GREEN – DUWAMISH WATERSHED
WATER QUALITY ASSESSMENT
COMPREHENSIVE MONITORING PROGRAM
SAMPLING AND ANALYSIS PLAN

Prepared by the
King County Department of Natural Resources and Parks
Water and Land Resources Division

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NAME OF PROJECT: Green – Duwamish Watershed Water Quality Assessment

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1 Introduction

The primary purpose of this project is to study water quality in the Green-Duwamish watershed and provide technical information to:

- the Wastewater Treatment Division Habitat Conservation Plan (WTD HCP) team,
- the WTD combined sewer overflow (CSO) control planning team,
- the Water Resources Inventory Area (WRIA) 9 Planning Work Group, Technical Committee and Steering Committee, and
- the Washington State Department of Ecology Total Maximum Daily Load (TMDL) effort

This Sampling and Analysis Plan (SAP) describes the planned scope of work, field sampling procedures, and laboratory analytical requirements for the Green-Duwamish Water Quality Assessment (GD-WQA) water quality model development. This SAP does not cover many other components of the GD-WQA that may be implemented, such temperature-specific studies, macroinvertebrate sampling, etc. If necessary, these other programs will be described in separate SAPs.

1.1 Project Background

The primary goal of this project is to develop analytical tools for evaluating current and future water quantity and quality issues in the Green-Duwamish watershed and to provide water quality information to a variety of clients internal and external to King County's Department of Natural Resources and Parks (DNRP). The GD-WQA will assist wastewater capital planning (including the Combined Sewer Overflow (CSO) program and habitat conservation planning), WRIA 9 salmon conservation planning, stormwater management efforts, and the Department of Ecology's TMDL (Total Maximum Daily Load) program by collecting water quality information, developing a watershed model, and using the model to evaluate resource management options. The scope of work includes water quality and hydrologic monitoring, land use / land cover modeling, water quality and quantity modeling, best management practice (BMP) evaluation, and ecological and human health risk assessment.

The GD-WQA will use a risk-based approach to assess water quality in the watershed. This approach will include a review of existing water quality data, sampling and analysis in the watershed, water quantity and quality modeling, risk assessment, and coordination and involvement with various stakeholders and jurisdictions in the watershed. Biological resource and habitat investigations will be conducted as necessary to meet the objectives of the project.

1.2 Project Objectives

The overall objectives of the GD-WQA are as follows:

1. To develop a watershed runoff water quantity and quality model for the Green-Duwamish River and tributaries from the Tacoma diversion dam to the mouth of the Duwamish River.
2. To assess existing water quality conditions for bacteria indicator organisms for the Green-Duwamish River and tributaries from the Tacoma diversion dam to the mouth of the Duwamish River.
3. To assess metals concentrations in the Green-Duwamish River and its major tributaries.
4. To assess conventional water quality parameters, such as temperature, dissolved oxygen, and suspended solids that may be of importance in salmon recovery efforts.
5. To assess future water quality conditions for the above parameters assuming a) buildout according to the King County Comprehensive Plan and Growth Management Act, b) no changes in management practices, and possibly c) intermediate development stages prior to complete buildout.
6. To assess existing and future loading of parameters of concern to the study area from various land use / land cover types.
7. To assess effectiveness of alternative BMPs for the control of parameters and sources of concern.
8. To assess the relative risk of pathogens (as measured by bacterial indicators) and metals to aquatic life, wild life and people for the purpose of prioritizing spatial and temporal control of these parameters in the watershed.
9. To provide this technical assessment information to the Department of Ecology for their use in the development of TMDLs.
10. To work closely with the regional stakeholders especially GD-WQA Technical Work Group to obtain input on project design and implementation.
11. To coordinate work with the sediment cleanup efforts in the Duwamish River (e.g., Superfund and CSO sediment project and the LDWG project).

1.3 Study Area Description

The Green-Duwamish Watershed includes a drainage area of approximately 484 square miles of varied terrain and land use from forested headwater areas at the crest of the Cascade Mountains to industrial and port facilities of the Duwamish estuary. The project study area encompasses the Green-Duwamish watershed from the Tacoma Diversion Dam at river mile 61 to the mouth of the Duwamish River at Elliott Bay (Figure 1), about 261 square miles. The upper Green River Basin (231 square miles) is not included in the study area.

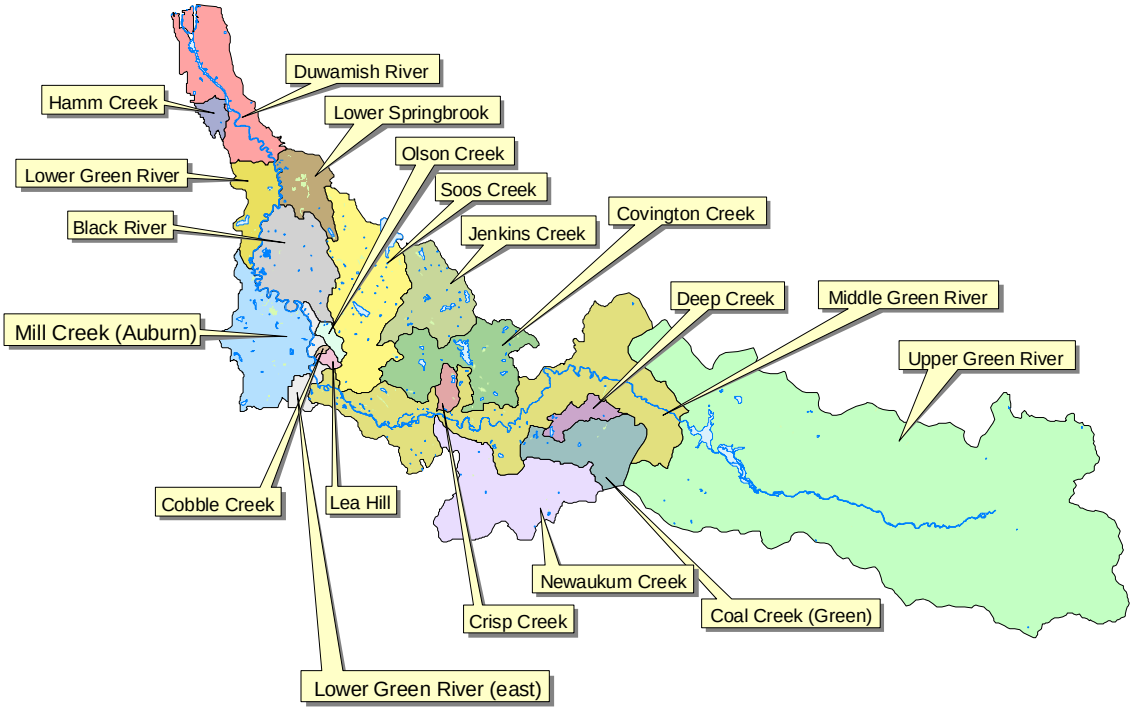

Figure 1. Green River subbasins.

2 Study Objectives

The objectives of the Green-Duwamish Watershed Water Quality Assessment, Comprehensive Monitoring Program are to:

- Measure in-stream water quality parameter concentrations resulting from different land use/land cover types within the stream drainage area;
- Measure in-stream water quality parameter concentrations as a function of the rise, peak, and fall of the corresponding stream hydrograph to determine peak concentrations and variability within a storm;
- Measure in-stream water quality parameter concentrations in different geographic areas of the watershed throughout the year, including mouths of major tributaries and boundary conditions of the Green River mainstem;
- Measure in-stream water quality parameter concentrations during both storm and baseflow conditions; and
- Collect sufficient data to allow development and calibration of a water quality model for the Green River watershed.

3 Project Team and Responsibilities

Project team members and their responsibilities are summarized in Table 1. All team members are staff of the King County Department of Natural Resources and Parks, either within the Water and Land Resources Division or Wastewater Treatment Division.

Table 1. Project team members and responsibilities.

