Green River
PCB Equipment Blank Study
Sampling and Analysis Plan

April 2015

Revised August 2015

Final

King County

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Science and Technical Support Section

Citation

King County. 2015. Green River PCB Equipment Blank Study – Sampling and Analysis Plan. Prepared by Debra Williston. King County Water and Land Resources Division, Science and Technical Support Section. Seattle, Washington.

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Acronyms

COC	chain of custody
DOC	dissolved organic carbon
EPA	U.S. Environmental Protection Agency
FSU	Field Science Unit
KCEL	King County Environmental Laboratory
LCS	laboratory control sample
LDW	Lower Duwamish Waterway
LIMS	Laboratory Information Management System
LMCL	lowest method calibration limits
MDL	method detection limit
ML	minimum level
OPR	ongoing precision and recovery
PCB	polychlorinated biphenyls
RDL	reporting detection limit
RO	reverse osmosis
RPD	relative percent difference
QA/QC	quality assurance/quality control
QC	quality control
SAP	sampling and analysis plan
SDL	specific detection limit
TOC	total organic carbon
TSS	total suspended solids

1.0. INTRODUCTION

This sampling and analysis plan (SAP) presents project information and sampling and analytical methodologies for a study to evaluate the potential for sampling equipment to cause contamination in samples analyzed for low level polychlorinated biphenyls (PCB). Equipment blank samples collected for previous studies suggest that autosampler equipment may be contributing PCBs to water samples. Two sampling methods will be used to collect whole surface water samples to better understand specific PCB congener contamination from autosampler equipment and evaluate the potential bias to middle and lower Green River surface water samples collected in previous King County Green River studies (King County 2011; 2013).

1.1 Project Background

King County is a member of the Source Control Work Group for the Lower Duwamish Waterway (LDW) Superfund site; other members include lead agency Washington Department of Ecology, U.S. Environmental Protection Agency (EPA), City of Seattle and the Port of Seattle. The Source Control Work Group works to understand potential chemical sources within the LDW Superfund site and to control and reduce sources that can contaminate waterway sediments. King County seeks to better understand the potential sources of contaminants of concern into combined sewer overflow basins which discharge to the LDW and also contaminant inputs to the LDW from upstream sources.

King County recently completed two surface water studies characterizing PCBs, polycyclic aromatic hydrocarbons and arsenic in the Green River and four major tributaries in the Green River Watershed (King County2014; 2015). Water quality in the Duwamish River is closely tied to water quality conditions in the Green River, which is the major source of water to the Duwamish River. Based on method and equipment blank results, PCBs were found to be biased high in Green River water samples collected using ISCO autosamplers; however, the degree of bias could not be estimated (King County 2015). The goal of this study is to better understand the magnitude of equipment contamination bias to total PCB congener results from the middle and lower Green River water samples as well as evaluate which piece(s) of the equipment contributes to the equipment blank contamination. The study contains two parts: (1) field sampling and analysis at two locations in the Green River, and (2) analysis of laboratory blank samples collected using specific autosampler equipment components and sample splitting tubing.

1.2 Scope of Work

This effort will involve collection of whole surface water samples for analysis of PCB congeners at two previously sampled locations in the Green River using two different sampling methods. Samples will be collected during both wet season storm events and dry season baseflow conditions, because the PCB congener pattern and influence of the equipment blank contamination to the total PCB concentration appeared to differ based on the type of sampling event. In addition, samples will be collected from two locations with differing land. PCB contamination associated with autosampler equipment appears to have a greater influence on the total PCB concentration in samples collected from the less developed drainage basin. However, it is also important to understand how the equipment may have influenced results from a more developed drainage basin where higher total PCB concentrations have been observed. Therefore, samples will be collected from the Green River at Kanaskat-Palmer State Park in the Middle Green River Basin where there is little development, and the Green River at the Foster Links Golf Course in the Lower Green River Basin, which has substantially more upstream urban and suburban development. Both PCB congeners and conventional parameters will be analyzed. The conventional parameter data will assist in data interpretation, such as estimating particulate bound PCBs as well as assessing natural variability at the site and comparability of the two sampling methods. At each location, three samples will be collected during dry season baseflow conditions and three samples during wet season storm event conditions. Samples will be collected using two sampling methods: autosamplers and composited hand-grabs. This will allow direct comparison of PCB results using two different sampling methods and provide an evaluation of bias from contamination associated with the autosampler equipment. Samples will be analyzed for PCB congeners, total organic carbon (TOC), dissolved organic carbon (DOC) and total suspended solids (TSS). In addition, laboratory water that has passed through sample tubing as well as equipment blank laboratory source water will be tested for PCB congeners to evaluate potential PCB contamination from these materials.

1.3 Study Schedule

Three dry season baseflow samples will be collected between July and September 2015. Three wet season storm event samples will be collected between April through June 2015 and October through December 2015. Chemical analysis will be completed within approximately 60 days of the last sampling event, followed by data validation.

1.4 Project Staff

The following staff members are responsible for project execution:

Jeff Stern, LDW Project Manager..206-477-5479

Wastewater Treatment Division Manager and Technical lead for all Lower Duwamish River studies

Debra Williston, Water and Land Resources Division Technical Lead 206-477-4870

Study project manager including responsible for study project execution and adherence to SAP and schedule and data report

Jeff Droker, Field Science Unit (FSU) Kanaskat-Palmer Site Field Lead 206-477-7145

Responsible for sample collection

Jean Power, FSU Foster Links Site Field Lead 206-477-7149

Responsible for sample collection

Fritz Grothkopp, King County Environmental Lab (KCEL) Project Manager...206-477-7114

Manages sample analysis, sample shipment, and data delivery

Carly Greyell, Data Validation Lead 206-477-4703

Responsible for all King County laboratory data validation

2.0. STUDY DESIGN

The goal of this study is to better understand the magnitude of equipment contamination to total PCB results from the middle and lower Green River water samples as well as evaluate which piece(s) of the equipment are contributing. The results from this study can also be useful to other studies that have used similar equipment for sampling PCB congeners. All samples will be analyzed for PCB congeners. Green River surface water samples will also be analyzed for TSS, TOC and DOC. Resulting data will allow King County to better understand the potential bias in PCB results to previous surface water data collected using autosamplers in the Green River Watershed. In addition, the study will generate additional PCB congener data for two locations in the Green River.

