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# Lower Duwamish Waterway Source Tracing in King County Combined Sewer System Sampling and Analysis Plan

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August 2011

Final



**King County**

Department of Natural Resources and Parks  
Water and Land Resources Division

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# Lower Duwamish Waterway Source Tracing in King County Combined Sewer System

## Sampling and Analysis Plan

### Prepared for:

King County Department of Natural Resources and Parks  
Wastewater Treatment Division Sediment Management Program

### Submitted by:

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Department of Natural Resources and Parks



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**Science and Technical Support Section**



## Acknowledgements

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## Citation

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# Table of Contents

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1	INTRODUCTION .....	1
1.1	Project Background.....	1
1.2	Scope of Work .....	1
1.3	Survey Schedule.....	2
1.4	Project Staff .....	2
2	SURVEY DESIGN.....	4
2.1	Data Quality Objectives.....	4
2.1.1	Precision, Accuracy, and Bias .....	4
2.1.2	Representativeness.....	4
2.1.3	Completeness .....	5
2.1.4	Comparability .....	5
2.1.5	Sensitivity .....	5
2.2	Sampling and Analytical Strategy .....	5
2.2.1	Sampling Station Locations and Sample Identification.....	6
2.2.2	Sample Acquisition and Analytical Parameters.....	6
3	SAMPLING PROCEDURES .....	8
3.1	In-Line Sediment Grab Sampling Methods .....	8
3.2	In-Line Sediment Trap Sampling Methods.....	9
3.3	Sampling Equipment.....	9
3.4	Equipment Decontamination .....	11
3.5	Sample Delivery and Storage.....	12
3.6	Chain of Custody .....	12
3.7	Sample Documentation.....	13
3.8	Field Replicates.....	13
4	ANALYTICAL METHODS AND DETECTION LIMITS .....	14
4.1	PCB Aroclors .....	16
4.2	Semivolatile Organic Compounds .....	17
4.3	Metals.....	21
4.4	Conventionals .....	23
4.5	Dioxins/furans.....	24
5	DATA VALIDATION, REPORTING AND RECORD KEEPING .....	27

5.1	Data Validation .....	27
5.2	Reporting.....	27
5.3	Record Keeping .....	27
6	REFERENCES .....	29

## Figures

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Figure 1.	King County CSOs and Associated Basins in Lower Duwamish Waterway. ....	31
Figure 2.	Inline sediment sampler .....	32
Figure 3.	Sediment trap bottle mounting bracket.....	33

## Tables

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Table 1.	Solids Sample Container, Preservation, Storage, and Hold Time Requirements .....	12
Table 2.	PCB Aroclor detection limit goals in µg/kg ww.....	16
Table 3.	PCB Aroclor QA/QC Frequency and Acceptance Criteria.....	17
Table 4.	SVOC Target Compounds and Detection Limit Goals in µg/kg, ww .....	18
Table 5.	SVOC QA/QC Frequency and Acceptance Criteria.....	19
Table 6.	Trace Metals Target Analytes and Detection Limit Goals in mg/kg ww .....	22
Table 7.	Mercury Detection Limit Goals in mg/kg ww .....	22
Table 8.	Trace Metals and Mercury QA/QC Frequency and Acceptance Criteria.....	23
Table 9.	Conventionals Target Analytes and Detection Limits Goals.....	24
Table 10.	Conventionals QA/QC Frequency and Acceptance Criteria .....	24
Table 11.	Labeled Surrogates and Recovery Standards Used for EPA Method 1613b Dioxins/Furans Congener Analysis .....	25
Table 12.	Dioxin/furan solids sample detection limit goals in pg/g and lower calibration limit goals by EPA method 1613b, AXYS Analytical Services method MLA 017.....	25
Table 13.	Dioxins/furans QA/QC Frequency and Acceptance Criteria.....	26

# ACRONYMS

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AXYS	AXYS Analytical Services Ltd.
COC	chain of custody
CSO	combined sewer overflow
CVAA	cold vapor atomic absorbance
DQOs	data quality objectives
Ecology	Washington Department of Ecology
EIM	environmental information management
EPA	Environmental Protection Agency
FSU	Field Science Unit
GC/ECD	gas chromatography/ electron capture detection
HRGC/HRMS	high-resolution gas chromatography/high-resolution mass spectroscopy
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
MRL	method reporting limit
OPR	ongoing precision and recovery
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyls
RDL	reporting detection limit
PQL	practical quantitation limit
PSD	particle size distribution
QA/QC	quality assurance/quality control
SAP	sampling and analysis plan
SRM	standard reference material
SVOC	semi-volatile organic compounds
TOC	total organic carbon
WTD	Wastewater Treatment Division

# 1 INTRODUCTION

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This sampling and analysis plan (SAP) presents project information and sampling and analytical methodologies to evaluate the relative magnitude of certain chemicals in the combined sewer system leading to the Duwamish River in Seattle, Washington. Figures referenced in the text follow Section 6, References. This SAP is being updated from the 2010 version (King County 2010) to account for modifications in analytical methods or procedures and to broaden the scope, which was originally focused on limited sampling in Brandon and Michigan combined sewer overflow (CSO) basins.

## 1.1 Project Background

This SAP documents the field and laboratory activities associated with source tracing samples collected in CSO basins of the Lower Duwamish Waterway (LDW).<sup>1</sup> This work supports King County source control investigations related to the LDW. Specifically, King County will perform this work to help identify sources of chemicals of potential concern and as a line of evidence to be used in evaluating whether these chemicals are present in sufficient amounts to potentially recontaminate sediments in the LDW.

The Duwamish River originates at the confluence of the Green and Black Rivers near Tukwila, Washington, and flows northwest for approximately 19 km (12 mi), splitting at the southern end of Harbor Island to form the East and West Waterways, prior to discharging into Elliott Bay, in Puget Sound, Seattle, Washington. The LDW is about 5 miles long and consists of the downstream portion of the Duwamish River, excluding the East and West Waterways. King County has eight CSOs and two emergency overflows that discharge into the LDW. These CSOs and their associated drainage basins are shown on Figure 1.

King County (KC) Wastewater Treatment Division (WTD) needs to better understand the current levels of certain chemicals and conventional parameters at CSO basins in the LDW. King County has recently completed sampling of CSO whole water at various CSOs in the Duwamish River Basin (King County 2009). The CSO solids data collected under this SAP will assist in source tracing activities in King County LDW CSO basins (Figure 1) and in understanding if CSO discharges could lead to recontamination of sediments following any designated remediation in the LDW identified by the US Environmental Protection Agency (EPA).

## 1.2 Scope of Work

The scope of source characterization and tracing of chemicals in the combined sewer basin will involve collection and analysis of solid (i.e., sediment) samples from pipes, wet wells or outfall weir structures located within the combined sewer collection system of the LDW Basin. Generally, CSO basins with discharges to the LDW of 5 times or more a year (on average; King

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<sup>1</sup> The LDW was added to US Environmental Protection Agency's National Priorities List (also known as Superfund) on September 13, 2001. The LDW was added to Ecology's Hazardous Sites List on February 26, 2002.

County 2011) will be prioritized for sampling (i. e., Brandon, Michigan, West Michigan, and Hanford #1 CSO basins) but other basins with smaller discharge frequencies may be sampled as well. Future sampling of other CSO basins could occur and this SAP will support that work. Sampling includes methods for collecting both in-line solid grab samples and sediment trap samples. Samples will be analyzed for select metals (including mercury), select organic compounds, percent solids, and total organic carbon, depending on sample mass/volume. Where sample mass allows, in-line solid grab and sediment trap samples will also be analyzed for particle size distribution and archived for potential future analyses.

