King County
Combined Sewer Overflow
Water Quality Assessment for the
Duwamish River and Elliott Bay

Appendix A: Problem Formulation, Analysis Plan, and Field Sampling Work Plan
A3: Field Sampling Work Plan

Prepared by the

Duwamish River and Elliott Bay

Water Quality Assessment Team

February 1999

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LIST OF ACRONYMS

BNA	Base/neutral/acid compounds
COC	Chain-of-custody
COD	Chemical oxygen demand
COPC	Constituents of potential concern
CRM	Certified reference materials
CSO	Combined sewer overflow
DMMP	Dredged Materials Management Program
DO	Dissolved oxygen
ICP-MS	Inductively coupled plasma-mass spectrophotmetry
KCEL	King County Environmental Laboratory
LIMS	Laboratory Information Management System
MDL	Method detection limit
PAHs	Polynuclear aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PSEP	Puget Sound Estuarine Program
QAPP	Quality assurance project plan
QA/QC	Quality assurance/quality control
RDL	Reporting detection limit
RPD	Relative percent difference
RWSP	Regional Wastewater Services Plan
SAP	Sampling and analysis plan
SCADA	Supervisory control and data acquisition
SEDQUAL	Sediment quality database
SPMD	Semipermeable membrane devices
SRM	Standard reference material
TOC	Total organic carbon
TSS	Total suspended solids
U.S. EPA	United States Environmental Protection Agency
WAC	Washington Administrative Code
WDFW	Washington Department of Fish and Wildlife
WERF	Water Environment Research Foundation
WQA	Water Quality Assessment
WSDOE	Washington State Department of Ecology

1. INTRODUCTION TO THE FIELD SAMPLING WORKPLAN

This work plan outlines the planned scope, sampling procedures, and laboratory analytical requirements of the field sampling program conducted in support of the Duwamish Estuary/Elliott Bay Water Quality Assessment (WQA) project. The WQA project will provide decision-makers in the Combined Sewer Overflow (CSO) Control Program information regarding the benefits of controlling CSO discharges to the Duwamish River and Elliott Bay. The CSO Control Program is a major element of King County's Regional Wastewater Services Plan (RWSP).

Included in this work plan are the project background, site description, sampling and analysis plan (SAP), and five quality assurance project plans (QAPPs). The SAP describes the specific activities, standard operating procedures, and quality assurance/quality control (QA/QC) procedures that were used during sample collection, laboratory analysis, and field testing. The QAPPs describe quality assurance objectives, laboratory analytical methods, method detection limits, and quality control methodologies. The five QAPPs (included as Subappendices A through E) encompass the specific field sampling tasks of: CSO and receiving water, sediment, transplanted mussel *in situ* bioassays, tissue, and benthic infauna survey.

This work plan presents the scope of work for generating data to be included in the project's water quality modeling effort and to be used in ecological and human health risk assessments.

2. PROJECT BACKGROUND

2.1 Overview of the RWSP

The RWSP is a comprehensive sewer plan that evaluates several means of providing wastewater treatment and related services to the growing population of King County over the next 30 years. These services include wastewater conveyance and treatment, CSO control, biosolids management, and water reuse. A draft RWSP was issued in May 1997 that included four alternative wastewater service strategies. Based on input from the public, decision-makers, and other stakeholders, one of the four alternatives was chosen by the King County Executive to be refined and released in April 1998 as the Executive's Preferred Plan. The King County Council will be deliberating on this plan through the summer and fall of 1998. The final plan is expected to be voted on by King County Council in 1999.

2.2 Role of the WQA Project in the RWSP

There are 16 King County CSO outfalls which discharge approximately 1.4 billion gallons of combined sewage and storm water into the Duwamish River and Elliott Bay in a year of average rainfall. King County is currently working to meet the Washington State Department of Ecology (WSDOE) requirement of reducing CSOs to one discharge per year at each outfall in a year of average rainfall. Meeting WSDOE's requirement involves a significant monetary investment.

While King County is committed to protecting human health and aquatic resources in the Duwamish River and Elliott Bay, it is not known at this time to what extent water and sediment quality is affected by CSOs and how much water and sediment quality will be improved by reducing CSO impacts. To gain a better understanding of CSO impacts, King County is conducting the WQA project, which includes the following tasks:

- Determining existing conditions by sampling, monitoring, and computer modeling of the water column and sediment. Computer modeling will also be used to assess situations that do not currently occur.

- Understanding the relative significance of CSO pollutants compared to other pollutant sources by studying CSO impacts on human health, aquatic life, and wildlife.

Results of the WQA project will allow decision-makers to steer the CSO control program toward meeting WSDOE's CSO requirement and providing cost-effective protection of the Duwamish River and Elliott Bay.

2.3 Project Organization

Figure 2-1 presents the management structure for the WQA project. The project manager is responsible for defining the requirements of the project and is assisted by four project

leaders. Additionally, a project consultant and two review panels provide added technical assistance in the design and implementation of the field-sampling program.

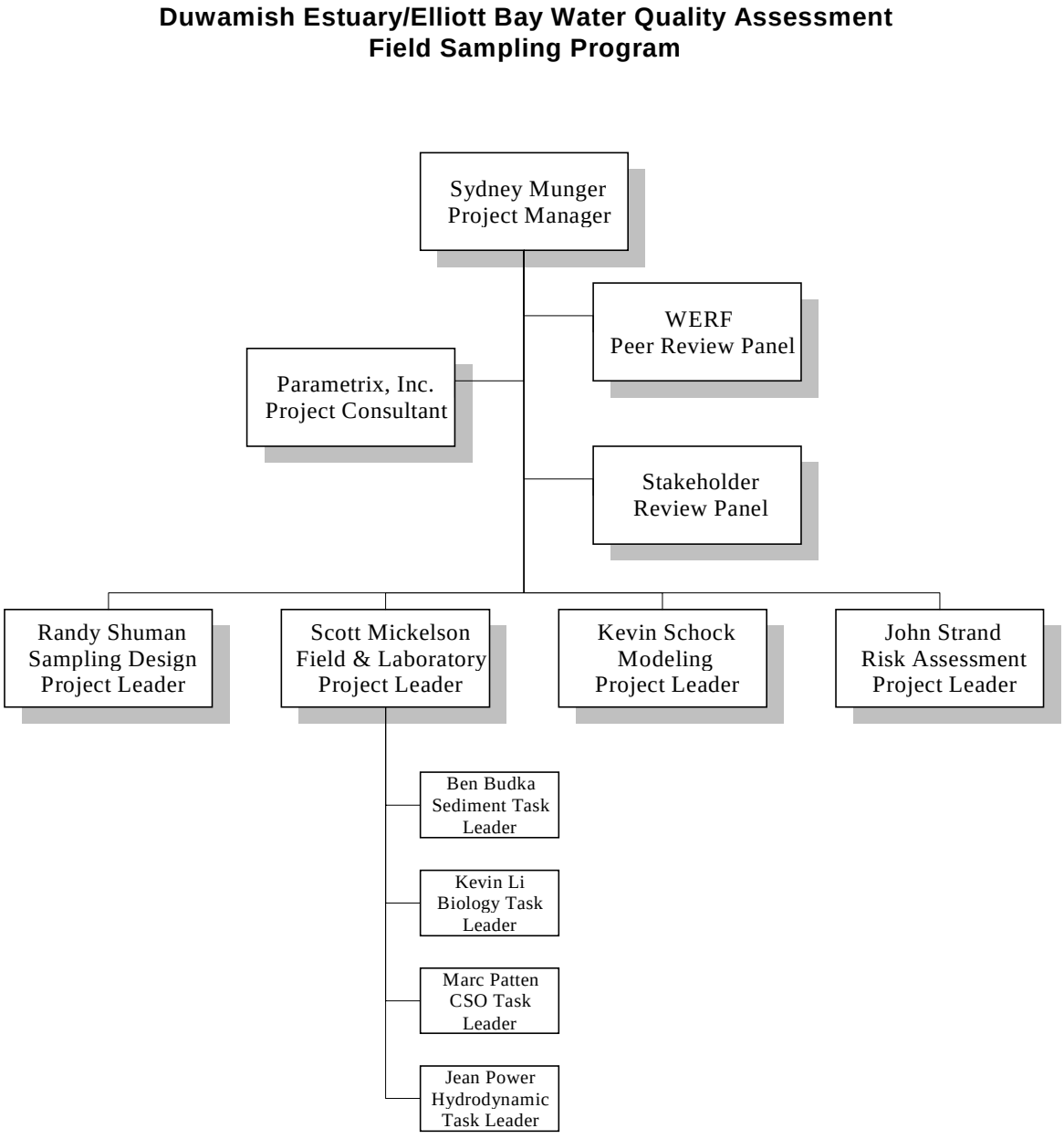


Figure 2-1. Project Management Organization

Sydney Munger of the King County Water and Land Resources Division is the WQA project manager. She is responsible for defining the requirements of the project as well as implementing the project within budget and schedule requirements.

Parametrix, Inc. is the project consultant. They provide expertise in risk assessment as well as technical assistance in the design and implementation of the field sampling program.

Water Environment Research Foundation (WERF) is a peer review panel. They provide technical assistance as well as an overall evaluation of the resulting conclusions of the project.

Stakeholder Review Panel is a panel comprised of regional organizations and individuals with an interest in the quality of the Duwamish River and Elliott Bay. They provide assistance with the formation of the project goals as well as a review of the resulting conclusions of the project.

Randy Shuman of the King County Water and Land Resources Division is the sampling design project leader. In conjunction with the modeling project leader, he is responsible for the overall design of the field program for sediment, receiving water, and CSO sampling. He also provides analysis and interpretation of water, sediment, and hydrodynamic data.

Scott Mickelson of the King County Environmental Laboratory is the field and laboratory project leader. He is responsible for implementing the field work performed in support of the project and coordination of laboratory analyses. He also provides quality QA/QC guidelines for sampling and analytical activities as well as QA/QC review of the resulting data. He is assisted by four task leaders for sediment sampling, biological field work, CSO effluent sampling, and hydrodynamic data collection.

Kevin Schock of the King County Wastewater Treatment Division is the modeling project leader. He is responsible for modeling water, sediment, and hydrodynamic data on the project. In conjunction with the sampling design project leader, he is responsible for the overall design of the field program for sediment, receiving water, and CSO sampling as well as the design of the hydrodynamic data collection program.

John Strand is the risk assessment project leader. He is responsible for the design of field studies supporting the ecological and human health risk assessments including tissue analysis, benthic community analysis, and *in situ* bioassays. He also provides analysis and interpretation of biological data.

3. SITE DESCRIPTION

The WQA study area, shown in Figure 3-1, includes the Green-Duwamish River from just upriver of the East Division Reclamation Plant (Renton Sewage Treatment Plant) downstream to where it enters Elliott Bay, a distance of approximately 24 kilometers (km). The study area also includes the portion of Elliott Bay east of an imaginary line drawn from Duwamish Head northward to Magnolia Bluff.

3.1 Duwamish Estuary

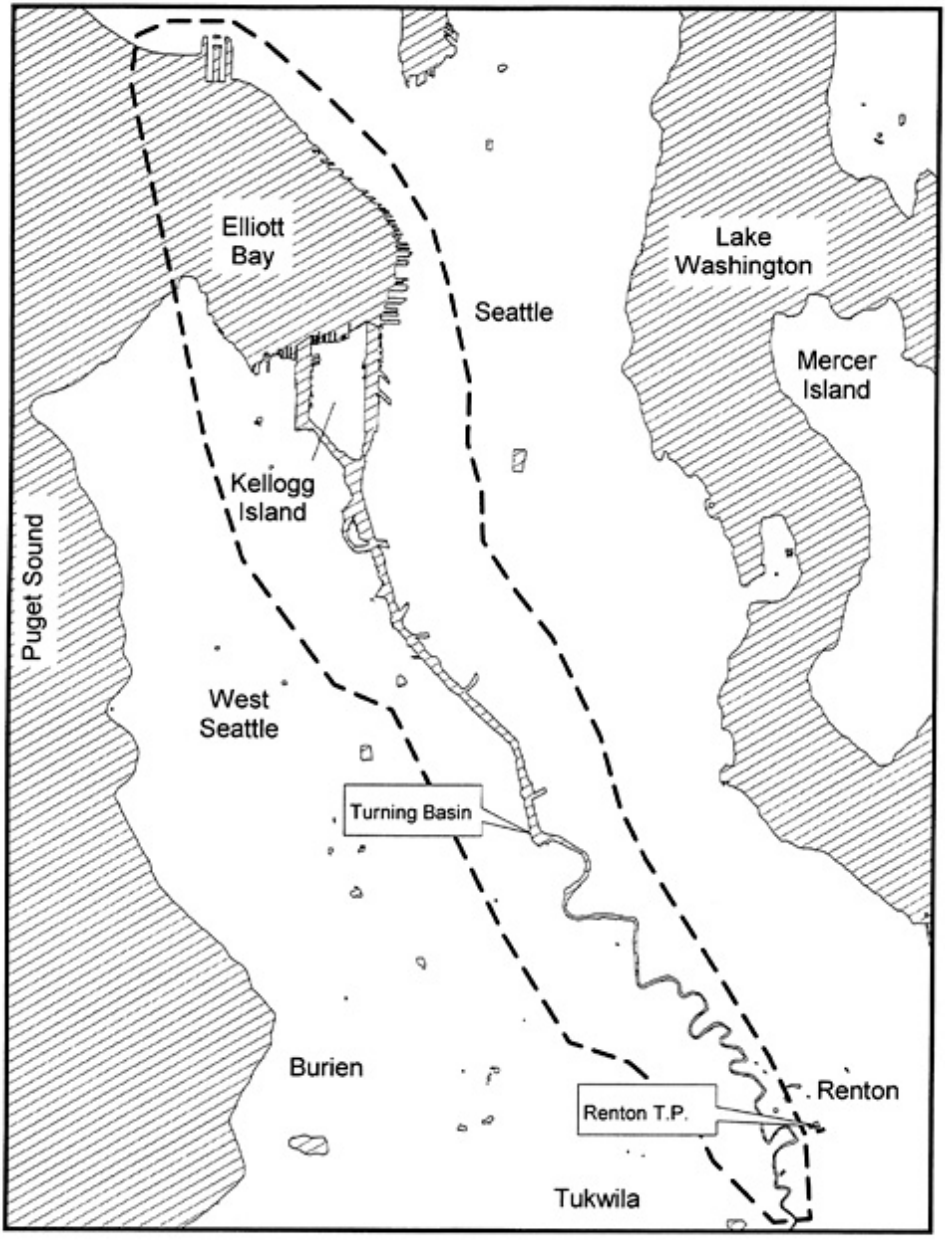
The lower Duwamish River is a highly industrialized, salt wedge estuary influenced both by river flow and tidal effects. At its mouth, the river splits into the East and West Waterways, flowing around Harbor Island into Elliott Bay. The river is considered an estuarine system, exhibiting both marine and freshwater characteristics. During periods of normal river flow, the salt wedge extends upriver approximately 13 km with its terminus or "toe" near the navigational turning basin. From the turning basin upriver to the Renton Sewage Treatment Plant, the river flows through areas of light commercial and residential uses.

The lower portion of the Duwamish River, below the turning basin, has been straightened, dredged, and rip-rapped to facilitate navigation and commerce. Upriver of the turning basin the river continues to flow through its historic channel. River depths range from approximately 17 meters (m) near the mouth to less than a meter in some areas of the upper portion of the study area. Bottom sediments range from coarse sand to fine silt depending on sediment sources and river hydrodynamics. River flows are largely controlled by releases from the Howard Hansen dam, located in the upper Green River watershed. Summer flows, gaged at Auburn, are in the range of 7 cubic meters per second (cms). Winter flows average approximately 45 to 55 cms with peak flows greater than 150 cms during storm events.

3.2 Elliott Bay

Elliott Bay, approximately 21 km^2 in area, forms the western boundary of the commercial core of Seattle. Land use surrounding the bay is mainly marine-oriented industrial and commercial with marine traffic on the bay heavy at all times of the year. The bay opens to the main basin of Puget Sound to the east.

Depths in the bay on the western edge of the study area range from 150 to 180 m while depths near the Seattle waterfront are in the range of 10 to 20 m. The open portion of Elliott Bay is dominated by Puget Sound marine water masses with the fresh water lens from the Duwamish River occupying the upper 5 m. Natural shorelines with intertidal zones are present along the northeast and southwest shores of the bay. In the commercially developed portions of the bay, piers, a sea wall, and rip-rapping have replaced natural shorelines. Bottom sediments in the bay range from fine sediments to coarse gravels and cobbles.



Water Quality Assessment Area - - - - -

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Figure 3-1.
Water Quality
Assessment Study Area

4. FIELD SAMPLING PROGRAM DESCRIPTION

The WQA field sampling program was designed to generate data to be used in the water quality model and the ecological and human health risk assessments. This section presents the objectives of the field sampling program and describes sampling locations, frequencies, and methodologies

4.1 Field Sampling Project for the Water Quality Model

The field sampling project for the water quality model generated data for three matrices: CSO effluent, receiving water, and sediment. These data will be used to model the chemical, physical, and microbiological characteristics of the Duwamish River and Elliott Bay during both storm and non-storm conditions. Sampling locations for this field project are presented in Figure 4-1.

4.1.1 CSO Effluent

Effluent samples were collected from five CSO locations according to the following scheme:

- Brandon Street CSO - A sequential autosampler and a composite autosampler were placed side-by-side at the outfall structure. This placement allows comparison of effluent concentrations at various times during the discharge event (sequential sampling) to concentrations over the entire duration of the discharge event (composite sampling).

- Chelan Avenue CSO - Three composite autosamplers were placed side-by-side at the regulator. The intakes for these autosamplers were placed at three different depths in the effluent stream; bottom, mid-depth, and surface. This placement allows comparison of effluent concentrations at different depths in the effluent stream.

- Connecticut Street CSO - A single composite autosampler was placed at the regulator.

- Hanford Street CSO - Two sequential autosamplers were placed side-by-side at the regulator. This placement allows field replication of effluent samples.

- King Street CSO - A sequential autosampler and a composite autosampler were placed side-by-side at the regulator. This placement allows comparison of effluent concentrations at various times during the discharge event to concentrations over the entire duration of the discharge event.

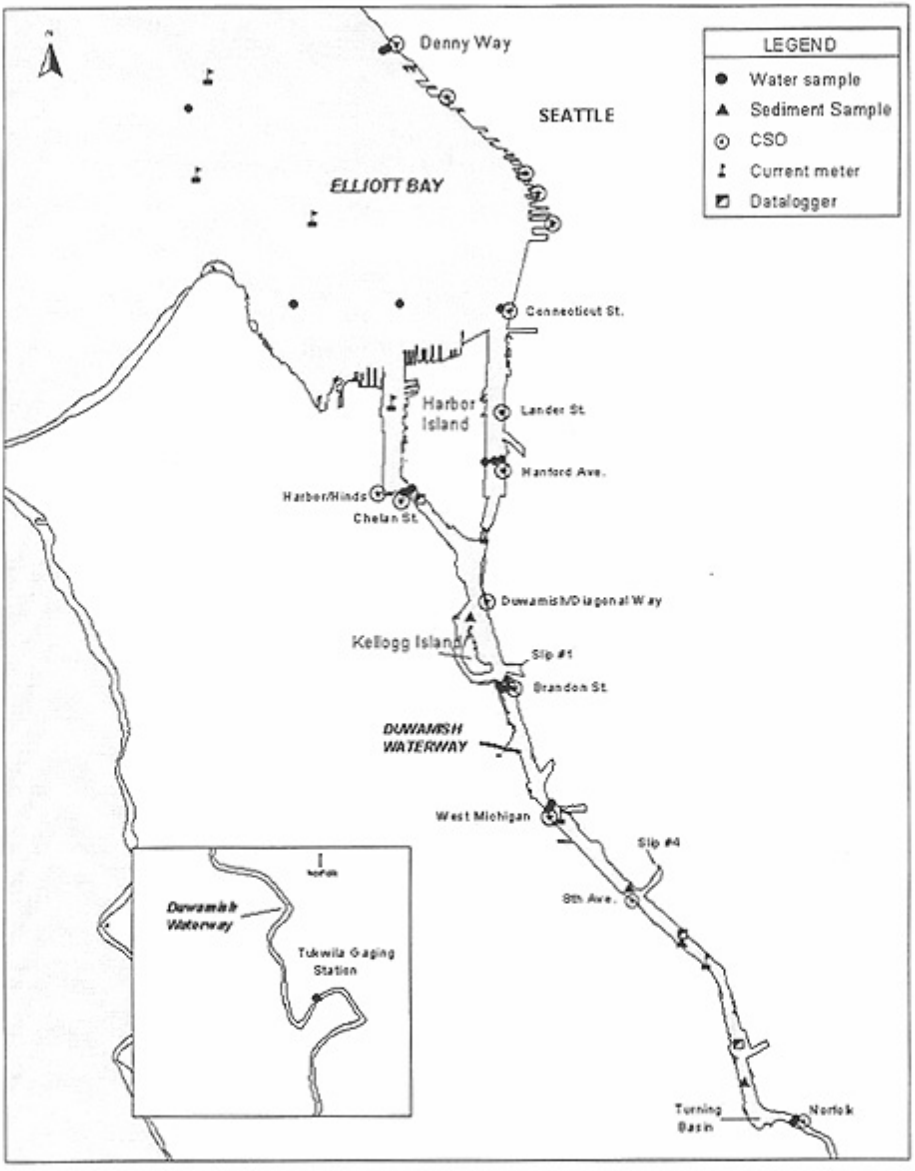


Figure 4-1. Locations of WQA Sampling and Field Instrument Sites

Intake lines for the autosamplers were placed in the wet well at each location. Sampling events were triggered by flow conditions monitored by King County's computerized flow-monitoring system SCADA (Supervisory Control and Data Acquisition). CSO effluent samples were analyzed for conventional, metal, organic, and microbiological parameters. Sampling procedures and the proposed analytical scheme are described in detail in the section CSO Effluent and Subappendix A, respectively. Subappendix A includes the quality assurance project plan for CSO analysis.

4.1.2 Receiving Water

Receiving water samples were collected from 21 stations in the Duwamish River and Elliott Bay to evaluate the chemical, physical, and microbiological characteristics of receiving water during both storm and non-storm conditions. Samples were collected over two 26-week periods according to the following scheme:

- At most stations in the river and the bay, samples were collected from two depths: one meter below the surface and one meter above the bottom (or a depth of 20 m at the deeper stations). Sampling at two depths allows an evaluation of the differences between the overlying fresh water and the salt water at each station.

- At shallow stations (Tukwila, Norfolk, and the Denny Way Outfall), samples were collected only at a depth of one meter.