2.1 Data Quality Objectives

The data quality objectives for this effort are to collect data of known and sufficient quality to meet study goals. Validation of study data will assess whether the data collected are of sufficient quality to meet the study goals. The data quality issues of precision, accuracy, bias, representativeness, completeness, comparability, and sensitivity are described in the following sections. Data validation is discussed in Section 5.0.

2.1.1 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 measured 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 one or more of the following quality control (QC) samples:

- analysis of various laboratory QC samples such as method blanks, spiked blanks, matrix spikes, laboratory control samples and laboratory duplicates or triplicates; and
- collection and analysis of field replicate samples.

Precision of replicates is expected to be within the limits specified in Section 4. If precision is considered too low for project needs, these data will be used to guide future sampling efforts.

Accuracy is assessed through matrix spikes, spike blanks, and with the ongoing precision and recovery sample control charts. Additionally, the isotopic dilution method chosen for this study is the most rigorous method for PCB congener analysis. This method uses isotopically-labeled congeners, to track the recovery performance of the range of congener homologs. Thus, each congener concentration is theoretically adjusted for the extraction efficiency and analytical performance of that specific sample.

2.1.2 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. Surface water samples will be collected from river locations to represent water quality during defined dry and wet season conditions. The samples are intended to generate data of sufficient quality to provide survey level water quality data for PCBs from the Green River.

Samples will be collected with ISCO® autosamplers in the same manner as conducted for previous studies to replicate any potential contamination associated with sampling equipment. All other aspects of the study will be conducted in such a manner as to minimize potential contamination and other types of degradation in the chemical and physical composition of the water. This can be achieved by following guidelines for sampler decontamination, sample acceptability criteria, sample processing, observation of proper hold-times and preservation, storage and preparation of samples.

2.1.3 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 submitted for analysis. Sampling with adherence to standardized sampling and testing protocols will aid in providing a complete set of data for this study. The goal for completeness is 100%. The samples from each event should produce acceptable data under the QC conditions described elsewhere in this SAP.

2.1.4 Comparability

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another. This goal is achieved through the use of standard techniques to collect and analyze representative samples, along with standardized data validation and reporting procedures. By following the guidance described in this SAP, the goal of comparability between this and future sampling events will be achieved. Although a different analytical laboratory will analyze samples for PCB congeners than was used for past studies (due to new King County contract), the same analytical method is being used. There will be some differences in co-elutions of specific PCB congeners due to the use of a different gas chromatography column as well as some differences in sample specific detection limits.

2.1.5 Sensitivity

Sensitivity is a measure of the capability of analytical methods to meet the study goal. The analytical method detection limits (MDLs) presented in Section 5 are sensitive enough to detect PCB congeners at concentrations sufficient to increase the understanding of PCB levels in the Green River and to evaluate the source and magnitude of PCB congener contamination from autosampler equipment.

2.2 Sampling and Analytical Strategy

The sampling strategy is designed to evaluate PCB sample bias associated with the autosampler equipment within two reaches of differing land development in the Green River. Additionally, the effort described here will provide water quality data at these two sites. The sampling effort will also provide data to evaluate the potential source of the PCB contamination from components of the sampling equipment. The sampling methods for the autosampler will follow the same procedures used during the previous Green River studies (King County 2011; 2013).

2.2.1 Field Sampling

Samples will be collected concurrently using both the ISCO® autosampler and composite hand-grabs. This will allow direct comparison of PCB results using two different sampling methods. Samples will be collected over a 3-hour period. Each method will result in collection of the same volume of water and the same number of aliquots over the sampling period. As such, samples will be collected approximately every 20 minutes over a three-hour period (total of 10 grabs per composite) per method at each location.

Flow at the sampling locations will be estimated from the USGS gage at Palmer WA (Gage 12106700) for Kanaskat-Palmer location and at USGS Auburn gage (Gage 12113000) for the Foster Links location. Precipitation will be tracked using the King County gauges BDIA in Black Diamond and TUKW in Tukwila.

Baseflow Sample Collection

Three composite samples will be collected from each of the two locations during dry season baseflow (July – September) conditions with an antecedent dry period of at least 3 days.

Storm Event Sample Collection

Collection of wet season (March-June and October-February) storm event samples from the two locations will be triggered by a rain event where 0.25 to 0.50” of precipitation is predicted. Three sets of storm event samples will be collected from each location. The intent is to capture wash-off events with the potential to transport target chemicals downstream. Storm event samples will be collected after rain event has begun and can be completed following the rain event; the goal is to capture samples representative of storm conditions.

2.2.2 Equipment Sampling

Silicone tubing has been associated with PCB congeners (e.g., 44, 45 and 68) (Perdih and Jan 1994; Rodenburg 2015) and it is a suspected source of the PCB equipment contamination. These three congeners were found at proportionately higher levels than other congeners in previous equipment blank samples (King County 2015). However, to confirm that substantive contamination is not originating from other tubing used for sample collection and processing or the King County Environmental Laboratory reverse osmosis (RO) water, additional testing will be conducted. Therefore, to evaluate the potential source of the PCB contamination from the autosampler equipment and sample splitting equipment, the following material will be evaluated:

- Silicone tubing used with the autosampler's peristaltic pump
- Teflon® tubing used with autosampler to collect river water
- KCEL sample splitting room silicone/Teflon combination tubing
- KCEL RO water used for equipment blanks

For the different tubing types, KCEL RO water will be exposed to the tubing and tested (see Section 3.1.2 for details). There will be 2 samples collected from each of the three tubing types: new silicone; new Teflon; and previously used splitting room silicone/Teflon tubing (total of 6 samples). KCEL RO water was used for previously collected equipment blanks and is the medium used to test the tubing listed above, as such it will also be tested.