### 1.3 Survey Schedule

Field reconnaissance for collection of in-line solid grab samples will begin in July 2011 and sample collection in August to September 2011 and continue as needed based on the results of prior sampling<sup>2</sup> or as new information becomes available suggesting a need to further characterize a CSO basin. Sediment traps are targeted for deployment in the summer of 2011 and continue as needed through 2012. Typically sediment traps are left in pipes for 6-9 months to allow adequate time for sufficient suspended solids to be captured for analysis. Analysis of samples is expected to continue through second quarter of 2012. It is anticipated that data from all sampling events will be validated, reviewed, and ready for release by the last quarter of 2012.

### 1.4 Project Staff

The following staff members are responsible for project execution:

Jeff Stern, LDW Project Manager.....	206-263-6447
Wastewater Treatment Division Manager and Technical lead for all Lower Duwamish River studies.	
Debra Williston, Study Project Manager .....	206-263-6540
Responsible for study project execution and adherence to SAP and schedule; technical support for all Lower Duwamish River studies.	
Richard Jack, Study Assistant Project Manager .....	206-205-5151
Assists project manager with study project execution.	
Bruce Tiffany, Industrial Waste Project Lead.....	206-263-3011
Provides technical advice on all aspects of the project; King County representative on the LDW Source Control Work Group.	

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<sup>2</sup> Contaminant concentrations targeting the need for additional source tracing in combined sewer systems have not been established at this time.

- David Robinson, Field Science Unit Field Lead.....206-684-2329  
Responsible for sample collection.
- Fritz Grothkopp, KC Environmental Laboratory Project Manager .....206-684-2327  
Manages sample analysis, sample shipment, and data delivery.
- Scott Mickelson, Data Validation Lead .....206-296-8247  
Responsible for all data validation.

## 2 SURVEY DESIGN

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The goal of this source tracing survey is to collect representative samples that reflect chemical concentrations found in solids (sediments) within King County combined sewer basins that discharge to the LDW. Another goal is to further refine or identify potential sources of chemicals of concern within the combined system to assist in source control actions for the LDW.

### 2.1 Data Quality Objectives

The data quality objectives (DQOs) are to collect data of known and sufficient quality to meet the survey goals. Validation of project data will assess whether the data collected are of sufficient quality to meet the survey 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 5.1.

#### 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) procedures:

- analysis of various laboratory QC samples such as blanks, surrogates, and replicates;
- collection and analysis of field replicate samples.

Because this project is a survey, and combined sewers are suspected to be variable in their flow rates, industrial discharges and stormwater inputs, precision is expected to be low. Precision of replicates will be compared to previous in-line grab and sediment trap results to evaluate data from this study.

Accuracy for polychlorinated biphenyls (PCB) Aroclor data is not quantifiable since certified reference materials do not exist for the in-line solid or sediment trap matrix from combined sewer systems. Since this study intends to track potential sources to combined sewers, and possible sources vary in both time and space, analytical bias only needs to be quantified relative to other in-line or trap samples.

#### 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. Solid samples will be collected from locations within the combined sewer system to represent one line of evidence of the solids fraction conveyed by the system. The selected locations contain sewage and stormwater that have discharged to the combined sewer system in the past under varying rainfall and operating conditions. The frequency that these locations

actually overflow to the LDW is variable and unpredictable, being primarily dependent on the intensity and duration of storm events. These samples are not intended to represent historic conditions in the pipe, rather to trace ongoing or episodic sources within these combined basins through the sampling of sediment traps and in-line solid grab 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 survey. The goal for completeness is 90%. If 90% completeness is not achieved, the project team will evaluate if the DQOs can still be met or if additional samples may need to be collected and analyzed.

### 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 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 between this and future sampling events will be achieved.

### 2.1.5 Sensitivity

Sensitivity is a measure of the capability of analytical methods to meet the survey goal. The analytical method detection limit goals presented in Section 4 should be sufficiently sensitive to detect mercury, metals, and other analytes at concentrations of interest to understand the magnitude of potential sources to the LDW from the combined sewer system.

## 2.2 Sampling and Analytical Strategy

The source control sampling strategy has been designed to build on existing knowledge of the collection system obtained through Industrial Waste and WTD monitoring programs. In-line solids grab samples will be collected from accessible conveyance lines with available solids material for the CSO basins targeted, such as Brandon and Michigan. Sediment traps will be deployed in accessible Brandon, Michigan, and West Michigan CSO conveyance lines. To the extent possible, sediment traps will be placed in areas that will capture suspended solids at access points close to an outfall structure or regulator station or after multiple conveyance lines have merged. Sampling from other CSO basins could be conducted in the future.

Both in-line solid grab samples and sediment trap samples will provide data to supplement the CSO whole water data and will help with source tracing of chemicals of potential concern. Sampling will be continued as deemed necessary based on results of current proposed sampling and consideration of the project schedule. Initial sampling, based on reconnaissance by King County Industrial Waste and King County Environmental Laboratory (KCEL) Field Science Unit (FSU) staff as well as results of in-line solid grab samples collected in 2010, will include in-line grab samples in basins that discharge to Brandon, Michigan, Terminal 115 and West

Michigan outfalls. Sediment traps are being targeted for conveyance line in the Brandon, Michigan and West Michigan CSO basins. Sample locations including coordinates will be included in the data report.

Samples from these systems will be submitted for total organic carbon (TOC) and total solids. Other parameters will be chosen based on receiving sediment concentrations close to the associated basin's outfall, previous results from the combined system, and available mass of solids collected from within the CSO conveyance lines. Analytes considered for analysis include: mercury, other metals, PCBs, select semivolatile organic compounds (SVOCs), 17 dioxin/furan congeners and particle size distribution (PSD). In general, all of these analytes except dioxin/furan congeners will be analyzed in samples if sufficient mass is available. Dioxin/furans will be limited to a subset of samples. When mass is limited, the project manager will be consulted for priority of analytes. The analyte priority will consider receiving sediment conditions close to the CSO basin's outfall. There may be situations where source tracing is being conducted for a particular analyte(s) and therefore the analyses will be limited to the analyte(s) of interest. Where ever, sufficient mass is available, archive jars will be collected and frozen.

Where possible, one field replicate sample will be collected for every ten in-line solid grab samples, or one per CSO basin if less than ten are collected in the basin. Field replicates are not expected for sediment traps because of the limited solid mass collected. If sufficient mass were to be collected from a sediment trap, then a field replicate would be collected and analyzed. In addition, field replicates for mercury will be collected at all locations sampled where sufficient mass is available and mercury is prioritized for analysis. Duplicates for mercury will be collected to help evaluate variability of mercury, which King County's laboratory has found to sometimes be very heterogeneous in sediment/solid matrices.

### 2.2.1 Sampling Station Locations and Sample Identification

Sample locations will be identified using a unique sample location or 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. Locations targeted for sampling are specified in this SAP because field reconnaissance is not complete; locations have to be confirmed by field staff depending on access and suitable in-line solids accumulations. In addition, sample locations may be added over time based on the findings of previous sampling results or as new information becomes available suggesting a need to further characterize sources in a CSO basin. Figure 1 shows the CSO basins for the LDW. Coordinates for locations sampled will either be determined by current GIS information or handheld GPS on site.

### 2.2.2 Sample Acquisition and Analytical Parameters

King County FSU staff will primarily conduct sampling; however, King County Industrial Waste and WTD facilities staff may provide assistance as needed. Sampling techniques are discussed in Section 3.