Name/Telephone	Title	Affiliation	Responsibility
John Brooker (206) 205-5151	Water Quality Planner	Science, Monitoring and Data Management	Risk Assessment, Macroinvertebrate Sampling
Jeff Burkey (206) 296-8390	Hydrologist	Science, Monitoring and Data Management	Modeling
Betsy Cooper (206) 263-3728	NPDES Administrator	Planning and Compliance (WTD)	WTD Representative
Curtis DeGasperi (206) 684-1268	Senior Engineer	Comprehensive Planning and Technical Resources (WTD)	Modeling
Colin Elliott (206) 684-2343	Quality Assurance Officer	Environmental Laboratory	Overall analytical and Field QA/QC
Eric Ferguson (206) 263-6512	Water Quality Planner	Science, Monitoring and Data Management	Groundwater and Temperature Investigations
David Funke (206) 296-8066	Senior Engineer	Science, Monitoring and Data Management	Gauging and auto-sampler set-up/operation
Fritz Grothkopp (206) 684-2327	Laboratory Project Manager	Environmental Laboratory	Coordination of sampling and analytical activities, laboratory QA/QC, and data reporting
Doug Henderson (206) 263-6317	Water Quality Planner	Science, Monitoring and Data Management	Risk Assessment
Lorin Reinelt (206) 296-1960	Senior Water Quality Planner	Science, Monitoring and Data Management	Assistant Manager for Green-Duwamish WQA.
Jim Simmonds (206) 296-1986	Senior Water Quality Planner	Science, Monitoring and Data Management	Manager for Green-Duwamish Watershed WQA
Stephanie Hess (206) 684-9101	Environmental Specialist	Environmental Laboratory	Coordination of routine field sampling activities, routine field analyses and routine field QA/QC
Curtis Nickerson (206) 267-1405	Consultant Team Project Manager	Taylor Associates, Inc.	Sample collection and splitting, autosampler programming, in-stream parameter measurements, and summary reporting

4 Schedule

Sampling will take place during water years 2002 and 2003 (October 2001 to September 2003). The level of monitoring is expected to reduce in the water year 2003. Special studies will be designed at a later date to answer specific questions that may arise and will be conducted in the 2003 water year.

5 Sample Design

In order to develop a water quality model for the Green River watershed to estimate peak concentrations and loadings as a function of land use/land cover and hydrographs, four different types of variability need to be characterized:

1. Variability of peak concentrations and loadings of in-stream parameters of interest as a function of land use/land cover.
2. Variability of in-stream parameter concentrations during the course of a storm. This will help determine how peak concentrations relate to the event mean concentrations (EMCs) and how sensitive concentrations are to flow rate.
3. Variability of in-stream parameter concentrations and loadings across subbasins in the Green River watershed based on unique subbasin factors other than land use/land cover (such as slope/gradient/topography, soils and presence of lakes/wetlands).
4. Seasonal variability of in-stream parameter concentrations and loadings that result from factors such as precipitation/runoff, leaf fall, plant uptake, and land use practices (e.g., livestock activities, cropping, logging, application of fertilizers/pesticides in urban areas).

Site locations, water quality parameters, and sampling frequency were selected to address these types of variability.

5.1 Site Locations

To characterize peak concentrations and loadings as a function of land use/land cover, sites that were characterized by homogeneous land use/land cover were targeted. However, no perennial streams in the Green River watershed were found that drained only one type of land use/land cover. Therefore, catchments dominated by one land use/land cover (such as low density residential, high density residential, commercial, agricultural, or forest) were selected. Furthermore, sites were selected to represent a wide geographic distribution across the Green-Duwamish watershed to address subbasin variability as well. Sample locations are shown in Figure 2 below.

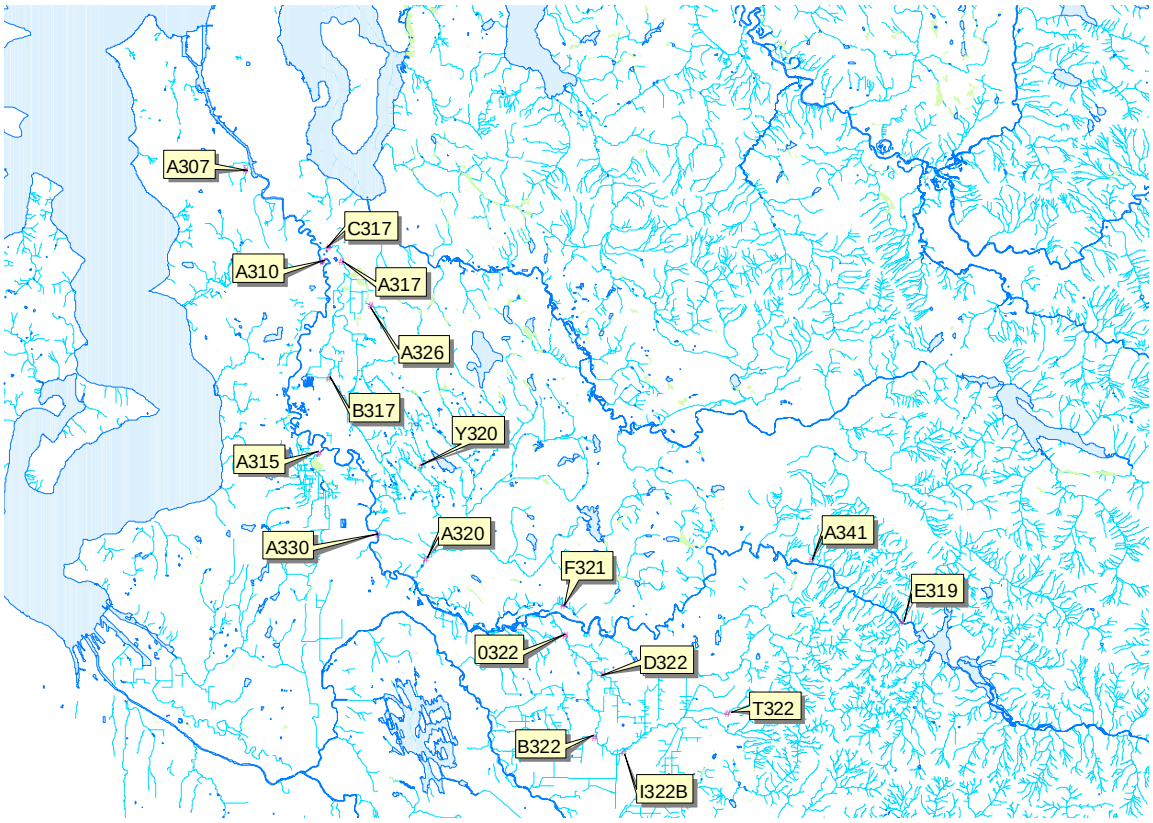

Figure 2. Green River Watershed WQA sampling sites.

5.2 Storm / Baseflow Conditions

Two types of stream samples will be collected for this project: Storm and baseflow (i.e., non-storm). Storm conditions are defined as ≥0.5 inches of precipitation in 12 hours. However, if few storms have been sampled as the wet season progresses, the precipitation criteria may be lowered in order to increase the number of samples collected. Specific dry antecedent conditions are not required so that the water quality model can be developed and calibrated under a full range of conditions. However, as stated above, sampling will target the rise and fall of the hydrograph; therefore, stream flows will have to be relatively stable prior to initiating sampling.

5.3 Sample Types

For both storm and baseflow samples, different collection methods will be employed at different locations. In order to evaluate the variability of parameter concentrations during the course of a storm, multiple discrete samples are to be collected at regular intervals after the onset of a storm. To do this at multiple sampling locations concurrently requires the use of autosamplers. The ideal sampling interval (in hours) required to define, with some known error, the true concentration of a given parameter as a function of river flow was calculated (King County 2000, Soerens et al. 1999). Ideally,

samples would be collected every one to four hours, capturing the rise, peak and fall of the hydrograph at all sampling locations. However, in some systems the water level returns to baseflow conditions very quickly, and in others it does not return to pre-storm levels for 48 hours or more; therefore, this ideal design will not always be feasible. Therefore, four hours was selected as the best sampling interval to capture the rise, peak and fall of the hydrograph. As a result, during storm conditions, six to ten discrete samples will be collected at a rate of one every four hours at the autosampler sites, depending on the duration of the elevated stream flow during and/or after the storm. For baseflow conditions, three discrete samples will be collected at a rate of one every four to eight hours (evenly spaced over 24 hours or less).

In addition, given the large size of the watershed and the variety of land use/land cover types targeted, 18 sites have been selected for monitoring (see Figure 2). Analytical capacity at the King County Environmental Laboratory would be exceeded if this multiple discrete grab sampling design were to be extended to all 18 sites. Therefore, at a small subset of the sites (e.g., four or five), water quality as a function of stream hydrograph will be characterized at this resolution using discrete samples. The remaining sites will be characterized by either flow-weighted composites (i.e., one sample) using autosamplers, or by single grab samples collected manually. Therefore, three types of samples for both storm and baseflow conditions will be employed: auto-sequential (discrete grabs), auto-composite and grab (manual). Once the first subset of automated discrete (auto-sequential) sites have been sufficiently characterized, these sites may be switched to flow-weighted composites or even single grabs to allow other sites to be similarly characterized at higher temporal resolution.

5.4 Frequency

Sample frequency will vary depending upon sample type (storm vs. baseflow).

5.4.1 Storm

Eight to ten storms will be targeted for sampling during the water year 2002. The number of storms targeted for water year 2003 will be dependent on the quantity and quality of the data collected in 2002 and model calibration needs. To ensure that the storms sampled are distributed throughout the year, no more than two storms will be sampled per month. In addition to seasonal variability, this also provides processing time for the laboratory to prepare equipment for the next sampling event.

