRGC/HRMS) method using an isotope dilution internal standard quantification. This method provides reliable analyte identification and very low detection limits. Labeled native and surrogate standards (Table 11) are added before samples are extracted. Data are “recovery-corrected” for losses in extraction and cleanup, and analytes are quantified against their labeled analogues or a related labeled compound.

AXYS will perform this analysis according to their Standard Operating Procedure (SOP) MLA-017 which is based on EPA Method 1613b Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS. Sample will be extracted followed by standard method clean-up, which includes layered Acid/Base Silica, Florisil, and Alumina.

Table 11. Labeled Surrogates and Recovery Standards Used for EPA Method 1613b Dioxins/Furans Congener Analysis

¹³C-labeled Congener Surrogate Standards	
Labeled analytes of interest are used for all dioxins and furans quantified except 1,2,3,7,8,9-HxCDD and OCDF	
³⁷Cl-labeled Cleanup Standards	
2,3,7,8 TCDD	
¹³C-labeled Internal (Recovery) Standards	
1,2,3,4 TCDD	1,2,3,7,8,9 HxCDD

Table 12 lists the 17 dioxin/furan congeners and their respective target SDL values. The reported SDLs for individual samples may differ from those in Table 12 since they are

determined by signal to noise ratios and changes to final volumes. Typical sample detection limits are shown.

Table 12. Dioxin/furan solids sample detection limit goals in pg/g and lower calibration limit goals

Analyte	Typical Detection Limit/SDL	LMCL based on Low Cal./RDL
Dioxins		
2,3,7,8 TCDD	0.5	2.0
1,2,3,7,8 PeCDD	0.1	5.0
1,2,3,4,7,8 HxCDD	0.1	5.0
1,2,3,6,7,8 HxCDD	0.1	5.0
1,2,3,7,8,9 HxCDD	0.1	5.0
1,2,3,4,6,7,8 HpCDD	0.1	5.0
OCDD	0.5	10.0
Furan		
2,3,7,8 TCDF	0.05	1.0
1,2,3,7,8 PeCDF	0.5	5.0
2,3,4,7,8 HxCDF	0.1	5.0
1,2,3,4,7,8 HxCDF	0.1	5.0
1,2,3,6,7,8 HxCDF	0.1	5.0
1,2,3,7,8,9 HxCDF	0.1	5.0
2,3,4,6,7,8 HxCDF	0.1	5.0
1,2,3,4,6,7,8 HpCDF	0.1	5.0
1,2,3,4,7,8,9 HpCDF	0.1	5.0
OCDF	0.55	10.0

SDL = sample detection limit

LMCL = lower method calibration limit

Note:SDL and LMCL based on EPA method 1613b, AXYS Analytical Services method MLA 017.

4.5 Quality Assurance/Quality Control (QA/QC) Practices

Chemistry data will undergo standard sediment QA1 review according to PSDDA guidelines (PTI, 1989a) and data will be flagged accordingly. This level of QA review is necessary to provide the project and program managers with the level of information needed to correctly interpret the data and allow evaluations of baseline sediment quality in the Green River watershed. QC data to be included with a QA1 review will include (but not be limited

t) results for matrix spikes and matrix spike duplicates, surrogate spikes, method blanks, certified reference materials, and analytical replicates.

4.5.1 Analyses by KCEL

The QC samples that will be analyzed in association with sediment conventional and chemical testing are summarized in Table 13.

Table 13. Sediment Chemistry Quality Control Samples

Analyte	Method Blank	Duplicate	Triplicate	Matrix Spike	SRM or LCS	Surrogates
PSD	No	No	Yes	No	No	No
TOC	Yes	No	Yes	Yes	Yes	No
pH	No	No	Yes	No	No	No
Total Solids	Yes	No	Yes	No	No	No
Acid Volatile Sulfide	Yes	No	Yes	Yes	No	No
Total Metals	Yes	Yes	No	Yes	Yes	No
SEM Metals	Yes	Yes	No	Yes	No	No
BNAs	Yes*	Yes	No	Yes**	Yes	Yes
Chlorinated Pesticides	Yes*	Yes	No	Yes**	Yes	Yes
EDC	Yes*	Yes	No	Yes**	No	Yes
PCBs	Yes*	Yes	No	Yes**	Yes	Yes

Yes* = A spiked blank will also be performed with each batch.