- Samples were collected weekly except in the event of storm conditions causing a significant discharge at two or more of the target CSOs. During storm conditions, samples were collected at all 21 locations daily for a period of three days following the CSO discharge event.

In addition to the receiving water sampling scheme described above, separate sampling tasks were undertaken for the evaluation of trace-level organics and mercury. Receiving water samples were analyzed for conventional, metal, organic, and microbiological parameters. Sampling procedures and the proposed analytical scheme are described in detail in the section Receiving Water and Subappendix A, respectively. Subappendix A contains the quality assurance project plan for receiving water analysis.

4.1.3 Sediment

Sediment samples were collected weekly from five locations in the Duwamish River according to the following scheme:

- Brandon Street CSO - Sediment samples were collected from this location for a period of 17 weeks.

- Eighth Avenue CSO - Sediment samples were collected from this location for a period of 14 weeks.

- Kellogg Island - Sediment samples were collected from this location for a period of 14 weeks.

- Hamm Creek Delta - Sediment samples were collected from this location for a period of four weeks.

- South Park - Sediment samples were collected from this location for a period of four weeks.

At each location, a single sample was composited from 10 sediment grabs, laid out on a 5-m square grid. Samples were collected from the top 2 centimeters (cm) at each grab station. Sediment samples were analyzed for conventional, metal, and organic parameters. Sampling procedures and the proposed analytical scheme are described in the section Sediment and Subappendix B, respectively. Subappendix B is the quality assurance project plan for sediment analysis.

4.2 Field Sampling Project for the Ecological and Human Health Risk Assessments

The field sampling project for the ecological and human health risk assessments will generated two types of data: chemical concentrations present in fish and shellfish tissue and abundance of benthic infaunal organisms. These data will be used directly in calculations used to ascribe risk to human health and the ecological receptors established as risk assessment endpoints for the WQA project. Sampling locations for this field project are presented in Figure 4-2.

4.2.1 Bioaccumulation of Chemicals in Fish and Shellfish

Chemical concentrations present in fish and shellfish from the Duwamish River and Elliott Bay were evaluated through two studies. An *in situ* bioassay using transplanted mussels was conducted twice near several CSO outfalls and in-river reference stations. Mussels were collected from a "clean" baseline location and transplanted into the Duwamish River and Elliott Bay for a period of one month, both during wet and dry season river-flow conditions. Mussel tissue was analyzed and chemical concentrations compared between transplanted mussels, ambient or wild mussels, and mussels from the baseline sampling location. Sampling procedures and analytical methods are described in Subappendix C, the quality assurance project plan for the *in situ* bioassay of transplanted mussels.

Chemical analysis of various fish and shellfish tissue was conducted on samples collected by Washington State Department of Fish and Wildlife (WDFW) personnel as part of their Puget Sound Ambient Monitoring Program work. Tissue was collected from English sole, quillback rockfish, Dungeness crab, spot prawn, and numerous small fish. In addition, samples of squid and benthic invertebrates were collected by King County personnel for chemical analysis. Sampling procedures and analytical methods are described in Subappendix D, the quality assurance project plan for other tissue analyses.

4.2.2 Benthic Infauna

The benthic communities in an area influenced by a CSO were compared with similar communities from an in-river reference area. Comparisons included numbers of individuals, number of species, and various diversity indices. Comparisons were also made to the reference value ranges for Puget Sound (Ecology 1996). In addition to the benthic analysis, the sediment samples were analyzed for chemical and physical characteristics.

Sediment samples were collected near the Duwamish/Diagonal CSO and storm drain outfalls and at the north end of Kellogg Island. Both sampling sites included a transect of five grab stations. Sampling procedures and analytical methods are described in Subappendix E, the quality assurance project plan for the benthic assessment survey.

5. DATA QUALITY OBJECTIVES

This section describes the data quality objectives of the WQA project and how data quality is measured.

5.1 End Use of Data

Data generated by the field sampling program for the WQA project will be used both in modeling of water and sediment quality in the Duwamish River and Elliott Bay and in risk assessment calculations. Data must be of sufficient quality to minimize potential uncertainties associated with modeling and risk assessment.

5.2 Measurements of Data Quality

The following measurements of data quality are fully described in Subappendices A through E, the quality assurance project plans for the WQA project. The procedures and practices described below are designed to generate data of sufficient quality to support project goals and allow thorough quality assurance review of all data.

5.2.1 Precision and Bias

Sampling and analytical precision may be assessed through the use of field replicates and laboratory replicates, respectively. Collection and analysis of field replicate samples allows evaluation of sampling precision while also allowing assessment of the homogeneity of the sampling matrix. Analysis of laboratory replicate samples allows evaluation of method precision. Analytical bias is assessed by reviewing data resulting from the analysis of laboratory method blanks, standard reference materials, blank spikes, and matrix spikes. Assessment of precision and bias for the benthic assessment survey is described in Subappendix E.

5.2.2 Data Completeness

Date completeness is judged by accounting for all projected data points, compliance with the data quality criteria, and compliance with required holding times (Subappendices A through E). The goal for these criteria is 100 percent completion. Where data are not complete, decisions regarding reanalysis are made by a collaborative process involving both data users and data generators.

5.2.3 Data Representativeness

Samples that are as representative as possible of the site from which they were collected is assured by following sampling methodologies specified in *Recommended Guidelines for Sampling Marine Sediment, Water Column, and Tissue in Puget Sound* (PSEP 1996). Proper attention to storage conditions and holding times helps prevent sample

degradation prior to analysis. Prior to chemical or physical analysis, each sample is thoroughly homogenized to assure that the analytical sample aliquot is representative of the contents of the sample container.

5.2.4 Data Comparability

Data comparability is enhanced through the use of sampling procedures that are standard to the Puget Sound region as well as applying standard analytical methodologies, units of measurement, and detection limits. Application of standard QC policies and a rigorous level of QA review provide data that are comparable to the highest-quality data in the region.

6. SAMPLE COLLECTION PROCEDURES

This section provides a brief overview of the sample collection procedures for the various matrices sampled for the WQA project.

6.1 Sample Collection

All samples were collected in accordance with methodologies suggested in PSEP (1996). A complete description of sampling procedures is included in Subappendices A through E.

6.1.1 CSO Effluent

CSO effluent was collected during discharge events either by autosampler or, for some parameters, by hand. Field measurements taken during collection of CSO effluent samples included temperature, conductivity/salinity, and pH. Field measurements were taken with electronic instrumentation calibrated prior to each sampling event.

Routine CSO effluent samples were collected using ISCO® autosamplers. Autosampler intakes were placed in the wet well at each sampling location and the autosamplers maintained in secure conditions at all times. The autosamplers were programmed for sample amount, duration of sampling event, and sampling interval according to project needs at each sampling location. CSO effluent samples collected for the analysis of low-level mercury were collected by hand at the outfall during discharge. Sample collection procedures for low-level mercury followed U.S. EPA Method 1669 the "clean hands/dirty hands" technique.

6.1.2 Receiving Water

Receiving water samples were generally collected as discrete grab samples. Field measurements taken during collection of receiving water samples included dissolved oxygen (DO), temperature, conductivity/salinity, and pH. Field measurements were taken with electronic instrumentation calibrated prior to each sampling event.

Routine Sample Collection. Routine receiving water samples were collected either from the King County Environmental Laboratory's research vessel *Liberty* or from shore. In non-navigable areas, receiving water samples were collected from bridges. Samples collected from bridges employed Van Dorn or Niskin bottles lowered by rope to the water surface. Sample bottles were lowered to a depth of approximately one meter below the surface and the closing mechanism tripped to facilitate the collection of a discrete sample.

Samples collected from the *Liberty* employed Niskin bottles deployed on a hydrowire. The Niskin bottles were lowered on the hydrowire to depths of one meter below the

surface and one meter above the bottom (or 20 meters in depth) simultaneously at each station.

Low-Level Mercury Sample Collection. To obtain the lowest possible detection limits, special sampling events for the collection of mercury samples were undertaken in association with Brooks Rand, Inc. of Seattle, Washington. Sampling from the *Liberty* employed a peristaltic pump and Teflon® tubing to allow virtually hands-free collection of water samples *in situ*. This minimizes contamination either from sampling equipment or the environment. Sampling from shore employed a Teflon® bailer and associated deployment equipment. Special precautions outlined in U.S. EPA Method 1669 were followed and several field QC samples were collected, including tubing blanks, atmosphere blanks, filter blanks, and bailer blanks. Sampling equipment was supplied by Brooks Rand.

Semipermeable Membrane Devices. To collect time-integrated samples for ultra-trace level organic analysis, semipermeable membrane devices (SPMD) were deployed at two locations in the Duwamish River. SPMD are pre-cleaned polyethylene sheets that accumulate organic compounds over time. The SPMD were deployed for a period of two weeks. The SPMD were attached to a rope-float-anchor assembly which was deployed and retrieved as quickly as possible to minimize contamination. To assess possible contamination by airborne organic compounds, a trip blank was exposed to the air for the same amount of time as one SPMD during deployment and retrieval.

6.1.3 Sediment

Sediments were collected as composites of ten grab samples on a 5-m grid. Sediment samples were collected from the *Liberty* using a modified, stainless steel Van Veen grab sampler. The grab sampler was lowered on a hydrowire and, upon retrieval, the sample was visually inspected for acceptability. If acceptable, a 200 cm^3 aliquot was collected from the sample, using a stainless steel cookie cutter, and placed in a stainless steel bowl. An aliquot was collected from each of the subsequent nine grab stations. Samples were thoroughly homogenized before placement in sample containers.

Redox, or oxidation-reduction potential, was measured in each of the ten individual grab samples with an electronic meter. The meter was calibrated prior to each sampling event according to manufacturers specifications.

6.1.4 Benthic Communities

Benthic sediment samples were collected to assess the abundance and diversity of the benthic infauna near a CSO and a reference site. Samples were collected by Striplin Associates personnel assisted by King County personnel. Sample collection followed methodologies suggested in PSEP (1996) and *Recommended Protocols for Sampling and Analyzing Subtidal Benthic Macroinvertebrate Assemblages in Puget Sound* (PSEP 1987).

6.1.5 Tissue

Most tissue samples for this project were collected by WDFW personnel. Tissue samples were resected, homogenized, and analyzed by King County personnel. Collection of benthic invertebrates and squid for chemical analysis was performed by King County personnel. All tissue collection was performed following methodologies suggested in PSEP (1996).

6.2 Sample Handling

All samples were maintained according to recommended storage and preservative guidelines. In most cases, this involved keeping the samples in ice-filled coolers to maintain an approximate ambient temperature of 4°C until delivery to the laboratory. Specific sample preservation requirements are included in Subappendices A through E.

6.3 Chain-of-Custody

Where required, chain-of-custody forms were completed and retained with samples between collection and delivery to the laboratory. Information included on the chain-of-custody form included: sample number, location, date and time of sample collection, field personnel, number of containers, and requested analyses. The form also included the date and time samples were relinquished to the laboratory as well as the signature of the person in whose custody the samples were retained. Samples subcontracted to another laboratory were accompanied by a completed chain-of-custody form completed by the KCEL sample manager. Custody was maintained by keeping the samples in sight of the sample custodian at any time they were not in a secured area. Secured areas were considered a locked vehicle, the sampling vessel, or a locked refrigerator.

6.4 Documentation

Documentation of field activities was recorded on computer-generated “field sheets” for routine sampling activities. Information on these field sheets included the sampling date and time, field personnel, field measurements, and specific observations. Calibration documentation for field meters is maintained in log books dedicated to each meter. Documentation for biological sampling will be maintained in log books or other documents specific to the agency performing the sampling.

7. PROPOSED ANALYTICAL SCHEME

This section provides an overview of the proposed analytical scheme for the WQA project. Full descriptions of analytical methodologies and associated QA/QC requirements are included in Subappendices A through E. Unless otherwise noted, analyses are performed by the King County Environmental Laboratory.

7.1 Conventional Parameters

Analysis of conventional parameters provides information about the physical properties of the sampling matrix such as solids content or organic content. Conventional parameters were measured both in the field and by laboratory analysis.

7.1.1 CSO Effluent and Receiving Water

CSO effluent was routinely analyzed for the following conventional parameters: chemical oxygen demand (COD), total organic carbon (TOC), volatile suspended solids, ammonia nitrogen, nitrate/nitrite nitrogen, and total suspended solids (TSS). COD, TOC, and volatile suspended solids provide an estimate of the organic content of the CSO effluent. Analysis of the various forms of nitrogen allows evaluation of the contribution of this nutrient to receiving water from CSO effluent. Field conventional measurements included temperature, conductivity, and pH.

Receiving water was routinely analyzed for: TOC, volatile suspended solids, ammonia nitrogen, nitrate/nitrite nitrogen, and TSS. Where the receiving water is fresh, analysis of COD was be performed. Field conventional measurements included DO, temperature, conductivity/salinity, and pH.

7.1.2 Sediment

Sediment was routinely analyzed for particle size distribution, total solids, TOC, ammonia nitrogen, and total sulfides. Particle size distribution and total sulfide analyses was performed by AmTest, Inc. in Redmond, Washington. Analysis of total solids allows sediment organic and metal data to be normalized to dry weight. Some organic data are also normalized to organic carbon for comparison to regulatory standards.

7.1.3 Tissue

Tissue samples were analyzed for total solids to allow normalization of tissue organic and metal data to dry weight.

7.2 Metal Parameters

Analysis of metals in various matrices allows the evaluation of both baseline concentrations of these potential toxicants and the possible contribution of metals to the river and bay by CSOs.

7.2.1 CSO Effluent and Fresh Water

CSO effluent and fresh receiving water were analyzed for the following thirteen priority pollutant metals: antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc.

Analysis of these samples was performed by inductively coupled plasma-mass spectrometer (ICP-MS) to obtain the lowest-possible detection limits. The samples were also analyzed by ICP for calcium and magnesium to allow a hardness calculation. Fresh water quality criteria for metals are hardness normalized.

7.2.2 Marine Water

Marine receiving water was analyzed for the same suite of metals mentioned in Section 7.2.1 above CSO Effluent and Fresh Water. The salinity and dissolved solids concentration of marine water, however, impart a high degree of interference to the ICP-MS analysis. Special sample preparation was conducted on marine water samples prior to analysis.

7.2.3 Low Level Mercury

To obtain the lowest possible detection limits for mercury, a separate low-level mercury study was undertaken for CSO effluent and receiving water. As previously stated in Section 1.1, sampling methodologies followed guidelines specified in U.S. EPA Method 1669, the “clean hands/dirty hands” technique. Collection of a greater number of field QC samples allows evaluation of the final quality of the data. Low level mercury analysis by cold vapor atomic fluorescence was performed by Brooks Rand, Inc. in Seattle, Washington.

7.2.4 Sediment

Sediment analysis included those metals regulated under the State of Washington Sediment Management Standards (arsenic, cadmium, chromium, copper, lead, mercury, silver, and zinc) as well as the remaining priority pollutant metals (antimony, beryllium, nickel, selenium, and thallium). The mineral metals, aluminum and iron, were also analyzed to provide a potential method for normalizing other metal concentrations to local geological conditions. Organic forms of metals, including butyltin isomers and methyl mercury, were also analyzed in sediment due to their potential toxicity through bioaccumulation. Methyl mercury analysis was performed by Frontier Geosciences, Inc. in Seattle, Washington.

7.2.5 Tissue

All tissue samples were analyzed for the thirteen priority pollutant metals mentioned above and butyltin isomers.

7.3 Microbiological Parameters

To evaluate the potential risk to human health posed by CSO effluent, fecal coliforms were analyzed in both water and tissue matrices. Fecal coliforms have been used as indicator organisms of other more harmful pathogens present in sewage.

7.3.1 CSO Effluent and Receiving Water

Fecal coliforms were routinely analyzed in both CSO effluent and receiving water during storm and non-storm conditions.

7.3.2 Tissue

Fecal coliforms were analyzed in tissue samples collected from wild mussels located near the Brandon Street CSO. Baseline samples were collected prior to a discharge event and additional samples collected following the discharge event. In addition to fecal coliforms, mussel tissue samples were analyzed for viruses, *Salmonella*, and *Yersinia* bacteria.

7.4 Organic Parameters

Analysis of organic compounds in various matrices allows the evaluation of both baseline concentrations of these potential toxicants and the possible contribution of organic compounds to the river and bay by CSOs.

7.4.1 CSO Effluent and Receiving Water

CSO effluent and receiving water were routinely analyzed for all of the priority pollutant base/neutral/acid (BNA) extractable semivolatile organic compounds. Included in the BNA analysis were caffeine and coprostanol, two compounds which act as tracers for the sewage component of CSO effluent.

7.4.2 Semipermeable Membrane Devices

Organic compounds are difficult to detect in ambient receiving water samples collected as discrete grabs. SPMDs were deployed to achieve lower detection limits for organic compounds. SPMD concentrate non-polar or lipophilic compounds over a specified time. The data are used to estimate the average receiving water concentrations by applying compound-specific partitioning coefficients. SPMD analysis was performed by Battelle Marine Sciences Laboratory in Sequim, Washington. SPMD parameters included

polynuclear aromatic hydrocarbon (PAH) compounds, chlorinated pesticides, PCB Aroclors®, and PCB congeners.

7.4.3 Sediment

Sediment samples were analyzed for all organic parameters specified in WSDOE's Sediment Management Standards (Chapter 173-204 WAC). These parameters include the BNA compounds and PCBs.

7.4.4 Tissue

All tissue samples were analyzed for BNA compounds (including caffeine and coprostanol), PCBs, and percent lipids.

7.5 Benthic Taxonomy

In addition to the taxonomic analysis, the benthic sediments were analyzed for the physical and chemical analyses summarized in the sections titled Sediment in the Conventionals, Metals, and Organics sections. This analysis provided data regarding the chemical and physical nature of the sediment in which the benthic organisms reside.

7.6 Laboratory Quality Control

A rigorous QA/QC program ensures data of the highest quality that will be comparable to other studies in the region and reduce the uncertainty associated with using the data in both modeling and risk assessment applications. Detailed descriptions of specific laboratory QA/QC procedures are included in Subappendices A through E.

8. DATA REVIEW, VALIDATION, AND REPORTING

This section describes data reporting and the levels of review that project data underwent prior to use in the computer model or risk assessment calculations.

8.1 Data Review and Validation

All project data underwent a rigorous program of data review and validation prior to posting to the King County Environmental Laboratory database (Laboratory Information Management System or LIMS) and reporting to data users. This review ensures the quality of the data at an analytical level. Peer review checks for overall quality of the data including transcription errors, calculation errors, correct data interpretation, and appropriate level of QA/QC. Validation of all project data was performed by the Laboratory Project Manager or QA/QC Officer. This validation step reviews the quality of the data on a project level. Sediment data underwent QA1 review as specified under Dredged Materials Management Program (DMMP) guidelines. Sediment QA1 review narratives were prepared that meet regulatory requirements for inclusion of the data on the WSDOE's SEDQUAL database. Other data underwent a similar level of review, however, the reporting requirements are not as rigorous as for sediment data. A technical memorandum was written for each data set describing the results of the analytical process, acceptability of the analytical QA/QC, and indicating possible analytical bias. An additional independent review of all analytical data will be performed by the project consultant prior to use in the risk assessment.

8.2 Data Reporting

All chemical, physical, and microbiological project data generated by the King County Environmental Laboratory and its subcontractors is maintained on the LIMS database. Data generated by the benthic assessment survey will not be maintained on the LIMS database.

8.2.1 Analytical Data

Analytical data are reported in Excel® spreadsheet format derived from the LIMS database. Data are reported on a wet-weight basis for all liquid matrices. When required, data are reported on a dry-weight basis for sediment samples. Some sediment data will also be normalized to organic carbon for comparison to regulatory standards. Tissue data are reported on a wet-weight basis and total solids data, when available, will also be reported to allow the data user to convert the tissue data to a dry weight basis if necessary.

8.2.2 Field Measurements

Field measurements are posted to the LIMS database and reported along with analytical data in Excel® spreadsheet format. Field measurements include both numeric data and mnemonic or other encoded recordings of field observations.

9. REFERENCES

Puget Sound Estuarine Program PSEP. 1987 Recommended protocols for sampling and analyzing subtidal benthic macroinvertebrate assemblages in Puget Sound. Prepared for the U.S. Environmental Protection Agency Region 10, Office of Puget Sound, Seattle Washington by Tetra Tech, Inc. Bellevue WA.

Puget Sound Estuarine Program PSEP. 1996. Recommended guidelines for sampling marine sediment, water column, and tissue in Puget Sound. Prepared for the U.S. EPA Region 10, Office of Puget Sound, Seattle Washington by King County Environmental Laboratory. Seattle Washington.

Washington State Department of Ecology (WSDOE). 1996. Development of reference value ranges for benthic infauna assessment endpoints in Puget Sound. Prepared by Striplin Environmental Associates, Inc. Olympia, Washington.

SUBAPPENDIX A

QUALITY ASSURANCE PROJECT PLAN

CSO AND RECEIVING WATER ANALYSES

PROJECT DESCRIPTION

Water samples are being collected and analyzed as part of the Duwamish Estuary Water Quality Assessment (WQA) Risk Assessment study. Chemical and microbiological analysis of the samples will aid in evaluating the impact of combined sewer overflow (CSO) discharges. Both CSO discharges and ambient water samples will be collected and used in modeling for risk assessments.

PROJECT ORGANIZATION AND RESPONSIBILITY

Sydney Munger directs the Water Quality Assessment (WQA). Randy Shuman manages the water phase of the WQA project. Scott Mickelson will facilitate sample collection and delivery and coordinate sample processing and analysis by the King County Environmental Laboratory (KCEL), including data evaluation and reporting.

DATA QUALITY OBJECTIVES

The procedures and practices described in this quality assurance (QA) plan are designed to generate data of sufficient quality to support project goals. Routine data quality objectives used for water analyses at KCEL will be applied. Project-specific data quality objectives for water analyses were established from discussions involving King County personnel and the project consultant, Parametrix. These two sets of objectives will be applied at different points in the project. The routine objectives will be applied during routine data review. Project-specific objectives will define how results may be used in the WQA model. The Data Review, Validation, and Reporting section (Section 8) addresses many of the procedures used to verify that data are meeting these quality objectives.

KCEL Routine Objectives

Precision

Laboratory precision will be assessed using laboratory duplicates for conventional and metals analyses and matrix spike/duplicate matrix spikes for organic parameters. Relative percent difference (RPD) will be calculated for duplicate analyses. At least one of the replicate sample results must exceed the reporting detection limit (RDL) in order for the RPDs to be evaluated against the acceptance limits (Table A-1). Results of precision measurements are evaluated against the objectives defined in Table A-1.