5.4.2 Baseflow

Baseflow conditions are defined as the flow rates that occur before the rise and after the drop in elevated stream flows resulting from precipitation. These flow rates generally require two to three days of no rainfall, depending on the site, so that recession of the hydrograph has occurred. Baseflow samples will be targeted for bimonthly sampling for one year for all parameters except organics. Priority pollutant organics (see below) will be targeted for sampling once per quarter.

5.5 Parameters

Sample parameters will vary depending upon sample type (storm vs. baseflow).

5.5.1 Storm

Water quality parameters to be analyzed for this project can be grouped into six general categories: Microbiology, conventionals, nutrients, metals, organics, and in-stream measurements. Specific analytes for each category are listed below:

- Microbiology – Fecal coliform, enterococcus, and E. coli.
- Conventionals – Alkalinity, biochemical oxygen demand, total suspended solids, turbidity and total and dissolved organic carbon.
- Nutrients – Ammonia, total nitrogen, nitrate/nitrite nitrogen, orthophosphorus, and total phosphorus.
- Metals – Total and dissolved aluminum, arsenic, cadmium, calcium, chromium, copper, iron, lead, magnesium, manganese, mercury, nickel, potassium, selenium, silver, sodium, and zinc; and total hardness.
- In-stream parameters – Temperature, pH, dissolved oxygen, and specific conductance.

5.5.2 Baseflow

The same parameters for storm samples will be collected for baseflow samples. In addition, priority pollutant organics will be collected:

- Priority pollutant organics – Base/neutral/acid organic compounds, Chlorinated Pesticides/PCBs, Organochlorine Herbicides and Organophosphorus Pesticides.

5.6 Proposed Design

Sample parameters and types for each location are provided in Table 2. Use of auto-composite, auto-sequential (discrete grabs), and manual grab samples at these locations is subject to change based upon feasibility of implementation, review of results, and analytical capacity of the laboratory.

Table 2. Proposed sample design for each location.

Description	Locator	Sample Type	Micro	Conv	Nutrients	Metals	In-stream params.	Organics
Low/Medium Intensity Development								
Hamm Creek	A307	AC/AS	S,B	S,B	S,B	S,B	S,B	--
Panther Creek	A326	GR	S,B	S,B	S,B	S,B	S,B	--
Soosette Creek	Y320	AC/AS	S,B	S,B	S,B	S,B	S,B	--
Green tributary (Lea Hill)	A330	GR	S,B	S,B	S,B	S,B	S,B	--
Higher Levels of Development								
Newaukum tributary (Enumclaw)	I322B	AC/AS	S,B	S,B	S,B	S,B	S,B	--
Mill Creek tributary (Springbrook basin)	B317	AC/AS	S,B	S,B	S,B	S,B	S,B	--
Agriculture/Pasture								
Newaukum tributary (236th Ave SE)	D322	AC/AS	S,B	S,B	S,B	S,B	S,B	--
Newaukum tributary (SE 424th St. – ditch)	B322	GR	S,B	S,B	S,B	S,B	S,B	--
Forest/Forestry Practices								
Newaukum tributary (Weyerhauser)	T322	AC/AS	S,B	S,B	S,B	S,B	S,B	--
Crisp Creek above fish hatchery	F321	GR	S,B	S,B	S,B	S,B	S,B	--
Green River tributary in foothills near TPU diversion (Parker home)	A341	AC/AS	S,B	S,B	S,B	S,B	S,B	--
Boundary Conditions and Subbasins								
Green River (Fort Dent Park)	A310	AC/AS	S,B	S,B	S,B	S,B	S,B	Q
Green River below HHD at USGS gaging station 12105900	E319	AC	S,B	S,B	S,B	S,B	S,B	Q
Newaukum Creek near mouth	0322	AC/AS	S,B	S,B	S,B	S,B	S,B	Q
Springbrook Creek near mouth	A317	AC/AS	S,B	S,B	S,B	S,B	S,B	Q
Black River Pump Station	C317	GR	S,B	S,B	S,B	S,B	S,B	Q
Mill Creek near mouth	A315	GR	S,B	S,B	S,B	S,B	S,B	Q
Soos Creek above fish hatchery	A320	GR	S,B	S,B	S,B	S,B	S,B	Q

AC = Auto-composite
AS = Auto-sequential (discrete grabs)
GR = Manual grab
S = Storm (8-10 per year)
B = Baseflow (bimonthly)
Q = Baseflow (quarterly)

5.7 Data Quality Objectives

The most critical requirements for data quality are driven by the needs of the model to accurately predict the appropriate endpoints. To meet these needs the following data quality objectives have been established.

5.7.1 Precision, Accuracy, and Bias of Field and Laboratory Measurements

Precision is the agreement of a set of results among themselves and is a measure of the ability to reproduce a result. Accuracy is an estimate of the difference between the true value and the determined mean value. The accuracy of a result is affected by both systematic and random errors. Bias is a measure of the difference, due to a systematic factor, between an analytical result and the true value of an analyte. Precision, accuracy, and bias for analytical chemistry may be measured by one or more of the following quality control (QC) procedures:

- Analysis of various laboratory QC samples such as method blanks, matrix spikes, certified reference materials, and laboratory duplicates (laboratory QC results will be evaluated against the control limits presented in Section 9).
- Collection and analysis of replicate field samples for laboratory and field measurement (replicate results should exhibit a relative percent difference less than 50% in order for the evaluation of the spatial and temporal chemical concentrations to be meaningful)
- Collection and analysis of total metals field blanks (results should be less than the method detection limit).

5.7.2 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. Samples for chemistry analysis will be collected from stations with preselected coordinates to represent specific site locations. Samples are to be collected to minimize potential contamination and other types of degradation in the chemical and physical composition of the water. Following the guidelines described for sampler decontamination, sample acceptability criteria, and sample processing (Section 7) will help ensure that samples are representative. Laboratory representativeness is achieved by proper preservation and storage of samples along with appropriate subsampling and preparation for analysis. The storm and baseflow conditions in Section 5.2 and 5.4 should also be met. Data that is not representative as defined above should not be used in the model.

The sampling design of this water quality project may cause some samples to arrive at the laboratory having exceeded either a parameter method holding time or a sampler

preparation/preservation time. These sample results will be flagged in the laboratory database with the "H" qualifier. The qualifier will be applied on a method/parameter-specific basis, as necessary. This situation may be unavoidable and will not necessarily be used to exclude data from use in model development and calibration.

5.7.3 Completeness

Completeness is defined as the total number of samples analyzed for which acceptable and representative analytical data are generated, compared to the total number of samples to be analyzed. Sampling at stations with known position coordinates in favorable conditions and at the appropriate time points, along with adherence to standardized sampling and testing protocols, will aid in providing a complete set of data for this project. The goal for completeness is 100%. Each storm and baseflow event should collect greater than 50% of the planned samples for the event. The samples from each event should produce greater than 90% acceptable chemical and biological data under the QC conditions mentioned in Section 9.

5.7.4 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. Changes or updates to analytical methods and sampling techniques midway into the project must be validated and shown to be equivalent to existing methods before being implemented.

6 Sample Collection Procedures

This section describes sample collection procedures that will be followed throughout the project to help ensure that project data quality objectives are met. Included in this section are health and safety requirements, geographic sample locations, sample collection and processing procedures, and field documentation. Sampling equipment will be prepared at the laboratory following appropriate procedures, and sampling personnel will be trained in the specialized sampling techniques.

6.1 General Health and Safety Requirements

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

- Sampling personnel will wear chemical-resistant gloves whenever coming into contact with samples.
- No eating, drinking, smoking, or tobacco chewing by sampling personnel will be allowed during active sampling operations.
- All accidents, "near misses," and symptoms of possible exposure will be reported to a sampler's supervisor within 24 hours of occurrence.
- All crewmembers will be aware of the potential hazards associated with chemicals used during the sampling effort.

6.2 Geographical Sample Locations

The samples for this effort will be collected at the following proposed coordinates that are shown in Table 3.

Table 3. Proposed sampling station coordinates (NAD 83).