Most in-line solid grab samples or sediment trap samples will be analyzed for the following, where sample mass is sufficient: total solids, TOC, PCB Aroclors, mercury, metals, select SVOCs, and PSD. Dioxin/furans will be analyzed in only a subset of samples. Where mass is

insufficient to analyze all parameters, the project manager/task manager will determine the priority for the location being sampled. The project manager/task manager will consider conditions of the receiving sediments close to the CSO outfall and previous sampling data for that basin. Where excess in-line solids are found, additional material will be collected in glass jars and archived for possible future analysis. Except for PSD analysis, all samples will be stored frozen. KCEL will conduct all chemical and conventional analyses except dioxin/furans. Dioxin/furans will be analyzed by AXYS Analytical Services (hereinafter AXYS).

## 3 SAMPLING PROCEDURES

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This section describes field procedures that will be utilized to ensure that samples are collected in a consistent manner and are representative of the matrix being sampled, and the data will be comparable to data collected by other existing and future monitoring programs. Procedures are described for collecting solid samples, collecting field quality control samples, decontaminating sampling equipment, and recording field measurements and conditions. Requirements for sample containers and preservation, sample identification, and field quality control procedures are also described.

### 3.1 In-Line Solid Grab Sampling Methods

In-line solid grab samples will be collected using stainless steel beakers and long-handled scoops. King County has a specially designed long handled scoop which is required to reach down to the bottom of large (e.g., 150-inch diameter, 3.81 m) combined sewer trunk lines without exposing staff to confined spaces. The beakers will be decontaminated between sampling locations (see Section 3.4). The vented long-handled scoop is illustrated in Figure 2.

Samples will be collected from the in-line solid accumulated in conveyance lines. Individual aliquots will be collected from at least three scoop dips at a given access point. Because wastewater is always present in sewer lines, overlying water collected with the solids will be allowed to decant from the sample container. This is accomplished through perforations in the sampling container designed specifically to allow wastewater to dewater from the solid sample. Once the overlying water has been decanted and returned to the sewer line, the solids in the sampling container will be placed in a stainless steel bowl. All sample locations will have dedicated stainless steel mixing bowls and spoons that will be pre-cleaned at KCEL. Once sufficient sediment has been collected in the stainless steel bowl (see Section 3.5 for approximate sample volumes by method); it will be thoroughly mixed. Any particles greater than 2 centimeters in size will be removed from the sample and returned to the sewer line. After mixing, samples will be placed into pre-cleaned sample containers provided by KCEL. Samples will be placed in a cooler and stored on ice until delivered to the analytical laboratory. Samples will be analyzed for the parameters outlined in Section 2.2.2. Where possible, sediment will be archived for potential future analyses.

Nitrile gloves will be worn at all times while collecting the samples. Descriptions of field observations (including oil sheens and potential contributing activities) and sample characteristics (odor, amount and type of particles being removed, size, description; e.g., wood, rocks, color) will be included in field notes recorded during sample collection. A digital photo will be taken of the sample while in the stainless steel bowl.

Field replicates for mercury will be collected at all locations where mercury is being analyzed (assuming sufficient mass is available). One field replicate for all analytes will be collected at a frequency of 1 per 10 environmental samples (or one per CSO basin sampled if less than 10 are collected in that basin). All field replicates will be collected using separate cleaned scoops and bowls. Suitable replicate locations are limited by the mass of in-line solids found and will be

decided in the field. It is possible not all CSO basins will have a field replicate collected if sufficient mass is not present.

One field blank sample will be collected from the long-handled scoops to evaluate the effectiveness of the field decontamination procedures for this piece of equipment. Laboratory reagent grade water will be poured through the scoop following field decontamination. This water will be collected in pre-cleaned sampling containers and stored on ice along with the in-line solid grab samples until delivery to KCEL. The field blanks will be collected once per every 20 stations. Field blanks will be analyzed for whichever analytes are selected for a given location based on review of receiving sediment concentrations and previous results. Methods and method detection limits (MDLs) for this water matrix are shown in Appendix B.

### 3.2 In-Line Sediment Trap Sampling Methods

Sediment trap samples will be collected in pre-cleaned, one-liter, wide-mouth Teflon<sup>®</sup> containers. Sediment traps will be mounted to the wall of the conveyance line above base flows to collect suspended solids associated with combined sewer flows (Figure 3 shows the sediment trap bottle mounting bracket). Each sediment trap consists of a stainless-steel bracket and housing that holds a Teflon<sup>®</sup> sample container. The sediment traps were fabricated for Seattle Public Utilities based on an initial design by Washington Dept. of Ecology (Ecology 1996) and modifications by the City of Tacoma.

Sediment traps would be deployed for approximately 6-month intervals to allow for sufficient sample volume to accumulate. If there is sufficient room in the pipe, two traps will be installed per location to increase the amount of suspended solids collected. If sufficient material has not accumulated in the six month interval, traps will be removed, processed and stored frozen and new traps placed, or they will be left in place so that additional material can be collected over the remaining wet season. If possible, sediment traps will be retrieved after a period of three days of dry weather to allow for additional settling of particulate and colloidal materials in the collected sample. Upon retrieval, the sample container will be capped with Teflon<sup>®</sup> lined lid, placed in sealed plastic bags, sealed and put on ice in a cooler for delivery to KCEL. At the laboratory, the height of solids within the sample container will be measured to the nearest millimeter and samples will be centrifuged in the original Teflon<sup>®</sup> container to separate solids from overlying water. After centrifuging, as much overlying water as possible will be siphoned off and the underlying solids and colloidal fraction will be analyzed. If necessary, samples from different deployment intervals will be combined to provide enough mass for analysis. Solids and colloidal fraction will be thoroughly mixed in pre-cleaned stainless steel bowl prior to adding to appropriate pre-cleaned sample containers for chemical analysis. Samples will be analyzed for the parameters outlined in Section 2.2.2, provided sufficient volume is available and collected. Any excess sample mass will be archived frozen for potential future analysis.

### 3.3 Sampling Equipment

If entry into the confined spaces is necessary for any sample collection it will be done by King County personnel who have the training and experience to safely enter these spaces. King County confined space entry requirements and safety protocols will be followed at all times.

Field staff members are confined-space entry certified through the WTD Permit-Required Confined Space Entry Program. All guidelines and requirements for confined space entry can be found in the WTD Permit-Required Confined Space Entry Program Manual (King County 1998). KCEL FSU staff will be responsible for sampling in-line solid grabs using a custom stainless steel bucket on a pole. This sampler allows them to remain safely outside of confined spaces. Figure 2 illustrates the sampler. If traffic control is necessary for sample collection, FSU flagger certified staff will be part of the sampling team. Additional field equipment is listed below.