Table A-1. Parameters and QC Objectives for Water Samples

Parameter	Lab Duplicate	Matrix Spike	Duplicate Matrix Spike	Blank Spike/SRM[a]	Method Blank (filter blank)[b]
Pesticide/PCBs	N/A	See Table A-2	See Table A-2	See Table A-2	< MDL
BNAs[c]	N/A	See Table A-2	See Table A-2	See Table A-2	< MDL
Metals[d]	≤ 20% RPD	80% to 120%	N/A	80% to 120%	< MDL
Metals by Reductive Precipitation[e]	≤ 20% RPD	80% to 120%	N/A	80% to 120%	< MDL
Mercury by CVAA[f]	≤ 20% RPD	80% to 120%	N/A	80% to 120%	< MDL
Fecal Coliform	≤ ELD RPD limits	N/A	N/A	N/A	< MDL and Negative response
Ammonia Nitrogen	≤ 25% RPD	70% to 130%	N/A	80% to 120%	< MDL
Nitrate+Nitrite Nitrogen	≤ 25% RPD	70% to 130%	N/A	80% to 120%	< MDL
TSS	≤ 25% RPD	N/A	N/A	N/A	< MDL
Volatile Suspended Solids	≤ 25% RPD	N/A	N/A	N/A	< MDL
COD	≤ 25% RPD	70% to 130%	N/A	N/A	< MDL
TOC	≤ 25% RPD	70% to 130%	N/A	N/A	< MDL
Hardness	≤ 25% RPD	80% to 120%	N/A	80% to 120%	< MDL
Microtox (effluents only)	≤ 25% RPD	N/A	N/A	80% to 120%	< MDL and Neutral response
Low-level Mercury (subcontracted)	≤ 24% RPD	75% to 125%	< 24% RPD	N/A	< 50 pg

[a] Includes positive control for fecal coliform analysis

[b] Includes negative control for fecal coliform

[c] EPA 8270 list plus caffeine and coprostanol

[d] Total and Dissolved metals (Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Ni, Se, Ag, Tl, Zn) analysis by ICP and ICP-MS (including hardness).

[e] Total and dissolved metals (Sb, As, Be, Cd, Cr, Co, Cu, Pb, Ni, Se, Ag, Tl, Zn,Vn) analysis by Reductive precipitation/ICP-MS.

[f] Cold vapor atomic absorption

SRM = Standard reference material

BNAs = Base/neutral/acid compounds

COD = Chemical oxygen demand

RPD = Relative percent difference

MDL = Method detection limit

N/A Not analyzed or not applicable

TOC = Total organic carbon

TSS = Total suspended solids

Bias

An indication of the bias or accuracy of the analytical data is provided by method blanks, standard reference materials (SRMs) or certified reference materials (CRMs), surrogate spikes, blank spikes, and matrix spikes. Tables A-1, A-2 and A-3 shows the objectives for quality control (QC) used to assess accuracy. Corrective action taken when acceptance limits are exceeded will be done at the discretion of the project manager and the laboratory. Analytical results for method blanks are to be less than the method detection limit (MDL) and, for metals, not less than the negative MDL value. A sample result will be flagged with the "B" qualifier if the method blank concentration for that analyte is greater than the MDL and if the sample response is less than five times the method blank response (ten times for metals and conventionals analyses).

Table A-2. Matrix Spike/Spiked Blank Recovery and Relative Percent Difference (RPD) Acceptance Limits Water Samples

Parameter	% Recovery	RPD
BNAs		
Phenol	12 to 110	42
2-Chlorophenol	27 to 123	40
1,4-Dichlorobenzene	36 to 97	28
N-Nitroso-di-n-propylamine	41 to 116	38
1,2,4-trichlorobenzene	39 to 98	28
4-chloro-3-methylphenol	23 to 97	42
Acenaphthene	46 to 118	31
4-Nitrophenol	10 to 80	50
2,4-Dinitrotoluene	24 to 96	38
Pentachlorophenol	9 to 103	50
Pyrene	26 to 127	31
Gamma-BHC	46 to 127	50
Pesticide/PCBs		
Heptachlor	35 to 130	31
Aldrin	34 to 132	43
Dieldrin	31 to 134	38
Endrin	42 to 139	45
DDT	23 to 134	50

Table A-3. Surrogate Recovery Acceptance Limits Water Samples

Surrogate	% Recovery
BNAs	
2,4,6-Tribromophenol	10 to 123
2-Fluorobiphenyl	43 to 116
2-Fluorophenol	21 to 110
d14-Terphenyl	33 to 141
d4-1,2-Dichlorobenzene	16 to 110
d4-2-Chlorophenol	33 to 110
d5-Nitrobenzene	35 to 114
d5-Phenol	10 to 110
Pesticide/PCBs	
2,4,5,6-TCMX	50 to 150
Decachlorobiphenyl	50 to 150

Representativeness

Standardized sampling protocols sensitive to program analytical requirements will be used to collect samples representative of the sampling locations. Proper sample storage will also insure that the sample will still be representative of the target site.

Comparability

Data comparability will be ensured through the application of standard sampling procedures, analytical methods, units of measurement and detection limits. Sampling methodologies, however, may change in order to obtain more accurate data. Comparability of the data for the reductive-precipitation method may be limited since this procedure does not directly follow a standardized method.

Completeness

Completeness will be judged by the following criteria:

- Accounting for the projected data points as detailed in this QA plan
- Compliance with the data quality criteria as presented in this section
- Compliance with required holding times

The goal for the above criteria is 100 percent complete. However, where data are not complete, decisions regarding reanalysis will be made by a collaborative process involving both data users and data generators. These decisions will take into account the project data quality objectives as presented above.

Quality Objectives for Modeling

The objectives to be met in order for data to be acceptable for modeling have been defined by Parametrix, the project consultant, following discussions with King County Staff. A copy of the document summarizing these objectives is included in an attachment.

Sampling Procedures

Sample Collection. For CSO effluents, composite autosamplers will be initiated when a sufficient overflow has occurred to meet project specifications. For receiving water samples, collection will be performed from both shoreline locations (land-based) and on-water locations (marine-based) using the KCEL research vessel *Liberty*. The land-based samples will be collected using a van Dorn sampler while the marine-based samples will be collected using Niskin samplers. To improve the accuracy of the results, modification of the sampling protocol may be necessary. Special sampling protocols for metals, such as those described in U.S. EPA Method 1669, will only be used for the low-level mercury analysis for this project. The low-level mercury samples will be collected by Brooks Rand personnel.

For samples collected by King County personnel, decontamination between collections will be performed using routine procedures such as a rinse with lab deionized water prior to sample collection.

Station Positioning. A differential geographic positioning system (DGPS) is to be used to position the *Liberty* during sampling of marine-based locations. The DGPS is a satellite-based navigation system that operates using a receiver to calculate ground position by triangulating data transmitted by a constellation of satellites operated by the Department of Defense (DOD). These signals are scrambled by the introduction of "white noise." The Coast Guard and King County operate "base stations" which are receivers/transmitters installed permanently on known points. The base stations receive the satellite information and calculate a correction, which is also broadcast. The DGPS receives both the satellite information and the correction information from the base station. It can then, in real time, provide an accurate survey position.

Sample Containers and Preservation. All sample containers will be supplied by KCEL. Sample containers will be provided in accordance with guidelines noted in Table A-4. These containers will be pre-washed and prepared for sampling in accordance with standard operating practice of KCEL. Samples must be filtered and preserved, if appropriate, within 24 hours of collection.

Table A-4. Sample Container, Preservation and Storage Conditions

Parameter	Sample Container	Storage Conditions to be Used	Hold Time
BNA	G with Teflon lid	4° C	7 days to extract 40 days to analyze
Pesticide/PCBs	G with Teflon lid	4° C	7 days to extract 40 days to analyze
Metals	P	Room temp. ultrapure HNO3 to < pH 2[a]	180 days
Mercury by CVAA[c]	P	Room temp. ultrapure HNO3 to < pH 2	28 days
Fecal Coliform	P	4° C	24 hours
Ammonia Nitrogen	P, G	4° C	48 hours[b]
Nitrate+ Nitrite Nitrogen	P, G	4° C	48 hours[b]
TSS, TDS	P	4° C	7 days
Volatile Susp. Solids	P	4° C	7 days
COD	P	4° C, H2SO4 to < pH 2	28 days
TOC	P	4° C, H2SO4 to < pH 2	28 days
Microtox	40 mL G VOA	4° C, no headspace	4 days
Low-level Mercury (EPA 1631)	Teflon	4° C, HCl and BrCl	6 months

[a] For reductive-precipitation samples, HNO3 was added to reach a concentration of 0.2%.

[b] Holding time can be extended to 28 days if the sample is filtered then preserved with Sulfuric acid to < pH 2 within 24 hours of collection.

[c] Cold vapor atomic absorption

P = plastic

G = glass

BNA = base/neutral/acid compounds

PCBs = Polychlorinated biphenyls

TSS = Total suspended solids

TDS = Total dissolved solids

COD = Chemical oxygen demand

TOC = Total organic carbon

VOA = Volatile organic analytes

Sample Delivery. Sample containers will be placed in an insulated cooler with ice immediately after subsampling to maintain a storage temperature of approximately 4°C until delivery to the laboratory. Samples will be packed in a manner that minimizes the possibility of breakage during transport. Samples should be delivered to the KCEL the same day they are collected.

Sample Receipt and Sample Log In. Samples will be logged into the Laboratory Information Management System (LIMS) by the laboratory sample management specialist. The following will be checked at that time:

- Correct use of sample ID and agreement with the field sheet
- Appropriate use of sample bottles and sample preservation
- Samples have been received within the holdtime

When applicable, the following will also be documented:

- Any applicable or unique safety hazards of the sample
- Subcontracted parameters are included in the requested suite of analytes

Samples collected by Brooks Rand for low-level mercury will be transferred directly to their laboratory. Log-in will be performed at KCEL such that the data may be entered into LIMS, even though no samples will be received.

Field Notes. At each sampling location, the following information will be recorded on waterproof field sheets: date and time of sample collection, sampling personnel, station location information, weather conditions, number and type of samples collected, any unusual ambient conditions, and any deviations from standard sampling procedures. Field sheets will be completed for each day of sampling. The field sheet(s) will be delivered to the lab along with the samples.

Field Measurements. Field measurements will be conducted for conductivity, pH, temperature, depth, and dissolved oxygen.

ANALYTICAL PROCEDURES

Table A-5 lists the analytical procedures and detection limits to be used in this project. Limitations in sample quantities may effect the detection limits for individual samples. Low-level mercury (EPA 1631) will be subcontracted to an outside laboratory. All other parameters will be analyzed at KCEL.

Table A-5. Laboratory Analysis Summary

Parameter	Reference	Method Detection Limit	Units
BNAs			
N-Nitrosodimethylamine	EPA 625	2.0	µg/L
Phenol	EPA 625	2.0	µg/L
Bis(2-chloroethyl)ether	EPA 625	0.3	µg/L
2-Chlorophenol	EPA 625	1.0	µg/L
1,3-Dichlorobenzene	EPA 625	0.3	µg/L
1,4-Dichlorobenzene	EPA 625	0.3	µg/L
1,2-Dichlorobenzene	EPA 625	0.3	µg/L
2,2'-Oxybis(1-chloropropane)	EPA 625	1.0	µg/L
N-Nitrosodi-n-propylamine	EPA 625	0.5	µg/L
Hexachloroethane	EPA 625	0.5	µg/L
Nitrobenzene	EPA 625	0.5	µg/L
Isophorone	EPA 625	0.5	µg/L
2-Nitrophenol	EPA 625	0.5	µg/L
2,4-Dimethylphenol	EPA 625	0.5	µg/L
Bis(2-chloroethoxy)methane	EPA 625	0.5	µg/L
2,4-Dichlorophenol	EPA 625	0.5	µg/L
1,2,4-Trichlorobenzene	EPA 625	0.3	µg/L
Naphthalene	EPA 625	0.8	µg/L
Hexachlorobutadiene	EPA 625	0.5	µg/L
4-Chloro-3-methylphenol	EPA 625	1.0	µg/L
Hexachlorocyclopentadiene	EPA 625	0.5	µg/L
2,4,6-Trichlorophenol	EPA 625	2.0	µg/L
2-Chloronaphthalene	EPA 625	0.3	µg/L
Acenaphthylene	EPA 625	0.3	µg/L
Dimethyl phthalate	EPA 625	0.2	µg/L

Table A-5. Laboratory Analysis Summary (continued)

Parameter	Reference	Method Detection Limit	Units
2,6-Dinitrotoluene	EPA 625	0.2	µg/L
Acenaphthene	EPA 625	0.2	µg/L
2,4-Dinitrophenol	EPA 625	1.0	µg/L
4-Nitrophenol	EPA 625	1.0	µg/L
2,4-Dinitrotoluene	EPA 625	0.2	µg/L
Fluorene	EPA 625	0.3	µg/L
Diethyl phthalate	EPA 625	0.5	µg/L
4-Chlorophenyl phenyl ether	EPA 625	0.3	µg/L
4,6-Dinitro-o-cresol	EPA 625	1.0	µg/L
N-Nitrosodiphenylamine	EPA 625	0.5	µg/L
1,2-Diphenylhydrazine	EPA 625	1.0	µg/L
4-Bromophenyl phenyl ether	EPA 625	0.2	µg/L
Hexachlorobenzene	EPA 625	0.3	µg/L
Pentachlorophenol	EPA 625	0.5	µg/L
Phenanthrene	EPA 625	0.3	µg/L
Anthracene	EPA 625	0.3	µg/L
Di-n-butyl phthalate	EPA 625	0.5	µg/L
Fluoranthene	EPA 625	0.3	µg/L
Benzidine	EPA 625	12	µg/L
Pyrene	EPA 625	0.3	µg/L
Benzyl butyl phthalate	EPA 625	0.3	µg/L
Benzo(a)anthracene	EPA 625	0.3	µg/L
Chrysene	EPA 625	0.3	µg/L
3,3'-Dichlorobenzidine	EPA 625	0.5	µg/L
Bis(2-ethylhexyl)phthalate	EPA 625	0.3	µg/L
Di-n-octyl phthalate	EPA 625	0.3	µg/L

Table A-5. Laboratory Analysis Summary (continued)

Parameter	Reference	Method Detection Limit	Units
Benzo(b)fluoranthene	EPA 625	0.8	µg/L
Benzo(k)fluoranthene	EPA 625	0.8	µg/L
Benzo(a)pyrene	EPA 625	0.5	µg/L
Indeno(1,2,3-cd)pyrene	EPA 625	0.5	µg/L
Dibenzo(a,h)anthracene	EPA 625	0.8	µg/L
Benzo(g,h,I)perylene	EPA 625	0.5	µg/L
Aniline	EPA 625	1.0	µg/L
Benzyl alcohol	EPA 625	0.5	µg/L
2-Methylphenol	EPA 625	0.5	µg/L
4-Methylphenol	EPA 625	0.5	µg/L
Benzoic acid	EPA 625	2.0	µg/L
4-Chloroaniline	EPA 625	1.0	µg/L
2-Methylnaphthalene	EPA 625	0.8	µg/L
2,4,5-Trichlorophenol	EPA 625	2.0	µg/L
2-Nitroaniline	EPA 625	2.0	µg/L
3-Nitroaniline	EPA 625	2.0	µg/L
Dibenzofuran	EPA 625	0.5	µg/L
4-Nitroaniline	EPA 625	2.0	µg/L
Carbazole	EPA 625	0.5	µg/L
Coprostanol	EPA 625	2.0	µg/L
Pesticide/PCBs			
4,4'-DDD	EPA 608	0.024	µg/L
4,4'-DDE	EPA 608	0.024	µg/L
4,4'-DDT	EPA 608	0.024	µg/L
Aldrin	EPA 608	0.024	µg/L
Alpha-BHC	EPA 608	0.024	µg/L

Table A-5. Laboratory Analysis Summary (continued)

Parameter	Reference	Method Detection Limit	Units
Aroclor 1016	EPA 608	0.24	µg/L
Aroclor 1221	EPA 608	0.24	µg/L
Aroclor 1232	EPA 608	0.24	µg/L
Aroclor 1242	EPA 608	0.24	µg/L
Aroclor 1248	EPA 608	0.24	µg/L
Aroclor 1254	EPA 608	0.24	µg/L
Aroclor 1260	EPA 608	0.24	µg/L
Beta-BHC	EPA 608	0.024	µg/L
Chlordane	EPA 608	0.12	µg/L
Delta-BHC	EPA 608	0.024	µg/L
Dieldrin	EPA 608	0.024	µg/L
Endosulfan I	EPA 608	0.024	µg/L
Endosulfan II	EPA 608	0.024	µg/L
Endosulfan sulfate	EPA 608	0.024	µg/L
Endrin	EPA 608	0.024	µg/L
Endrin aldehyde	EPA 608	0.024	µg/L
Gamma-BHC (Lindane)	EPA 608	0.024	µg/L
Heptachlor	EPA 608	0.024	µg/L
Heptachlor epoxide	EPA 608	0.024	µg/L
Methoxychlor	EPA 608	0.12	µg/L
Toxaphene	EPA 608	0.24	µg/L
Metals (ICP-MS)			
Aluminum	EPA 200.8	10	µg/L
Antimony	EPA 200.8	0.5	µg/L
Arsenic	EPA 200.8	0.5	µg/L
Barium	EPA 200.8	0.5	µg/L

Table A-5. Laboratory Analysis Summary (continued)

Parameter	Reference	Method Detection Limit	Units
Beryllium	EPA 200.8	0.5	µg/L
Cadmium	EPA 200.8	0.2	µg/L
Chromium	EPA 200.8	0.5	µg/L
Cobalt	EPA 200.8	0.5	µg/L
Copper	EPA 200.8	0.4	µg/L
Lead	EPA 200.8	0.5	µg/L
Nickel	EPA 200.8	0.5	µg/L
Molybdenum	EPA 200.8	0.5	µg/L
Selenium	EPA 200.8	1.0	µg/L
Silver	EPA 200.8	0.3	µg/L
Thallium	EPA 200.8	0.5	µg/L
Tin	EPA 200.8	0.5	µg/L
Zinc	EPA 200.8	0.5	µg/L
Metals (Reductive Precipitation/ICP-MS)			
Antimony	EPA 200.8	0.01	µg/L
Arsenic	EPA 200.8	0.03	µg/L
Beryllium	EPA 200.8	0.015	µg/L
Cadmium	EPA 200.8	0.007	µg/L
Chromium	EPA 200.8	0.042	µg/L
Cobalt	EPA 200.8	0.0056	µg/L
Copper	EPA 200.8	0.028	µg/L
Lead	EPA 200.8	0.005	µg/L
Nickel	EPA 200.8	0.014	µg/L
Selenium	EPA 200.8	0.15	µg/L
Silver	EPA 200.8	0.12	µg/L
Thallium	EPA 200.8	0.005	µg/L

Table A-5. Laboratory Analysis Summary (continued)

Parameter	Reference	Method Detection Limit	Units
Zinc	EPA 200.8	0.15	µg/L
Vanadium	EPA 200.8	0.02	µg/L
Metals (CVAA)			
Mercury	EPA 245.2	0.2	µg/L
Metals (Low-level Mercury)			
Low-level Mercury	EPA 1631	0.11	ng/L
Conventionals			
Ammonia nitrogen	SM4500-NH3-H	0.02	mg/L
Nitrate+nitrite nitrogen	SM4500-NO3-F	0.05	mg/L
TSS	SM 2540-D	0.5	mg/L
Volatile suspended solids	SM 2540-E	0.5	mg/L
COD	SM5220-D	3	mg/L
TOC	SM5310-B	0.5	mg/L
TDS	SM 2540-C	0.5	mg/L

BNAs = Base/neutral/acid compounds

PCBs = Polychlorinated biphenyls

ICP/MS = Inductively coupled plasma-mass spectrometer

CVAA = Cold vapor atomic absorption

TSS = Total suspended solids

COD = Chemical oxygen demand

TOC = Total organic carbon

TDS = Total dissolved solids

DATA REDUCTION, REVIEW AND REPORTING

Field and lab data will be loaded into LIMS, where they will be available for authorized users. A copy of the LIMS "COMP" and "QC" reports will be prepared by the lab project manager along with the narrative of the data review (see Section 8 of Appendix A3).

Method Blank Subtraction

To meet the project requirements for high sensitivity for metals analyses, a reductive precipitation procedure was developed for the receiving water samples. This procedure provides both preconcentration and elimination of saltwater interferences such that a ten-fold increase in sensitivity has been achieved. Due to the high sensitivity of the procedure, certain metals in the method blanks were being detected. Following efforts to minimize and control contamination, it was decided that blank subtraction could be used to minimize the effects of contamination on the sample results. Evaluation of the method blanks from multiple batches of analyses indicate that certain metal contaminants could be accurately characterized by the method blank and therefore the blank responses may be subtracted from sample results. Five metals: cadmium, chromium, cobalt, copper, and nickel meet the criteria for method blank subtraction. Three method blanks will be ran per batch and for these five metals, the method blank average will be subtracted from all sample and QC results. The use of method blank subtraction shows a clear improvement in the observed accuracy of the results for the CRM. The improvement in accuracy of sample results can also be expected since the CRMs are a close match to the samples. Blank subtraction will not be performed on any other metals, even those which routinely were detectable in the method blanks (lead and zinc). The responses detected for these two elements are deemed too variable such that the method blank average would not be representative of the batch and should not be subtracted.

Data Corrections Based on Field Blank Responses

To meet project requirements, data manipulations based on field blank responses for metals analyses by reductive precipitation, ICP-MS may be employed. These calculations may improve the accuracy of the data but results should still be treated as estimated values and may not be acceptable for regulatory purposes.

QUALITY CONTROL PROCEDURES

Field Quality Control Procedures

Field blanks for metals will be collected for selected sample sets to be analyzed for reductive-precipitation ICP-MS. For the land-based samples, the single field blank per sampling event will consist of lab deionized water, sampled through the Van Dorn bottle prior to the collection of samples. For the marine-based samples, two field blanks per sampling set will be collected using the Niskin sampler filled with lab deionized water before and after sample collection. Routine decontamination procedures will be applied to the samplers prior to field blank collection.

For the low-level mercury analysis, field QC samples include tubing blanks, atmosphere blanks, bailer blanks, field filter blanks, and field replicates.

Laboratory Quality Control Procedures

KCEL is accredited by the Washington State Department of Ecology (WSDOE) and participates in audits and inter-laboratory studies by WSDOE and U.S. EPA. These performance and system audits have verified the adequacy of the laboratory QC procedures that follow the U.S. EPA guidelines found in 40 CFR 136.