Station Number	Station Name	Northing (ft)	Easting (ft)
0322	Newaukum mouth	102390	1336841
A307	Hamm Creek	191355	1275651
A310	Green River (Fort Dent)	174004	1290319
A315	Mill Creek mouth	137218	1289725
A317	Springbrook mouth	173897	1293904
A317G	Springbrook mouth grab site	174418	1293694
A320	Soos Creek above fish hatchery	116821	1309972
A326	Panther Creek	165415	1299518
A330	Green trib (Lea Hill)	121797	1300926
A341	Green River trib in foothills near TPU diversion (Parker home)	116629	1383830
B317	Mill Creek trib (Springbrook basin)	151362	1291526
B322	Newaukum trib (SE 424th St. – ditch)	82958	1342366
C317	Black River Pump Station	176500	1291794
D322	Newaukum trib (236th Ave SE)	106907	1344160
E319	Green River below HHD (USGS 12105900)	104678	1401243
F321	Crisp Creek above fish hatchery	108123	1336395
I322B	Newaukum trib (Enumclaw)	79976	1348486
T322	Newaukum trib (Weyerhauser)	85543	1342779
Y320	Soosette Creek	134795	1309050

6.3 Field Measurements and Analysis

Field measurements will be taken at each sampling location either just prior or just after grab sampling for chemical analysis. A Hydrolab Mini sonde or a YSI probe will be used to analyze the stream stormwater for temperature, pH, specific conductance and dissolved oxygen. The field meters will be calibrated according to Environmental Support Services (ESS) Standard Operating Procedure (SOP # 02-01-005) within 24 hours of the sampling event. See Section 9.3 for specific QC requirements for field measurements.

6.4 Stream Stormwater Sampling

6.4.1 Grab Sampling

Grab samples will be collected according to ESS SOP # 02-02-13 (Clean Surface Grab Sampling) which follows U.S. EPA Method 1669 (U.S. EPA 1996). Grab samples will be collected while facing upstream to minimize contamination from field equipment. Whenever possible, the sampling should be conducted while facing the prevailing winds. Sampling personnel will wear multiple layers of clean PVC gloves including a pair of

shoulder length gloves for personal protection and to prevent contamination of the samples. The low-level pre-concentration metal sample bottles (two for ICP-MS and two for mercury), which will be doubled-bagged prior to going into the field, will be filled first using the U.S. EPA "clean hand/dirty hands", low-level metal sampling technique (U.S. EPA Method 1669). The remaining sample bottles will be filled after the metals sample bottles.

The metals sample bottles will be rinsed three times with stream water prior to filling with the actual sample. The bottle will be immersed in the stream with the neck facing down, filled with 50 to 100 ml of stream water. The bottle will be shaken several times and then drained into the stream. The draining is done downstream and away from the sampling personnel. This is repeated two more times, and then the sample bottle will be filled, leaving some headspace to allow room to add preservative. For metals analyses, one set of field blank bottles filled with de-ionized water will accompany the sample bottles in a cooler with ice for the duration of the sampling event. At one randomly selected site, the field blank bottles will be opened using the same "clean hands/dirty hands" techniques, and exposed to the atmosphere for approximately the same duration that is required to fill the sample bottles. The microbiology sample bottle will be filled by lowering the bottle, open with the neck faced down, into the stream to a depth of 1 to 3 inches. The bottle is rotated and allowed to fill up just below the top shoulder of the bottle. The extra headspace is required so that the bottle may be agitated before filtering. The bottle is not to be rinsed with sample. Finally, the conventional analysis bottles are filled in a similar manner as the microbiology sample, using face down immersion and capping after the container is removed from the stream flow. All sample and blank containers will be placed in a cooler with ice until transported to sample receiving at the laboratory.

6.4.2 Autosampler-Sequential

Discrete grabs using sequential autosamplers will be done with ISCO 3700 series autosamplers and 24-bottle sampler bases. The samplers will be set up to collect samples every four hours during a storm. The method used to trigger the autosamplers will depend on the storm conditions and will be either manual (sampler is set to start a specified time) or automatically triggered by liquid-level activator switch upon stage level rise. The sampler will be programmed to fill four sequential bottles once every four hours. These four bottles will constitute a sample. At an appropriate time during the storm, the autosampler base will be exchanged for another base with clean, empty bottles. This is required as one base can only hold up to six samples (24 bottles); therefore, two bases are needed in order to collect the target of ten samples. The autosampler bottles will be capped for transport to the laboratory. The autosampler bases with filled sample bottles will be brought to the laboratory sample receiving area. The autosampler base with bottles will be iced for the transport to the laboratory.

The contents of the autosampler bottles will be transferred into the appropriate laboratory sample containers. There will be four autosampler bottles filled in sequence for each sample. The first two bottles in the sequence will be used for filling conventional and

nutrient analysis bottles, the next bottle will be used for microbiological analysis bottles, and the fourth and last bottle will be used for metals analysis bottles.

The transfer procedure for the autosampler bottles will be as follows:

- The laboratory analysis bottles for each group (conventionals including nutrients, microbiology, and metals) will be opened as needed.
- The first autosampler bottle will be shaken periodically during sample transfer and used to fill the TSS analysis bottle.
- The second autosampler bottle will be shaken periodically during sample transfer and used to fill the remaining conventionals bottles.
- The third autosampler bottle will be shaken periodically during sample transfer and used to fill the microbiology bottle.
- The remaining liquid in the third autosampler bottle will be used to fill the first metals analysis bottle (Teflon bottle for mercury analysis).
- The fourth and final autosampler bottle will be shaken periodically during sample transfer and used to fill the remaining two metal analysis bottles.

Care must be taken to ensure that the autosampler bottle contents go into the appropriate laboratory sample container for the sampling location where the autosampler collected the sample. If there is insufficient volume to complete all of the requested analyses, priority shall be given to conventional parameters, followed by microbiological analyses, metals, and finally nutrients.

6.4.3 Autosampler-Composite

Composite samples will be collected using ISCO 3700 series autosampler filled with 15-liter HDPE sample carboys. Composite samples will be collected over a 24-hour period with two samples for a 40-hour storm. The collection volume will be proportional to the flow of the stream. The method used to trigger the autosamplers will depend on the storm conditions and will be either manual (sampler is set to start at a specified time) or automatically triggered by liquid-level activator switch upon stage level rise. Composite sampling equipment and containers will be set up to minimize contamination of the sample for metals analysis. The composite sample containers will be fitted with a special cap designed to prevent contamination of the sample during the sampling process. The sample will remain capped until a standard cap is fitted onto the carboy for transportation to the laboratory. Once in the laboratory, the carboy is opened for splitting into laboratory sample containers.

Composite samples will be brought back to the laboratory to transfer to appropriate laboratory sample containers. The transfer will consist of continuous agitation of the sample in the 10-litre carboy and transfer of the sample to the laboratory containers using a Teflon siphon tube. Each sample container will be filled ½ full while the sample is flowing from the autosampler carboy and then the sample containers will be filled to the appropriate level. This procedure will insure a representative sample from the carboy in each laboratory sample container. As with the autosampler discrete grab samples, if there

is insufficient volume to complete all of the requested analyses, priority shall be given to conventional parameters, followed by microbiological analyses, metals, and finally nutrients.

6.4.4 Autosampler Deployment, Setup, Maintenance, and Field Blanks

All autosamplers will be sited at each location inside secure enclosures at a point close to the stream or creek. The locations will be positioned above the high water mark of the stream to prevent potentially flooding the enclosure during a storm. The sample lines will be deployed to a position in the stream at least three feet from shore and at least one foot under water. Each sample line will be fitted with a custom, pre-cleaned, non-contaminating screen to prevent large material from entering the autosampler containers. The sample lines will be back-flushed with laboratory de-ionized water, usually just prior to start-up for the next event. Autosampler pump and sample tubing will be replaced as needed with pre-cleaned tubing. Because the sample bottles will remain open inside the sequential autosampler for the duration of a storm or baseflow sampling event, the potential for metals contamination is increased. However, the sequential autosampling equipment will be assembled in such a manner as to reduce metals contamination from the sampling equipment. In addition, bottles used in the sequential autosampler will be cleaned to minimize metals contamination of the sample from the bottles. See Section 7.3 for details on cleaning and preparation of the autosampler sample containers and tubing.

Full autosampler system blanks were analyzed at the laboratory at the beginning of the project and will not be repeated in the field. Field blanks will be run with selected sequential autosamplers. A pair of field blank bottles will be placed, open, in the center of the autosampler base at the beginning of each sample event. Four bases will be monitored during each event. A different set of locations will be chosen for a field blank for each event. Field blanks will not be used for the composite autosamplers as they will not be exposed to the atmosphere except under laboratory conditions.

6.5 Stream Baseflow Sampling

All sample locations sampled during storms will be sampled during baseflow conditions. The techniques and requirements for sampling will be the same as those detailed in section 6.4. The only difference will be the frequency of baseflow event sampling and the inclusion of organic parameter analyses at various locations (see Section 5). Baseflow conditions are defined as the flow rates that occur before the rise and after the drop in elevated stream flows resulting from precipitation. These flow rates generally require two to three days of no rainfall, depending on the site, so that recession of the hydrograph has occurred.

6.6 Field QC

In addition to the field blanks described in Section 6.4, field duplicates will be collected once per storm or baseflow event. Duplicate samples at one randomly selected grab site will be collected for all parameters. A field duplicate is a separate sample collection done

repeating the sampling steps and appropriate rinsing procedures but with separate sample containers.