2.3 Sampling Station Locations and Sample Identification

Sample locations will be identified using a unique locator name. The locator name, collection date and the unique sample identification number generated by KCEL will identify individual samples collected at each location. The two sampling locations are shown in Figure 1. The corresponding locator numbers and sample coordinates are shown in Table 1.

Table 1. Upper Green River and Tributary Sampling Locations and Locator Names.

Locator	Locator Description	Approximate River Mile[a]	Northing[b]	Easting[b]
KP319	**Green River at Kanaskat-Palmer State Park** – west of day use shelters	52	119148	1373725
FL319	**Green River – Foster Links** Golf Course, downstream location	10	177997	1288012

[a] River Miles are based on south end of Harbor Island (lower boundary of LDW Superfund site) as river mile 0.0. Tributary river miles are approximately where they discharge into the Green River

[b] State plane coordinates in North American Datum 1983 (NAD83) Washington State Plane North (4601)

The samples associated with the tubing and RO water will also have a unique sample identification number generated by KCEL. In place of locator name, samples will be identified as silicone tubing, Teflon tubing, splitting room tubing and KCEL RO water.

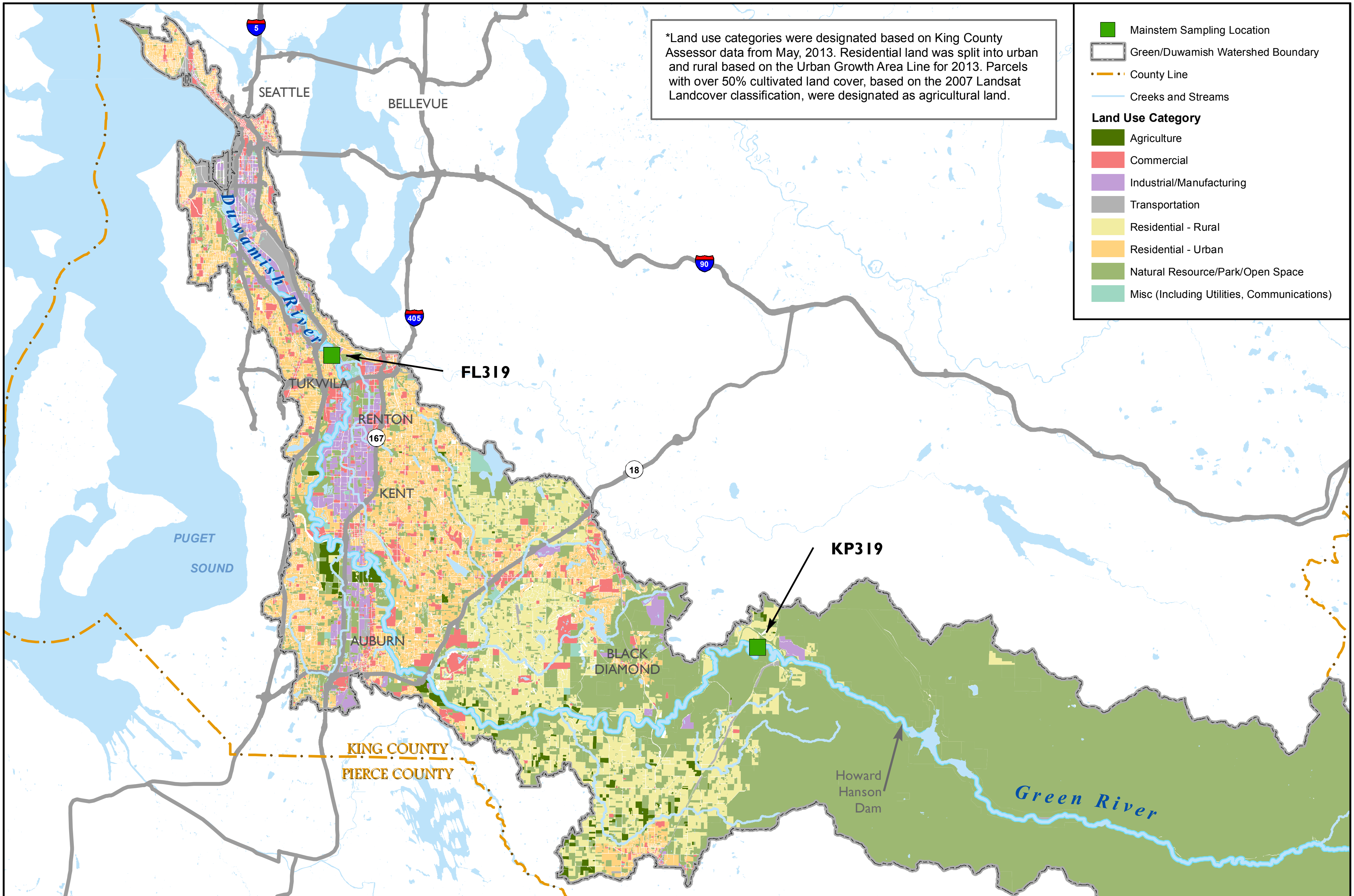
2.4 Sample Acquisition and Analytical Parameters

King County FSU staff will primarily conduct sampling; however, other King County Water and Land Resources staff may provide assistance as needed. Sampling techniques are discussed in Section 3. Each Green River sample will be analyzed for 209 PCB congeners

TOC, DOC, and TSS. All equipment tubing and equipment blank water will be analyzed for 209 PCB congeners. Table 2 summarizes the number of samples to be collected for the study, at each location, as well as the estimated number of sample replicates. PCB congener analysis will be conducted by Pacific Rim Laboratories in Vancouver, British Columbia. All conventional analyses will be conducted by the KCEL.