Frequency of Lab Quality Control Samples

For samples analyses performed at KCEL, the frequency of QC samples to be performed for this project is shown in Table A-6. Analysis of matrix spikes and duplicates may not be possible if insufficient sample is available.

DATA ASSESSMENT PROCEDURES

Data assessment will be conducted by reviewing QC data supplied from the laboratory. Data assessment using both routine lab protocol and the guidelines defined by Parametrix (see the attachment) will be summarized by the lab project manager in the format of a case narrative. Professional judgment will be used to evaluate situations where data quality objectives have not been met. Completeness will be calculated by dividing the number of valid values by the total number of values.

Table A-6. Laboratory Quality Control Samples

Parameter	Method Blank	Lab Duplicate	Matrix Spike	Duplicate Matrix Spike	CRM[a]	Surrogates	Spiked Blank
Chemical Oxygen Demand	1 per batch	5% minimum, 1/batch	5% minimum, 1/batch	N/A	N/A	N/A	N/A
Total Organic Carbon	1 per batch	5% minimum, 1/batch	5% minimum, 1/batch	N/A	N/A	N/A	N/A
Fecal Coliform Microtox	(Negative Control)1 per batch	5% minimum, 1/batch	N/A	N/A	N/A	N/A	N/A
Ammonia Nitrogen	1 per batch	5% minimum, 1/batch	5% minimum, 1/batch	N/A	5% minimum, 1/batch	N/A	N/A
Nitrate+ Nitrite Nitrogen	1 per batch	5% minimum, 1/batch	5% minimum, 1/batch	N/A	5% minimum, 1/batch	N/A	N/A
TSS, TDS	1 per batch	5% minimum, 1/batch	N/A	N/A	N/A	N/A	N/A
Volatile Suspended Solids	1 per batch	5% minimum, 1/batch	N/A	N/A	N/A	N/A	N/A
Metals [b]	1 per batch [c]	5% minimum, 1/batch	5% minimum, 1/batch	N/A	1 per batch	N/A	1 per batch
Mercury [b] (EPA 245.2)	1 per batch	5% minimum, 1/batch	5% minimum, 1/batch	N/A	1 per batch	N/A	1 per batch
Low-level Mercury (EPA 1631)	1 per batch	N/A	N/A	5% minimum, 1/batch	1 per batch	N/A	1 per batch
Semivolatile Organics (BNAs and Pest/PCBs)	1 per batch	N/A	5% minimum, 1/extraction batch	5% minimum, 1/extraction batch	1 per batch	Yes	1 per batch

[a] Certified reference material. Blank spike may be used if CRM not available.

[b] Pre- and post filter blanks will be prepared and analyzed with each set of samples analyzed for dissolved metals.

[c] For reductive-precipitation, 3 method blanks are analyzed per batch.

Note: Batch is generally defined as a set of 20 samples or less, prepared and analyzed using the same reagents and equipment and by the same analyst(s).

N/A = Not applicable or not available

TSS = Total suspended solids

TDS = Total dissolved solids

REFERENCES

Puget Sound Estuarine Program (PSEP). 1996. Recommended quality assurance and quality control guidelines for the collection of environmental data in Puget Sound. Prepared for U.S. EPA, Region 10, Office of Puget Sound, Seattle, Washington. Prepared by King County Environmental Laboratory. Seattle, Washington.

Puget Sound Estuarine Program (PSEP). 1989. Recommended guidelines for measuring selected environmental variables. Prepared for U.S. EPA, Region 10, Office of Puget Sound, Seattle, Washington. Prepared by Tetra Tech, Inc. Bellevue, Washington.

ATTACHMENT A

OBJECTIVES FOR MODELING DATA QUALITY

April 1997

INTRODUCTION

The purpose of this document is to delineate which data collected from water samples are acceptable for use in the water quality assessment (WQA) model, and which data should be excluded.

Certain results may need to be treated as non-detects based on laboratory and field blanks, even though a numerical result is reported. These non-detects, in conjunction with the appropriate quality control sample results, may be used to exclude additional results from the WQA model. Criteria for non-detect designation and results rejection were derived using standard procedures developed by the U.S. Environmental Protection Agency (U.S. EPA 1994, 1995).

IDENTIFICATION OF ANALYSIS TYPES

This section identifies each analytical group for which results may either be treated as non-detects or rejected from use in the WQA model:

- Semivolatile BNAs (U.S. EPA SW8270 plus caffeine and coprostanol)
- Total metals (Priority Pollutant list, minus mercury)
- Dissolved metals (Priority Pollutant list, minus mercury)
- Low-level mercury (subcontracted to Brooks Rand)
- Total organic carbon (TOC)
- Ammonia

The analytical groups that are also being analyzed, but will not be reviewed for rejection, are:

- Hardness
- Microtox
- Fecal coliform
- Nitrate+nitrite
- Total solids
- Total volatile solids
- Chemical oxygen demand (COD)
- Field Measurements - dissolved oxygen (DO), pH, temperature, conductivity

LABORATORY AND FIELD BLANKS

A minimum of one method blank for each matrix should have been extracted and analyzed with each batch. No contaminants should be found in the blanks. If an analyte is found in the blank, but not in any of the samples in the associated extraction batch, no action is taken. Any analyte (other than common phthalate contaminants) identified in a sample that was also detected in the associated extraction batch method blank, should be treated as a non-detect if the sample concentration is less than 5 times (5x) the blank concentration. If the sample concentration is greater than 5 times (5x) the blank concentration, the sample result should be treated as a detected result.

If a common semivolatile phthalate contaminant (i.e., bis(2-ethylhexyl)phthalate, di-n-butylphthalate) is detected in a blank, a "10 times (10x)" criteria should be used in an identical manner.

The criteria defined above also apply to aqueous field blanks, except that compounds identified in the field blank will be used to qualify aqueous results associated with samples collected on the same day as the blank.

HOLDING TIMES

Semivolatile BNAs

The maximum time that may elapse from the date of sample collection to sample extraction is 14 days. If this holding time is exceeded for one or more samples by a factor of 2 (28 days), all non-detects in the affected samples will be rejected.

The maximum time that may elapse from the date of sample extraction to sample analysis is 40 days. If this holding time is exceeded for one or more samples by a factor of 2 (80 days), all non-detects in the affected samples will be rejected.

Metals, Mercury, Ammonia, TOC

The holding time criteria are as follows:

Metals: 6 months to analysis, defined as 180 days

Mercury: 28 days to analysis

Ammonia: 28 days to analysis

TOC: 28 days to analysis

If the holding times are exceeded by a factor of 2, all non-detects for the associated samples will be rejected. For example, if a sample that underwent ammonia analysis was analyzed 56 days after collection and the result was a non-detect (based on laboratory determination or based on the associated blanks), the result would be rejected.

SURROGATES

Semivolatile surrogate (system monitoring) compounds are added to each sample analyzed for semivolatile BNAs. The surrogate compound percent recoveries should fall within the appropriate method limits. If any surrogate compound shows less than 10 percent recovery, the affected fraction must be determined (i.e. acid, base/neutral, or both). This depends on the number and type of internal standards utilized by the laboratory. Non-detected semivolatile target compounds in the relevant fraction shall be rejected.

MATRIX SPIKES AND MATRIX SPIKE DUPLICATES

Semivolatile Samples

Matrix spikes and matrix spike duplicate samples should be extracted and analyzed at a frequency of one per 20 samples of a similar matrix. Percent recoveries and relative percent differences should fall within method requirements. If the matrix spike and matrix spike duplicate results for a compound have recoveries below the lower acceptance limit, non-detected semivolatile target compounds for environmental samples in the corresponding extraction batch should be rejected.

Metals, Mercury, Ammonia, and TOC

The spike recovery for these analytes must be within the method requirements (typically 75 percent to 125 percent). However, spike recovery limits do not apply when the sample concentration exceeds the predicted spiked concentration by a factor of 4 or more. If the matrix spike results for an analyte have recoveries less than 30 percent, non-detected results for the affected analytes in environmental samples in the corresponding extraction batch should be rejected.

LABORATORY CONTROL SAMPLES & BLANK SPIKES

Semivolatile Samples

Laboratory control samples, also known as blank spikes, should be extracted and analyzed at a frequency of one per 20 samples of a similar matrix. Percent recoveries for semivolatile compounds should be within the method recovery limits.

If the laboratory control sample results for a compound have a recovery below the lower acceptance limit and recoveries in the corresponding matrix spike/matrix spike duplicate are less than the lower acceptance limit, then results for the same semivolatile compound in the corresponding batch only are rejected, if not detected.

If more than half of the laboratory control sample results have recoveries less than the lower acceptance limit, then all non-detected semivolatile target compounds in the corresponding batch are rejected.

Metals, Mercury, Ammonia, and TOC

Blank spikes and matrix spikes should be extracted and analyzed at a frequency of one per 20 samples of a similar matrix. If the blank spike results for an analyte have a recovery less than 30 percent and recoveries in the corresponding matrix spike are less than the appropriate recovery limits (typically 75 percent), then non-detected analytes in the corresponding batch only are rejected.

REFERENCES

U.S. EPA. 1994. U.S. EPA contract laboratory program national functional guidelines for organic data review. February 1994. U.S. EPA Office of Solid Waste and Emergency Response. Washington DC.

U.S. EPA. 1995. Test methods for evaluating solid waste. Volume IB: Laboratory manual physical/chemical methods. November 1986, 3rd edition. U.S. EPA Office of Solid Waste and Emergency Response. Washington DC.

ADDENDUM TO QUALITY ASSURANCE PROJECT PLAN CSO AND RECEIVING WATER ANALYSES

DEPLOYMENT OF SEMIPERMEABLE MEMBRANE DEVICES AND RESULTING ANALYSIS OF ORGANIC PARAMETERS

Task Description

Organic compounds are difficult to detect in ambient receiving water samples collected as discrete grabs and analyzed by standard methodology. To better understand the existing organic compound concentrations in receiving water, semipermeable membrane devices (SPMD) were employed to collect time-integrated water samples. SPMD concentrate non-polar or lipophilic compounds from water over a specified time period. Resulting data can be used to estimate average receiving water concentrations by applying compound-specific partitioning coefficients.

Data Quality Objectives

The procedures described in this Addendum to the Receiving Water Quality Assurance Project Plan were designed to generate data of sufficient quality to support the project goals of evaluating organic chemical constituents in the Duwamish River at concentrations lower than those detectable by routine sampling and analytical methodologies.

Precision. Sampling and analytical precision, as well as matrix variability, was evaluated by the collection and analysis of a field replicate.

Accuracy. Sampling and analytical accuracy were evaluated by the collection and analysis of a trip blank, as well as analytical quality control (QC) samples including method blanks, blank spikes, surrogates, and internal standards. Analytical results for the trip and method blanks were used as an indicator of sampling or laboratory bias through contamination. Evaluation of the surrogate and internal standard recoveries provided an indication of method performance and accuracy of analytical results.

Representativeness. Adherence to standardized sampling protocols suggested by Battelle Marine Sciences Laboratory (Battelle) in Sequim, Washington, as well as collection and analysis of a trip blank and field replicate, helped ensure that samples collected were as representative as possible of the sampling locations and that representativeness could be evaluated based on sample analytical results.

Comparability. Data comparability was ensured by the application of standard sampling procedures and analytical methodologies developed by Battelle. Previous SPMD work performed by Battelle in the Duwamish River allowed data comparison between the two projects and a further check of data quality and representativeness.

Sampling Procedures

The SPMD were pre-cleaned, lay-flat polyethylene sheets fabricated at Battelle. The SPMD were received at the King County Environmental Laboratory (KCEL) and kept in their air-tight containers until deployment. The SPMD were deployed at two locations in the Duwamish River from March 26 to April 8, 1997. The 13-day deployment was considered sufficient for the analytes of interest to reach equilibrium between the SPMD and the river

water. Three SPMD, including one field duplicate were deployed just offshore of the Duwamish/Diagonal combined sewer overflow (CSO) and two SPMD were deployed just offshore of the Brandon Street CSO.

Both sets of SPMD were deployed in approximately five meters of water (referenced to mean lower low water) at depths of one meter and three meters below the surface. The SPMD were attached to a rope-float-anchor assembly, which was deployed and retrieved as quickly as possible to minimize contamination. To assess possible contamination by airborne organic compounds, a trip blank was exposed to the air for the same amount of time as one SPMD during deployment and retrieval. Deployment and retrieval was performed from King County's Boston Whaler research vessel.

Analytical Procedures

The SPMD samples were submitted to Battelle on April 8, 1997 and were received at the laboratory on April 9. Samples were analyzed for chlorinated pesticides, polychlorinated biphenyl (PCB) Aroclors®, PCB congeners, and polynuclear aromatic hydrocarbon (PAH) compounds. QC samples included method blanks, blank spikes, surrogates and internal standards, and analysis of the field duplicate sample and trip blank.

Analytical Methodologies

SPMD were extracted on April 11, 1997, three days after retrieval. The SPMD were extracted in hexane under ambient conditions. Extracts were cleaned using silica/alumina chromatography followed by a high performance liquid chromatography (HPLC) cleanup. Analysis was completed within 40 days of extraction. Chlorinated pesticide and PCB analysis was performed according to methodology based on U.S. EPA Method 8080 and PAH analysis was performed according to methodology based on U.S. EPA Method 8270 using selected ion monitoring (SIM).

Quality Control

Several methods of QC were employed to meet the data quality objectives of precision, accuracy, representativeness, and comparability.

Field QC. Field QC samples included a field replicate to assess sampling precision and a trip blank to assess field contamination. The duplicate SPMD was deployed at the Duwamish/Diagonal site, at a depth of one meter below the surface. The SPMD was attached to the deployment rope next to the original SPMD for that depth. The trip blank consisted of a SPMD, which was exposed to the atmosphere both during deployment and retrieval of one SPMD. Analysis of the trip blank allowed evaluation of target analytes that may have been imparted to the SPMD from atmospheric contamination.

Analytical Parameters

The analytical parameters included in the SPMD study are summarized in Table A-7.

Table A-7. SPMD Analytical Parameters

Pesticides	PCB Congeners	PCB Aroclors®	PAHs
a-BHC	PCB8	Aroclor 1242	1,4-Dichlorobenzene
g-BHC	PCB18	Aroclor 1248	Naphthalene
Heptachlor	PCB28	Aroclor 1254	Acenaphthylene
Aldrin	PCB52	Aroclor 1260	Acenaphthene
b-BHC	PCB49		Fluorene
d-BHC	PCB44		Dibenzothiop
Heptachlor epoxide	PCB66		Phenanthrene
2,4' DDE	PCB101		Anthracene
Endosulfan I	PCB87		Fluoranthene
g-Chlordane	PCB77		Pyrene
a-Chlordane	PCB118		Benzo(a)anthracene
4,4' DDE	PCB184		Chrysene
Dieldrin	PCB153		Benzo(b)fluoranthene
2,4' DDD	PCB105		Benzo(k)fluoranthene
Endrin	PCB138		Benzo(e)pyrene
2,4' DDT	PCB187		Benzo(a)pyrene
4,4' DDD	PCB183		Perylene
Endosulfan II	PCB126		Indeno(1,2,3-c,d)pyrene
4,4' DDT	PCB128		Dibenzo(a,h)anthracene
Endrin aldehyde	PCB180		Benzo(g,h,i)perylene
Endosulfan sulfate	PCB170		
	PCB195		
	PCB206		
	PCB209		

Analytical QC. Analytical QC samples included method or matrix blanks, to assess possible laboratory contamination, and blank spikes, surrogates, and internal standards, to assess method accuracy.

Data Reduction, Review, And Reporting

Data received from Battelle included a narrative report discussing methodologies, sample results, and QC. Spreadsheets summarized analytical and QC results as well as partitioning coefficients (K_{poly}) and estimated average water analyte concentrations.

Data Validation. Data validation included a review of holding times, extraction and analytical methodologies, method blank results, and blank spike, surrogate, and internal standard recoveries. Analytical results for QC samples were compared to method control

limits established by Battelle. A technical memorandum was prepared narrating the results of the data validation review.

Blank Correction of Analytical Results. Calculations of estimated water concentrations performed and reported by Battelle did not take into account either trip or method blank contamination. Based on the data validation review of analytical results for both the method and trip blanks, it was decided that estimated water concentrations should be blank-corrected during the calculation.

Data Reporting. Estimated water concentrations were recalculated and reported as "blank-corrected" values, summarized in spreadsheets. The final data report included spreadsheets of the blank-corrected, estimated water concentrations calculated by King County, spreadsheets provided by Battelle, the data validation review narrative technical memorandum, and a task-summary technical memorandum.

SUBAPPENDIX B

QUALITY ASSURANCE PROJECT PLAN

SEDIMENT PROJECT

PROJECT DESCRIPTION

Sediment samples are being collected and analyzed as part of the Duwamish Estuary Water Quality Assessment (WQA) Risk Assessment study. A limited sediment sampling program will focus on five sites in the Duwamish River. Chemical analysis of sediment samples will aid in evaluating the potential impact of combined sewer overflow (CSO) discharges on nearby sediment quality. Combined with existing data the results will be used in modeling for risk assessments.

PROJECT ORGANIZATION AND RESPONSIBILITY

Sydney Munger directs the WQA. Randy Shuman manages the sediment phase of the WQA project. Ben Budka will facilitate sample collection and delivery and coordinate sample processing and analysis by the King County Environmental Laboratory (KCEL), including data reduction and reporting.

DATA QUALITY OBJECTIVES

The procedures and practices described in this quality assurance (QA) plan are designed to generate data of sufficient quality to support project goals and will allow a QA1 review and use of SEDQUAL data qualifiers as defined by the Dredged Material Management Program (DMMP). Procedures to attain these data quality objectives are discussed throughout this document. The quality control procedures section (Section 7.0) addresses many of the procedures used to verify the data is meeting the quality objectives described in this section.

Precision

Laboratory precision will be assessed using laboratory duplicates for organics and metals analyses and triplicates for conventionals parameters. Relative percent difference (RPD) will be calculated for duplicate analyses while relative standard deviation (RSD) will be calculated for triplicate results. At least one of the replicate sample results must exceed the reporting detection limit (RDL) in order for the RPDs or RSDs to be evaluated against the acceptance limits. Results of precision measurements are evaluated against the objectives defined in Table B-1 and those that exceed the acceptance limits will be qualified as specified in Table B-2.

Bias

An indication of the bias or accuracy of the analytical data is provided by method blanks, standard reference materials (SRMs) or certified reference materials (CRMs), blank spikes, and matrix spikes. Table B-1 shows the objectives for quality control (QC) samples used to assess accuracy. When acceptance limits are exceeded, data will be qualified according

to Table B-2. Corrective action taken when data require qualification will be done at the discretion of the project manager and the laboratory. Analytical results for method blanks

Table B-1. Parameters and QC Objectives for Sediment Samples

Parameter	Lab Replicate	Matrix Spike	Duplicate Matrix Spike	Blank Spike	CRM*	Method Blank
Ammonia Nitrogen	≤ 20% RSD	70% to 130%	N/A	80% to 120%	N/A	< MDL
BNAs[a]	≤ 100% RPD	50% to 150%	100% RPD	50% to 150%	80% to 120%	< MDL
Metals[b]	≤ 20% RPD	75% to 125%	N/A	80% to 120%	≤ 120%	< MDL
Methyl Mercury (Subcontracted)	≤ 100% RPD	50% to 150%	100% RPD	N/A	80% to 120%	< MDL
Particle Size Distribution (Subcontracted)	≤20% RSD	N/A	N/A	N/A	N/A	N/A
PCBs[c]	≤ 100% RPD	50% to 150%	100% RPD	50% to 150%	80% to 120%	< MDL
TOC	≤ 20% RSD	70% to 130%	N/A	N/A	80% to 120%	< MDL
Total Sulfide (Subcontracted)	≤ 20% RSD	65% to 135%	N/A	N/A	65% to 135%	< MDL
Total Solids	≤ 20% RSD	N/A	N/A	N/A	N/A	< MDL
Tributyltin	≤ 100% RPD	50% to 150%	100% RPD	50% to 150%	N/A	< MDL

[a] EPA 8270 list plus caffeine and coprostanol. Surrogate recovery limits = 50% to 150%.

[b] Metals = Priority pollutant metals plus iron and aluminum

[c] PCB surrogate recovery limits = 50% to 150%.

* CRM certified values for metals are generated using a different digestion method, therefore data are not qualified based on low recoveries.

RPD = Relative percent difference

RSD = Relative standard deviation

MDL = Method detection limit

N/A = Not analyzed or not applicable

TOC = Total organic carbon

Table B-2. Summary of Data Qualifiers

Condition to Qualify	KCEL Data Qualifier	Organics QC Limits	Metals QC Limits	Conventionals QC Limits	Comment
Very low matrix spike recovery	X	< 10 %	< 10 %	N/A	
Low matrix spike recovery	G	< 50%	< 75%	N/A	
High matrix spike recovery	L	> 150%	>125%	N/A	
Low SRM recovery	G	< 80%*	N/A	< 80%*	
High SRM recovery	L	>120%*	>120%	>120%*	
High duplicate RPD	E	>100 %	>20%	> 20 %	Use duplicate as routine QC for organics
High triplicate RSD	E	> 100%	N/A	> 20 %	Use triplicate as routine QC for conventionals
Less than the reporting detection limit	< RDL	N/A	N/A	N/A	
Less than the method detection limit	< MDL	N/A	N/A	N/A	
Contamination reported in blank	B	> MDL	> MDL	> MDL	
Very biased data, based on surrogate recoveries	X	All fraction surrogates are <10%	N/A	N/A	Use average surrogate recovery for BNA

Table B-2. Summary of Data Qualifiers (Continued)

Condition to Qualify	KCEL Data Qualifier	Organics QC Limits	Metals QC Limits	Conventionals QC Limits	Comment
Biased data, based on low surrogate recoveries	G	All fraction surrogates are < 50%	N/A	N/A	Use average surrogate recovery for BNA
Biased data, based on high surrogate recoveries	L	All fraction surrogates are >150%	N/A	N/A	Use average surrogate recovery for BNA
Estimate based on presumptive evidence	J# used to indicate the presence of TIC's	N/A	N/A	N/A	
Rejected, unusable for all purposes	R	N/A	N/A	N/A	
A sample handling criteria has been exceeded	H	N/A	N/A	N/A	Includes container, preservation, hold time, sampling technique

* Note that DMMP guidance uses a 95% confidence window for this parameter/qualification.

RDL = Reported detection limit

N/A = Not applicable

TIC = Tentatively identified compounds

BNA = Base/neutral/acid

are to be less than the method detection limit (MDL). A sample result will be flagged with the "B" qualifier if the method blank concentration for that analyte is greater than the MDL and if the sample response is less than 5 times the method blank response (10 times for metals and organic analyses).