6.7 Sample Documentation

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

6.7.1 Sample Numbers and Labels

Unique sample numbers will be assigned to each sampling location for which stream water samples are collected for chemical and microbiological analysis. Sample numbers will be assigned prior to the sampling event and waterproof labels generated for each sample container.

6.7.2 Field Notes

Field notes will be maintained for all field activities, including the collection of samples and the gathering of field meter data. Field notes will be kept on water-resistant paper and all field documentation will be recorded in indelible, black ink. Field notes will be recorded on pre-printed field sheets prepared specifically for this project. A sample field sheet is shown in Figure 3. Information recorded on field notes will include, but not be limited to:

- name of recorder,
- sample or station number,
- sample station locator information,
- date and time of sample collection,
- results for all field measurements (temperature, pH, dissolved oxygen, and conductivity),
- staff height.

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

Figure 3. Sample field sheet.

Fieldsheet ID: 421235_22JUN1999_101133 Page: 1

MAJOR LAKES (wtr col)

Project Number: 421235 Personnel: _____

Sample Number	P15790-1	P15790-2	P15790-3	
Locator	0618	0623	0625	
Short Loc. Desc.		Rosemnt SD	Sammslough	
Locator Desc.		LAKE SAMM/WEST SHORE-ROSEMONT STOR	Lake Sammamish	
Site	MAJOR LAKES	MAJOR LAKES	MAJOR LAKES	
Sample Depth				
Collect Date				
Comments				
EH, FIELD				
SED DEPTH				
SED SAMP RANGE				
SED TYPE				
TIME				
Dept., Matrix, Prod				
	3 FRSHWTRSED AVS	3 FRSHWTRSED AVS	3 FRSHWTRSED AVS	
	3 FRSHWTRSED NH3	3 FRSHWTRSED NH3	3 FRSHWTRSED NH3	
	3 FRSHWTRSED PSD	3 FRSHWTRSED PSD	3 FRSHWTRSED PSD	
	3 FRSHWTRSED TOC	3 FRSHWTRSED TOC	3 FRSHWTRSED TOC	
	3 FRSHWTRSED TOTP	3 FRSHWTRSED TOTP	3 FRSHWTRSED TOTP	
	3 FRSHWTRSED TOTS	3 FRSHWTRSED TOTS	3 FRSHWTRSED TOTS	
	3 FRSHWTRSED TOTSULFIDE	3 FRSHWTRSED TOTSULFIDE	3 FRSHWTRSED TOTSULFIDE	
	6 FRSHWTRSED HG-CVAA	6 FRSHWTRSED HG-CVAA	6 FRSHWTRSED HG-CVAA	
	6 FRSHWTRSED PP ICPMS	6 FRSHWTRSED PP ICPMS	6 FRSHWTRSED PP ICPMS	
	7 FRSHWTRSED BNA	7 FRSHWTRSED BNA	7 FRSHWTRSED BNA	
	7 FRSHWTRSED CHLOROBENZENES	7 FRSHWTRSED CHLOROBENZENES	7 FRSHWTRSED CHLOROBENZENES	
	7 FRSHWTRSED CLPESTPCB	7 FRSHWTRSED CLPESTPCB	7 FRSHWTRSED CLPESTPCB	
	7 FRSHWTRSED HERB	7 FRSHWTRSED HERB	7 FRSHWTRSED HERB	
	7 FRSHWTRSED OPPEST	7 FRSHWTRSED OPPEST	7 FRSHWTRSED OPPEST	
	7 FRSHWTRSED TRIBUTYLTIN	7 FRSHWTRSED TRIBUTYLTIN	7 FRSHWTRSED TRIBUTYLTIN	
	7 FRSHWTRSED WTPH-HCID	7 FRSHWTRSED WTPH-HCID	7 FRSHWTRSED WTPH-HCID	

End of Fieldsheet.

6.7.3 Field Analytical Results

Field analytical and QC results will be recorded on field sheets in a manner that easily identifies the information as analytical or QC data. Daily field instrument calibration records will be recorded in instrument-specific logbooks. All entries will be recorded in waterproof, indelible black ink.

7 Sample Handling Procedures

Consistent sample handling procedures are necessary to maintain sample integrity and provide data that is as defensible and as high a quality as possible under the sampling conditions. This section provides requirements for proper sample containers, labeling, preservation and storage, autosampler bottle preparation, and chain-of-custody practices.

7.1 Sample Containers and Labels

All samples will be collected or split into pre-cleaned, laboratory-supplied containers affixed with computer-generated labels. All low-level metals analysis sample bottles will be double bagged in ziplock closure bags. The low-level metals analysis sample bottles will be bagged in a clean room environment at the King County Environmental Laboratory. Information contained on sample labels will include: a unique sample number; information about the sampling location; the collection date; the requested analyses; and information about any chemical used in sample preservation. Sample containers required for the various analyses are summarized in Table 4.

Table 4. Sample containers, preservation, and holding times.

Analysis	Container	Preservation	Holding Time*
Total Suspended Solids 0.45	1-Liter HDPE, CWM	Refrigerate, 4 °C	7 days
Total Suspended Solids	1-Liter HDPE, CWM	Refrigerate, 4 °C	7 days
Nutrients (NH3, NO23, OrthoP)	125ml HDPE, CWM	Filter and Freeze @ -20 ^{o}C	14 days @ -20^{o}C**
Alkalinity	500-ml HDPE,CWM	Refrigerate, 4 °C	14 days
Total Phosphorus, Total Nitrogen	125ml HDPE, CWM	Refrigerate, 4 °C	2 days w/o pres. 28d H_2SO_4, pH<2
Turbidity	500-ml HDPE,CWM	Refrigerate, 4 °C	2 days
Mercury, Total and Dissolved (by CVAF)	500-ml Teflon, Acid washed, double bagged	BrCl, pH <2 (within 48 hours)	28 days **
Mercury, Total and Dissolved (by CVAA)	500-ml Teflon, Acid washed	HCl, pH <2	28 days **
Other Metals, Total and Dissolved, by ICP-MS-PC	500-ml HDPE, Acid washed, double bagged	HNO_3, pH <2	180 days **
Other Metals, Total and Dissolved, by ICP-MS-routine	500-ml HDPE, Acid washed	HNO_3, pH <2	180 days **
Other Metals, Total and Dissolved by ICP	500-ml HDPE	HNO_3, pH <2	180 days **
Fecal Coliform, Enterococcus, E. coli	500-ml HDPE, sterile	Refrigerate, 4 °C	24 hours
Total Organic Carbon	2 x 40ml amber glass	H_3PO_4, pH <2, Refrigerate, 4 °C	28 days
Dissolved Organic Carbon	125-ml HDPE, CWM	Filter, H_3PO_4,, pH <2, Refrigerate, 4 °C	28 days ***
Biochemical Oxygen Demand	2-L HDPE	Refrigerate, 4 °C	2 days
Organic Analysis, Herbicides	250-ml Amber Glass with Septum cap	Refrigerate, 4 °C	7 days
Organic Analysis, BN-LVI, A-LVI, Chlorinated Pest. / PCB, OP Pest.	1000-ml Amber Glass with Teflon lined cap	Refrigerate, 4 °C	7 days

* The start of the holding time for grab samples is the time collected in the field. For composite samples (collected over 24 hrs or less) the holding time starts immediately at the end of the compositing period.
** Filter the dissolved portion within 24 hours.
*** Filter DOC within 24 hours.

7.2 Sample Preservation and Storage Requirements

Stream stormwater samples will be stored refrigerated at a temperature of approximately 4° C, or preserved appropriately. Sample preservation requirements and storage conditions as well as analytical holding times are summarized in Table 4, above.

7.3 Autosampler Equipment Preparation

Sequential (discrete) and composite autosampler bottles will be cleaned prior to each sampling event. The sequential sampler bottles will be cleaned as follows. The bottles are first washed in a laboratory dishwasher, inverted in racks. The newly washed bottles are allowed to drain completely. The bottles are then filled with de-ionized water (DIW) and laboratory detergent (Detergent 8) and soaked overnight. They are emptied the next day and rinsed with DIW. The bottles are then filled with 5% sulfuric acid solution and soaked overnight. The next morning, the acid solution is removed, and the bottles are given a final rinse with DIW before drying, inverted on a drying rack. Once the sequential bottles are dry, they are capped and stored in a clean storage container. The composite sample carboys are rinsed with DIW. Then the carboys are filled with DIW and laboratory detergent and soaked overnight. The carboys are rinsed with DIW the next day, drained, and then filled with a 5% sulfuric acid solution and soaked overnight. The carboys are drained of the acid solution the following morning, and then thoroughly rinsed with DIW. The carboys are allowed to dry, and finally are stored, capped in a clean storage area. Caps for both the autosampler-sequential and autosampler-composite bottles are cleaned using the laboratory dishwasher. The caps are then allowed to dry in a non-contaminating drying rack. They dry caps are stored in clean ziplock polybags until needed.