1) Sampling Equipment:

- a) Appropriate sample containers supplied by laboratory (Table 1)
- b) Stainless steel scoops and/or extension pole with swivel attachment
- c) Stainless steel mixing bowls
- d) Stainless steel spoons

2) Sampling supplies:

- a) Ziploc® bags
- b) Cooler with ice
- c) Nitrile gloves

3) Safety equipment:

- a) Hard hat
- b) Safety vest
- c) Safety shoes and glasses
- d) Appropriate traffic control equipment and personnel where applicable (FSU supervisor will approve safety plan)
- e) Documentation supplies:
- f) Field notebook
- g) Sample labels
- h) Chain-of-custody forms
- i) 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 (e.g., street intersection, identification number for County-owned structures)
- Weather conditions
- Number and type of samples collected

- Field measurements
- Log of photographs taken
- Comments on the working condition of the sampling equipment
- Deviations from sampling procedures
- Unusual conditions (e.g., water color or turbidity, presence of oil sheen, odors, and land disturbances)
- Visual observations of color, texture (estimate particle size fractions per standard soil classification), and amount and type of debris

### 3.4 Equipment Decontamination

All sampling equipment, including the trap and stainless-steel scoop and beaker, and other stainless-steel materials will be decontaminated after each sampling event. The following decontamination procedures will be followed:

Sediment trap Teflon<sup>®</sup> sample bottles (to be completed by KCEL)

- Phosphate-free detergent wash and tap water rinse
- 10 percent ultra-pure hydrochloric acid rinse
- Reagent-grade water rinse
- Air dry
- Cap on during transport to site

Stainless-steel scoop and beaker will be cleaned at the lab before each day's use and again by field staff in between each sampling location. The dedicated stainless-steel bowl and mixing spoon for each sampling location will be pre-cleaned at the lab before each day's use. Below are the procedures for cleaning stainless-steel items:

- Phosphate-free detergent wash and tap water rinse
- Reagent-grade water rinse
- Air dry
- Wrapped in new uncoated aluminum foil

After the decontamination procedures have been completed, the sampling equipment will be capped or sealed with new uncoated aluminum foil and the sampling device will be protected and kept clean until needed. A field blank will be collected once per every 20 sampling stations. It will entail using laboratory supplied reagent grade water to rinse the cleaned and dried sampling scoop. This scoop rinse water will then be analyzed for PCB Aroclors, SVOCs, mercury, and metals. Methods and MDLs for water blanks are listed below in Appendix B.

### 3.5 Sample Delivery and Storage

All samples will be kept in ice-filled coolers until delivery to KCEL on the same day that they are collected. No additional preservative is required for solids samples. Table 1 shows sample handling and storage requirements for all possible analyses. Archived solids will be placed in glass jars and held frozen at -18°C. Dioxin/furan samples will be wrapped in individual ziplock bags and shipped frozen in coolers with ice or frozen gel packs to AXYS via overnight delivery within four 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.

**Table 1. Solids Sample Container, Preservation, Storage, and Hold Time Requirements**

Analyte in priority	Container*	Preferred Storage Conditions	Hold Time**	Acceptable Storage Conditions	Hold Time
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
Total Organic Carbon (TOC)	4-oz. glass or polypropylene	freeze at -18°C	6 months to analyze	refrigerate at 4°C	14 days to analyze
Total Solids (collect with TOC)	4-oz. glass or polypropylene	freeze at -18°C	6 months to analyze	refrigerate at 4°C	14 days to analyze
Mercury	4-oz polypropylene	freeze at -18°C	28 days to analyze	N/A	N/A
Semi-Volatile Organic 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
Other Metals	4-oz polypropylene	freeze at -18°C	2 years to analyze	refrigerate at 4°C	6 months to analyze
Archive jars (2)	2x 16-oz. glass	freeze at -18°C	Analyte specific		
Particle Size Distribution	16-oz. glass or polypropylene	refrigerate at 4°C	6 months to analyze	N/A	N/A

\* Containers to be filled approximately ¾ full to allow space for expansion upon freezing (except for Particle Size Distribution).

\*\* Holding time begins the date the sample is removed from the CSO conveyance system.

### 3.6 Chain of Custody

Chain of custody (COC) will commence at the time the in-line solids grabs are collected. For sediment traps, chain of custody will begin at the time the traps are removed from the combined sewer lines. Thereafter, all samples will be under direct possession and control of King County field staff. For chain of custody purposes, closed/latched sewer lines and field vehicles will be considered “controlled areas.” All sample information will be recorded on a COC form (Appendix A). This form will be completed in the field and will accompany all samples during transport and delivery to KCEL. Upon arrival at the KCEL, 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

at this time. Copies of COC form will accompany dioxin/furan samples being shipped to AXYS. Once completed, original COC forms will be archived in the project file at KCEL.

Samples delivered to KCEL after regular business hours will be stored in a secure refrigerator after hours until the next day using established procedures for delivery.

### 3.7 Sample Documentation

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

- Field sheets generated by King County's Laboratory Information Management System (LIMS) will be used at all stations and will include the following information:
  1. sample ID number
  2. station name
  3. in-pipe station water depth at time of sampling.
  4. sampling time
  5. initials of all sampling personnel
  6. any deviations from these sampling procedures
- LIMS-generated container labels will identify each container with a unique sample number, station and site names, collect date, analyses required, and preservation method.
- COC documentation will consist of KCEL COC form, which is used to request analyses and track release-receipt of each sample from collection to arrival at the lab.

### 3.8 Field Replicates

Field replicates for mercury will be collected at all in-line grab sampling locations where mercury is being analyzed (assuming sufficient mass is available). At least one field replicate for all analytes will be collected at a frequency of 1 in 10 (or one per CSO basin sampled if less than 10 are collected in that basin) during the sampling of in-line solid grab samples. The field crew will determine locations where sufficient in-line solids are available for analysis of all target parameters. Each field replicate will be collected with a separate, cleaned set of sampling equipment. Field replicates will be identified by unique sample identification number but have the same locator and sample collection date as the primary sample.

Sediment trap samples are not expected to result in sufficient volume to create field replicate samples. However, if there is sufficient mass collected, a field replicate will be created.

## 4 ANALYTICAL METHODS AND DETECTION LIMITS

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

EPA's Office of Wastewater generally defines the practical quantitation limit (PQL) as the minimum concentration of a chemical constituent that can be reliably quantified while the MDL is defined as the minimum concentration of a chemical constituent that can be detected. The KCEL LIMS RDL is analogous to the PQL for all analyses. It is verified either by including it on the calibration curve or by running a low level standard near the PQL value during the analytical run.

For the majority of Trace Metals, Conventionals and Trace Organic PCB Aroclor (gas chromatography/electron capture detection[GC/ECD]) analyses, KCEL LIMS MDLs are typically two to five times higher than the statistically derived MDLs that are calculated by the 40 CFR Part 136, Appendix B procedure (Federal Register, Appendix B. 2007). In the case of some Metals and Conventionals tests, MDLs are evaluated by the procedure listed in Appendix D of 40 CFR Part 136. 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. In the case of organic mass spectral analyses, a standard analyzed near the MDL concentration during calibration must produce a valid mass spectra and this standard is used to define the MDL.

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 and TOC values). When sample extracts are diluted because the concentrations for one or more target analytes exceeded 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 particularly for dioxin/furan 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) 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.

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:

- A method blank is an aliquot of clean reference matrix that is generally processed through the entire analytical procedure. Analysis of the method blank is used to evaluate the levels of contamination that might be associated with the processing and analysis of samples in the laboratory. All method blank results should be less than the method detection limit.
- 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 between the results should be within method-specified, SAP-specified or performance-based quality control limits. In the case of SVOCs and mercury a matrix spike duplicate may be used in lieu of a laboratory duplicate due to the large number of non-detects frequently encountered in these analyses.
- 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/standard reference material (LCS/SRM). 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 should 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 is LIMS.