Representativeness

Samples representative of the target site will be collected by following the guidelines in Recommended Guidelines for Sampling Marine Sediment, Water Column, and Tissue in Puget Sound (PSEP 1996). Proper sample storage will also insure that the sample will still be representative of the target site. Prior to analysis within the laboratory, each individual sample will be homogenized to ensure that the analytical subsample is representative of the sample container contents.

Comparability

Data comparability will be ensured through the application of standard sampling procedures, analytical methods, units of measurement and detection limits. Additionally, the QC criteria based on DMMP guidelines will provide for an adequate level of analytical performance and will produce comparable data.

Completeness

Completeness will be judged by the following criteria:

- Accounting for the projected data points as detailed in this QA plan
- Compliance with the data quality criteria as presented in this section
- Compliance with required holding times

The goal for the above criteria is 100 percent complete. However, where data are not complete, decisions regarding reanalysis will be made by a collaborative process involving both data users and data generators. These decisions will take into account the project data quality objectives as presented above.

SAMPLING PROCEDURES

Sample collection also followed guidelines suggested in PSEP (1996).

Station Positioning

A differential geographic positioning system (DGPS) is to be used to position the KCEL research vessel *Liberty* during sampling. The DGPS is a satellite-based navigation system that operates using a receiver to calculate ground position by triangulating data transmitted by a constellation of satellites operated by the Department of Defense (DOD).

These signals are scrambled by the introduction of "white noise." The Coast Guard and King County operate "base stations" which are receivers/transmitters installed permanently on known points. The base stations receive the satellite information and calculate a correction, which is also broadcast. The DGPS receives both the satellite information and the correction information from the base station. It can then, in real time, provide an accurate survey position.

Sample Collection

Surface sediment grabs are collected with a stainless steel 0.1-m^2 van Veen grab sampler. The grab sampler is decontaminated between sampling stations by scrubbing with a brush to remove excess sediment and rinsing on board, followed with a thorough in-situ rinsing. After a sample has been obtained, the grab sampler is raised slowly off the bottom to allow it to close slowly. Care will be taken in rough conditions to ensure that minimal sample disturbance occurs when bringing the grab sampler on board. After the grab sampler has been secured on board, the sampler will be opened and examined for acceptability. Ideally, 4 to 5 cm should be collected for a sediment subsample of 0 to 2 cm. Sediment depth is measured with a ruler and recorded on the field sheet. If sample acceptability criteria are met, the overlying water is carefully siphoned off. Prior to subsampling, appropriate field measurements and observations are recorded on field sheets.

Subsamples are removed by using stainless steel "cookie cutters" designed to subsample from 0 to 2 cm. The cookie cutter is driven into the sample and the aliquot collected by placing a stainless steel "spatula" underneath the cookie cutter to transfer the aliquot to the composting bowl. If sample aliquots are to be collected from multiple sampler deployments, the stainless steel bowl should be covered with aluminum foil between deployments to minimize contamination from the immediate environment.

Sample Identification

For chemical analysis, a unique laboratory sample number, assigned to each sampling location and event will identify each sample. A single sample number will be used for all parameters analyzed from the same sample. Sample numbers will be assigned and sample containers labeled with these numbers prior to use. Sample labels will also include information about the sampling location, sampling date, project number, sample matrix, requested analytical parameters, and preservation information.

Sample Containers and Preservation

All sample containers will be supplied by KCEL. Sample containers will be provided in accordance with guidelines noted in Table B-3. These containers will be prewashed and prepared for sampling in accordance with standard operating practice of KCEL.

Sample Delivery

Sample containers will be placed in an insulated cooler with ice immediately after subsampling to maintain a storage temperature of approximately 4°C until delivery to the laboratory. Samples will be packed in a manner that minimizes the possibility of breakage during transport. Samples with more than one container will be grouped and placed in plastic bags to facilitate sample receipt and log-in. Samples should be delivered to the KCEL the same day they are collected.

Table B-3. Sample Containers, Preservation, and Storage Conditions

Parameter	Sample Container	Storage Conditions to be Used	Hold Time	Source of Storage Requirements*
BNAs	G with Teflon lid	freeze at -18° C	1 year to extract 40 days to analyze	PSEP and PSDDA ARM
PCBs	G with Teflon lid	freeze at -18° C	1 year to extract 40 days to analyze	PSEP and PSDDA ARM
Metals	P	freeze at -18° C	2 years to analyze	PSEP and PSDDA ARM
Mercury	P	freeze at -18° C	28 days to analyze	PSEP and PSDDA ARM
Methyl Mercury	G or Teflon	freeze at -18° C	28 days to analyze	No guidance available
Ammonia	P, G	refrigerate at 4° C	7 days	PSEP and PSDDA ARM
Particle Size Distribution	G	refrigerate at 4° C	6 months	PSEP and PSDDA ARM
Total Solids	G with Teflon lid	freeze at -18° C	6 months to analyze	PSEP and PSDDA ARM
TOC	G with Teflon lid	freeze at -18° C	6 months to analyze	PSEP and PSDDA ARM
Total Sulfides	G with no headspace	refrigerate at 4° C Zn acetate preserved	7 days	PSEP and PSDDA ARM
Tributyltin	G with Teflon lid	freeze at -18° C	1 year to extract 40 days to analyze	No guidance available

* ARM = Minutes of Third PSDDA *Annual Review Meeting*[1].

Note: Samples to be refrigerated at 4°C after thawing. Mercury storage conditions have been used for methyl mercury. Recommended sample containers are based on guidance from laboratories that perform this test. Organic semivolatile storage conditions have been used for Tributyltin.

BNAs = Base/neutral/acid compounds

PCBs = Polychlorinated biphenyls

P = plastic

G = glass

[1] This document summarizes many program/industry hold time standards. Those to be used for this project are listed in table.

Chain-of-Custody

A laboratory work order, which serves as a chain-of-custody form, will be used for samples analyzed by KCEL. The form will be completed in the field and accompany all samples during transport and delivery to the laboratory. For chain-of-custody purposes, the research vessel is considered a "controlled area".

The sample release section of the laboratory work order form is completed at the time of sample transfer to the laboratory. Date and time of sample delivery as well as the signature of the individual delivering the samples (Relinquished By) must be filled out at this time. The sample recipient (Received By) completes the laboratory work order form and maintains the original in a project file. Samples delivered after regular business hours will be stored in a locked chain-of-custody refrigerator.

Samples delivered to a subcontracted laboratory will be accompanied by a properly completed KCEL chain-of-custody form with custody seals placed on the cooler if samples are delivered by an outside courier. Subcontracted laboratories provide a copy of the completed chain-of-custody form to the lab project manager to become a part of the analytical data package.

Sample Receipt and Sample Log-In

Samples will be logged into the Laboratory Information Management System (LIMS) by the laboratory sample management specialist. The following will be checked at that time:

- Correct use of sample ID and agreement with the field sheet
- Appropriate use of sample bottles and sample preservation
- Samples have been received within the holdtime

When applicable, the following will also be documented:

- Any applicable or unique safety hazards of the sample
- Subcontracted parameters are included in the requested suite of analytes

Field Notes

At each sampling location, the following information will be recorded on waterproof field sheets: date and time of sample collection, sampling personnel, station location information, weather conditions, number and type of samples collected, any unusual ambient conditions, and any deviations from standard sampling procedures. Field sheets will be completed for each day of sampling. The field sheet(s) will be delivered to the lab along with the samples.

Field Measurements

Field measurements of the oxidation-reduction potential will be recorded for each grab sample collected. Characterization of a sediment sampling location as oxidizing or reducing can aid in evaluating other chemical characteristics such as the amount of organic matter present or metals speciation. The physical parameters of sample depth, sediment depth and tide height will also be recorded for each grab sample.

ANALYTICAL PROCEDURES

Samples will be analyzed using the analytical procedures and detection limits appropriate to PSEP studies. These are listed in Table B-4. All results (except total solids) will be reported on a dry weight basis and non-ionizable organic compounds will be normalized using the total organic carbon (TOC) results for each sample.

Methyl mercury, particle size distribution (PSD) and total sulfides will be subcontracted to outside laboratories. All other parameters will be analyzed at KCEL.

Table B-4. Laboratory Analysis Summary

Parameter	Reference	Nominal Method Detection Limit[b]	Units
BNAs			
1,2,4-Trichlorobenzene	EPA 8270 (SIM)	1.4	µg/Kg
1,2-Dichlorobenzene	EPA 8270 (SIM)	1.4	µg/Kg
1,2-Diphenylhydrazine	EPA 8270	110	µg/Kg
1,3-Dichlorobenzene	EPA 8270 (SIM)	1.4	µg/Kg
1,4-Dichlorobenzene	EPA 8270 (SIM)	1.4	µg/Kg
2,4,5-Trichlorophenol	EPA 8270	220	µg/Kg
2,4,6-Trichlorophenol	EPA 8270	220	µg/Kg
2,4-Dichlorophenol	EPA 8270	54	µg/Kg
2,4-Dimethylphenol	EPA 8270	54	µg/Kg
2,4-Dinitrophenol	EPA 8270	110	µg/Kg
2,4-Dinitrotoluene	EPA 8270	22	µg/Kg
2,6-Dinitrotoluene	EPA 8270	22	µg/Kg

Table B-4. Laboratory Analysis Summary (continued)

Parameter	Reference	Nominal Method Detection Limit[b]	Units
2-Chloronaphthalene	EPA 8270	32	µg/Kg
2-Chlorophenol	EPA 8270	110	µg/Kg
2-Methylnaphthalene	EPA 8270	85	µg/Kg
2-Methylphenol	EPA 8270	54	µg/Kg
2-Nitroaniline	EPA 8270	220	µg/Kg
2-Nitrophenol	EPA 8270	54	µg/Kg
3,3'-Dichlorobenzidine	EPA 8270	54	µg/Kg
3-Nitroaniline	EPA 8270	220	µg/Kg
4,6-Dinitro-o-cresol	EPA 8270	110	µg/Kg
4-Bromophenyl phenyl ether	EPA 8270	22	µg/Kg
4-Chloro-3-methylphenol	EPA 8270	110	µg/Kg
4-Chloroaniline	EPA 8270	110	µg/Kg
4-Chlorophenyl phenyl ether	EPA 8270	32	µg/Kg
4-Methylphenol	EPA 8270	54	µg/Kg
4-Nitroaniline	EPA 8270	220	µg/Kg
Acenaphthene	EPA 8270	22	µg/Kg
Acenaphthylene	EPA 8270	32	µg/Kg
Aniline	EPA 8270	110	µg/Kg
Anthracene	EPA 8270	32	µg/Kg
Benzidine	EPA 8270	1300	µg/Kg
Benzo(a)anthracene	EPA 8270	32	µg/Kg
Benzo(a)pyrene	EPA 8270	54	µg/Kg
Benzo(b)fluoranthene	EPA 8270	85	µg/Kg
Benzo(g,h,l)perylene	EPA 8270	54	µg/Kg

Table B-4. Laboratory Analysis Summary (continued)

Parameter	Reference	Nominal Method Detection Limit[b]	Units
Benzo(k)fluoranthene	EPA 8270	85	µg/Kg
Benzoic acid	EPA 8270	220	µg/Kg
Benzyl alcohol	EPA 8270	54	µg/Kg
Benzyl butyl phthalate	EPA 8270	32	µg/Kg
Bis(2-chloroethoxy)methane	EPA 8270	54	µg/Kg
Bis(2-chloroethyl)ether	EPA 8270	32	µg/Kg
Bis(2-chloroisopropyl)ether	EPA 8270	110	µg/Kg
Bis(2-ethylhexyl)phthalate	EPA 8270	32	µg/Kg
Caffeine	EPA 8270	11	µg/Kg
Carbazole	EPA 8270	54	µg/Kg
Chrysene	EPA 8270	32	µg/Kg
Coprostanol	EPA 8270	220	µg/Kg
Di-n-butyl phthalate	EPA 8270	54	µg/Kg
Di-n-octyl phthalate	EPA 8270	32	µg/Kg
Dibenzo(a,h)anthracene	EPA 8270	85	µg/Kg
Dibenzofuran	EPA 8270	54	µg/Kg
Diethyl phthalate	EPA 8270	54	µg/Kg
Dimethyl phthalate	EPA 8270	22	µg/Kg
Fluoranthene	EPA 8270	32	µg/Kg
Fluorene	EPA 8270	32	µg/Kg
Hexachlorobenzene	EPA 8270	1.4	µg/Kg
Hexachlorobutadiene	EPA 8270	54	µg/Kg
Hexachlorocyclopentadiene	EPA 8270	54	µg/Kg
Hexachloroethane	EPA 8270	54	µg/Kg

Table B-4. Laboratory Analysis Summary (continued)

Parameter	Reference	Nominal Method Detection Limit[b]	Units
Indeno(1,2,3-cd)pyrene	EPA 8270	54	µg/Kg
Isophorone	EPA 8270	54	µg/Kg
N-Nitrosodi-n-propylamine	EPA 8270	54	µg/Kg
N-Nitrosodimethylamine	EPA 8270	220	µg/Kg
N-Nitrosodiphenylamine	EPA 8270	54	µg/Kg
Naphthalene	EPA 8270	85	µg/Kg
Nitrobenzene	EPA 8270	54	µg/Kg
Pentachlorophenol	EPA 8270	54	µg/Kg
Phenanthrene	EPA 8270	32	µg/Kg
Phenol	EPA 8270	220	µg/Kg
Pyrene	EPA 8270	32	µg/Kg
PCBs			
Aroclor 1016	EPA 8080	26	µg/Kg
Aroclor 1221	EPA 8080	26	µg/Kg
Aroclor 1242	EPA 8080	26	µg/Kg
Aroclor 1248	EPA 8080	26	µg/Kg
Aroclor 1254	EPA 8080	26	µg/Kg
Aroclor 1260	EPA 8080	26	µg/Kg
Butyltin			
Tri-n-butyltin	NOAA 1989	0.17	µg/Kg
Methyl Mercury			
Methyl mercury	Frontier Geo. 1993	0.006	µg/Kg
Metals			
Aluminum	EPA 6010	10	mg/Kg

Table B-4. Laboratory Analysis Summary (continued)

Parameter	Reference	Nominal Method Detection Limit[b]	Units
Antimony	EPA 6010	3	mg/Kg
Arsenic	EPA 6010	5	mg/Kg
Beryllium	EPA 6010	0.1	mg/Kg
Chromium	EPA 6010	0.5	mg/Kg
Copper	EPA 6010	0.4	mg/Kg
Iron	EPA 6010	5	mg/Kg
Lead	EPA 6010	3	mg/Kg
Mercury	EPA 7471	0.04	mg/Kg
Nickel	EPA 6010	2	mg/Kg
Selenium	EPA 6010	5	mg/Kg
Silver	EPA 6010	0.4	mg/Kg
Thallium	EPA 6010	20	mg/Kg
Zinc	EPA 6010	0.5	mg/Kg
Conventionals			
Particle Size Distribution	PSEP	0.1	%
Total Organic Carbon	SM 5310-B	10	mg/Kg
Total Solids	SM 2540-B	0.005	%
Total Sulfide	SW846 9030	20	mg/Kg
Ammonia Nitrogen	SM 4500-NH3[1]	1	mg/Kg

[a] Sediment extraction by: Methods Manual for forest soil and plant analysis (Y.P. Kalra and D.J. Maynard 1991).

[b] Nominal detection limits based on an estimated percent solids of 50%.

DATA REDUCTION, REVIEW AND REPORTING

Field and lab data will be loaded into LIMS, where it will be available for authorized users. A copy of the LIMS "COMP" and "QC" reports will be prepared by the lab project manager along with the narrative of the QA1 data review (see Section 8 of Appendix A3).

Quality Control Procedures

Field Quality Control Procedures

Since each sample is a homogenized composite of 10 grab samples, it is assumed that sample collection variability will be minimized and therefore no field duplicates will be collected.

Laboratory Quality Control Procedures

KCEL is accredited by the Washington State Department of Ecology (WSDOE) and participates in audits and inter-laboratory studies by WSDOE and U.S. EPA. These performance and system audits have verified the adequacy of the laboratory standard operating procedures, which include preventative maintenance and data reduction procedures.

Frequency of Lab Quality Control Samples

For samples performed at KCEL, the frequency of QC samples to be performed for this project is shown in Table B-5.

DATA ASSESSMENT PROCEDURES

Data assessment will be conducted by reviewing QC data supplied from the laboratory. Data assessment using QA1 guidelines will be summarized by the lab project manager in the format of a case narrative. Professional judgment will be used to evaluate situations where data quality objectives have not been met.

Completeness will be assured by comparing valid sample data with this QA project plan and the chain-of-custody records. Completeness will be calculated by dividing the number of valid values by the total number of values.

Table B-5. Laboratory Quality Control Samples

Parameter	Blank	Replicate	Triplicate	Matrix Spike	CRM[a]	Surrogates
TOC	1 per batch	5% minimum, 1/batch	5% minimum, 1/batch	N/A	1 per batch	N/A
Total Solids	1 per batch	N/A	5% minimum, 1/batch	N/A	N/A	N/A
Total Sulfides and Ammonia Nitrogen	1 per batch	N/A	5% minimum, 1/batch	5% minimum, 1/batch	As available	N/A
Particle Size Distribution	N/A	N/A	5% minimum, 1/batch	N/A	N/A	N/A
Metals	1 per batch	5% minimum, 1/batch	N/A	5% minimum, 1/batch	1 per batch	N/A
Mercury	1 per batch	5% minimum, 1/batch	N/A	5% minimum, 1/batch	1 per batch	N/A
BNAs	1 per batch	5% minimum, 1/extraction batch	N/A	5% minimum, 1/extraction batch	1 per extraction batch	Yes
PCBs	1 per batch	5% minimum, 1/extraction batch	N/A	5% minimum, 1/extraction batch	1 per extraction batch	Yes
Other organic tests; Methyl Mercury, Tributyltin	1 per batch	5% minimum, 1/extraction batch	N/A	5% minimum, 1/extraction batch	As available	As available

[a] Certified Reference Material. Blank spike may be used if CRM not available.

Note: Batch is generally defined as a set of 20 samples or less, prepared and analyzed using the same reagents and equipment and by the same analyst(s).

N/A = Not applicable

BNAs = Base/neutral/acid compounds

PCBs = Polychlorinated biphenyls

REFERENCES

Kalra Y.P. and D.G. Maynard. 1991. Methods manual for forest soil and plant analysis. Forestry Canada, NW Region. NW Forestry Center, Edmonton Alberta, Canada. Information report NOR-X-319.

Puget Sound Estuarine Program (PSEP). 1996. Recommended quality assurance and quality control guidelines for the collection of environmental data in Puget Sound. Prepared by King County Environmental Laboratory. Seattle Washington.

Puget Sound Estuarine Program (PSEP). 1989. Recommended guidelines for measuring selected environmental variables. Prepared for U.S. EPA, Region 10, Office of Puget Sound, Seattle, Washington. Prepared by Tetra Tech, Inc. Bellevue, Washington.

SUBAPPENDIX C

QUALITY ASSURANCE PROJECT PLAN

IN SITU BIOASSAY USING TRANSPLANTED MUSSELS

PROJECT DESCRIPTION

Objective

"Clean" transplanted mussels will be placed in the Duwamish River and Elliott Bay during September 1996 to measure dry season baseline levels of bioaccumulatable metals and organic chemicals. The transplanted mussels, *Mytilis galloprovinciallis*, will be deployed below three CSOs and at nearby reference stations for a period of four weeks. Identical deployments will occur in March 1997 to measure the mussels wet season pollutant uptake. The reference stations are either upriver or across the river and outside the zone of immediate CSO influence.

Data on bioconcentratable contaminants will also be collected from semipermeable membrane devices (SPMDs) deployed in March 1997 with the caged mussels. SPMDs are made of polyethylene sheets with a thickness of 4 mil and mimic biological membranes. They are potential surrogates for mussels and other organisms.

Additionally, data on bioaccumulatable chemicals will be obtained from wild mussels, *Mytilis trossulus*. These data will be compared with the data from the mussel transplants and the SPMDs. This approach will provide important information on the bioavailability of contaminants from both baseline and without CSO sources. This information will be used in validating model estimates for bioaccumulation that will support both the ecological and the human health risk assessments.

Mortality and growth of the mussels transplanted to the Duwamish River and Elliott Bay will also be measured. Growth will be determined by following changes in total animal weight and valve (shell) length over the duration of exposure. Growth data will be correlated with concentrations of contaminants deposited in mussel tissues and contaminants found in nearby sediments. Growth is a commonly used indicator of environmental stress that exhibits a quantifiable dose-response relationship.

PROJECT ORGANIZATION AND RESPONSIBILITY

Sydney Munger directs the water quality assessment. John Strand assisted by Kim Stark, Cathy Laetz, and Kristie Silver will conduct the *in situ* bioassay using transplanted mussels. Scott Mickelson will provide logistic support to mussel deployment and recovery. He also will facilitate sample delivery and coordinate sample processing and analysis by the King County Environmental Laboratory (KCEL).

DATA QUALITY OBJECTIVES

The procedures and practices described in this quality assurance (QA) plan are designed to generate data of sufficient quality to support decision making described in the project description section and follow the guidelines of the Puget Sound Ambient Monitoring

Program (PSAMP). Procedures to attain these data quality objectives are discussed throughout this document. The quality control (QC) procedures section (Section 7.0 of Appendix A3) addresses many of the procedures necessary to obtain data which meet the data quality objectives described in this section.

Precision

Laboratory precision will be assessed using laboratory duplicates. One of the duplicate sample results must exceed the reporting detection limit (RDL) in order for the relative percent differences (RPD) to be evaluated against the acceptance limits. RPDs for duplicate samples with both responses below the RDL are provided for informational purposes only. Table C-1 shows the QC objectives for lab duplicates. For organics analyses, a matrix spike/matrix spike duplicate will also be analyzed to assess method precision.

Bias

An indication of the bias or accuracy of the analytical data is provided by method blanks, standard reference materials (SRMs), blank spikes and matrix spikes. Table C-1 shows the objectives for QC samples used to assess accuracy. The laboratory will use professional judgment regarding interpretation of data quality and any subsequent action taken as a result of recoveries outside these limits.

Bias will also be judged by the evaluation of method blank data. Analytical results for method blanks are to be less than the method detection limit (MDL). A sample result will be flagged with the "B" qualifier if the method blank is greater than the MDL and if the sample response is less than 5 times the method blank response.

Representativeness

Sample representativeness will be addressed at two distinct steps of the data collection process. During sample collection, five replicate samples will be obtained and analyzed separately. Prior to analysis within the laboratory, each individual sample will be homogenized to ensure that the analytical subsample is representative of the sample container contents.