The sequential bottle and carboy cleaning procedure was thoroughly evaluated using randomly selected bottles for blank testing. All blanks were found to be clean for the parameters of interest for this project. The cleaning process was deemed acceptable and no further testing has been conducted.

Autosampler pump and sample tubing will be cleaned using the following procedure. The newly purchased sample and pump tubing will be flushed with a solution of 5% sulfuric acid in DIW for ten minutes. The line will then be flushed with DIW for a minimum of 30 minutes to remove all residues of the acid cleaning solution. The cleaned lines will be capped with non-contaminating material and stored in their original containers until deployment in the field.

7.4 Chain-of-Custody Practices

During sample collection, all sample bottles will be either locked in a secure housing with the autosamplers, or in the custody of the sampling personnel. After splitting the autosampler-collected samples into the appropriate containers, sampling personnel will deliver all samples to Sample Receiving and enter them into the Logbook, as described in ESS SOP # 01-01-003-001 (Sample Management). If any samples require analyses that are to be conducted by a subcontracting laboratory, then samples are released according to ESS SOP # 11-02-002-000 (Subcontracting Samples).

7.5 Sample Retention and Disposal

The laboratory will hold, where practical, any unused sample that has not exceeded holding time for at least 30 days after the release of results. Unused samples categorized as hazardous according to state or federal guidelines will either be returned to the client or special arrangements will be made to dispose of the samples at the laboratory.

8 Laboratory Analytical Methods

Adherence to standardized analytical protocols and associated QA/QC guidelines for both chemical and biological testing will help produce data able to meet the project goals and objectives.

8.1 Chemical Testing

This section presents the chemical analytical methodologies that will be employed during this project, along with associated detection limits. The King County Environmental Laboratory distinguishes between a *method* detection limit (MDL) and a *reporting* detection limit (RDL).

- The MDL is defined as *the minimum concentration of a chemical constituent that can be detected*.
- The RDL is defined as *the minimum concentration of a chemical constituent that can be reliably quantified*.

8.1.1 Conventional Analyses and Detection Limits

Conventional analyses, analytical methods, and associated detection limits are summarized in Table 5. All conventional analyses will be performed at the King County Environmental Laboratory with the exception of Biochemical Oxygen Demand, which may be subcontracted to the King County WTD process laboratories or other commercial laboratories. Subcontracting may be necessary, depending on in-house capacity. The specific sites requiring Biochemical Oxygen Demand (BOD) analysis to be subcontracted will be kept to a minimum to ensure comparability of data over the course of the project.

Table 5. Conventional analyses.

Analysis/Method	Method Summary	MDL (mg/L)	RDL (mg/L)
Total Suspended Solids SM 2540 D	Gravimetric	0.5	1
Total Suspended Solids, 0.45 SM 2540 D	Gravimetric	0.5	1
Turbidity SM 2130-B	Nephelometry (Units = NTU)	0.5	2
Alkalinity SM 2320-B	Titration (Units = mg CaCO3/L)	0.2	10
Ammonia Nitrogen SM 4500-NH_3-G	Colorimetric, Automated	0.010	0.020
Nitrate+Nitrite Nitrogen SM 4500-NO_3-F	Colorimetric, Cd Red., Automated	0.020	0.040
Orthophosphate SM 4500-P-F	Colorimetric, Automated	0.002	0.005
Total Phosphorus SM 4500-P-B, FMOD	Colorimetric, Automated	0.005	0.010
Total Nitrogen SM 4500-N-C	Colorimetric, Cd Red., Automated	0.050	0.100
Total Organic Carbon SM 5310-B	High Temperature Combustion, Catalytic Conversion, IR Detection	0.5	1.0
Dissolved Organic Carbon SM 5310-B	High Temperature Combustion, Catalytic Conversion, IR Detection	0.5	1.0
Biochemical Oxygen Demand SM 2510-B	Oxygen Depletion Following 5-Day Incubation @ 20 °C	2*	10*

* May vary depending on subcontracting laboratory capability

8.1.2 Metal Analyses and Detection Limits

Target elements, analytical methods and associated detection limits are summarized in Table 6. Sample collection methods and methods of analysis are designed to achieve the multiple project goals. Grab samples collected using clean techniques (EPA Method 1669) will be analyzed using the most sensitive methods to achieve the lowest detection limits. Samples collected using autosamplers (sequential and composite) will be analyzed using less sensitive methods. The King County Environmental Laboratory will perform all metals analyses with the exception of low-level mercury by Cold Vapor Atomic Fluorescence (CVAF), which will be analyzed at Frontier Geosciences Inc., of Seattle, Washington. Analysis of mercury by Cold Vapor Atomic Absorption Spectroscopy (CVAA), a less sensitive method than CVAF, will be performed at the King County Environmental Laboratory. All other elements will be analyzed by either Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES) or Inductively

Coupled Plasma Mass Spectroscopy (ICP-MS), depending upon the concentration of the element in the samples. ICP-MS analysis is more sensitive and capable of lower detection limits than ICP-OES. Mineral elements (calcium, iron, magnesium, potassium and sodium) and other elements detected will be reported by ICP-OES analysis. For all samples, all elements not detected by ICP-OES, except the minerals, will be analyzed by ICP-MS as required to achieve a lower detection limit. Grab samples only will be analyzed for trace elements by the most sensitive pre-concentration ICP-MS method for elements not detected by routine ICP-MS.

Table 6. Total and dissolved metal analyses for water samples.

ICP-MS Pre-Concentration Analysis

Element	Analytical Method	MDL (mg/L)	RDL (mg/L)
Arsenic	Pre-concentration/ICP-MS (EPA 1638)	0.0001	0.0005
Cadmium	Pre-concentration/ICP-MS (EPA 1638)	0.00001	0.00005
Chromium	Pre-concentration/ICP-MS (EPA 1638)	0.00005	0.00025
Copper	Pre-concentration/ICP-MS (EPA 1638)	0.0001	0.0005
Lead	Pre-concentration/ICP-MS (EPA 1638)	0.000025	0.000125
Nickel	Pre-concentration/ICP-MS (EPA 1638)	0.00005	0.00025
Selenium	Pre-concentration/ICP-MS (EPA 1638)	0.0005	0.0025
Silver	Pre-concentration/ICP-MS (EPA 1638)	0.000025	0.000125
Zinc	Pre-concentration/ICP-MS (EPA 1638)	0.00015	0.00075

ICP-MS Routine Analysis

Element	Analytical Method	MDL (mg/L)	RDL (mg/L)
Aluminum	ICP-MS (EPA 200.8)	0.002	0.01
Arsenic	ICP-MS (EPA 200.8)	0.0005	0.0025
Cadmium	ICP-MS (EPA 200.8)	0.0001	0.0005
Chromium	ICP-MS (EPA 200.8)	0.0004	0.002
Copper	ICP-MS (EPA 200.8)	0.0004	0.002
Lead	ICP-MS (EPA 200.8)	0.0002	0.001
Manganese	ICP-MS (EPA 200.8)	0.0002	0.001
Nickel	ICP-MS (EPA 200.8)	0.0003	0.0015
Selenium	ICP-MS (EPA 200.8)	0.0015	0.0075
Silver	ICP-MS (EPA 200.8)	0.0002	0.001
Zinc	ICP-MS (EPA 200.8)	0.0005	0.0025

ICP-OES Analysis

Element	Analytical Method	MDL (mg/L)	RDL (mg/L)
Aluminum	ICP-OES (EPA 200.7)	0.1	0.5
Arsenic	ICP-OES (EPA 200.7)	0.05	0.25
Cadmium	ICP-OES (EPA 200.7)	0.003	0.015
Calcium	ICP-OES (EPA 200.7)	0.05	0.25
Chromium	ICP-OES (EPA 200.7)	0.005	0.025
Copper	ICP-OES (EPA 200.7)	0.004	0.02
Iron	ICP-OES (EPA 200.7)	0.05	0.25
Lead	ICP-OES (EPA 200.7)	0.03	0.15
Magnesium	ICP-OES (EPA 200.7)	0.03	0.15
Manganese	ICP-OES (EPA 200.7)	0.002	0.01
Nickel	ICP-OES (EPA 200.7)	0.02	0.1
Potassium	ICP-OES (EPA 200.7)	2	10
Sodium	ICP-OES (EPA 200.7)	0.5	2.5
Selenium	ICP-OES (EPA 200.7)	0.05	0.25
Silver	ICP-OES (EPA 200.7)	0.004	0.02
Zinc	ICP-OES (EPA 200.7)	0.005	0.025
Hardness	ICP-OES (EPA 200.7)	0.25	1.25

Total and Dissolved Mercury Analysis

Element	Analytical Method	MDL (mg/L)	RDL (mg/L)
Mercury	CVAA (245.1)	0.000005	0.000015
Mercury	CVAF (EPA 1631b)	0.0000001	0.0000005

8.1.3 Organic Analyses and Detection Limits

Organic analyses, methodologies, and associated detection limits are summarized in Table 7. All organic analyses will be performed by the King County Environmental Laboratory, except for the Chlorinated Herbicides, which will be sent to Severn-Trent-Laboratories (STL-Seattle) of Tacoma, Washington.