Yes** = A matrix spike duplicate will also be performed with each batch.

SRM – Standard Reference Material

LCS- Laboratory Control Sample

The recommended QC limits associated with sediment conventional and chemistry testing are summarized in Table 14. Laboratory performance-based QC limits are presented in appendices A and B for metals and organic compounds, respectively.

Table 14. QC Acceptance Criteria for Sediment Chemistry Samples

Analyte	Method Blank	Duplicate	Triplicate	Matrix Spike	SRM/LCS	Surrogates
PSD	N/A	N/A	RSD \leq 20% _s	N/A	N/A	N/A
TOC	< MDL	N/A	RSD \leq 20%	75 - 125%	80 - 120%	N/A
pH	N/A	N/A	RSD < 5%	N/A	N/A	N/A

Analyte	Method Blank	Duplicate	Triplicate	Matrix Spike	SRM/LCS	Surrogates
Total Solids	< MDL	N/A	RSD \leq 20%	N/A	N/A	N/A
Acid Volatile Sulfide	< MDL	N/A	RSD \leq 20%	65 – 135%	N/A	N/A
Metals/SEM Metals	< MDL	RPD \leq 20%	N/A	75 - 125%	perf-based	N/A
BNAs	< MDL	RPD \leq 35%	N/A	perf-based	perf-based	perf-based
Chlor. Pesticides	< MDL	RPD \leq 35%	N/A	perf-based	perf-based	perf-based
PCBs	< MDL	RPD \leq 35%	N/A	perf-based	perf-based	perf-based

< MDL - Method Blank result should be less than the method detection limit.

RPD - Relative Percent Difference

RSD - Relative Standard Deviation

N/A - Not Applicable

Metals matrix spike limits of 75 to 125% apply when the sample concentration is less than 4 times the spike concentration.

Metals performance based SRM acceptance criteria are listed in Table A1

QC results for matrix spike, SRM, and surrogates are in *percent recovery of analyte*.

Perf-based - The laboratory's performance-based control limits that are in effect at the time of analysis will be used as quality control limits.

4.5.2 Dioxin/Furans

Quality control samples include method blanks, ongoing-precision and recovery (OPR) samples, and surrogate spikes. Method blanks and OPR samples are each included with each batch of samples. Surrogate spikes are labeled compounds that are included with each sample. The sample results are corrected for the recoveries associated with these surrogate spikes as part of the isotope dilution method. In addition, a laboratory duplicate will be conducted with each batch of samples. Note that a matrix spike and matrix spike duplicate are not required, nor meaningful under Method 1613b. Method 1613b has specific requirements for method blanks that must be met before sample data can be reported (see section 9.5.2 of Method 1613b). The OPR samples must show acceptable recoveries, according to Method 1613b, in order to samples to be analyzed and data to be reported. A summary of the quality control samples are shown in Table 15.

Table 15. Dioxins/furans QA/QC Frequency and Acceptance Criteria

	Method Blank	Lab Duplicate (RSD)	OPR (% Recovery)	Surrogate Spikes
Frequency	1 per batch*	1 per batch*	1 per batch*	Each sample
Dioxins/furans	<LMCL ^a	RPD <50%	laboratory QC limits ^b	laboratory QC limits ^b

batch = 20 samples or less prepared as a set

^aEPA Method 1613B blank criteria (see Table 2 of the published method) is to be below the Minimum Levels: 0.5, 1.0, and 5 pg/g for the tetra, penta through hepta, and octa respectively

^bThe laboratory's performance-based control limits that are in effect at the time of analysis will be used as quality control limits.

LMCL = Lowest Method Calibration Limit

RSD = Relative Standard Deviation
 OPR = ongoing precision and recovery

4.6 Data Qualifiers

The data qualification flags which will be used by the KCEL for this project are presented in Table 16. These data qualifiers address situations that require qualification and conform to QA1 guidance (PTI, 1989a). The KC Lab qualifiers indicating <MDL and <RDL have been used as replacements for the *T* and *U* qualifier flags specified under QA1 guidance. QC results that do not meet the acceptance criteria outlined in this SAP will be evaluated to determine if the unacceptable data indicate that the reported results may be biased or otherwise impacted. Laboratory information management system (LIMS) products and list types are presented in Appendix C.