Comparability

Data comparability will be ensured through the application of standard sampling procedures, analytical methods, units of measurement and detection limits. Additionally, the QC criteria based on PSAMP guidelines will provide for an adequate level of analytical performance and will produce comparable data.

Table C-1. Parameters and QC Objectives for Tissue Samples

Parameter	Lab Duplicate	Matrix Spike/Duplicate Matrix Spike	Surrogate	Blank Spike	Method Blank	Standard Ref. Material
BNAs[a]	RPD < 50%	50% to 150%	50% to 150%	50% to 150%	< MDL	N/A
Pesticide/PCBs	RPD < 100%	50% to 150%	50% to 150%	50% to 150%	< MDL	N/A
Metals	RPD < 20%	80% to 120%	N/A	80% to 120%	< MDL	80% to 120%
Mercury	RPD < 20%	80% to 120%	N/A	80% to 120%	< MDL	80% to 120%
Butyltin Isomers	RPD < 30%	50% to 150%	40% to 120%	50% to 150%	< MDL	N/A
Percent Lipids	RPD < 100%	N/A	N/A	N/A	N/A	N/A

[a] EPA 8270 list plus caffeine and coprostanol

BNAs = Base/neutral/acid compounds

PCBs = Polychlorinated Biphenyls

RPD = Relative percent difference

MDL = Method detection limit

N/A = Not analyzed

Completeness

Completeness will be judged by the following criteria:

- Accounting for the projected data points as detailed in this QA plan
- Compliance with the data quality criteria as presented in this section
- Compliance with required holding times

The goal for the above criteria is 100 percent complete. However, where data are not complete, decisions regarding reanalysis will be made by a collaborative process involving both data users and data generators. These decisions will take into account the project data quality objectives as presented above.

SAMPLING PROCEDURES AND MEASUREMENT OF BIOEFFECTS

Sample Identification

For chemical analysis, each sample will be identified by a unique laboratory sample number, assigned to each sampling location and event. A single sample number will be used for all parameters analyzed from the same sample. Sample numbers will be assigned and sample containers labeled with these numbers prior to use. Sample labels will also include information about the sampling location, sampling date, project number, sample matrix, requested analytical parameters, and preservation information.

Sample Containers

All sample containers will be supplied by KCEL. Sample containers will be provided in accordance with guidelines noted in Table C-2. These containers will be prewashed and prepared for sampling in accordance with standard operating practice of KCEL.

Table C-2. Sample Containers, Preservation, and Storage Conditions

Parameter	Matrix	Reference	Sampling Container	Sample Size	Preservative	Hold Time
Metals	Tissue	PSEP (1989)	HDPE	30 g	freeze(-18°C)	2 years (Hg = 28 days)
Semivolatiles	Tissue	PSEP (1989)	Glass	60 g	freeze(-18°C)	1 year*
Lipids	Tissue	PSEP (1989)	Glass	30 g	freeze(-18°C)	1 year
TBT	Tissue	PSEP (1989)	Glass	10 g	freeze(-18°C)	1 year

* 1-year storage time between collection and extraction, 40 days between extraction and analysis.

HDPE = High density polyethylene

TBT = Tributyltin

Sample Preservation

Samples (either transplanted or wild mussels) will be preserved in accordance with the guidelines and references listed in Table C-2. Sample preservation will be performed in the lab, upon sample receipt. Samples will be preserved as soon as possible after collection and always within 24 hours of sampling. After collection, all samples will immediately be placed in an insulated cooler to maintain ambient temperature. Transplanted mussels are already in mesh bags. Wild mussels are wrapped in aluminum foil prior to placement in the cooler. No ice is used.

Sample Delivery

All samples will be delivered to the laboratory in sufficient time to allow the laboratory to meet sample hold times specified in the table above.

A field sheet will be completed for each day of sampling. The field sheet will be delivered to the lab along with the samples.

Sample Receipt and Sample Log In

Samples will be logged into the Laboratory Information Management System (LIMS) by the laboratory sample management specialist. The following will be checked at that time:

- Correct use of sample ID and agreement of the sample ID with the field sheet

- Appropriate sample bottles and sample preservation have been employed
- Samples have been received within the holdtime
- Samples have been kept at ambient field temperatures

When applicable, the following will also be documented:

- • Any applicable or unique safety hazards of the sample
- • Subcontracted parameters are included in the requested suite of analytes

Field Notes

At each sampling location, the following information will be recorded on waterproof field notes: date and time of sample collection, sampling personnel, station location information, weather conditions, number and type of samples collected, any unusual ambient conditions, and any deviations from standard sampling procedures.

Sampling Procedures

Sampling and analytical strategies are provided in the following sections.

Sampling Locations

Transplanted mussels will be deployed in the Duwamish River at the Brandon Street CSO, at a primarily storm water source (former Duwamish/Diagonal CSO), and at two reference sites. Additionally, transplanted mussels will be deployed in Elliott Bay at the Denny Way CSO and at a marine reference site. Installation will be as close to the CSOs as practical and in the water column at -1 meter and -3 meters mean lower low water (MLLW) but at least 1 meter above the bottom.

One reference site (Slip #1) is located approximately 500 meters below the CSO at Brandon Street on the east side of the river. This reference site was previously sampled as part of the Elliott Bay Action Program (PSEP 1988) and was designated KG 02. It is intertidal between dolphins 3 and 4 N of Slip 1 (East Coordination1627505; North Coordination 207185). The sediments at this site are relatively clean (no SQS exceedances) for either metals or organics.

The second reference site is located equidistant between the last two sets of dolphins at the furthest downstream point of Kellogg Island. This location is approximately 300 meters west of the Duwamish/Diagonal CSO. Little is known about the site except that there appears to be little or no remaining commercial activity on Kellogg Island near the

site. Where mussels are purchased (Taylor United, Olympia) will be considered a third reference site.

Deployment Duration

Transplanted mussels will first be deployed in September 1996 to establish dry season levels of bioconcentratable metals and organic contaminants. Exposure will continue until the first overflow events occur, hopefully a period of 4 to 6 weeks. Transplanted mussels will be similarly deployed in March 1997 to establish wet season levels of bioconcentratable contaminants, with particular interest in those discharged from CSOs. This subsequent exposure is scheduled for 4 to 6 weeks.

Measurement of Bioconcentratable Contaminants

The proposed approach to measure bioaccumulatables follows the general recommendations of Salazar and Salazar (1995). The sampling strategy for both dry and wet seasons is summarized in Table C-3. Additionally, wild mussels will be collected following the strategy shown in Table C-4.

Table C-3. Sampling Strategy for Bioaccumulatables

Location	Matrix Sampled	Deployment Time Frame	Event Sampled	Total Measures	
Taylor United	Mussel tissue	9/96	Pre-deployment	5	
		10/96	Post deployment	5	
		3/97	Pre-deployment	5	
		4/97	Post deployment	5	
				-1m	**-3m**
Brandon CSO	Mussel tissue	9/96 to 10/95	Post deployment	5	5
		3/97 to 4/97	Post deployment	5	5
Reference No.1	Mussel tissue	9/96 to 10/96	Post deployment	5	5
		3/97 to 4/97	Post deployment	5	5
Duwamish CSO	Mussel tissue	9/96 to 10/96	Post deployment	5	5
		3/97 to 4/97	Post deployment	5	5
Denny Way CSO	Mussel tissue	9/96 to 10/96	Post deployment	5	5
		3/97 to 4/97	Post deployment	5	5
Reference No.2	Mussel tissue	9/96 to 10/96	Post deployment	5	5

		3/97 to 4/97	Post deployment	5	5

Table C-4. Wild Mussel Sampling Strategy

Location	Sampling matrix	Collection Dates	Total Measures
Brandon CSO	Mussel tissue	10/96	5
		4/97	5
Duwamish CSO	Mussel tissue	10/96	5
		4/97	5
Terminal 107	Mussel tissue	10/96	5
		4/97	5
Hanford/Lander	Mussel tissue	10/96	5
		4/97	5
Slip #4	Mussel tissue	4/97	5
Elliott Bay	Mussel tissue	4/97	5

Measurement of Bioeffects

Transplanted mussels will also be used to estimate potential bioeffects. We propose to measure growth of juvenile mussels deployed over a 4 to 6 week period of exposure, by measuring total weights and shell lengths, at the beginning and at the end of this period. Mortality also will be recorded. Following the general recommendations of Salazar and Salazar (1995), at least 50 juvenile mussels 25 to 40 mm in length will constitute each sample. At each site, each sample will be replicated five times. The number of mussels in each sample could increase to 75 if only small (<25 mm) mussels are available from the grower. It is critical to have at least 100 g of tissue per sample at the end of the study to conduct chemical analyses. The sampling strategy for use of transplanted mussels to assess bioeffects is summarized in Table C-5.

Table C-5. Strategy for Measuring Bioeffects

Location	Endpoints	Time Frame	Event sampled	Total Measures
Taylor United	Weight	9/96 to 10/96	Post deployment	3000
	Shell length			
	Mortality			250
	Weight			
	Shell length			
Brandon St. CSO	Mortality	9/96 to 10/96	Post deployment	250
	Weight			
	Shell length			
Reference No. 1	Mortality	9/96 to 10/96	Post deployment	250
	Weight			
	Shell length			
Duwamish CSO	Mortality	9/96 to 10/96	Post deployment	250
	Weight			
	Shell length			
Denny Way CSO	Mortality	9/96 to 10/96	Post deployment	250
	Weight			
	Shell length			
Reference No. 2	Mortality	9/96 to 10/96	Post deployment	250
	Weight			
	Shell length			

DEPLOYMENT PROCEDURES

Animals will be obtained from the grower and transported in an ice chest to a suitable site for sorting and sizing. The animals will be maintained in ambient seawater while being sorted and sized. Ideally, the size of all mussels to be used in the growth study should be the same but in practicality will vary slightly. Selection of a final target size will be

somewhat dependent on the size of mussels on the day of their purchase from the grower. The grower from whom we will purchase mussels indicated that mussels of the size 25 to 40 mm are available in September, the time of scheduled dry-season deployment. It is assumed that that we will be able to purchase a sufficient number of mussels of the same size to support the parallel wet-season study.

The size of mussels in each sample should not exceed a range of 25 to 40 mm as determined by plastic vernier caliper or similar device. Prior to loading into each mussel bag, a representative sample (10) of the mussels will again be sized and also weighed to the nearest 0.001 g. These data will be recorded.

As the mussels are sized and weighed, they are loaded in sequence into individual compartmentalized mesh bags. The first and last compartments will be numbered or otherwise marked to preserve the sequence of mussels for post-exposure measurements. Oyster clutch netting (15-mm mesh size) will be used for this purpose. Individual compartments will be constructed using plastic cable ties. These materials can be purchased from NorPlex Inc., Auburn, Washington. The mussels once in their respective mussel bags, will be maintained overnight in ambient (unfiltered) seawater.

The next day the mussels will be transported in cool ice chests without seawater and deployed at each study site. The transplanted mussels in mesh bags will be suspended by a float anchored at each study site.

At the end of the exposure period, the mussel bags will be retrieved by boat. They will be immediately and individually wrapped in foil (dull side in) and placed in individually coded plastic bags for transport in cool ice chests to the laboratory. At the lab, the mesh bags will be placed in a constant temperature room (4°C) without seawater, until processing the next day.

DATA COLLECTION

Measurement of Bioeffects

The next day the mussel bags will be opened and processed in the blind. The scientist making the measurements will not know from which location a sample comes. Mortality will be recorded and each mussel will again be sized and weighed. Mussels exhibiting dense fouling with algae will be brushed and rinsed with seawater before weighing. The data will be recorded.

After sizing and weighing, the mussels will be carefully shucked and the available tissue collected for chemical analyses. Puget Sound Estaurine Protocols (PSEP 1989) will be followed for the excision, processing, and storage of tissue for chemical analyses, for both transplanted and wild mussels. Clean storage vessels as specified in Table C-2 will

be used to segregate aliquots of tissue for analyses of metals, organics, and lipids will be provided by the lab.

Measurement of Bioconcentratable Contaminants

We are assuming that over a 4 to 6 week period, the 50 or more juvenile mussels will grow and will provide at least 110 grams of tissue for chemical analyses. The 110 grams of tissue per sample is the target wet weight required by the lab to complete the required chemical analyses. Most references we hold indicate that 50 to 100 juvenile mussels (tissues are pooled) will be required to obtain a measured concentration of an analyte within +/- 10 percent of the population mean, with a probability of 95 percent. The data, in this case concentration of analyte, will be expressed in mg or µg/Kg wet weight of tissue. Levels of organics accumulated in mussel tissue will be correlated with levels of organic compounds concentrated by semipermeable membrane devices.

Statistical Analysis

Chemical concentrations and growth data across study locations will be compared by an Analysis of Variance (ANOVA) and Duncan's New Multiple Range Test. At the discretion of the project statistician, a nonparametric procedure may be used to compare data across transplant locations.

ANALYTICAL PROCEDURES

Samples will be analyzed using the analytical procedures and detection limits appropriate to PSAMP studies. Analysis for all parameters listed in Table C-6 may not have been done for the mussel samples collected in April 1997.

Table C-6. Laboratory Analysis Summary

Parameter	Reference	Method Detection Limit	Units
BNAS			
1,2,4-trichlorobenzene	EPA 8270	16	µg/Kg
1,2-dichlorobenzene	EPA 8270	16	µg/Kg
1,2-diphenylhydrazine	EPA 8270	53	µg/Kg
1,3-dichlorobenzene	EPA 8270	16	µg/Kg
1,4-dichlorobenzene	EPA 8270	16	µg/Kg
2,4,5-trichlorophenol	EPA 8270	110	µg/Kg

2,4,6-trichlorophenol	EPA 8270	110	µg/Kg
2,4-dichlorophenol	EPA 8270	27	µg/Kg

Table C-6. Laboratory Analysis Summary (continued)

Parameter	Reference	Method Detection Limit	Units
2,4-dimethylphenol	EPA 8270	27	µg/Kg
2,4-dinitrophenol	EPA 8270	53	µg/Kg
2,4-dinitrotoluene	EPA 8270	11	µg/Kg
2,6-dinitrotoluene	EPA 8270	11	µg/Kg
2-chloronaphthalene	EPA 8270	16	µg/Kg
2-chlorophenol	EPA 8270	53	µg/Kg
2-methylnaphthalene	EPA 8270	43	µg/Kg
2-methylphenol	EPA 8270	27	µg/Kg
2-nitrophenol	EPA 8270	27	µg/Kg
3,3'-dichlorobenzidine	EPA 8270	27	µg/Kg
3-nitroaniline	EPA 8270	110	µg/Kg
4-bromophenyl phenyl ether	EPA 8270	11	µg/Kg
4-chloro-3-methylphenol	EPA 8270	53	µg/Kg
4-chlorophenyl phenyl ether	EPA 8270	16	µg/Kg
4-methylphenol	EPA 8270	27	µg/Kg
4-nitroaniline	EPA 8270	110	µg/Kg
Acenaphthene	EPA 8270	11	µg/Kg
Acenaphthylene	EPA 8270	16	µg/Kg
Anthracene	EPA 8270	16	µg/Kg
Benzidine	EPA 8270	640	µg/Kg
Benzo(a)anthracene	EPA 8270	16	µg/Kg
Benzo(b)fluoranthene	EPA 8270	43	µg/Kg
Benzo(g,h,I)perylene	EPA 8270	27	µg/Kg

Benzo(k)fluoranthene	EPA 8270	43	µg/Kg
Benzoic acid	EPA 8270	110	µg/Kg
Benzyl alcohol	EPA 8270	27	µg/Kg

Table C-6. Laboratory Analysis Summary (continued)

Parameter	Reference	Method Detection Limit	Units
Benzyl butyl phthalate	EPA 8270	16	µg/Kg
Bis(2-chloroethoxy)methane	EPA 8270	27	µg/Kg
Bis(2-chloroethyl)ether	EPA 8270	16	µg/Kg
Bis(2-ethylhexyl)phthalate	EPA 8270	16	µg/Kg
Caffeine	EPA 8270	5.3	µg/Kg
Carbazole	EPA 8270	27	µg/Kg
Chrysene	EPA 8270	16	µg/Kg
Coprostanol	EPA 8270	110	µg/Kg
Di-n-butyl phthalate	EPA 8270	27	µg/Kg
Di-n-octyl phthalate	EPA 8270	16	µg/Kg
Dibenzo(a,h)anthracene	EPA 8270	43	µg/Kg
Dibenzofuran	EPA 8270	27	µg/Kg
Diethyl phthalate	EPA 8270	27	µg/Kg
Dimethyl phthalate	EPA 8270	11	µg/Kg
Fluoranthene	EPA 8270	16	µg/Kg
Fluorene	EPA 8270	16	µg/Kg
Hexachlorobenzene	EPA 8270	16	µg/Kg
Hexachlorobutadiene	EPA 8270	27	µg/Kg
Hexachlorocyclopentadiene	EPA 8270	27	µg/Kg
Hexachloroethane	EPA 8270	27	µg/Kg
Indeno(1,2,3-cd)pyrene	EPA 8270	27	µg/Kg
Isophorone	EPA 8270	27	µg/Kg
N-nitrosodi-n-propylamine	EPA 8270	27	µg/Kg
N-nitrosodimethylamine	EPA 8270	110	µg/Kg
Naphthalene	EPA 8270	43	µg/Kg
Nitrobenzene	EPA 8270	27	µg/Kg

Table C-6. Laboratory Analysis Summary (continued)

Parameter	Reference	Method Detection Limit	Units
Pentachlorophenol	EPA 8270	27	µg/Kg
Phenanthrene	EPA 8270	16	µg/Kg
Pyrene	EPA 8270	16	µg/Kg
Pesticides/PCBs			
4,4'-DDD	EPA 8080	1.3	µg/Kg
4,4'-DDE	EPA 8080	1.3	µg/Kg
4,4'-DDT	EPA 8080	1.3	µg/Kg
Aldrin	EPA 8080	1.3	µg/Kg
Alpha-BHC	EPA 8080	1.3	µg/Kg
Aroclor 1016	EPA 8080	13	µg/Kg
Aroclor 1221	EPA 8080	13	µg/Kg
Aroclor 1232	EPA 8080	13	µg/Kg
Aroclor 1248	EPA 8080	13	µg/Kg
Aroclor 1260	EPA 8080	13	µg/Kg
Beta-BHC	EPA 8080	1.3	µg/Kg
Chlordane	EPA 8080	6.7	µg/Kg
Delta-BHC	EPA 8080	1.3	µg/Kg
Dieldrin	EPA 8080	1.3	µg/Kg
Endosulfan I	EPA 8080	1.3	µg/Kg
Endosulfan II	EPA 8080	1.3	µg/Kg
Endosulfan sulfate	EPA 8080	1.3	µg/Kg
Endrin aldehyde	EPA 8080	1.3	µg/Kg
Gamma-BHC (Lindane)	EPA 8080	1.3	µg/Kg
Heptachlor	EPA 8080	1.3	µg/Kg
Heptachlor epoxide	EPA 8080	1.3	µg/Kg
Methoxychlor	EPA 8080	6.7	µg/Kg

Table C-6. Laboratory Analysis Summary (continued)

Parameter	Reference	Method Detection Limit	Units
Toxaphene	EPA 8080	13	µg/Kg
Butyltin			
Di-n-Butyltin	NOAA 1989	1.3	µg/Kg
Mono-n-Butyltin	NOAA 1989	1.7	µg/Kg
Total butyltin	NOAA 1989	0.35	µg/Kg
Tri-n-Butyltin	NOAA 1989	0.35	µg/Kg
Metals			
Mercury	EPA 7471	0.0040	mg/Kg
Chromium	EPA 6010	0.050	mg/Kg
Zinc	EPA 6010	0.050	mg/Kg
Antimony	EPA 6020	0.020	mg/Kg
Arsenic	EPA 6020	0.020	mg/Kg
Cadmium	EPA 6020	0.0081	mg/Kg
Cobalt	EPA 6020	0.020	mg/Kg
Copper	EPA 6020	0.020	mg/Kg
Lead	EPA 6020	0.020	mg/Kg
Molybdenum	EPA 6020	0.020	mg/Kg
Nickel	EPA 6020	0.020	mg/Kg
Silver	EPA 6020	0.012	mg/Kg
Vanadium	EPA 6020	0.020	mg/Kg

Quality Control Procedures

Field Quality Control Procedures

No specific field QC samples are to be submitted for analysis. Information on field precision may be derived from the five replicate tissue samples collected at each station and individually analyzed.

Laboratory Quality Control Procedures

KCEL is accredited by the Washington State Department of Ecology (WSDOE) and participates in audits and inter-laboratory studies by WSDOE and U.S. EPA. These performance and system audits have verified the adequacy of the laboratory standard operating procedures, which include preventative maintenance and data reduction procedures. All tissue samples will be analyzed by KCEL. For samples performed at KCEL, the frequency of QC samples to be performed for this project is shown in Table C-7.

Table C-7. Laboratory Quality Control Samples

QC Sample	Description	Frequency
Method Blank	An aliquot of a clean solid matrix carried through the analytical process and used as an indicator of contamination.	1 per sample batch. Maximum sample batch size equals 20 samples.
Standard Reference Material (SRM)	Sample of similar matrix and of known analyte concentration, processed through the entire analytical procedure and used as an indicator of method accuracy.	1 per 50 samples. SRMs may not be available for all analyses.
Spike Blank	Known concentration of target analyte(s) introduced to a clean solid matrix, processed through the entire analytical procedure and used as an indicator or method performance.	1 per sample batch. Maximum sample batch size equals 20 samples.
Surrogate Recovery	Surrogate compounds are added to the sample aliquot at the start of processing. Recovery results indicate method accuracy.	Added to all Organics analyses, including all QC samples.
Lab Duplicate	A second aliquot of a sample, processed concurrently and identically with the initial sample, used as an indicator of method precision.	Over the course of the project, 1 per 20 samples.
Matrix Spike	An aliquot of sample to which known quantities of analyte(s) are added. Used as an indicator of sample matrix effect on recovery of target analyte(s).	Over the course of the project, 1 per 20 samples.
Matrix Spike duplicate	An additional matrix spike sample used as an indicator of matrix effect on sample recovery and method precision.	Over the course of the project, 1 per 20 samples. (For Organics analyses only)

DATA ASSESSMENT PROCEDURES

Data assessment will be conducted by reviewing QC data supplied from the laboratory. Holding times will be compared to the date received versus when the analysis was performed. A review will be made of the detection limits obtained in relation to matrix interferences. Duplicate samples will be evaluated for their RPDs. Surrogates, spiked samples, blank spikes and SRMs will be reviewed for their percent recoveries. Method blanks will also be compared to individual MDLs. Data assessment will be summarized by the lab project manager in the format of a case narrative. Professional judgment will be used to evaluate situations where data quality objectives have not been met.