Table 2. Sample numbers by type and analysis

Location/ Equipment	Sample Number and Type		Analysis			
			PCBs	TSS	TOC	DOC
Field						
	Baseflow	**Storm**				
Kanaskat-Palmer	3-autosampler 3-hand grab composites	3-autosampler 3-hand grab composites	X	X	X	X
Foster Links	3-autosampler 3-hand grab composites	3-autosampler 3-hand grab composites	X	X	X	X
Replicates - Foster Links	1-autosampler 1- hand grab composite	1-autosampler 1- hand grab composite	X	X	X	X
Equipment						
Silicone Tubing	2-equipment blanks		X			
Teflon Tubing	2-equipment blanks		X			
Splitting Tubing	2-equipment blanks		X			
KCEL Reverse Osmosis Water	2-equipment blanks		X			
Total number of samples			**36**	**28**	**28**	**28**



King County
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March 2015

Figure 1

Sampling Locations And Land Use In The Green/Duwamish Watershed

3.0. SAMPLING PROCEDURES

This section describes procedures for field and equipment sample collection, including sampling equipment decontamination and use, field replicates, and procedures for recording field measurements and conditions. Requirements for sample containers and preservation, and sample custody procedures are also described.

3.1 Sample Collection

Field samples will be collected concurrently using the ISCO® autosampler and by composite hand-grabs. The method for each sampling procedure is described below. This section also describes the methods for equipment sample collection.

3.1.1 Field Sampling Methods

Autosamplers

Composite water quality samples will be collected using ISCO® autosamplers equipped with 5-gallon glass carboys. The treatment of tubing used for sampling will replicate the treatment used in previous sampling efforts at each location. At the Kanaskat-Palmer Green River location, autosamplers will be fitted with new, pre-cleaned, site-dedicated silicone tubing in the peristaltic pump for each sampling event; the silicone tubing will be cleaned prior to each sampling event as described in Section 3.3. At the Foster Links Green River location, the silicone tubing used with the peristaltic pump will be new and pre-cleaned for each sampling event. Teflon® tubing and stainless steel fittings shall be used for all other tubing needs. Teflon® tubing will also be dedicated to a sampling location and cleaned prior to each sampling event as described in Section 3.3.

The ISCO® autosampler will be deployed on the stream bank and the sample collection tubing will be placed in the river at a water depth similar to that where the composite grabs are collected. The ISCO® autosampler will be programmed to collect a 1-liter sample every 20 minutes. A target volume of approximately 10 liters of water will be collected over a 3-hour period to coincide with the composite grab samples. During the sampling period, the carboy will be kept cool with ice within the autosampler container. When collection of the integrated composite sample is complete, the ISCO® autosampler will also be turned off. At the conclusion of sampling, the carboy will be sealed with a Teflon® lined lid and transported on ice in a cooler to KCEL.

Composite Grabs

All grab samples will be collected at 20 minute intervals over a three hour period. Two slightly different approaches for grab samples will be used at each location, as described below. Once collected, the individual grab sample will then be transferred to a glass carboy in the field creating a composite sample for each sampling event at each location. A target volume of approximately 10 liters of water will be collected over the course of each sampling event.

All grab samples at the Kanaskat-Palmer location will be collected using a proofed 1-liter glass jar[1] with lid; approximately 1-liter grabs will be collected at 20 minute intervals over a three hour period. Field personnel will wade into the river to a water depth of approximately ½ to 1 meter[2] and submerge the 1-liter glass jar approximately 6-inches below the water surface upstream of their position to collect the grab sample. The collection point will also be downstream of the autosampler intake location and positioned so the substrate is not disturbed upstream of the autosampler collection point. In between collection periods, the glass jar will be capped to prevent contamination.

All grabs samples at the Foster Links location will be collected using a proofed 1-liter glass jar with lid; approximately 1-liter grabs will be collected at 20 minute intervals over a three hour period. Field personnel will attach the jar to an adjustable fiberglass pole that will extend into the river parallel or just downstream of the autosampler intake line. The jar will be submerged approximately 6-inches below the water surface to obtain grab sample. This will not disturb the bottom substrate or negatively influence the autosampler collection point. In between collection periods, the glass jar will be capped to prevent contamination. Grabs will be collected at the same frequency as at Kanaskat-Palmer location.

Following collection of each grab sample, FSU staff will place the sample in the carboy. The carboy will be stationed in a cooler with ice throughout the sampling event. In between sampling intervals and at the conclusion of sampling, the carboy will be sealed with a Teflon® lined lid. Once sampling is complete, the carboy will be transported to KCEL on ice in a cooler.

Field Replicates

Two field replicates will be collected at the Foster Links location using the same methods as described above. One set of replicates will be collected during baseflow sample collection and a second set will be collected during storm event sample collection for a total of four replicates samples (see Table 2). A second autosampler will be used to collect the replicate samples. For the composite grab samples, a second grab sample will be collected following the first grab per that 20 minute interval cycle and placed in a separate glass carboy. Field replicates will be analyzed for all parameters and will provide a measure of variability at the sampling locations.

3.1.2 Equipment Sampling Methods

The methods used to evaluate the autosampler equipment and splitting room tubing are described here. For each sample collection, 4 1-liter samples will be collected; two of these will be archived at KCEL and the other two shipped to Pacific Rim Labs for PCB congener

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[1] Proofed clean PCB sampling containers will be supplied by Pacific Rim.

[2] If river conditions are not safe to wade to the target depth (minimum of ½ meter), the field personnel will record the water depth for which the samples were collected.

analysis. These equipment blank samples shall be preserved, stored, and analyzed for PCBs in the same manner as environmental samples.