Table 16. KCEL Data Qualifier Flags and Conditions to Qualify

Condition to Qualify	Flag	Comment
Low matrix spike recovery	JG	
High matrix spike recovery	JL	
Low standard reference material recovery	JG	
High standard reference material recovery	JL	
High duplicate relative percent difference	J	
High triplicate relative standard deviation	J	
Less than the reporting detection limit	<RDL	
Less than the method detection limit	<MDL	
Contamination detected in method blank	B	>MDL and <5 times MB result ¹
Contamination detected in method blank	B2	Common Lab Contaminants ²
Contamination detected in method blank	B3	All other parameters between 5 and 10 times MB result ¹
Biased data based on low surrogate recoveries	JG	At least 2 surrogates < limit for BNAs
Biased data based on high surrogate recoveries	JL	At least 2 surrogates > limit for BNAs
Rejected – unusable for all purposes	R	
A sample handling criteria has not been met	SH	Container, preservation
Holding time not met	H	

¹Comparison of the method blank and sample results for applying B flags must be done on a wet-weight basis.

²Common Lab Contaminants: bis(2-ethylhexyl) phthalate, benzyl butyl phthalate, di-n-butyl phthalate.

5.0. DATA REVIEW AND RECORD KEEPING

5.1 Data Review

All sediment chemistry data will be reported in QA1 format (PTI 1989a). The final QA1 report will contain the following information and deliverables:

- A QA1 narrative discussing data quality in relation to study objectives and data criteria;
- All associated QC data (LIMS QC reports and worklists);
- Copies of field sheets and COC forms;
- A comprehensive report containing all analytical and field data (including data qualifier flags); and
- Data files in Environmental Information Management System (EIMS) format for delivery to Ecology.

All KCEL generated chemical analysis and associated conventional data will be validated against requirements of the reference methods as well as the requirements of this SAP. Data validation will be performed by the King County WLRD for all data generated by KCEL.

All necessary data needed for independent review of dioxin/furan data will be provided by AXYS. Data validation for dioxin/furan data may be conducted by either an outside party for this survey or by King County WLRD. A data validation memorandum will be produced and maintained along with the analytical data as part of the project records.

Chemical data generated during this project will be validated according to accepted Environmental Protection Agency (EPA) guidelines (EPA 2001, 2004 and 2005), where applicable. Validation of data generated by KCEL will be EPA Stage 2a. This level of validation includes reviews of holding times, method blanks, and QA/QC samples.

5.2 Record Keeping

All field and sampling records, custody documents, raw lab data, and summaries and narratives will be archived according to KCEL policy, for a minimum of 10 years from the date samples were collected.

These records will include both hard copy and electronic data. Conventional, Trace Metals and Trace Organics analytical data produced by the KCEL will be maintained on its LIMS database in perpetuity. AXYS will provide electronic deliverables of data and associated quality control results to King County. While KCEL will maintain a copy of deliverables from AXYS Analytical, copies of full data packages pertaining to King County samples analyzed by AXYS will be maintained by AXYS for 10 years from the analysis date.

6.0. HEALTH AND SAFETY REQUIREMENTS

The following general health and safety guidelines have been provided in lieu of a site-specific Health and Safety Plan. These guidelines will be read and understood by all members of the sampling crew prior to any sampling activities.

- Sampling personnel will wear chemical-resistant gloves whenever coming into contact with sediment.
- All sampling operations will be conducted during daylight hours.
- All accidents, “near misses,” and symptoms of possible exposure will be reported to a sampler’s supervisor within 24 hours of occurrence.
- All field members will be aware of the potential hazards associated with chemicals used during the sampling effort.

Contact with sediment at some sampling stations may present a health hazard from chemical constituents of the sediment. Potential routes of exposure to chemical hazards include **inhalation, skin and eye absorption, ingestion, and injection.**

Field staff will exercise caution to avoid coming into contact with sediment at all stations during sampling operations. Protective equipment will include chemical-resistant gloves, safety glasses or goggles, and protective clothing (e.g., chemical resistant coveralls, etc.). Field staff will exercise good personal hygiene prior to eating or drinking.