Completeness will be assured by comparing valid sample data with this QA project plan and chain-of-custody records. Completeness will be calculated by dividing the number of valid values by the total number of values.

REFERENCES

Puget Sound Estuarine Program (PSEP). 1988. Elliott Bay action program: analysis of toxic problem areas. Prepared for U.S. EPA, Region 10, Office of Puget Sound, Seattle, Washington. Prepared by PTI Environmental Services and Tetra Tech, Inc. Bellevue, Washington.

Puget Sound Estuarine Program (PSEP). 1989. Recommended guidelines for measuring selected environmental variables. Prepared for U.S. EPA, Region 10, Office of Puget Sound, Seattle, Washington. Prepared by Tetra Tech, Inc. Bellevue, Washington.

Salazar, M.H., and S.M. Salazar. 1995. *In situ* bioassays using transplanted mussels: I. estimating chemical exposure and bioeffects with bioaccumulation and growth. *In*: environmental toxicology and risk assessment - Third Volume, ASTM STP 1218. J.S. Hughes, G.R. Biddinger, and E. Mones, Eds., American Society for Testing and Materials. Philadelphia, Pennsylvania. pp 216-241.

SUBAPPENDIX D

QUALITY ASSURANCE PROJECT PLAN

TISSUE ANALYSES FOR RISK ASSESSMENT

PROJECT DESCRIPTION

Tissue samples from the Duwamish River and Elliott Bay were collected and analyzed for metals, organics, tributyltin and lipids. In addition to the raw tissue, cooked portions of certain samples were analyzed. Results of these analyses were used in a risk assessment of the Duwamish Estuary.

PROJECT ORGANIZATION AND RESPONSIBILITY

Sydney Munger directs the Water Quality Assessment (WQA). John Strand manages the tissue study portion of WQA and, assisted by Sandy O'Neill of the Washington Department of Fisheries and Wildlife (WDFW), collected the samples and performed the cooking of selected tissue. Scott Mickelson facilitated sample delivery and coordinated sample processing and analysis by the King County Environmental Laboratory (KCEL).

DATA QUALITY OBJECTIVES

The procedures and practices described in this quality assurance (QA) plan are designed to generate data of sufficient quality to support decision making described in the project description section and follow the guidelines of the Puget Sound Ambient Monitoring Program (PSAMP). Procedures to attain these data quality objectives are discussed throughout this document. The QC procedures section (Section 7.0) addresses many of the procedures necessary to obtain data which meet the data quality objectives described in this section.

Precision

Laboratory precision is assessed using laboratory duplicates. One of the duplicate sample results must exceed the reporting detection limit (RDL) in order for the relative percent differences (RPDs) to be evaluated against the acceptance limits (for metals, both must exceed the RDL). Table D-1 shows the quality control (QC) objectives for lab duplicates. For organics analyses, a matrix spike/matrix spike duplicate were analyzed to assess method precision.

Bias

An indication of the bias of the analytical data is provided by standard reference materials (SRMs), surrogate spikes, blank spikes and matrix spikes. Table D-1 shows the objectives for QC samples used to assess bias. The laboratory uses professional judgment regarding interpretation of data quality and any subsequent action taken as a result of recoveries outside these limits.

Table D-1. Parameters and QC Objectives for Tissue Samples

Parameter	Lab Duplicate	Matrix Spike / Dup Matrix Spike	Surrogate	Blank Spike	Method Blank	Standard Reference Material
BNAs[a]	RPD < 100%	50% to 150%	50% to 150%	50% to 150%	< MDL	80% to 120%
PCBs	RPD < 100%	50% to 150%	50% to 150%	50% to 150%	< MDL	N/A
Metals	RPD < 20%	75% to 125% *	N/A	80% to 120%	< MDL	≤120%
Mercury	RPD < 20%	75% to 125% *	N/A	80% to 120%	< MDL	80% to 120%
Tributyl Tin	RPD < 100%	50% to 150%	50% to 150%	50% to 150%	< MDL	N/A
Percent Lipids	RPD < 100%	N/A	N/A	N/A	N/A	N/A

* Matrix spikes only (no duplicate matrix spikes) analyzed for metals and mercury.

[a] EPA 8270 list (may be limited to the compounds of potential concern for WQA)

BNAs = Base/neutral/acid compounds

PCBs = Polychlorinated biphenyls

RPD = Relative percent difference

MDL = Method detection limit

N/A = Not analyzed

Bias is also judged by the evaluation of method blank data. Analytical results for method blanks are to be less than the method detection limit (MDL). Method blanks for metals must also be greater than the negative MDL. A sample result will be flagged with the "B" qualifier if the method blank is greater than the MDL and if the sample response is less than 5 times the method blank response (10 times for metals parameters).

Representativeness

Prior to analysis within the laboratory, each individual sample was homogenized to ensure that the analytical subsample is representative of the sample container contents.

Comparability

Data comparability is ensured through the application of standard sampling procedures, analytical methods, units of measurement and detection limits. Additionally, the quality control criteria based on PSAMP guidelines provides for an adequate level of analytical performance and produces comparable data.

Completeness

Completeness is judged by the following criteria:

- Accounting for the projected data points as detailed in this QA plan
- Compliance with the data quality criteria as presented in this section
- Compliance with required holding times

The goal for the above criteria is 100 percent complete. However, where data are not complete, decisions regarding reanalysis will be made by a collaborative process involving both data users and data generators. These decisions take into account the project data quality objectives as presented above.

SAMPLING AND PREPARATION PROCEDURES

Sample Collection

With the exception of the small invertebrates and market squid, all the tissues in Table D-2 were collected jointly by the staffs at WDFW and King County Department of Natural Resources. The collections were made aboard the MV *Chasita* from April 14 through April 24, 1997. Puget Sound Estuary Program (PSEP) protocols were followed for the collection and handling of the fish and shellfish samples. A commercial otter trawl that contained a 1-1/2 inch mesh liner was employed to collect the target species at three locations: (1) the Duwamish River, (2) in Elliott Bay, and (3) at Port Susan. The latter is

a clean reference site. Each trawl was of short duration, usually five minutes. After each haul, the net was brought aboard the vessel and the contents dumped onto a sorting table. The catch was first sorted for English sole and rockfish, and then sorted for several other species of finfish including shiner perch and all juveniles under 15 cm in length. Dungeness crab, red rock crab, and spot prawn were also collected. The quantity of fish and shellfish taken was dictated by the need to provide the lab approximately 130 grams per sample for chemical analyses. We also archived some samples for possible analyses at a later date. All samples, with the exception of shiner perch, were wrapped in aluminum foil, dull side in, and placed in ice chests containing bags of ice.

Table D-2. Summary of Tissues

Tissue Type	Study Area			Total
	Duwamish River	Elliott Bay	Reference Site	
Dungeness Crab	2 uncooked	4 uncooked	3 uncooked	9
	2 cooked	3 cooked	3 cooked	8
Crab Hepatopancreas	1 uncooked	2 uncooked	1 uncooked	4
		1 cooked	1 cooked	2
Large Sole Fillet	3 uncooked	3 uncooked	3 uncooked	9
	3 cooked	3 cooked	3 cooked	9
Large Sole Carcass	3	3	3	9
Rockfish Fillets		3	3	6
Small Fish	3	3	3	9
Invertebrates	1	1	2	4
Spot Prawns		1	2	3
Market Squid		3 cleaned		3
		3 whole		3
Total	18	33	27	78

After collections were made on April 14th and April 17th 1997, the samples (with the exception of one half of the crabs) were brought back to the lab and frozen at -20°C. The other half of the crab samples from each site was first cooked, then frozen. All other collections (other crabs from Elliott Bay collected on April 15th and April 16th, and fish and crabs collected on April 24th from Port Susan) were frozen onboard the MV *Chasita* the day of collection. Shiner perch were placed in glass jars and frozen for whole body analysis. The additional crabs from Elliott Bay were transported to the lab in an ice chest

containing ice on April 17th. The fish and crabs from Port Susan were transported to the lab on April 25th.

The small invertebrate samples were collected by staff from the King County Department of Natural Resources. They contained mostly amphipods screened from intertidal sediments in the Duwamish River and at a reference area (McAllister Creek on the Nisqually Delta). Collections in the Duwamish River occurred on May 8th and 9th, 1997. Collections from McAllister Creek occurred June 16 and 19 and July 3, 1997. The samples were washed and concentrated back at the lab and frozen at -20°C. Market squid were collected from Elliott Bay on December 11 and 12, 1997 employing rod and reel. Squid were placed in glass jars and frozen whole until dissection.

Sample Processing

No less than 130 grams of tissue were composited for each sample. On average, composite samples consisted of an equal amount of tissue from either 20 English sole, 1 rockfish, 3 Dungeness crabs, 10 spot prawns, 10 shiner perch, 10 squid, and 2,000 intertidal invertebrates. Clean, stainless steel knives were used in the dissections. Excised tissues were placed into clean glass jars and refrozen at -20°C. Powder-free surgical gloves were worn when excising the tissues and both clean implements and gloves were used for each sample.

Composite samples of English sole contained approximately 10 grams from each of 20 fish. There were three composite samples from each sampling site, each composite sample representing a different size group (small, medium, large). The sole was filleted in a similar manner for both the raw and cooked samples using opposite sides of the same fish, except that the lateral line was retained as part of the cooked portion. The skin of each fish was carefully removed before dissection and collection of the underlying muscle tissue. Composite samples made from English sole carcasses contained equal amounts of skin, fins and tail, viscera, backbone, and head (including jaws and gills). There again were three composite samples from each site, each composite sample representing a different size group. Rockfish were filleted similarly but were not composited. A single rockfish was dissected for each sample.

Cooking of English sole fillets consisted of frying in a Teflon® pan on medium heat for eight minutes. A small amount of PAM® (a commercially available cooking lubricant) was added to the pan prior to frying. The cooked fillets were returned to their respective glass jars following a 10-minute cooling period and refrozen at -20°C.

The raw samples of crab contained all soft parts with the exception of hepatopancreas, which was dissected free of the carcass and analyzed separately. Crab, cooked whole before dissection and analysis was segregated such that only edible tissue was used for analysis. The cooked hepatopancreas was dissected free of the whole cooked crab carcass and analyzed separately. Cooking, in the case of crabs, was boiling for 25 minutes in a ceramic-coated cooking pot. Crabs were cooked in their shells, cooled, then dissected.

Shiner perch and half of the market squid samples consisted of the whole body homogenized for analysis. The other halves of the squid samples were cleaned by removing the quill, beak, and viscera. Spot prawn samples consisted of only edible muscle tissues collected from the tail of the animal. The tails were severed from the cephalothorax and their shells, intestine, and dorsal abdominal aorta removed.

As a final step to sample preparation, each fish and shellfish sample was homogenized in a blender prior to freezing at -20°C. The homogenizer was outfitted with titanium blades. The samples were homogenized for three minutes at 6,000 rpm. The cooked samples of English sole and Dungeness crab were homogenized at a lower rpm (3,000) for the first two minutes due to less moisture remaining in the cooked sample. The rpms were then slowly increased to 6,000 and maintained at this level for two minutes. As part of the planned analyses, the percent moisture was also determined.

Sample Identification

For chemical analysis, each sample is identified by a unique laboratory sample number, assigned to each sampling location and event. A single sample number is used for all parameters analyzed from the same sample. Sample numbers are assigned and sample containers labeled with these numbers prior to use. Sample labels also include information about the sampling location, sampling date, project number, sample matrix, requested analytical parameters, and preservation information.

Sample Containers

All sample containers are supplied by KCEL. Sample containers will be provided in accordance with guidelines noted in Table D-3. These containers are purchased as precleaned by the manufacturer or are prewashed and prepared for sampling in accordance with standard operating practice of KCEL. These containers are typically used following the preparation of the tissues (dissection, grinding, or cooking).

Table D-3. Sample Containers, Preservation, and Storage Conditions

Parameter	Matrix	Reference	Sampling Container	Sample Size	Preservative	Hold Time[a]
Metals	Tissue	PSEP (1989)	HDPE	30 g	Freeze(-18°C)	2 years[b]
Semivolatiles	Tissue	PSEP (1989)	Glass	30 g	Freeze(-18°C)	1 year[c]
Lipids	Tissue	PSEP (1989)	Glass	20 to 30 g	Freeze(-18°C)	1 year
TBT	Tissue	PSEP (1989)	Glass	8 to 20 g	Freeze(-18°C)	1 year

[a] Holding times are initiated upon receipt of the sample in its final form for analysis (cooked or filleted, etc.) rather than from the date collected.

[b] Unpublished KCEL data indicate that mercury is stable in tissue samples for up to 6 months when frozen.

[c] 1 year storage time between collection and extraction, 40 days between extraction and analysis.

HDPE = High density polyethylene

Sample Receipt and Sample Log In

Samples are logged into the Laboratory Information Management System (LIMS) by the laboratory sample management specialist. The following are checked at that time:

- Correct use of sample ID and agreement of the sample ID with the field sheet
- Appropriate sample bottles and sample preservation have been employed
- Samples have been received within the holding times

ANALYTICAL PROCEDURES

Samples are analyzed using the analytical procedures and detection limits appropriate to PSAMP studies. These are listed in Table D-4. MDLs for individual samples may differ due to differences in sample sizes or final extract volumes.

Table D-4. Laboratory Analysis Summary

Parameter	Reference	Method Detection Limit	Units
BNAs			
1,2,4-trichlorobenzene	EPA 8270	16	µg/Kg
1,2-dichlorobenzene	EPA 8270	16	µg/Kg
1,2-diphenylhydrazine	EPA 8270	53	µg/Kg
1,3-dichlorobenzene	EPA 8270	16	µg/Kg
1,4-dichlorobenzene	EPA 8270	16	µg/Kg
2,4,5-trichlorophenol	EPA 8270	110	µg/Kg
2,4,6-trichlorophenol	EPA 8270	110	µg/Kg
2,4-dimethylphenol	EPA 8270	27	µg/Kg
2,4-dinitrophenol	EPA 8270	53	µg/Kg
2,4-dinitrotoluene	EPA 8270	11	µg/Kg

2,6-dinitrotoluene	EPA 8270	11	µg/Kg
2-chloronaphthalene	EPA 8270	16	µg/Kg
2-chlorophenol	EPA 8270	53	µg/Kg

Table D-4. Laboratory Analysis Summary (continued)

Parameter	Reference	Method Detection Limit	Units
2-methylnaphthalene	EPA 8270	43	µg/Kg
2-methylphenol	EPA 8270	27	µg/Kg
2-nitroaniline	EPA 8270	110	µg/Kg
2-nitrophenol	EPA 8270	27	µg/Kg
3,3'-dichlorobenzidine	EPA 8270	27	µg/Kg
3-nitroaniline	EPA 8270	110	µg/Kg
4,6-dinitro-o-cresol	EPA 8270	53	µg/Kg
4-bromophenyl phenyl ether	EPA 8270	11	µg/Kg
4-chloro-3-methylphenol	EPA 8270	53	µg/Kg
4-chloroaniline	EPA 8270	53	µg/Kg
4-chlorophenyl phenyl ether	EPA 8270	16	µg/Kg
4-methylphenol	EPA 8270	27	µg/Kg
4-nitroaniline	EPA 8270	110	µg/Kg
4-nitrophenol	EPA 8270	53	µg/Kg
Acenaphthene	EPA 8270	11	µg/Kg
Acenaphthylene	EPA 8270	16	µg/Kg
Aniline	EPA 8270	53	µg/Kg
Anthracene	EPA 8270	16	µg/Kg
Benzidine	EPA 8270	640	µg/Kg
Benzo(a)anthracene	EPA 8270	16	µg/Kg
Benzo(a)pyrene	EPA 8270	27	µg/Kg
Benzo(b)fluoranthene	EPA 8270	43	µg/Kg
Benzo(g,h,I)perylene	EPA 8270	27	µg/Kg
Benzo(k)fluoranthene	EPA 8270	43	µg/Kg
Benzoic acid	EPA 8270	110	µg/Kg

Table D-4. Laboratory Analysis Summary (continued)

Parameter	Reference	Method Detection Limit	Units
Benzyl alcohol	EPA 8270	27	µg/Kg
Benzyl butyl phthalate	EPA 8270	16	µg/Kg
Bis(2-chloroethoxy)methane	EPA 8270	27	µg/Kg
Bis(2-chloroethyl)ether	EPA 8270	16	µg/Kg
Bis(2-chloroisopropyl)ether	EPA 8270	53	µg/Kg
Bis(2-ethylhexyl)phthalate	EPA 8270	16	µg/Kg
Carbazole	EPA 8270	27	µg/Kg
Chrysene	EPA 8270	16	µg/Kg
Coprostanol	EPA 8270	110	µg/Kg
Di-n-butyl phthalate	EPA 8270	27	µg/Kg
Di-n-octyl phthalate	EPA 8270	16	µg/Kg
Dibenzo(a,h)anthracene	EPA 8270	43	µg/Kg
Diethyl phthalate	EPA 8270	27	µg/Kg
Dimethyl phthalate	EPA 8270	11	µg/Kg
Fluoranthene	EPA 8270	16	µg/Kg
Fluorene	EPA 8270	16	µg/Kg
Hexachlorobenzene	EPA 8270	16	µg/Kg
Hexachlorobutadiene	EPA 8270	27	µg/Kg
Hexachlorocyclopentadiene	EPA 8270	27	µg/Kg
Hexachloroethane	EPA 8270	27	µg/Kg
Indeno(1,2,3-cd)pyrene	EPA 8270	27	µg/Kg
Isophorone	EPA 8270	27	µg/Kg
N-nitrosodi-n-propylamine	EPA 8270	27	µg/Kg
N-nitrosodimethylamine	EPA 8270	110	µg/Kg
N-nitrosodiphenylamine	EPA 8270	27	µg/Kg

Table D-4. Laboratory Analysis Summary (continued)

Parameter	Reference	Method Detection Limit	Units
Naphthalene	EPA 8270	43	µg/Kg
Nitrobenzene	EPA 8270	27	µg/Kg
Pentachlorophenol	EPA 8270	27	µg/Kg
Phenanthrene	EPA 8270	16	µg/Kg
Phenol	EPA 8270	110	µg/Kg
Pyrene	EPA 8270	16	µg/Kg
PCBs			
Aroclor 1016	EPA 8080	5.3	µg/Kg
Aroclor 1221	EPA 8080	5.3	µg/Kg
Aroclor 1232	EPA 8080	5.3	µg/Kg
Aroclor 1242	EPA 8080	5.3	µg/Kg
Aroclor 1248	EPA 8080	5.3	µg/Kg
Aroclor 1254	EPA 8080	5.3	µg/Kg
Aroclor 1260	EPA 8080	5.3	µg/Kg
Butyltin			
Tri-n-Butyltin	NOAA 1989	0.2	µg/Kg
Metals			
Mercury	PSEP 1996 (CVAA)	0.0040	mg/Kg
Chromium	PSEP 1996 (ICP)	0.050	mg/Kg
Zinc	PSEP 1996 (ICP)	0.050	mg/Kg
Antimony	PSEP 1996 (ICP-MS)	0.020	mg/Kg
Arsenic	PSEP 1996 (ICP-MS)	0.020	mg/Kg
Cadmium	PSEP 1996 (ICP-MS)	0.0081	mg/Kg
Beryllium	PSEP 1996 (ICP-MS)	0.020	mg/Kg
Copper	PSEP 1996 (ICP-MS)	0.020	mg/Kg

Table D-4. Laboratory Analysis Summary (continued)

Parameter	Reference	Method Detection Limit	Units
Lead	PSEP 1996 (ICP-MS)	0.020	mg/Kg
Selenium	PSEP 1996 (ICP-MS)	0.040	mg/Kg
Nickel	PSEP 1996 (ICP-MS)	0.020	mg/Kg
Silver	PSEP 1996 (ICP-MS)	0.012	mg/Kg
Thallium	PSEP 1996 (ICP-MS)	0.020	mg/Kg

DATA REDUCTION, REVIEW AND REPORTING

Tissue results are reported on a "wet weight" basis. Lab data will be loaded into LIMS, where it will be available for authorized users. A copy of the LIMS "COMP" and "QC" reports along with a case narrative will be prepared by the lab project manager following a project level review of the results.

Quality Control Procedures

Field Quality Control Procedures

No specific field QC samples are to be submitted for analysis. Cooking blanks for both the frying and the boiling processes will be submitted for analysis. Sodium sulfate will be used as the solid medium for the cooking blank prepared by frying (for organics analyses) and tap water will be used for the boiling blank.

Laboratory Quality Control Procedures

KCEL is accredited by the Washington State Department of Ecology (WSDOE) and participates in audits and inter-laboratory studies by WSDOE and U.S. EPA. These performance and system audits have verified the adequacy of the laboratory standard operating procedures, which include preventative maintenance and data reduction procedures. All tissue samples were analyzed by KCEL. For analyses performed at KCEL, the frequency of QC samples performed for this project is shown in Table D-5.

Table D-5. Laboratory Quality Control Samples

QC Sample	Description	Frequency
Method Blank	An aliquot of a clean solid matrix (if available) carried through the analytical process and used as an indicator of contamination.	1 per sample batch. Maximum sample batch size equals 20 samples.
Standard Reference Material (SRM)	Sample of similar matrix and of known analyte concentration, processed through the entire analytical procedure and used as an indicator of method accuracy.	1 per batch. SRMs may not be available for all analyses and may be a similar but not identical matrix.
Spike Blank	Known concentration of target analyte(s) introduced to a reagent blank, processed through the entire analytical procedure and used as an indicator or method performance.	1 per sample batch. Maximum sample batch size equals 20 samples.
Surrogate Recovery	Surrogate compounds are added to the sample aliquot at the start of processing. Recovery results indicate method accuracy.	Added to all Organics analyses, including all QC samples (except Lipids).
Lab Duplicate	A second aliquot of a sample, processed concurrently and identically with the initial sample, used as an indicator of method precision.	1 per matrix and batch (each unique tissue type and whether it was cooked or raw is considered a separate matrix)
Matrix Spike	An aliquot of sample to which known quantities of analyte(s) are added. Used as an indicator of sample matrix effect on recovery of target analyte(s).	1 per matrix and batch (each unique tissue type and whether it was cooked or raw is considered a separate matrix)
Matrix Spike duplicate	An additional matrix spike sample used as an indicator of matrix effect on sample recovery and method precision.	1 per matrix and batch (each unique tissue type and whether it was cooked or raw is considered a separate matrix). (For organics analyses only)

DATA ASSESSMENT PROCEDURES

Data assessment is conducted by reviewing QC data supplied from the laboratory. Holding times are evaluated and a review is made of the detection limits obtained in relation to matrix interferences. Duplicate samples are evaluated for their relative percent difference and surrogates; spiked samples, blank spikes and SRMs are reviewed against the limits defined in Table D-1. Method blanks are compared to individual MDLs shown in Table D-1. Data assessment is summarized by the lab project manager in the format of

a case narrative. Professional judgment is used to evaluate situations where data quality objectives have not been met.