Autosampler Silicone Tubing

The peristaltic pump in the ISCO® autosampler uses silicone tubing. New silicone tubing, following equipment decontamination procedures described in Section 3.3, will be tested. During previous Green River sampling, autosamplers were programed to collect approximately 12 liters of river water over a 24-hour period. To simulate the contact time the river water had with silicone tubing, the ISCO® autosampler will be set up to transfer 12 liters of KCEL RO water from a pre-cleaned glass carboy to another pre-cleaned glass carboy. The sample collection period would be approximately 7-8 hours, resulting in approximately 16 - 750 mL aliquots being collected. Four 1-liter analytical containers for PCB analysis will then be filled from the carboy using new silicone tubing (the same batch/stock used for this equipment test) and a peristaltic pump system; no Teflon tubing will be used. Alternatively, the sample water will be filled directly into the sample bottles from the carboy. Two samples will be collected at a minimum of 1 week apart. Each sample collection will be done with new pre-cleaned silicone tubing.

Autosampler Teflon® Tubing

The ISCO® autosampler uses Teflon® tubing (connected to the silicone tubing) to retrieve water from the river. New pre-cleaned Teflon® tubing will be tested. Because the KCEL RO water used in the Teflon® blank sample cannot come into contact with silicone tubing, a peristaltic pump cannot be used to collect the sample. Therefore, a house (lab) vacuum system will be used to draw RO water from one pre-cleaned glass carboy to another. The same twelve liters of RO water will be drawn through the Teflon tubing approximately 5 times to simulate field sampling conditions. Four 1-liter analytical containers for PCB analysis will then be filled from the carboy using this same Teflon tubing and house (lab) vacuum system or the sample water will be filled directly into the sample bottles from the carboy. Two samples will be collected at a minimum of 1 week apart. Each test will be conducted with new pre-cleaned Teflon® tubing.

Splitting Room Tubing

When samples are received in the laboratory, they are split into the appropriate analytical containers. This is accomplished with a peristaltic pump and Teflon/silicone/Teflon tubing combination that has been decontaminated between uses. The contact time of the sample with the tubing is very short, approximately 10-15 minutes; the time it takes transfer sample from the glass carboy to all sample containers. Therefore, splitting room tubing that had been used in past sample processing will be decontaminated (see Section 3.3) and used to draw approximately 10 liters of KCEL RO water from a pre-cleaned glass carboy to another pre-cleaned glass carboy. Four 1-liter analytical containers for PCB analysis will then be filled using this same splitting room tubing. Two samples will be collected at a minimum of 1 week apart. The same splitting room tubing will be used for each sampling event.

KCEL RO Water

The RO water will be transferred from the KCEL system directly to four 1-liter analytical containers for PCB analysis. The RO water will not come into contact with any silicone or Teflon tubing. Two samples will be collected approximately 1 week apart.

3.2 Field Sampling Equipment

In addition to the autosamplers discussed in Section 3.1, the field equipment listed below will be available for field staff.

1) Sampling supplies:
   a) Cooler with ice
   b) Nitrile gloves
   c) 1-liter proofed glass jar with lid
   d) Glass carboys
2) Safety equipment:
   a) Personal Floatation Device
   b) Waders
   c) Field vest (reflective)
3) Documentation supplies:
   a) Field notebook
   b) Sample labels
   c) Chain-of-custody forms
   d) Camera

When visiting the sampling station, field personnel will record the following information on field forms that are maintained in a waterproof field notebook.

- Date
- Time of sample collection or visit
- Name(s) of sampling personnel
- Description of sampling location
- Weather conditions
- Number and type of samples collected
- Log of photographs taken, if any taken
- Deviations from sampling procedures
- Unusual conditions (e.g., water color or turbidity, presence of oil sheen, odors, and land disturbances)

3.3 Equipment Decontamination

Prior to the first sampling event, the glass carboys will be prepared by (1) cleaning with Detergent 8 laboratory detergent; (2) a hot water rinse; and (3) KCEL RO water rinse. Following this preparation, the carboy will be dedicated to each site until the sampling for this study is completed. Following sample collection, all re-usable equipment will be decontaminated using the method described above.

The silicone and Teflon® tubing will be cleaned in the following manner: (1) a hot water rinse; and (2) a KCEL RO water rinse.

Proofed clean PCB sampling containers will be supplied by Pacific Rim. Proper personal protective equipment (new powder-free gloves) will be worn during sampling activities and during decontamination processes.

3.4 Sample Delivery and Storage

Field samples will be kept in ice-filled coolers during transport and until received by KCEL; sample delivery will occur on the day of collection. Equipment samples will be collected at KCEL. Additional sample preservation, where required, will be performed at KCEL following sample splitting.

Upon arrival at KCEL, all samples will be split out into the appropriate analytical containers. This will be done by continuously agitating the sample in the carboy while transferring sample aliquots to the appropriate laboratory containers. For samples collected with autosampler, the standard splitting room tubing procedure will be used and for hand-composite grabs a new Teflon® siphon tube and a house (lab) vacuum system will be used. Each sample container will be filled to the appropriate level from the carboy. This procedure will ensure a representative sample from the carboy in each analytical container.

Containers for PCB congener analysis will be delivered to Pacific Rim within 1 to 3 months of sample collection. Samples will be held at KCEL at the appropriate temperature until delivery date. Samples will be maintained in coolers with ice and/or ice packs during the delivery process. Samples will either be driven to Pacific Rim or shipped via overnight express delivery service. Table 3 shows sample handling and storage requirements.