7.0. REFERENCES

- EPA, 1991. Analytical Method for Determination of Acid Volatile Sulfide and Selected Simultaneously Extractable Metals in Sediment. Office of Science and Technology. Washington, D.C.
- EPA, 1999. Field Sampling Guidance Document #1215 Sediment Sampling. USEPA Region 9 Laboratory. Richmond, California.
- EPA 2001. USEPA Contract Laboratory Program National Functional Guidelines for Low Concentration Organic Data Review. United States Environmental Protection Agency. Washington, D.C.
- EPA 2004. USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review. Available at:
<http://www.epa.gov/superfund/programs/clp/download/inorgfg10-08-04.pdf>
- EPA. 2005. National functional guidelines for chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs) data review. OSWER 9240.1-51. EPA 540-R-05-001. Office of Superfund Remediation and Technology Innovation, US Environmental Protection Agency, Washington, DC.
- King County, 2004. Sampling and Analysis Plan for the Stream Sediment Monitoring Program. King County Water and Land Resources Division. Seattle, WA.
- King County, 2011. Green River Study – Sampling and Analysis Plan. Prepared by King County Water and Land Resources Division. Seattle, WA.
- PTI Environmental Services, 1989a. Data Validation Guidance Manual for Selected Sediment Variables. Washington State Department of Ecology. Olympia, WA.
- PTI Environmental Services, 1989b. Puget Sound Dredged Disposal Analysis Guidance Manual; Data Quality Evaluation for Proposed Dredged Material Disposal Projects. Washington State Department of Ecology. Olympia, WA.
- PSEP, 1996. Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound. Puget Sound Estuary Program. Olympia, WA.
- Smith, S.S., D.D. MacDonald, K.A. Keenleyside, C.G. Ingersoll, and L.J. Field. 1996. A preliminary evaluation of sediment quality assessment values for freshwater ecosystems. *J. Great Lakes Res.* 22(3): 624-638. *Internat. Assoc. Great Lakes Res.*

Washington State Department of Ecology & Avocet Consulting. 2003. Development of Freshwater Sediment Quality Values for Use in Washington State Phase II Report: Development and Recommendation of SQVs for Freshwater Sediments in Washington State Washington State Department of Ecology, Olympia, WA. September 2003.

<https://fortress.wa.gov/ecy/publications/publications/1109054.pdf>

THIS PAGE INTENTIONALLY LEFT BLANK

Appendix A

METALS PERFORMANCE-BASED QC LIMITS

TABLES A-1 THROUGH A-3

Table A-1

Laboratory QC Limits for Sediment Metals, Buffalo River Sediment LCS Recoveries

Parameter	Lower Limit (%)	Upper Limit (%)
Silver	n/a	n/a
Arsenic	80	120
Cadmium	76	116
Chromium	40	80
Copper	81	105
Lead	71	111
Mercury	n/a	n/a
Nickel	80	120
Zinc	69	109

Table A-2

Laboratory QC Limits for Sediment Metals, ERA Soil LCS Recoveries

Parameter	Lower Limit (%)	Upper Limit (%)
Silver	66	134
Arsenic	80	120
Cadmium	80	120
Chromium	80	120
Copper	80	120
Lead	80	120
Mercury	71	129
Nickel	80	120
Zinc	80	120

Table A-3

Laboratory QC Limits for Sediment Metals, WQB-1 LCS Recoveries

Parameter	Lower Limit (%)	Upper Limit (%)
Mercury	80	120

APPENDIX B

TRACE ORGANICS PERFORMANCE-BASED QC LIMITS FOR SEDIMENTS

TABLES B-1 THROUGH B-10

Performance-based control limits are statistically derived, reviewed and potentially updated on an annual basis. The limits below are accurate for the 2012 calendar year.