## 4.1 PCB Aroclors

Samples will be prepared by sonication extraction as detailed in method SW846 3550B, and analyzed for PCB Aroclors by method SW846 8082A (GC/ECD), KCEL SOP 757. Table 2 lists the PCB Aroclors and their respective target MDL and RDL goals. The reported MDLs and RDLs for individual samples may differ from those in Table 2 due to changes in the mass of sample extracted or the final extract volume. These MDL/RDLs are based upon taking 30 g of sample to 1 mL with a 3/8 loss due to a GPC cleanup. Every effort will be made to meet these limits, however depending upon the organic content of the samples it may not be possible to obtain this concentration factor. KCEL will report each individual Aroclor result and calculate Total Aroclors (i.e., total PCBs) as the sum of detected Aroclors<sup>3</sup>. If no Aroclors are detected the reported MDL/RDL for Total Aroclors will be the highest MDL/RDL reported for the individual Aroclors in that sample.

**Table 2. PCB Aroclor detection limit goals in µg/kg ww**

Analyte	MDL	RDL
Aroclor 1016	1.3	2.67
Aroclor 1221	2.7	5.33
Aroclor 1232	2.7	5.33
Aroclor 1242	1.3	2.67
Aroclor 1248	1.3	2.67
Aroclor 1254	1.3	2.67
Aroclor 1260	1.3	2.67

MDL = Method detection limit  
 RDL = Reporting detection limit  
 ww = wet weight

In addition to the surrogates and internal standards, which assess sample accuracy and bias, a method blank, laboratory duplicate, spike blank, matrix spike, matrix spike duplicate and an SRM duplicate sample will be analyzed with each set of 20 samples, or one per batch. Quality assurance/quality control (QA/QC) frequency and acceptance criteria for Aroclor analysis are as shown in Table 3.

<sup>3</sup> When Aroclors are detected, the reported MDL/RDL for the Total Aroclors parameter will be lowest MDL/RDL of the individual Aroclors.

**Table 3. PCB Aroclor QA/QC Frequency and Acceptance Criteria**

	Method Blank	Spike Blank (% Recovery)**	Matrix Spike (% Recovery)**	Matrix Spike or Spike Blank Duplicate (RPD)	Lab Duplicate (RPD)	Standard Reference Material and SRM Dup (% Recovery)**
Analyte/Frequency	1 per Extraction batch*	1 per Extraction batch*	1 per QC batch	1 per QC batch	1 per QC batch	1 per QC batch
Aroclor 1016	<MDL	NA	NA	NA	50	NA
Aroclor 1260	<MDL	40 -131	20 -132	50	50	NA
Aroclor 1254	<MDL	NA	NA	NA	50	57-139
Aroclor 1221	<MDL	NA	NA	NA	50	NA
Aroclor 1232	<MDL	NA	NA	NA	50	NA
Aroclor 1242	<MDL	36-117	45 -139	50	50	NA
Aroclor 1248	<MDL	NA	NA	NA	50	NA
<b>Surrogates - Added to all samples and QC</b>		<b>Surrogate (% Recovery)**</b>				
2,4,5,6-Tetrachloro-m-xylene		20-110				
Decachloro-biphenyl		25-150				

\*QC Extraction batch = 20 samples or less prepared within a 12 hour shift

\*\* These are empirically derived performance-based laboratory control limits. These limits may be updated once per calendar year and the limits in effect at the time of analysis will be used as accuracy limits for spike blank, matrix spike/matrix spike duplicate, laboratory control sample, and ongoing precision and accuracy samples.

Note: As of August 22, 2011 Aroclor 1242 will be used with Aroclor 1260 instead of Aroclor 1016 for spike blanks and matrix spikes. The recovery limits will remain unchanged.

Note: SRM will be run in duplicate to provide information on the analytical precision of the method. The RPD limit is 35%.

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

RPD = Relative Percent Difference

NA = Not Applicable

## 4.2 Semivolatile Organic Compounds

Semivolatile organics analyzed for this survey will consist of the compounds in the KCEL Base-Neutral-Acid-Sediment Management Standards (BNASMS) list type (see Table 4). The samples will be prepared by sonication extraction as detailed in method SW846 3550B, and analyzed by method SW846 8270D, KCEL SOP 753. Wet weight MDL and RDL goals are as shown and are based upon taking 30 g of sample to 1 mL with a 3/8 loss due to a GPC cleanup. Every effort will be made to meet these limits, however depending upon the organic content and total solids of the samples, it may not be possible to obtain this concentration factor. KCEL will report individual polycyclic aromatic hydrocarbon (PAH) results.

In addition, KCEL will report total high molecular weight PAHs (HPAHs) and total low molecular weight PAHs (LPAHs) as the sum of detected HPAHs or LPAHs, respectively<sup>4</sup>. If no PAHs are detected within the LPAH or HPAH class, the reported MDL/RDL for these totals will be the highest MDL/RDL reported for the individual PAHs in that class. When individual PAHs in HPAH or LPAH are detected, the reported MDL/RDL for these totals will be the lowest MDL/RDL from the respective LPAH or HPAH class.

**Table 4. SVOC Target Compounds and Detection Limit Goals in µg/kg, ww**

Analyte	MDL	RDL
1,2,4-Trichlorobenzene	0.53	1.07
1,2-Dichlorobenzene	5.33	5.33
1,4-Dichlorobenzene	8.00	8.00
2,4-Dimethylphenol	5.3	10.7
2-Methylnaphthalene	5.3	10.7
2-Methylphenol	5.3	10.7
3-,4-Methylphenol	27	53.3
Acenaphthene	5.3	10.7
Acenaphthylene	5.3	10.7
Anthracene	5.3	10.7
Benzo(a)anthracene	5.3	10.7
Benzo(a)pyrene	5.3	10.7
Benzo(b,j,k)fluoranthene	5.3	10.7
Benzo(g,h,i)perylene	5.3	10.7
Benzoic Acid	107	107
Benzyl Alcohol	13.3	13.3
Benzyl Butyl Phthalate	8.00	8.00
Bis(2-Ethylhexyl)Phthalate	11	21.3
Chrysene	5.3	10.7
Dibenzo(a,h)anthracene	5.3	10.7
Dibenzofuran	5.3	10.7
Diethyl Phthalate	11	21.3
Dimethyl Phthalate	10.7	10.7
Di-N-Butyl Phthalate	11	21.3
Di-N-Octyl Phthalate	10.7	10.7
Fluoranthene	5.3	10.7
Fluorene	5.3	10.7
Hexachlorobenzene	0.53	1.07
Hexachlorobutadiene	2.7	5.33
Indeno(1,2,3-Cd)Pyrene	5.3	10.7

<sup>4</sup> When PAHs are detected, the reported MDL/RDL for the total LPAH or total HPAH parameter will be lowest MDL/RDL of the individual LPAHs or HPAHs, respectively.

Analyte	MDL	RDL
Naphthalene	5.3	10.7
N-Nitrosodiphenylamine	13.3	13.3
Pentachlorophenol	80.0	80.0
Phenanthrene	5.3	10.7
Phenol	27	80.0
Pyrene	5.3	10.7

NOTE: The MDL/RDL limits are calculated on an extraction of 30 grams to a final volume of 1.0 mL with a 3/8 loss for GPC cleanup. MDL/RDL limits will vary depending on amount extracted and final volume.

ww = wet weight

In addition to the surrogates and internal standards, which assess sample accuracy and bias, a method blank, laboratory duplicate, spike blank, matrix spike, matrix spike duplicate an SRM and an SRM duplicate sample will be analyzed with each set of 20 samples, or one per batch. QA/QC frequency and acceptance criteria for SVOC analysis are as shown in Table 5.