Table 3. Sample Container, Preservation, Storage, and Hold Time Requirements

Analyte	Container	Preservation	Storage	Hold Time
Dissolved Organic Carbon	125 mL amber wide mouth HDPE	0.45 µm filtration, then H_3PO_4 to pH<2 within 1 day	refrigerate at <6^oC	28 days
Total Organic Carbon	125 mL amber narrow-mouth glass	H_3PO_4 to pH<2 within 1 day	refrigerate at <6^oC	28 days
Total Suspended Solids	1-L clear wide mouth HDPE	None	refrigerate at <6^oC	7 days
PCB Congeners	2 x 1-L amber glass	None	refrigerate at 4^oC in the dark	1 year
Archive	2 x 1-L amber glass	None	refrigerate at 4^oC in the dark	1 year

3.5 Chain of Custody

Chain of custody (COC) will commence at the time of sample collection. All samples will be under direct possession and control of FSU staff or locked in a controlled area. All sample information will be recorded on a COC form. This form will be completed in the field (or KCEL for equipment samples) and will accompany all samples during transport and delivery to the laboratory. Upon arrival at the KCEL, the samples will be split into the appropriate containers then relinquished to the sample login staff. The date and time of sample delivery will be recorded and both parties will then sign off in the appropriate sections on the COC form. Once completed, original COC forms will be archived in the project file.

Samples delivered to KCEL after regular business hours will be stored in a secure refrigerator until the next day. Samples delivered to Pacific Rim will be accompanied by a properly-completed COC form and custody seals will be placed on the shipping cooler. Pacific Rim will be expected to provide a copy of the completed COC form as part of their analytical data package.

3.6 Sample Documentation

Sampling information and sample metadata will be documented using the methods noted below.

- Field sheets generated by KCELs Information Management System (LIMS) will be used at all stations and will include the following information:
    1) Sample ID number
    2) Location name
    3) Number of grab samples per composite and sample interval between grab samples
    4) Date and time of sample collection (start and end times of the compositing period)
    5) Initials of all sampling personnel
- LIMS-generated container labels will identify each container with a unique sample number, station and site name, collect date, analyses required, and preservation method.
- The field sheet will contain records of collection times, general weather and the names of field crew staff. For equipment samples, field sheets will record all but general weather conditions.
- COC documentation will consist of KCEL's standard COC form, which is used to track release and receipt of each sample from collection to arrival at the lab.

4.0. ANALYTICAL METHODS AND DETECTION LIMITS

Analytical methods are presented in this section, along with analyte-specific detection limit goals. For the selected conventional analytes, the terms MDL and reporting detection limit (RDL), used in the following subsections, refer to method detection limit and reporting detection limit, respectively. The KCEL reports both the LIMS RDL and the LIMS MDL for each sample and parameter, where applicable.

For conventionals analyses, LIMS MDLs are typically two to five times higher than the statistically derived MDLs that are calculated using the 40 CFR Part 136, Appendix B procedure. In the case of some conventional parameter tests, MDLs are evaluated by the procedure listed in the appendix of 40 CFR Part 136[3]. The detection limits derived from this approach are also typically two to five times the statistically derived MDLs that are calculated by the 40 CFR Part 136, Appendix B procedure.

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 upon available sample volumes. Every effort will be made to meet the MDL/RDL goals listed in the SAP.

For PCB 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 particularly for PCB congener analyses are sample specific detection limits and lowest method calibration limits. Sample specific detection limit (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. Lowest method calibration limits (LMCL), also called estimated quantitation limits (EQL) are based on calibration points from standard solutions. They are prorated by sample size and are supported by statistically-derived method reporting limit values.

The PCB congener data will be reported to LMCLs and flagged down to the SDL value. In most cases the SDL may be below the LMCL. Method 1668C defines a Minimum Level (ML) value for each congener. The ML value is used to evaluate levels in the method blank. The ML is based on the lowest method calibration limit (LMCL) and any laboratory performing the method should be able to achieve at least that level. Pacific Rim uses an additional calibration point that is lower than the calibration points specified in the method; as such they are able to quantify congeners below the ML specified in the method.

[3] Appendix D: DQ FAC Single Laboratory Procedure v2.4 of the *Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs Final Report 12/28/0.7*

Details regarding the frequency of required QC samples are provided in the individual analytical sections shown below. In general for all methods, this frequency is 1 in 20 samples or 1 per batch whichever is more frequent. Below are general descriptions of types of laboratory QC samples:

- Analysis of method blanks is used to evaluate the levels of contamination that might be associated with the processing and analysis of samples in the laboratory and introduce bias into the sample result. Method blank results for all target analytes (other than PCB congeners) should be "less than the MDL."
- A laboratory duplicate is a second aliquot of a sample, processed concurrently and in an identical manner with the original sample. The laboratory duplicate is processed through the entire analytical procedure along with the original sample in the same quality control batch. Laboratory duplicate results are used to assess the precision of the analytical method and the relative percent difference (RPD) between the results should be within method-specified or performance-based quality control limits.
- A spike blank is a spiked aliquot of clean reference matrix used for the method blank. The spiked aliquot is processed through the entire analytical procedure. Analysis of the spike blank is used as an indicator of method accuracy. It may be conducted in lieu of a laboratory control sample. A spike blank duplicate should be analyzed whenever there is insufficient sample volume to include a sample duplicate or matrix spike duplicate in the batch.
- The ongoing precision and recovery (OPR) samples must show acceptable recoveries, according to the respective methods for data to be reported without qualification. The OPR sample is typically called a Lab Control Sample (LCS) or Spiked Blank in LIMS.

4.1 PCB Congeners

PCB congener analysis will follow EPA Method 1668 Revision C (EPA 2010), 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. An extensive suite of labeled surrogate standards (Table 4) is added before samples are extracted. Data are "recovery-corrected" for losses in extraction and clean-up, and analytes are quantified against their labeled analogues.

Pacific Rim will perform this analysis according to their SOP LAB02. A one-liter sample will be extracted followed by standard method clean-up, which includes an acid wash followed by Acid Silica and Alumina column chromatography. Analysis is performed with an SGE HT-8 column. Method 1668C requires that if a sample contains more than 1% total solids, the solids and liquid will be extracted and analyzed separately.