Table B-1
Laboratory QC Limits for Sediment BNAs – Matrix Spike Recoveries

Parameter	Lower Limit (%)	Upper Limit (%)	Parameter	Lower Limit (%)	Upper Limit (%)
1,2,4-Trichlorobenzene	22	95	Chrysene	47	141
1,2-Dichlorobenzene	20	110	Di-N-Butyl Phthalate	64	150
1,4-Dichlorobenzene	20	105	Di-N-Octyl Phthalate	43	150
2,4-Dimethylphenol	27	126	Dibenzo(a,h)anthracene	39	150
2-Methylnaphthalene	22	109	Dibenzofuran	49	135
2-Methylphenol	21	126	Diethyl Phthalate	71	130
3-,4-Methylphenol	24	129	Dimethyl Phthalate	66	128
Acenaphthene	37	129	Fluoranthene	53	144
Acenaphthylene	44	134	Fluorene	52	150
Anthracene	37	150	Hexachlorobenzene	51	149
Benzo(a)anthracene	52	149	Hexachlorobutadiene	20	133
Benzo(a)pyrene	62	136	Indeno(1,2,3-Cd)Pyrene	41	150
Benzo(b,j,k)fluoranthene	48	135	N-Nitrosodiphenylamine	58	140
Benzo(g,h,i)perylene	27	150	Naphthalene	20	112
Benzoic Acid	20	150	Pentachlorophenol	35	134
Benzyl Alcohol	28	111	Phenanthrene	51	136
Benzyl Butyl Phthalate	27	150	Phenol	21	142
Bis(2-Ethylhexyl)Phthalate	54	150	Pyrene	59	143

Table B-2
Laboratory QC Limits for Sediment BNAs – Blank Spike Recoveries

Parameter	Lower Limit (%)	Upper Limit (%)	Parameter	Lower Limit (%)	Upper Limit (%)
1,2,4-Trichlorobenzene	39	94	Chrysene	45	150
1,2-Dichlorobenzene	44	105	Di-N-Butyl Phthalate	71	142
1,4-Dichlorobenzene	40	103	Di-N-Octyl Phthalate	43	150
2,4-Dimethylphenol	20	121	Dibenzo(a,h)anthracene	41	150
2-Methylnaphthalene	20	128	Dibenzofuran	52	133
2-Methylphenol	20	123	Diethyl Phthalate	75	131
3-,4-Methylphenol	22	119	Dimethyl Phthalate	70	129
Acenaphthene	43	126	Fluoranthene	56	143
Acenaphthylene	45	132	Fluorene	57	150
Anthracene	48	149	Hexachlorobenzene	53	150
Benzo(a)anthracene	51	150	Hexachlorobutadiene	20	135
Benzo(a)pyrene	61	140	Indeno(1,2,3-Cd)Pyrene	42	150
Benzo(b,j,k)fluoranthene	45	143	N-Nitrosodiphenylamine	57	136
Benzo(g,h,i)perylene	28	150	Naphthalene	28	109
Benzoic Acid	20	92	Pentachlorophenol	25	135
Benzyl Alcohol	26	111	Phenanthrene	47	141
Benzyl Butyl Phthalate	36	150	Phenol	26	136
Bis(2-Ethylhexyl)Phthalate	61	150	Pyrene	60	144

Table B-3
Laboratory QC Limits for Sediment BNAs – Surrogate Recoveries

Parameter	Lower Limit (%)	Upper Limit (%)
2,4,6-Tribromophenol	45	150
2-Fluorophenol	20	136
d5-Phenol	20	142
d5-Nitrobenzene	22	126
d4-2-Chlorophenol	20	127
2-Fluorobiphenyl	22	135
d14-Terphenyl	25	150

Table B-4
Laboratory QC Limits for Sediment BNAs – SRM Recoveries

Parameter	Lower Limit (%)	Upper Limit (%)
Benzo(a)anthracene	48	127
Benzo(a)pyrene	48	119
Benzo(b,j,k)fluoranthene	50	126
Benzo(g,h,i)perylene	42	141
Chrysene	64	150
Dibenzo(a,h)anthracene	54	200
Fluoranthene	56	137
Indeno(1,2,3-Cd)Pyrene	40	130
Phenanthrene	49	124
Pyrene	58	123

Table B-5
Laboratory QC Limits for Sediment Pesticides and PCBs
Matrix Spike Recoveries

Parameter	Lower Limit (%)	Upper Limit (%)
4,4'-DDD	53	108
4,4'-DDE	59	106
4,4'-DDT	50	110
Aldrin	63	92
Alpha-BHC	65	90
Alpha-Chlordane	59	113
Beta-BHC	62	101
Delta-BHC	63	105
Dieldrin	62	104
Endosulfan I	20	113
Endosulfan II	33	99
Endosulfan Sulfate	47	99
Endrin	66	112
Endrin Aldehyde	30	68
Gamma-BHC (Lindane)	67	91