**Table 5. SVOC QA/QC Frequency and Acceptance Criteria**

	Method Blank	Spike Blank (% Recovery)**	Matrix Spike (% Recovery)**	Matrix Spike or Spike Blank Duplicate (RPD)**	Lab Duplicate (RPD)	Standard Reference Material and SRM Dup (% Recovery)**
Analyte/ Frequency	1 per Extraction batch*	1 per Extraction batch*	1 per QC batch	1 per QC batch	1 per QC batch	1 per QC batch
1,2,4-Trichlorobenzene	<MDL	21-115	35-117	50	50	
1,2-Dichlorobenzene	<MDL	21-118	25-74	50	50	
1,4-Dichlorobenzene	<MDL	32-78	19-76	50	50	
2,4-Dimethylphenol	<MDL	5-80	5-115	50	50	
2-Methylnaphthalene	<MDL	25-129	10-111	50	50	
2-Methylphenol	<MDL	10-100	20-90	50	50	
3-,4-Methylphenol	<MDL	10-125	10-163	50	50	
Acenaphthene	<MDL	40-100	40-95	50	50	
Acenaphthylene	<MDL	48-111	41-112	50	50	
Anthracene	<MDL	55-112	10-150	50	50	28-98
Benzo(a)anthracene	<MDL	68-130	40-158	50	50	66-124
Benzo(a)pyrene	<MDL	62-113	32-143	50	50	60-116
Benzo(b,j,k)fluoranthene	<MDL	61-126	31-153	50	50	52-190

*Lower Duwamish Waterway Source Tracing in King County Combined Sewer System Sampling and Analysis Plan*

	Method Blank	Spike Blank (% Recovery)**	Matrix Spike (% Recovery)**	Matrix Spike or Spike Blank Duplicate (RPD)**	Lab Duplicate (RPD)	Standard Reference Material and SRM Dup (% Recovery)**
Analyte/ Frequency	1 per Extraction batch*	1 per Extraction batch*	1 per QC batch	1 per QC batch	1 per QC batch	1 per QC batch
Benzo(g,h,i)perylene	<MDL	36-126	20-121	50	50	15-121
Benzoic Acid	<MDL	10-150	5-130	50	50	
Benzyl Alcohol	<MDL	10 -90	10 -95	50	50	
Benzyl Butyl Phthalate	<MDL	46-147	30-150	50	50	
Bis(2-Ethylhexyl)Phthalate	<MDL	49-129	30-160	50	50	
Chrysene	<MDL	59-110	41-127	50	50	77-136
Dibenzo(a,h)anthracene	<MDL	53-137	37-129	50	50	10-200
Dibenzofuran	<MDL	44-106	14-129	50	50	
Diethyl Phthalate	<MDL	40-138	26-142	50	50	
Dimethyl Phthalate	<MDL	41-128	31-127	50	50	
Di-N-Butyl Phthalate	<MDL	50-150	34-146	50	50	
Di-N-Octyl Phthalate	<MDL	54-146	50-155	50	50	
Fluoranthene	<MDL	50-120	10-168	50	50	45-126
Fluorene	<MDL	45-109	18-131	50	50	
Hexachlorobenzene	<MDL	36-112	20-130	50	50	
Hexachlorobutadiene	<MDL	17-92	21-78	50	50	
Indeno(1,2,3-Cd)Pyrene	<MDL	54-127	35-123	50	50	33-121
Naphthalene	<MDL	29-100	15-107	50	50	10-29
N-Nitrosodiphenylamine	<MDL	5-128	20-135	50	50	
Pentachlorophenol	<MDL	20-121	30-151	50	50	
Phenanthrene	<MDL	58-106	10-146	50	50	51-106
Phenol	<MDL	17-92	30-105	50	50	
Pyrene	<MDL	50-125	20-150	50	50	36-135
<b>Surrogates - Added to all samples and QC</b>		<b>Surrogate (% Recovery)</b>				
2-Fluorophenol		20-120				
D5-Phenol		17-103				
D5-Nitrobenzene		16-103				

	Method Blank	Spike Blank (% Recovery)**	Matrix Spike (% Recovery)**	Matrix Spike or Spike Blank Duplicate (RPD)**	Lab Duplicate (RPD)	Standard Reference Material and SRM Dup (% Recovery)**
Analyte/ Frequency	1 per Extraction batch*	1 per Extraction batch*	1 per QC batch	1 per QC batch	1 per QC batch	1 per QC batch
D4-2-Chlorophenol		13-101				
D4-1,2-Dichlorobenzene		20-140				
2-Fluorobiphenyl		22-135				
2,4,6-Tribromophenol		20-150				
D14-Terphenyl		45-150				

\* QC Extraction batch = 20 samples or less prepared within a 12 hour shift

\*\* These are empirically derived performance-based laboratory control limits. These limits may be updated once per calendar year and the limits in effect at the time of analysis will be used as accuracy limits for LCS, SB, MS/MSD, and ongoing precision and accuracy samples.

Note: SRM will be run in duplicate to provide information on the analytical precision of the method. The RPD limit is 35%.

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

RPD = Relative Percent Difference

NA = Not Applicable

### 4.3 Metals

Metals samples will be analyzed by EPA Method 3050B / 6010C (Inductively Coupled Plasma [ICP]), KCEL SOP 612 for the analytes listed in Table 6. If any metals are not detected in a sample, those samples will be analyzed and reported by EPA Method 3050B / 6020A (Inductively Coupled Plasma-Mass Spectrometry [ICP-MS]), KCEL SOP 623. Mercury will be analyzed by EPA Method 7471B (Cold Vapor Atomic Absorption [CVAA]), KCEL SOP 604, high-range; however, if mercury is not detected in the sample, it will be re-analyzed using mid-range.

The following detection limit goals are targeted for metals and mercury (Tables 6 and 7). The CVAA MDL is based upon digesting a 1 g sample aliquot, resulting in a final volume of 100 mL. ICP MDLs are based upon digesting a 1 g sample aliquot and diluting the resulting solution to a final volume of 50 mL. ICP-MS MDLs are based upon digesting a 1 g sample aliquot and diluting the resultant solution to a final volume of 250 mL. MDL and RDL values for actual samples will be calculated based on exact amount of sample digested and will be reported to 2 and 3 significant figures, respectively.

**Table 6. Trace Metals Target Analytes and Detection Limit Goals in mg/kg ww**

**Method = EPA 3050B / 6010C (ICP)**

Analyte	MDL	RDL
Arsenic	1.3	6.28
Cadmium	0.11	0.503
Chromium	0.16	0.754
Copper	0.21	1.01
Lead	1.1	5.03
Nickel	0.26	1.26
Silver	0.21	1.01
Vanadium	0.51	2.52
Zinc	0.26	1.26

**Method = EPA 3050B / 6020A (ICP-MS)**

Analyte	MDL	RDL
Arsenic	0.025	0.126
Cadmium	0.013	0.0628
Chromium	0.05	0.25
Copper	0.1	0.503
Lead	0.025	0.126
Nickel	0.025	0.126
Silver	0.01	0.05
Vanadium	0.019	0.0942
Zinc	0.13	0.628

**Table 7. Mercury Detection Limit Goals in mg/kg ww**

Analyte / Range	MDL	RDL
Mercury / Mid Range	0.005	0.05
Mercury / High Range	0.02	0.2

Sample accuracy and bias will be evaluated by a laboratory duplicates, spike blanks, and matrix spike/matrix spike duplicate samples and will be analyzed with each set of 20 samples, or one

per batch. QA/QC frequency and acceptance criteria for metals and mercury analysis are as shown in Table 8.