Table 7. Organic analyses.

Analysis/Method	Method Summary	MDL (µg/L)	RDL (µg/L)
BNA LVI EPA 3520C/8270C LVI	Gas Chromatography with Mass Spectroscopy	0.01 to 0.75	0.025 to 5.0
Chlorinated Pesticides/PCBs EPA 3520C/8081, 8082	Gas Chromatography with Electron Capture Detector	0.005 to 0.05	0.01 to 0.1
Chlorinated Herbicides EPA 8151 GCMS Modified	Gas Chromatography with Mass Spectroscopy	0.21 to 0.45	0.19 to 0.56
Orthophosphorus Pesticides EPA 3520C/8270C SIM	Gas Chromatography with SIM Mass Spectroscopy	0.027 to 0.048	0.50

8.2 Microbiology Analyses and Detection Limits

Microbiology analyses, methodologies, and associated detection limits are summarized in Table 8. The King County Environmental Laboratory will perform all microbiology analyses.

Table 8. Microbiology analyses.

Analysis/Method	Method Summary	MDL (cfu/100ml)	RDL (cfu/100ml)
Fecal coliform by Membrane Filtration	Std Method 19th ed., 9222D	1	N/A
Enterococcus by Membrane Filtration	Std Method 19th ed., 9230C	1	N/A
E. coli by Membrane Filtration	Std Method 19th ed., 9213D	1	N/A

9 Quality Control (QC) Practices

9.1 QC Practices for Chemistry Analysis

The QC samples that will be analyzed in association with chemical testing are summarized in Table 9.

Table 9. Chemistry QC samples for water analysis.

Parameter	Blank[1]	Replicate[2]	Matrix Spike	Blank Spike Duplicate[3]	LCS[4] / CS[5]	Surrogates
Turbidity	No	1 Per Batch[6]	No	No	1 Per Batch	No
Alkalinity	No	1 Per Batch	No	No	1 Per Batch	No
Ammonia Nitrogen	1 Per Batch	1 Per Batch	1 Per Batch	No	1 Per Batch	No
Nitrate+Nitrite Nitrogen	1 Per Batch	1 Per Batch	1 Per Batch	No	1 Per Batch	No
Orthophosphate	1 Per Batch	1 Per Batch	1 Per Batch	No	1 Per Batch	No
Total Phosphorus	1 Per Batch	1 Per Batch	1 Per Batch	No	1 Per Batch	No
Total Nitrogen	1 Per Batch	1 Per Batch	1 Per Batch	No	1 Per Batch	No
Total Suspended Solids	1 Per Batch	1 Per Batch	No	No	1 Per Batch	No
Total Suspended Solids, 0.45	1 Per Batch	1 Per Batch	No	No	1 Per Batch	No
Mercury (CVAF only)	1 Per Batch	No	1 Per Batch	No	1 Per Batch	No
Mercury (CVAA only)	1 Per Batch	1 Per Batch	1 Per Batch	No	1 Per Batch	No
Other Metals	1 Per Batch	1 Per Batch	1 Per Batch	No	1 Per Batch	No
Total Organic Carbon	1 Per Batch	1 Per Batch	1 Per Batch	No	1 Per Batch	No
Dissolved Organic Carbon	1 Per Batch	1 Per Batch	1 Per Batch	No	1 Per Batch	No
BNA, LVI	1 Per Batch	1 Per Batch	1 Per Batch	1 Per Batch	No	Yes
Chlorinated Pest./PCBs	1 Per Batch	1 Per Batch	1 Per Batch	1 Per Batch	No	Yes
Chlorinated Herbicides	1 Per Batch	1 Per Batch	1 Per Batch	1 Per Batch	No	Yes
Orthophosphorus Pesticides	1 Per Batch	1 Per Batch	1 Per Batch	1 Per Batch	No	No
Biochemical Oxygen Demand	1 Per Batch	No	No	1 Per Batch	No	No

[1]For dissolved parameters a filter blank will be prepared and analyzed with each batch

[2]Replicate - Duplicate analysis for all conventional parameters, duplicate analysis for metal parameters, and matrix spike duplicate (MSD) for organic parameters and Mercury by CVAF.
[3]A Blank Spike Duplicate will be prepared and analyzed in the absence of sufficient sample for Matrix Spike & Duplicate. An LCS may be substituted in metals analysis. For BOD, a single spike blank is run for each batch.
[4]Laboratory Control Standard
[5]Check Standard
[6]Batch - A group of samples analyzed together for QC purposes containing a maximum of 20 samples.

The recommended QC limits associated with chemistry testing are summarized in Table 10.

Table 10. Recommended chemistry QC limits for water samples.

Parameter	Blank[1]	Replicate[2]	Matrix Spike[3]	Blank Spike[3]	LCS/CS[3]	Surrogates[3]
Total Suspended Solids	< MDL	≤ 25%	N/A	N/A	80 – 120%	N/A
Total Suspended Solids, 0.45	< MDL	≤ 25%	N/A	N/A	80 – 120%	N/A
Alkalinity	N/A	≤ 10%	N/A	N/A	85 – 115%	N/A
Ammonia Nitrogen	< MDL	≤ 20%	75 – 125%	N/A	85 – 115%	N/A
Nitrate+Nitrite Nitrogen	< MDL	≤ 20%	75 – 125%	N/A	85 – 115%	N/A
Orthophosphate	< MDL	≤ 20%	75 – 125%	N/A	85 – 115%	N/A
Total Phosphorus	< MDL	≤ 20%	75 – 125%	N/A	85 – 115%	N/A
Total Nitrogen	< MDL	≤ 20%	75 – 125%	N/A	85 – 115%	N/A
Turbidity	N/A	≤ 20%	N/A	N/A	90 – 110%	N/A
Mercury CVAF	< 25 pg total	< 24%[4]	71 – 125%	N/A	Not defined	N/A
Mercury CVAA	< MDL	≤ 20%	80 – 120%	85 – 115%	80 – 120%	N/A
Other Metals	< MDL	≤ 20%	80 – 120%	85 – 115%	80 – 120%	N/A
Total Organic Carbon	< MDL	≤ 20%	75 – 125%	N/A	85 – 115%	N/A
Dissolved Organic Carbon	< MDL	≤ 20%	75 – 125%	N/A	85 – 115%	N/A
BNAs	< MDL	Cmpd Spec[5]	Cmpd Spec[5]	Cmpd Spec[5]	N/A	Cmpd Spec[5]
Chlorinated Pest./PCBs	< MDL	Cmpd Spec[5]	Cmpd Spec[5]	Cmpd Spec[5]	N/A	Cmpd Spec[5]
Chlorinated Herbicides	< MDL	Cmpd Spec[5]	Cmpd Spec[5]	Cmpd Spec[5]	N/A	50 – 135%
Orthophosphorus Pesticides	< MDL	≤ 100%	50 – 150%	50 – 150%	N/A	50 – 150%
Biochemical Oxygen Demand	< MDL	N/A	N/A	80 – 120%	N/A	N/A

[1]Concentration of all analytes should be less than the method detection limit (< MDL).

[2]Relative percent difference (RPD) for duplicate analysis.
[3]Percent recovery for matrix spike, standard reference material, and surrogates.
[4]Acceptance limits for the Relative Percent Difference of the Matrix Spike and Matrix Spike Duplicate
[5]Compound Specific
N/A = Not applicable.

9.2 QC Practices for Microbiology Analysis

Routine QC analyses for Microbiology monitor method performance of each sample analysis batch for each method. A sample analysis batch should not exceed 20 samples of the same matrix which are all prepared together and analyzed using the same reagents, media, equipment and by the same analyst(s). The QC samples to be tested with this set of samples are described below:

9.2.1 Laboratory Duplicates

Laboratory duplicates are prepared for each matrix type at a frequency of 1 per batch or 5%, whichever is more frequent. The duplicate must be processed through all preparation and incubation steps used for the original sample. The acceptance limits are based on a 95% confidence limit as described in the appropriate reference methods.

9.2.2 Negative Controls

A negative control is prepared at a frequency of 1 per batch or 5%, whichever is more frequent. The negative control should show an appropriate qualitative response for the test organism and should not be identified as containing the target organism.

- For Enterococci, the negative control organism is *Streptococcus pyogenes or Staphylococcus epidermidis.*
- For Fecal Coliform, the negative control organism is *Proteus sp*. or *Enterobacter sp*.
- For E. coli, the negative control organism is *Proteus sp. or Enterobacter sp.*

9.2.3 Positive Control

A positive control is prepared at a frequency of 1 per batch or 5%, whichever is more frequent. The positive control should show an appropriate qualitative response for the test organism.