Parameter	Lower Limit (%)	Upper Limit (%)
Heptachlor	60	102
Heptachlor Epoxide	62	97
Methoxychlor	63	107
Trans-Chlordane	40	131
Aroclor 1242	57	111
Aroclor 1260	33	105

Table B-6
Laboratory QC Limits for Sediment Pesticides and PCBs
Blank Spike Recoveries

Parameter	Lower Limit (%)	Upper Limit (%)
4,4'-DDD	57	107
4,4'-DDE	62	99
4,4'-DDT	47	131
Aldrin	51	71
Alpha-BHC	35	77
Alpha-Chlordane	69	98
Beta-BHC	54	90
Delta-BHC	53	98
Dieldrin	60	102
Endosulfan I	27	104
Endosulfan II	40	105
Endosulfan Sulfate	55	95
Endrin	63	106
Endrin Aldehyde	36	63
Gamma-BHC (Lindane)	39	82
Heptachlor	40	81
Heptachlor Epoxide	54	94
Methoxychlor	60	107
Trans-Chlordane	52	105
Aroclor 1242	23	92
Aroclor 1260	52	103

Table B-7
Laboratory QC Limits for Sediment Pesticides SRM and Surrogate Recoveries

Parameter	Lower Limit (%)	Upper Limit (%)
Alpha-Chlordane	69	136
Decachlorobiphenyl	47	122
2,4,5,6-Tetrachloro-m-xylene	20	134

Table B-8
Laboratory QC Limits for Sediment PCBs SRM and Surrogate Recoveries

Parameter	Lower Limit (%)	Upper Limit (%)
Aroclor 1254 (HS-2, Option 1)	41	133
Aroclor 1260 (Du/Di, Option 2)	38	167
Decachlorobiphenyl	55	120
2,4,5,6-Tetrachloro-m-xylene	20	115

Table B-9
Laboratory QC Limits for Sediment EDCs
Matrix Spike Recoveries

Parameter	Lower Limit (%)	Upper Limit (%)
Bis(2-ethylhexyl)adipate	20	150
Bisphenol A	20	150
Total 4-nonylphenols	20	150
Coprostanol	20	150

Table B-10
Laboratory QC Limits for Sediment EDCs
Blank Spike Recoveries

Parameter	Lower Limit (%)	Upper Limit (%)
Bis(2-ethylhexyl)adipate	20	150
Bisphenol A	20	150
Total 4-nonylphenols	20	150
Coprostanol	20	150

APPENDIX C

LABORATORY INFORMATION MANAGEMENT SYSTEM (LIMS) PRODUCTS AND LIST TYPES

TABLE C-1

Table C-1

**King County Environmental Laboratory
Laboratory Information Management System (LIMS)
Products and List Types**

Parameter	LIMS Product	LIMS List Type
PSD	PSD	CVPSD
TOC	TOC	CVTOC
Total Solids	TOTS	CVTOTS
Acid Volatile Sulfide	AVS	CVAVS
Mercury by CVAA-M (Sediments)	HG-CVAA-M	MTHG-MIDS, 6-SED
Mercury - SEM (Sediments)	HG-SEM, EXT	MTHG-SEM, 6-SEM
Total Metals by ICPMS (Sediments)	AG-ICPMS, AS-ICPMS, CD-ICPMS, CR-ICPMS, CU-ICPMS, PB-ICPMS, NI-ICPMS, P-ICPMS, ZN-ICPMS	MTICPMS-SED, 6-SED
Total Metals - SEM (Sediments)	AG-SEM, EXT, AS-SEM, EXT, CD-SEM, EXT, CR-SEM, EXT, CU-SEM, EXT, PB-SEM, EXT, NI-SEM, EXT, ZN-SEM, EXT	MTICP-SEM, 6-SEM
BNA SMS List *	BNASMS *	ORBNASMS *
Chlorinated Pesticides	CLPEST	ORCLPEST
EDCs	EDC	OREDC
PCBs	PCB	ORPCB

* Carbazole will be added to the ORBNASMS list type for the purposes of this project only.

CVAA – Cold vapor atomic absorption spectroscopy.

ICP – Inductively coupled plasma optic emission spectroscopy.

ICPMS – Inductively coupled plasma mass spectrometry

SEM – Simultaneously Extractable Metals