**Table 8. Trace Metals and Mercury QA/QC Frequency and Acceptance Criteria**

	Method Blank	Spike Blank (% Re-recovery)	Lab Duplicate	Matrix Spike Duplicate	Matrix Spike (% Re-recovery)	LCS (% Re-recovery) <sup>a</sup>	SRM (% Re-recovery) <sup>a</sup>
<b>Analyte/ Frequency</b>	<b>1 per batch*</b>	<b>1 per batch*</b>	<b>1 per batch</b>	<b>1 per batch</b>	<b>1 per batch</b>	<b>1 per batch</b>	<b>1 per batch</b>
Total Metals by ICP	< MDL	85 – 115%	RPD ≤ 20%	NA	75 - 125%	laboratory QC limits <sup>b</sup>	NA
Total Metals by ICP-MS	< MDL	85 – 115%	RPD ≤ 20%	NA	75 - 125%	laboratory QC limits <sup>b</sup>	NA
Total Mercury	< MDL	85 – 115%	RPD ≤ 20%	RPD ≤ 20%	75 - 125%	NA	80-120%

<sup>a</sup> The LCS or SRM samples will be run in duplicate with an expected RPD <20%

<sup>b</sup>The laboratory’s performance-based control limits that are in effect at the time of analysis will be used as quality control limits.

\*batch = 20 samples or less prepared as a set

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

RPD = Relative Percent Difference

LCS = Lab Control Sample

SRM = Standard Reference Material

NA = Not Applicable

## 4.4 Conventionals

For all samples, total organic carbon and total solids will be analyzed. In a subset of samples with sufficient volume, particle size distribution may also be analyzed. All conventional analyses will follow Standard Methods (SM) (American Public Health Association [APHA] 1998), EPA, Puget Sound Estuary Program (PSEP), and/or American Society for Testing and Materials (ASTM) method protocols. Table 9 presents the analytical methods, detection limits, and units for conventional analyses.

**Table 9. Conventionals Target Analytes and Detection Limits Goals**

Analyte	Method	KCEL SOP	Units	MDL	RDL
Total Organic Carbon	EPA 9060/PSEP 96	337	mg/Kg wet weight	500	1000
Total Solids	SM 2540-G	307	% wet weight	0.005	0.01
Particle Size Distribution	ASTM D422	318	% dry weight	0.1 (gravel and sand) 0.5 (silt and clay)	1.0 (all)

PSEP = Puget Sound Estuary Program

SM = Standard methods

ASTM = American Society for Testing and Materials

Detection limits will vary slightly from sample to sample, depending on the exact amount of sample mass used for analysis. Table 10 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 10. Conventionals QA/QC Frequency and Acceptance Criteria**

	Method Blank	Lab Triplicate (RSD)	Spike Blank (% Recovery)	Matrix Spike (% Recovery)	LCS (% Recovery)	SRM (% Recovery)
Analyte/ Frequency	1 per batch*	1 per batch*	1 per batch*	1 per batch*	1 per batch* (if available)	1 per batch* (if available)
Total Organic Carbon	<MDL	20%	80-120%	75-125%	N/A	80-120%
Total Solids	<MDL	20%	N/A	N/A	N/A	N/A
Particle Size Distribution	N/A	20%	N/A	N/A	N/A	N/A

\*batch = 20 samples or less prepared as a set

< MDL = less than the Method Detection Limit.

RSD = Relative Standard Deviation

LCS = Lab Control Sample

SRM = Standard Reference Material

N/A = not applicable

## 4.5 Dioxins/furans

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 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**

<b><sup>13</sup>C-labeled Congener Surrogate Standards</b>	
Labeled analytes of interest are used for all dioxins and furans quantified except 1,2,3,7,8,9-HxCDD and OCDF	
<b><sup>37</sup>Cl-labeled Cleanup Standards</b>	
2,3,7,8 TCDD	
<b><sup>13</sup>C-labeled Internal (Recovery) Standards</b>	
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 2 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 by EPA method 1613b, AXYS Analytical Services method MLA 017.**

<b>Dioxin</b>	<b>Typical Detection Limit/SDL</b>	<b>LMCL based on Low Cal./RDL</b>
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
<b>Furan</b>		
2,3,7,8 TCDF	0.05	1.0

Dioxin	Typical Detection Limit/SDL	LMCL based on Low Cal./RDL
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

Quality control samples include method blanks, 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 13.

**Table 13. Dioxins/furans QA/QC Frequency and Acceptance Criteria**

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

batch = 20 samples or less prepared as a set

<sup>a</sup>EPA 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

<sup>b</sup>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

RSD = Relative Standard Deviation

OPR = ongoing precision and recovery

## 5 DATA VALIDATION, REPORTING AND RECORD KEEPING

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

### 5.1 Data Validation

Chemical data generated during this survey will be validated according to accepted Environmental Protection Agency (EPA) guidelines (EPA 2001, 2004 and 2005), where applicable. KCEL will develop “QA 1 (Ecology 1989) or EPA Stage 2a data packages allowing for this level of validation. This level of validation includes reviews of holding times, method blanks, and QA/QC samples. An EPA Stage 2b validation will be performed on approximately 20% of the metals and organic batches. This level of validation includes a review of summary forms for calibrations, instrument performance, and internal standard summaries. All necessary data needed for independent review of dioxin/furan data will be provided by Axys. All other chemical analysis and associated 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 WLRD for all data generated by KCEL. Data validation for dioxin/furan data maybe conducted by either an outside party for this survey or by King County WLRD. Data validation memoranda will be produced and maintained along with the analytical data as part of the project records.

### 5.2 Reporting

All data and supporting information will be documented in a data report for data collected in 2011. Sample results associated with sediment trap samples may also be included in this data report depending on receipt date of analytical results. In addition, samples collected in 2010 under the previous version of this SAP will be included in the data report containing 2011 data. If further source tracing samples are collected in 2012, a separate data report will be produced. All in-line solid grab and sediment trap data will be reported in dry weight using sample specific percent solids data. Data validation memoranda will be included in the data report, as will copies of COC forms. In addition, if appropriate data fields can be generated in Ecology’s Environmental Information Management (EIM) database, data will be submitted for loading into the EIM 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, Trace Metals and Trace Organics analytical data produced by the KCEL will be