Table 4. Labeled Surrogates and Recovery Standards Used for EPA Method 1668 PCB Congener Analysis

^{13}C-labeled PCB Congener Surrogate Standards				
1	54	114	157	206
3	81	105	169	209
4	77	126	188	
15	104	155	202	
19	123	167	205	
37	118	156	208	
^{13}C-labeled Cleanup Standards				
28	111	178		
^{13}C-labeled Internal (Recovery) Standards				
9	52	101	138	194

Table 5 lists the 209 PCB congeners and their respective target SDL and LMCL values. The reporting limits for individual samples may differ from those in Table 5 since they are determined by signal to noise ratios and changes to final volumes. Typical sample detection limits are shown. Note that several of the congeners co-elute and a single SDL or LMCL value is provided for the congeners in aggregate.

Table 5. PCB Congener water detection limit goals

PCB(s)	SDL (pg/L)	LMCL (pg/L)
PCB-001	2.0	10
PCB-002	2.1	10
PCB-003	2.5	10
PCB-004	2.5	10
PCB-005/008	1.7	10
PCB-006	1.7	10
PCB-007	1.7	10
PCB-009	1.7	10
PCB-010	1.7	10
PCB-011	1.8	10

PCB(s)	SDL (pg/L)	LMCL (pg/L)
PCB-068	0.8	10
PCB-070	1.0	10
PCB-071	0.7	10
PCB-073	0.9	10
PCB-074	0.9	10
PCB-076	0.9	10
PCB-077	0.8	10
PCB-078	0.9	10
PCB-079	0.9	10
PCB-081	1.0	10

PCB(s)	SDL (pg/L)	LMCL (pg/L)
PCB-143	0.7	10
PCB-144	1.1	10
PCB-145	0.9	10
PCB-146	0.6	10
PCB-147	1.3	10
PCB-150	0.8	10
PCB-151	1.1	10
PCB-152	0.8	10
PCB-153	0.6	10
PCB-154	1.0	10

PCB(s)	SDL (pg/L)	LMCL (pg/L)
PCB-012/013	1.8	10
PCB-014	1.6	10
PCB-015	2.0	10
PCB-016	1.7	10
PCB-017	1.8	10
PCB-018	1.5	10
PCB-019	2.0	10
PCB-020/033	1.0	10
PCB-021	1.2	10
PCB-022	1.1	10
PCB-023	0.8	10
PCB-024	1.4	10
PCB-025	0.9	10
PCB-026	0.7	10
PCB-027	0.9	10
PCB-028	0.9	10
PCB-029	0.7	10
PCB-030	1.2	10
PCB-031	0.7	10
PCB-032	1.5	10
PCB-034	1.0	10
PCB-035	1.1	10
PCB-036	1.0	10
PCB-037	1.4	10
PCB-038	1.2	10
PCB-039	1.1	10
PCB-040/057	1.1	10
PCB-041	1.5	10
PCB-042	1.3	10
PCB-043/049	1.2	10
PCB-044	1.5	10

PCB(s)	SDL (pg/L)	LMCL (pg/L)
PCB-082	1.3	10
PCB-083/109	1.0	10
PCB-084	1.0	10
PCB-085	1.1	10
PCB-086/117	1.0	10
PCB-087/115	1.0	10
PCB-088	1.0	10
PCB-089	1.0	10
PCB-090	1.1	10
PCB-091/121	0.9	10
PCB-092	1.2	10
PCB-093/098/102	1.0	10
PCB-094	1.1	10
PCB-095	1.0	10
PCB-096	0.7	10
PCB-097/116	1.0	10
PCB-099	0.9	10
PCB-100	0.9	10
PCB-101	1.0	10
PCB-103	0.8	10
PCB-104	2.7	10
PCB-105/127	0.5	10
PCB-106	0.6	10
PCB-107/108	0.6	10
PCB-110	0.8	10
PCB-111	0.8	10
PCB-112/119	0.8	10
PCB-113	0.8	10
PCB-114	0.5	10
PCB-118	0.5	10
PCB-120	0.8	10

PCB(s)	SDL (pg/L)	LMCL (pg/L)
PCB-155	3.8	10
PCB-156	0.4	10
PCB-157	0.4	10
PCB-158	0.5	10
PCB-159	0.5	10
PCB-163/164	0.6	10
PCB-165	0.6	10
PCB-166	0.5	10
PCB-167	0.4	10
PCB-168	0.6	10
PCB-169	0.4	10
PCB-170	0.7	10
PCB-171	0.7	10
PCB-172	0.7	10
PCB-173	0.9	10
PCB-174	0.8	10
PCB-175	0.8	10
PCB-176	0.6	10
PCB-177	0.7	10
PCB-178	0.8	10
PCB-179	0.5	10
PCB-180	0.7	10
PCB-181	0.8	10
PCB-182/187	0.8	10
PCB-183	0.7	10
PCB-184	0.5	10
PCB-185	0.8	10
PCB-186	0.6	10
PCB-188	1.2	10
PCB-189	0.3	10
PCB-190	0.4	10

PCB(s)	SDL (pg/L)	LMCL (pg/L)
PCB-045	1.2	10
PCB-046	1.4	10
PCB-047/048	1.3	10
PCB-050	1.1	10
PCB-051	1.1	10
PCB-052/069	1.0	10
PCB-053	1.1	10
PCB-054	1.2	10
PCB-055/080	0.9	10
PCB-056	0.9	10
PCB-058	0.9	10
PCB-059	0.9	10
PCB-060	1.0	10
PCB-061	1.0	10
PCB-062	1.0	10
PCB-063	0.8	10
PCB-064/072	0.9	10
PCB-065/075	0.8	10
PCB-066	0.8	10
PCB-067	0.9	10