- For Enterococci, the positive control organism is *Enterococcus faecalis* or *faecium.*
- For Fecal Coliform, the positive control organism is *E. coli*.
- For E. coli, the positive control organism is *E. coli.*

9.2.4 Sterility Controls

Pre-filtration and post-filtration blanks are prepared each working day to evaluate the sterility of the dilution water and filtration equipment. These sterility controls are considered acceptable if no growth is detected.

9.3 QC Practices for Field Measurements

Calibration QC requirements for attended Hydrolab field measurements involve determination of post-deployment calibration drift for the parameters of interest (except temperature). Calibration drift is determined by measuring the check standard solution at the conclusion of the field measurements. This check must be done within 12 hours of the last field measurement. The post-deployment checks must be done in the same order used for initial calibration and must be done before any maintenance or calibrations are performed.

Table 11. Acceptance limits for post-deployment calibration checks.

Parameter	Calibration Drift Check
Dissolved Oxygen	± 4 %
Temperature	Done annually only
Conductivity	± 10 %
pH	± 0.2 pH units

QC for field measurements is typically limited to measuring precision by collection of replicate field measurements. Replicates are done at a minimum frequency of 5% of measurements or at a minimum, once per day. A field replicate is defined as a separate in-situ measurement made following all procedures typically done between individual samples. The probe would typically be removed from the water body then returned to the same depth and position used in the original measurement. The following table describes the acceptance limits for field replicates.

Table 12. Acceptance limits for field replicates measurements.

Parameter	Duplicate Samples
Dissolved Oxygen	RPD[1] ≤ 20%
Temperature	± 0.5 °C
Conductivity	RPD ≤ 20%
pH	± 0.2 pH units

[1] RPD (Relative Percent Difference) = $\mathbf{100 \times [(r_1 - r_2)] / ((r_1 + r_2)/2)}$, where r_1 = result 1 r_2 = result 2

Data sets that do not meet the field QC acceptance limits may require that the field measurement data be flagged. Comments on field QC results should be included in the QA review.

10 Data Analysis, Record Keeping, and Reporting

The King County Environmental Laboratory will provide a 30-day turnaround time for all analytical data with the exception of metals, starting upon receipt of the last sample collected per event. Each laboratory section will provide a narrative describing the contents of their data package, including any notable information of immediate interest to the recipient. All data received from subcontractor laboratories will be reported to the King County Environmental Laboratory in a format that will allow an appropriate level of QA/QC review.

10.1 Interpretation of Chemical and Microbiological Data

Analytical results will be used to develop and calibrate the watershed water quality model. These results will also be combined with the model output to conduct the risk based water quality assessment.

10.2 Quality Assurance Reviews

Chemistry, microbiology and field measurement data will undergo standard QA review within each laboratory group according to the Environmental Laboratory QA document and method-specific SOPs. Data will be flagged accordingly. A description of the laboratory qualifiers is provided in Table 13. The LPM will review the section QC results and provide a summary of the QC information in narrative form. This narrative will accompany the data when it is transmitted to the project and program managers. All reviews will be done on an event basis. This level of QA review is necessary to provide the project and program managers with the level of information needed to correctly interpret the data.

Table 13. Laboratory qualifiers.

Qualifier	Description
General	
H	Indicates that a sample handling criterion was not met in some manner prior to analysis. The sample may have been compromised during the sampling procedure or may not comply with holding times, storage conditions, or preservation requirements. The qualifier will be applied to applicable analyses for a sample.
R	Indicates that the data are judged unusable by the data reviewer. The qualifier is applied based on the professional judgment of the data reviewer rather than any specific set of QC parameters and is applied when the reviewer feels that the data may not or will not provide any useful information to the data user. This qualifier may or may not be analyte-specific.
<MDL	Applied when a target analyte is not detected or detected at a concentration less than the associated method detection limit (MDL). MDL is defined as the lowest concentration at which an analyte can be detected. The MDL is the lowest concentration at which a sample result will be reported.
<RDL	Applied when a target analyte is detected at a concentration greater than or equal to the associated MDL but less than the associated reporting detection limit (RDL). RDL is defined as the lowest concentration at which an analyte can reliably be quantified. The RDL represents the minimum

Qualifier	Description
	concentration at which method performance becomes quantitative and is not subject to the degree of variation observed at concentrations between the MDL and RDL.
RDL	Applied when a target analyte is detected at a concentration that, in the raw data is equal to the RDL.
TA	Applied to a sample result when additional narrative information is available in the text field. The additional information may help to qualify the sample result but is not necessarily covered by any of the standard qualifiers.
Chemistry	
B	Applied to a sample result when an analyte was detected at a concentration greater than the MDL in the associated batch method blank. The qualifier is applied in Organics analyses when the sample analyte concentration is less than five times the blank concentration and is applied in Conventionals and Metals analysis when the sample concentration is less than ten times the blank concentration. The qualifier indicates that the analyte concentration in the sample may include laboratory contamination. This is an analyte-specific qualifier.
J#	Applied to tentatively identified compounds (Tic's) reported for organics analysis. A TIC is a non-target analyte that appears on a chromatogram during sample analysis. The analyst compares the analyte peak to a reference library to obtain the best possible match. The number associated with the J qualifier is the confidence level of the analyte library match. The confidence level varies from 1 (highest confidence) to 4 (lowest confidence). The reported concentration is an estimated value.
P	Applied to indicate the presence of the reported analyte above the regulatory reporting limit for the test method.
>MR	Applied when a target analyte concentration exceeds the instrument or method capacity to measure accurately. The qualifier is primarily in the organics section. It is applied when the detected analyte concentration exceeds the upper instrument calibration limit and further dilution is not feasible. The reported value is an estimated analyte concentration.
Biology	
AD	Applied to Benthic data when an adult form of an organism was identified in the sample. Benthic samples are subcontracted.
C	Applied to Microbiology data when the sample analysis exhibits confluent growth of organisms. The value reported is an estimate and can be reliably used as an indicator of relative abundance, however, it can not be used as a reliable or accurate count of the associated organism.
D	Applied to Microbiology data to indicate that a target organism was evaluated to be the dominant or largest sub-population recovered from the sample. The evaluation is based on biomass.
E	Applied to microbiological data when a standard method for estimation of microorganisms has been employed during analysis rather than an actual count. The associated value is an estimate.
LV	Applied to Benthic data when a larval form of an organism was identified in the sample. Benthic samples are subcontracted.
>#####	Applied when a population count exceeds the method capacity to measure accurately. The qualifier is applied in Microbiology analyses when the population count exceeds the procedural capacity to measure accurately. The number in the qualifier is the highest procedural count possible. A value is not reported for the sample result. The actual population count is at least as great as or greater than the value shown in the qualifier. This qualifier is used only in microbiology.
NF	Applied to Microbiology data to indicate that a target organism was not recovered or identified in a sample.
P	Applied to Microbiology data to indicate that a target organism was recovered or identified in a sample.
PU	Applied is applied to Benthic data when a pupal form of an organism was identified in the sample. Benthic samples are subcontracted.

Qualifier	Description
S	Applied to Microbiology data to indicate that a target organism was evaluated to be the second largest contributory sub-population recovered from the sample. The evaluation is based on biomass.

10.3 Record Keeping

All field analysis and sampling records, custody documents, raw laboratory data, data summaries, and case narratives will be stored according to King County Environmental Laboratory policy.

10.4 Reporting

Project data will be presented to the project and program managers in a format that will include the following:

- King County Environmental Laboratory Comprehensive Reports consisting of spreadsheets of chemical, microbiological and field parameters;
- Section narratives of chemistry and microbiology data including supporting QC documentation (provided by the King County Environmental Laboratory);
- A technical memorandum, summarizing field sampling, analytical work, and interpretation of the QC results (provided by the King County Environmental Laboratory).

11 References

American Public Health Association (APHA). 1995. Standard methods for the examination of water and wastewater. 19th Edition. American Public Health Association. Washington, D.C.

King County. 1999. Combined Sewer Overflow Water Quality Assessment for the Duwamish River and Elliott Bay. Prepared by Parametrix, Inc. and King County Department of Natural Resources. Seattle, Washington.

King County 2000. Theoretical Number of Sample Intervals Required to Define The Chemical Wash-off Graph. Kevin Schock (unpublished).

Soerens, T. S., Nelson, M. A., and Spooner, J. 1999. Optimum Sampling for Determining Pollution Loads in Streams. Proceedings of the 1999 International Water Resources Engineering Conference, Seattle, Washington.

U.S. EPA 1996. EPA Method 1669: Sampling ambient water for trace metals at EPA water quality criteria levels. U.S. Environmental Protection Agency, Office of Water, Washington, D.C.