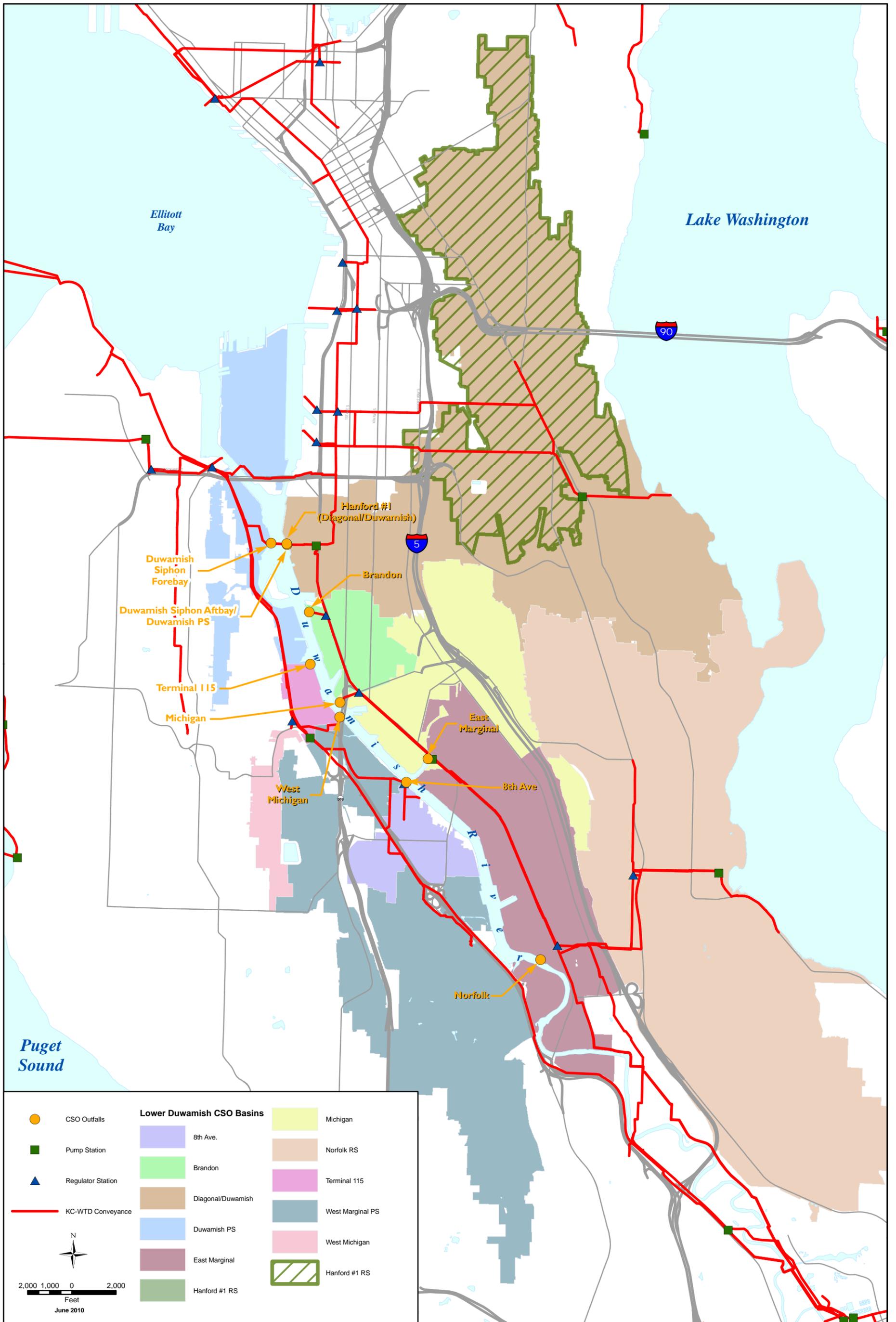
maintained on its LIMS database in perpetuity. AXYS will provide electronic deliverables of data and associated quality control results to King County. While KCEL will maintain a copy of deliverables from AXYS, copies of full data packages pertaining to King County samples analyzed by AXYS will be maintained by AXYS for 10 years from the analysis date.

## 6 REFERENCES

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**Figure 2. In-line solid grab sampler**



**Figure 3. Sediment trap bottle mounting bracket**



# APPENDIX A: CHAIN-OF-CUSTODY FORM







## APPENDIX B: RINSATE BLANK METHODS AND MDLS

### **Trace Organics Target Analytes and Detection Limits (ug/L)**

#### **PCB Aroclors**

Rinsate blanks will be prepared by liquid-liquid extraction as detailed in method SW846 35520C, and analyzed for PCB Aroclors by method SW846 8082A (gas chromatography electron capture detection [GC/ECD]), KCEL SOP 757. The following table lists the PCB Aroclors and their respective target MDL and RDL goals for the rinsate blanks. These MDL/RDLs are based upon extraction of 1000 mL of sample and concentration to 1.0 mL final volume. The reported MDLs and RDLs for individual rinsate blanks may differ from those shown below due to changes in the volume of sample extracted or the final extract volume. Every effort will be made to meet these limits, however depending upon the organic content of the samples it may not be possible to obtain this concentration factor.

#### **Method = SW846 3520C / 8082A (GC/ECD)**

<b>Analyte</b>	<b>MDL</b>	<b>RDL</b>
Aroclor 1016	0.025	0.05
Aroclor 1221	0.05	0.1
Aroclor 1232	0.05	0.1
Aroclor 1242	0.025	0.05
Aroclor 1248	0.025	0.05
Aroclor 1254	0.025	0.05
Aroclor 1260	0.025	0.05

#### **SVOCs**

Rinsate blanks will be prepared by liquid-liquid extraction as detailed in method SW846 35520C, and analyzed for semivolatile organics by method SW846 8270D (GC/MS), KCEL SOP 731. Semivolatile organics analyzed in the rinsate blanks will consist of the compounds included in the KCEL Base-Neutral-Acid-Sediment Management Standards (BNASMS) list type (although an alternative list type – applicable to liquids – may be used). The following table lists the BNASMS compounds and their respective target MDL and RDL goals for the rinsate blanks. These MDL/RDLs are based upon extraction of 1000 mL of sample and concentration to 1.0 mL final volume. The reported MDLs and RDLs for individual rinsate blanks may differ from those shown below due to changes in the volume of sample extracted or the final extract volume.

Every effort will be made to meet these limits, however depending upon rinsate blank volume it may not be possible to obtain this concentration factor.

**Method = SW846 3520C / 8270D (GC/MS)**

Analyte	MDL	RDL	Analyte	MDL	RDL
1,2,4-Trichlorobenzene	0.30	0.50	Chrysene	0.30	0.50
1,2-Dichlorobenzene	0.30	0.50	Dibenzo(a,h)anthracene	0.80	1.50
1,4-Dichlorobenzene	0.30	0.50	Dibenzofuran	0.50	1.00
2,4-Dimethylphenol	0.50	1.00	Diethyl Phthalate	0.50	1.00
2-Methylnaphthalene	0.80	1.50	Dimethyl Phthalate	0.20	0.30
2-Methylphenol	0.50	1.00	Di-N-Butyl Phthalate	0.50	1.00
3-,4-Methylphenol	0.50	1.00	Di-N-Octyl Phthalate	0.30	0.50
Acenaphthene	0.20	0.40	Fluoranthene	0.30	0.60
Acenaphthylene	0.30	0.50	Fluorene	0.30	0.50
Anthracene	0.30	0.50	Hexachlorobenzene	0.30	0.50
Benzo(a)anthracene	0.30	0.50	Hexachlorobutadiene	0.50	1.00
Benzo(a)pyrene	0.50	1.00	Indeno(1,2,3-Cd)Pyrene	0.50	1.00
Benzo(b,j,k)fluoranthene	0.80	1.50	Naphthalene	0.80	1.50
Benzo(g,h,i)perylene	0.50	1.00	N-Nitrosodiphenylamine	0.50	1.00
Benzoic Acid	2.00	3.00	Pentachlorophenol	0.50	1.00
Benzyl Alcohol	0.50	1.00	Phenanthrene	0.30	0.50
Benzyl Butyl Phthalate	0.30	0.50	Phenol	2.00	3.00
Bis(2-Ethylhexyl)Phthalate	0.30	0.50	Pyrene	0.30	0.50

**Trace Metals Target Analytes and Detection Limits (ug/L)**

**Method = EPA 245.1 (CVAA)**

Analyte / Range	MDL	RDL
Mercury / Mid Range	0.05	0.15

**Method = EPA 200.8 (ICP-MS)**

<b>Analyte</b>	<b>MDL</b>	<b>RDL</b>
Arsenic	0.1	0.5
Cadmium	0.05	0.25
Chromium	0.2	1
Copper	0.4	2
Lead	0.1	0.5
Nickel	0.1	0.5
Silver	0.04	0.2
Vanadium	0.075	0.375
Zinc	0.5	2.5