PCB(s)	SDL (pg/L)	LMCL (pg/L)
PCB-122	0.6	10
PCB-123	0.6	10
PCB-124	0.5	10
PCB-125	0.8	10
PCB-126	0.4	10
PCB-128/162	0.6	10
PCB-129	0.7	10
PCB-130	0.8	10
PCB-131	0.8	10
PCB-132/161	0.6	10
PCB-133	0.7	10
PCB-134	0.9	10
PCB-135	1.3	10
PCB-136/148	1.0	10
PCB-137	0.7	10
PCB-138/160	0.6	10
PCB-139/149	1.2	10
PCB-140	0.6	10
PCB-141	0.7	10
PCB-142	0.7	10

PCB(s)	SDL (pg/L)	LMCL (pg/L)
PCB-191	0.5	10
PCB-192	0.6	10
PCB-193	0.5	10
PCB-194	0.5	10
PCB-195	0.5	10
PCB-196	0.7	10
PCB-197	0.6	10
PCB-198	0.6	10
PCB-199	0.9	10
PCB-200	0.6	10
PCB-201	0.6	10
PCB-202	0.9	10
PCB-203	0.7	10
PCB-204	0.6	10
PCB-205	0.3	10
PCB-206	0.8	10
PCB-207	0.8	10
PCB-208	0.9	10
PCB-209	0.6	10

SDL = sample detection limit
LMCL = lower method calibration limit
pg/L = picograms per liter

Quality assurance/quality control (QA/QC) samples include method blank, OPR sample, and surrogate spikes. Method blanks and OPR, which are the same as spike blanks, 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 1668C. Method 1668C has specific requirements for method blanks that must be met before sample data can be reported (see section 9.5.2 of Method 1668). The OPR samples must show acceptable recoveries, according to Method 1668C, in order to samples to be analyzed and data to be reported. A summary of the quality control samples are shown in Table 6.

Table 6. PCBs QA/QC Frequency and Acceptance Criteria

Frequency	Method Blank	Lab Duplicate (RPD)	OPR (% Recovery)	Surrogate Spikes
	1 per batch	**1 per batch**	**1 per batch**	**Each sample**
PCB Congeners	<LMCL[a]	RPD <50%[b]	laboratory QC limits [c]	laboratory QC limits [c]

batch = 20 samples or less prepared as a set
[a]EPA Method 1668 blank criteria (see Table 2 of the published method) is to be below the Minimum Levels: 2, 10, 50 pg/congener depending on the congener with the sum of all congeners below 300 pg/sample. Higher levels are acceptable when sample concentrations exceed 10x the blank levels.
[b]provided both samples have results >10 pg/L
[c]The 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
RPD = Relative Percent Difference (difference / mean)
OPR = ongoing precision and recovery

4.2 Conventionals

All conventional analyses will follow Standard Methods protocols (American Public Health Association [APHA] 2012). Table 7 presents the analytical methods, detection limits and units for conventional analyses.

Table 7. Conventionals Analytical Methods and Detection Limit Goals in mg/L

Analyte	Method	KCEL SOP	MDL	RDL
Dissolved Organic Carbon	SM5310-B	336	0.5	1.0
Total Organic Carbon	SM5310-B	336	0.5	1.0
Total Suspended Solids	SM2540-D	309	0.5	1.0

SOP = standard operating procedures

Detection limits will vary slightly from sample to sample, depending on the exact amount of sample volume used for analysis. Table 8 describes the minimum QC required for the conventionals analysis. Conventional QC samples will be analyzed at the frequency of one per QC batch of 20 or less samples.

Table 8. Conventionals QA/QC Frequency and Acceptance Criteria

Analyte / Frequency	Method Blank	Lab Duplicate (RPD)	Spike Blank (% Recovery)	Matrix Spike (% Recovery)	LCS (% Recovery)
	1 per batch*	1 per batch*	1 per batch*	1 per batch*	1 per batch*
Dissolved Organic Carbon	<MDL	20%	80-120%	75-125%	85-115%
Total Organic Carbon	<MDL	20%	80-120%	75-125%	85-115%
Total Suspended Solids	<MDL	25%	N/A	N/A	80-120%

* batch = 20 samples or less prepared as a set
< MDL = less than the Method Detection Limit.
RPD = Relative Percent Difference
LCS = Lab Control Sample
N/A = Not Applicable

5.0. DATA VALIDATION, REPORTING AND RECORD KEEPING

This section presents the data validation, reporting and record keeping for the samples collected under this SAP.

5.1 Data Validation

Conventional data generated during this study will be validated according to acceptance limits listed in this SAP. KCEL will develop QC data allowing for validation based on reviews of holding times, method blanks, and QA/QC samples. For analyses performed by KCEL, the validator will also review data anomaly forms generated by the laboratory. These forms include any issues related to calibrations and instrument performance. PCB data will undergo a Level III data validation per EPA Region 10 guidelines (EPA 1995). All necessary data needed for independent review of PCB congener data will be provided by Pacific Rim. All other conventional water quality 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 Water and Land Resources Division staff for all data generated by KCEL. Data validation for PCB congener data will be conducted by an outside party for this study. Data validation memoranda will be produced and maintained along with the analytical data as part of the project records.

5.2 Reporting

All analytical data collected for this study and any supporting information will be documented in a data report. Data validation memoranda will be included in the data report, as will copies of COC forms. Green River analytical data will be submitted for loading into the Washington Department of Ecology's Environmental Information Management database.

5.3 Record Keeping

All hard-copy field sampling records, custody documents, raw lab data, and laboratory summaries and narratives generated by KCEL will be archived according to KCEL policy for LDW Superfund records. These records will include both hard copy and electronic data. Conventional data produced by the KCEL will be maintained on its LIMS database in perpetuity. Pacific Rim will provide electronic data deliverables and associated quality control results to King County. While KCEL will maintain a copy of deliverables from Pacific Rim, copies of full data packages pertaining to King County samples analyzed by Pacific Rim will be maintained by Pacific Rim for 10 years from the analysis date.

6.0. REFERENCES

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