MDLs may not be achievable due to potential interferences for some of the unique tissue types analyzed in this study. Since a separate MDL study is not practical for each tissue type, the lab project manager will review the data relative to matrix spike recoveries and chromatographic interferences (for GC methods only) in order to estimate a multiplier for the MDL for problem tissue types. A case narrative will be used to summarize this information.

BNA surrogate and matrix spike recoveries for the constituents of potential concern (COPCs) for WQA for each tissue type are used to determine if the data will need to be qualified. Samples where surrogate and matrix spike recoveries for the BNA, COPCs are less than 50 percent are flagged with a "G". For samples reported as <MDL, the "G" indicate that the MDL is higher than the reported value.

Completeness is assured by comparing valid sample data with this QA project plan and the chain-of-custody records. Completeness will be calculated by dividing the number of valid values by the total number of values.

REFERENCES

Puget Sound Estuarine Program (PSEP). 1988. Elliott Bay action program: analysis of toxic problem areas. Prepared for U.S. EPA, Region 10, Office of Puget Sound, Seattle, Washington. Prepared by PTI Environmental Services and Tetra Tech, Inc. Bellevue, Washington.

Puget Sound Estuarine Program (PSEP). 1989. Recommended guidelines for measuring selected environmental variables. Prepared for U.S. EPA, Region 10, Office of Puget Sound, Seattle, Washington. Prepared by Tetra Tech, Inc. Bellevue, Washington.

SUBAPPENDIX E

QUALITY ASSURANCE PROJECT PLAN

CSO BENTHIC ASSESSMENT SURVEY

PROJECT DESCRIPTION

Objective

The benthic assessment survey results will be used to validate aquatic life risk assessment predictions based on modeled chemical exposure/toxicity and modeled sedimentation effects (smothering).

Approach

Numbers of invertebrate species present in an area influenced by a combined sewer overflow (CSO) will be compared with similar data from an in-river reference area. Additional comparisons (impacted vs. reference) will be made employing proposed standard reference species numbers and other indices developed by the Washington State Department of Ecology (WSDOE) for Puget Sound. A replicated survey design based on Puget Sound Estuary Program (PSEP) protocol requirements will be followed. This approach includes the collection of sediments for both biological and physical-chemical analyses. This quality assurance (QA) project plan defines the plans for collection and identification of the benthic organisms and chemical-physical analysis of the associated sediments.

Justification

Benthic invertebrate species are recognized as sensitive indicators of chemical and physical impacts. Benthic communities inhabiting sediments in the vicinity of CSOs can be subjected to both chemical and physical stress following discharge events. Chemicals tend to accumulate and persist in depositional areas downstream from CSOs and sedimentation can smother shellfish and other benthos. Altered water quality may affect the abundance of individuals of a species as well as the numbers of species present. The benthos is an important food resource for commercially and recreationally important salmon and other fish and shellfish, which have significant societal value.

Attempting to understand how CSOs affect the many species of the benthic community and their separate populations addresses the need to include in the risk assessment an approach that goes beyond the individual level of ecological organization. Some of the most informative yet simplest measures of community structure include: numbers of species, numbers of individuals of a species, and numbers of dominant, pollution sensitive, or pollution tolerant species.

PROJECT ORGANIZATION AND RESPONSIBILITY

Sydney Munger directs the water quality assessment (WQA). John Strand manages the benthic assessment phase of the WQA project and will facilitate sample collection and delivery. Scott Mickelson will coordinate sample processing and analysis by the King County Environmental Laboratory (KCEL), including data reduction and reporting.

DATA QUALITY OBJECTIVES

The procedures and practices described in this QA plan are designed to generate data of sufficient quality to support project goals. Procedures to attain these data quality objectives are discussed throughout this document. Specific objectives for sample collection plus biological and chemical analyses are defined below.

Field Collection

The sediment sample upon collection should be carefully examined before acceptance. The following data quality objectives will be satisfied:

- Sediment is not extruding from the sampler so that organisms can escape.
- Overlying water is present indicating minimum leakage.
- The sediment surface is relatively flat indicating minimum disturbance.
- The entire surface of the sample is included in the sampler.
- The following penetration depths (i.e., The maximum depth of sediment sampled) are achieved at a minimum:
    - 4 to 5 cm for medium-coarse sand
    - 6 to 7 cm for fine sand
    - >10 cm for muddy sediment

If a sediment sample does not meet these objectives, the sample is rejected and another collected.

Biological Analyses

At least 20 percent of each sample will be resorted for QA/quality control (QC) purposes. Re-sorting is defined as the examination of a sample or subsample that has been sorted once and is considered free of organisms. Re-sorting will be done by an individual other than the one who sorted the original sample. A sorting efficiency of 95 percent of the total number of individuals is considered acceptable. When a subsample is found that does not meet this data quality objective, the entire sample is re-sorted

Taxonomic identifications will be verified with a reference collection. To ensure that identifications are correct and consistent, at least five percent of all samples identified by one taxonomist will be re-identified by another taxonomist. At least three specimens of each taxon will be given to the second taxonomist for verification. An identification accuracy of 95 percent is considered acceptable. When a sample is found that does not meet this data quality objective, additional verifications will be conducted. A decision to drop back to a higher taxonomic level may be required.

Chemical Analyses

The QC procedures for sediment chemical analyses, described in Section 7.0 address many of the procedures used to verify the data are meeting the quality objectives described in this section.

Precision

Laboratory precision will be assessed using laboratory duplicates for organics and metals analyses and triplicates for conventionals parameters. Relative percent difference (RPD) will be calculated for duplicate analyses while relative standard deviation (RSD) will be calculated for triplicate results. At least one of the replicate sample results must exceed the reporting detection limit (RDL) in order for the RPDs or RSDs to be evaluated against the acceptance limits. Results of precision measurements are evaluated against the objectives defined in Table E-1 and those that exceed the acceptance limits will be qualified as specified in Table E-2.

Bias

An indication of the bias or accuracy of the analytical data is provided by method blanks, standard reference materials (SRMs) or certified reference materials (CRMs), blank spikes, and matrix spikes. Table E-1 shows the objectives for QC samples used to assess accuracy. When acceptance limits are exceeded, data will be qualified according to Table E-2. Corrective action taken when data requires qualification will be done at the discretion of the project manager and the laboratory. Analytical results for method blanks are to be less than the method detection limit (MDL). A sample result will be flagged with the "B" qualifier if the method blank concentration for that analyte is greater than the MDL.

Representativeness

Samples representative of the target site will be collected by following the guidelines in *Recommended Guidelines for Sampling Marine Sediment, Water Column, and Tissue in Puget Sound* (PSEP 1996). Proper sample storage will also insure that the sample will still be representative of the target site. Prior to analysis within the laboratory, each individual sample will be homogenized to ensure that the analytical subsample is representative of the sample container contents.

Table E-1. Chemical Laboratory Parameters and QC Objectives for Sediment Samples

Parameter	Lab Replicate	Matrix Spike	Duplicate Matrix Spike	Blank Spike	CRM	Method Blank
Ammonia Nitrogen	≤ 20% RSD	70% to 130%	N/A	80% to 120%	N/A	< MDL
BNAs[a]	≤ 100% RPD	50% to 150%	100% RPD	50% to 150%	80% to 120%	< MDL
Metals[b]	≤ 20% RPD	75% to 125%	N/A	80% to 120%	≤ 120%*	< MDL
PCBs[c]	≤ 100% RPD	50% to 150%	100% RPD	50% to 150%	80% to 120%	< MDL
TOC	≤ 20% RSD	70% to 130%	N/A	N/A	80% to 120%	< MDL
Total Solids	≤ 20% RSD	N/A	N/A	N/A	N/A	< MDL
Tributyltin	≤ 100% RPD	50% to 150%	100% RPD	50% to 150%	N/A	< MDL

[a] Base/neutral/acid compounds—EPA 8270 list plus caffeine and coprostanol. Surrogate recovery limits = 50% to 150%.

[b] Metals = Priority pollutant metals including mercury.

[c] PCB surrogate recovery limits = 50% to 150%.

* Certified Reference Material—certified values for metals are generated using a different digestion method, therefore data are not qualified based on low recoveries.

RPD = Relative percent difference

RSD = Relative standard deviation

MDL = Method detection limit

N/A = Not analyzed or not applicable

TOC = Total organic carbon

PCBs = Polychlorinated biphenyls

Table E-2. Summary of Data Qualifiers

Condition to Qualify	KCEL Data Qualifier	Organics QC Limits	Metals QC Limits	Conventionals QC Limits	Comment
Very low matrix spike recovery	X	< 10 %	< 10 %	N/A	
Low matrix spike recovery	G	< 50%	< 75%	N/A	
High matrix spike recovery	L	> 150%	>125%	N/A	
Low SRM recovery	G	< 80%*	N/A	< 80%*	
High SRM recovery	L	>120%*	>120%	>120%*	
High duplicate RPD	E	>100 %	>20%	> 20 %	Use duplicate as routine QC for organics
High triplicate RSD	E	> 100%	N/A	> 20 %	Use triplicate as routine QC for conventionals
Less than the reporting detection limit	< RDL	N/A	N/A	N/A	
Less than the method detection limit	< MDL	N/A	N/A	N/A	
Contamination reported in blank	B	> MDL	> MDL	> MDL	
Very biased data, based on surrogate recoveries	X	All fraction surrogates are <10%	N/A	N/A	Use average surrogate recovery for BNA
Biased data, based on low surrogate recoveries	G	All fraction surrogates are <50%	N/A	N/A	Use average surrogate recovery for BNA
Biased data, based on high surrogate recoveries	L	All fraction surrogates are >150%	N/A	N/A	Use average surrogate recovery for BNA
Estimate based on presumptive evidence	J# indicate the presence of TICs	N/A	N/A	N/A	

Table E-2. Summary of Data Qualifiers

Condition to Qualify	KCEL Data Qualifier	Organics QC Limits	Metals QC Limits	Conventionals QC Limits	Comment
Rejected, unusable for all purposes	R	N/A	N/A	N/A	
A sample handling criteria has been exceeded	H	N/A	N/A	N/A	Includes container, preservation, hold time, sampling technique

* Note that DMMP guidance uses a 95% confidence window for this parameter/qualification.

N/A = Not applicable

SRM = Standard reference material

RPD = Relative percent difference

RSD = Relative standard deviation

RDL = Reporting detection limit

MDL = Method detection limit

BNA = Base/neutral/acid compounds

TIC = Tentatively identified compound

Comparability

Data comparability will be ensured through the application of standard sampling procedures, analytical methods, units of measurement and detection limits. Additionally, the QC criteria based on dredged materials management program (DMMP) guidelines will provide for an adequate level of analytical performance and will produce comparable data.

Completeness

Completeness will be judged by the following criteria:

- Accounting for the projected data points as detailed in this QA plan
- Compliance with the data quality criteria as presented in this section
- Compliance with required holding times

The goal for the above criteria is 100 percent complete. However, where data are not complete, decisions regarding reanalysis will be made by a collaborative process involving both data users and data generators. These decisions will take into account the project data quality objectives as presented above.

SAMPLING PROCEDURES

Sample collection also followed guidelines suggested in *Recommended Guidelines for Sampling Marine Sediment, Water Column, and Tissue in Puget Sound* (PSEP 1996).

Station Positioning

A differential geographic positioning system (DGPS) is to be used to position KCEL research vessel Liberty during sampling. The DGPS is a satellite-based navigation system that operates using a receiver to calculate ground position by triangulating data transmitted by a constellation of satellites operated by the Department of Defense (DOD). These signals are scrambled by the introduction of "white noise." The Coast Guard and King County operate "base stations" which are receivers/transmitters installed permanently on known points. The base stations receive the satellite information and calculate a correction, which is also broadcast. The DGPS receives both the satellite information and the correction information from the base station. It can then, in real time, provide an accurate survey position.

Sample Collection

Sediment grabs are collected with a modified stainless steel 0.1-m^2 van Veen grab sampler. Seven replicate sediment samples will be collected at each station. The grab sampler is decontaminated between sampling stations by scrubbing with a brush to remove excess sediment and rinsing on board, followed with a thorough *in-situ* rinsing.

After a sample has been obtained, the grab sampler is raised slowly off the bottom to allow it to close slowly. Care will be taken in rough conditions to ensure that minimal sample disturbance occurs when bringing the grab sampler on board. Prior to subsampling, appropriate field measurements and observations are recorded on field sheets. Sampling procedures will follow the PSEP protocols for sampling and analyzing benthic macroinvertebrate assemblages (Tetra Tech 1987).

The first five grabs will be collected for biological analyses. Each of these samples will be screened through a 1-mm sieve and the collected contents of the sample fixed and thoroughly mixed in the field using 15 percent borax-buffered formalin. Samples of sediment (150 grams for organics including TBT, 50 grams for metals, 150 grams for conventionals) from the 0 to 10 cm horizon from both the sixth and seventh replicate grabs will be archived for chemical analyses. Sediment (100 grams) from the seventh replicate grab will be analyzed in the field for grain size. Sediments for chemical analyses will be collected following the Puget Sound Ambient Monitoring Program procedures (PSAMP 1996).

Sample Identification

For both biological and chemical analyses, each sample will be identified by a unique laboratory sample number, assigned to each sampling location and event. A single sample number will be used for all parameters analyzed from the same sample. Sample numbers will be assigned and sample containers labeled with these numbers prior to use. Sample labels will also include information about the sampling location, sampling date, project number, sample matrix, requested analytical parameters, and preservation information.

Sample Containers and Preservation

All sample containers for chemistry parameters will be supplied by KCEL. Sample containers will be provided in accordance with guidelines noted in Table E-3. These containers will be prewashed and prepared for sampling in accordance with standard operating practice of KCEL.

Sample containers for biological samples (invertebrates retained on 1-mm screen) will be 10-liter plastic bags. These containers will be furnished by Striplin Environmental Associates. Biological samples will be preserved in the field with 15 percent borax-buffered formalin immediately following screening.

Sample Delivery

Sample containers will be placed in an insulated cooler with ice immediately after subsampling to maintain a storage temperature of approximately 4°C until delivery to the laboratory. Samples will be packed in a manner that minimizes the possibility of breakage during transport. Samples with more than one container will be grouped and placed in plastic bags to facilitate sample receipt and log-in. Samples should be delivered to the KCEL the same day they are collected. Samples for biological analyses will be delivered to Jeff Cordell at the University of Washington as soon as practical but within 72 hours of sample collection. A field sheet will be completed for each day of sampling and delivered to the KCEL laboratory at the University of Washington along with the samples.

Table E-3. Sample Containers, Preservation, and Storage Conditions

Parameter	Sample Container	Storage Conditions to be Used	Hold Time	Source of Storage Requirements*
BNAs	G with Teflon lid	freeze at -18°C	1 year to extract 40 days to analyze	PSEP and PSDDA ARM
PCBs	G with Teflon lid	freeze at -18°C	1 year to extract 40 days to analyze	PSEP and PSDDA ARM
Metals	P	freeze at -18°C	2 years to analyze	PSEP and PSDDA ARM
Mercury	P	freeze at -18°C	28 days to analyze	PSEP and PSDDA ARM
Methyl Mercury	G or Teflon	freeze at -18°C	28 days to analyze	No guidance available
Ammonia	P, G	refrigerate at 4°C	7 days	PSEP and PSDDA ARM
Particle Size Distribution	G	refrigerate at 4°C	6 months	PSEP and PSDDA ARM
Total Solids	G with Teflon lid	freeze at -18°C	6 months to analyze	PSEP and PSDDA ARM
TOC	G with Teflon lid	freeze at -18°C	6 months to analyze	PSEP and PSDDA ARM
Total Sulfides	G with no headspace	refrigerate at 4°C Zn acetate preserved	7 days	PSEP and PSDDA ARM
Tributyltin	G with Teflon lid	freeze at -18°C	1 year to extract 40 days to analyze	No guidance available

Note: Samples to be refrigerated at 4°C after thawing. Mercury storage conditions have been used for methyl mercury. Recommended sample containers are based on guidance from laboratories that perform this test. Organic semivolatile storage conditions have been used for tributyltin.

* ARM = Minutes of Third PSDDA *Annual Review Meeting.* This document summarizes many program/industry hold time standards.

BNA = Base/neutral/acid compounds

P = plastic

G = glass

TOC = Total organic carbon

Chain-of-Custody

Samples delivered to a subcontracted laboratory will be accompanied by a properly completed KCEL chain-of-custody form with custody seals placed on the cooler if samples are delivered by an outside courier. Subcontracted laboratories provide a copy of the completed chain-of-custody form to the lab project manager to become a part of the analytical data package.

Sample Receipt and Sample Log In

Samples will be logged into the Laboratory Information Management System (LIMS) by the laboratory sample management specialist. The following will be checked at that time:

- Correct use of sample ID and agreement with the field sheet
- Appropriate use of sample bottles and sample preservation
- Samples have been received within the holdtime

When applicable, the following will also be documented:

- Any applicable or unique safety hazards of the sample
- Subcontracted parameters are included in the requested suite of analytes

Field Notes

At each sampling location, the following information will be recorded on waterproof field sheets: date and time of sample collection, sampling personnel, station location information, depth, gross characteristics of surficial sediment (texture, color, presence of biological structures, debris, oily sheen, odor), gross characteristics of vertical profile (presence of redox potential discontinuity), maximum penetration of the grab sampler, and comments (deviations from standard sampling procedures). Field sheets will be completed for each day of sampling. The field sheet(s) will be delivered to the lab along with the samples.

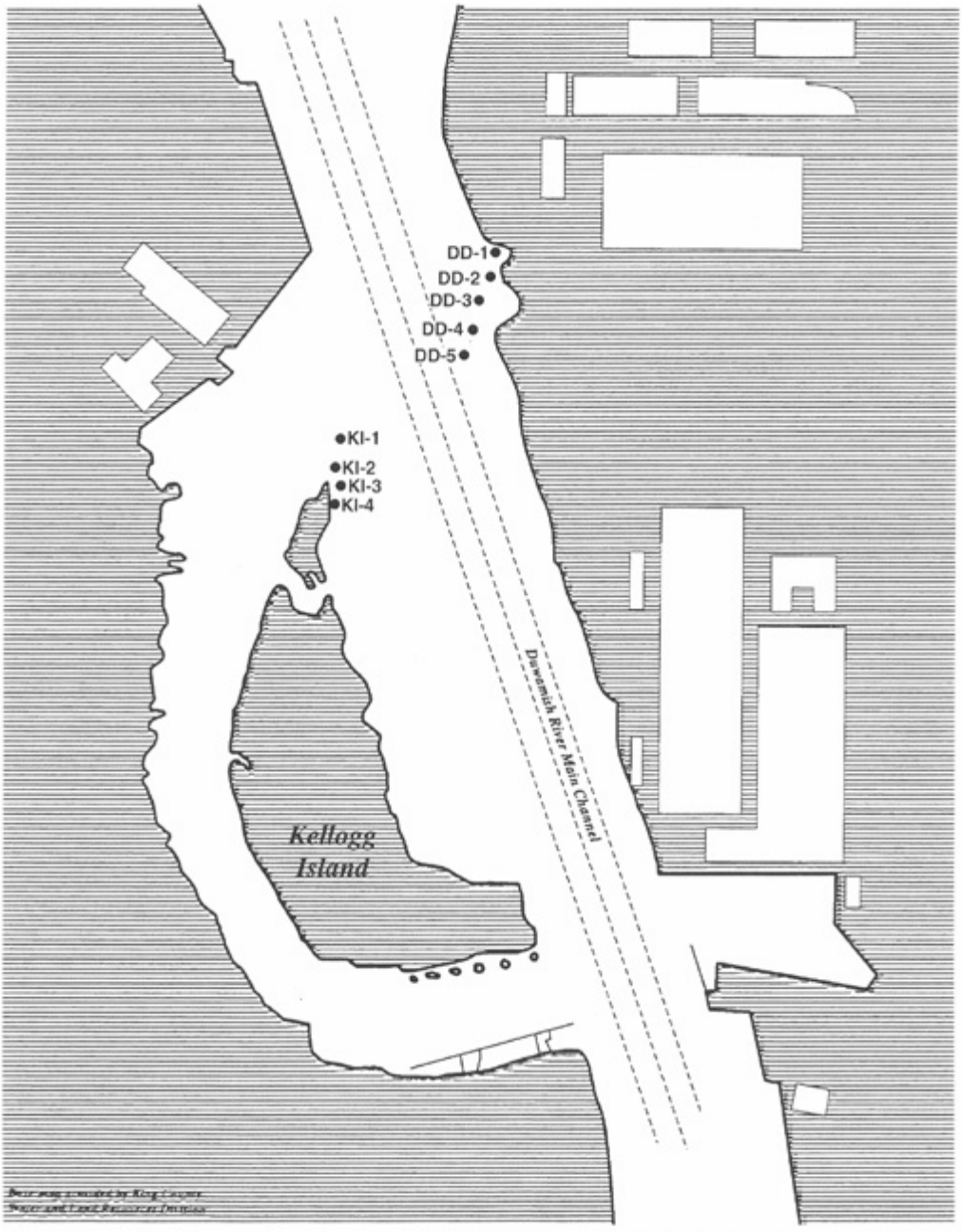
Sampling Locations

As shown in Figure E-1, benthic sampling will be conducted along two transects. The first transect is located at the Duwamish/Diagonal CSO and tends in a southwesterly direction away from the CSO. Five stations at the Duwamish/Diagonal CSO sampled in either 1994 or 1995 will be re-occupied using the original GPS coordinates. The second transect is located near the north tip (most down river point) of Kellogg Island and again tends in a southwesterly direction. Four stations will be occupied and sampled. One of these stations, KI-2 has been repeatedly sampled in 1997 as part of the WQA. The GPS

coordinates of all stations are entered in Table E-4. Station locations on each transect were selected based on having similar sediment grain size and TOC levels. Sediment chemistry is also available for all stations on the Duwamish/Diagonal transect and for one station on the Kellogg Island transect.

Table E-4. GPS Station Coordinates for Duwamish/Diagonal and Kellogg Island Benthic Assessment Survey

STATION NAME	NORTHING	EASTING
DD-1 (DUD001)	209120	1267153
DD-2 (DUD006)	209059	1267092
DD-3 (DUD022)	208929	1267040
DD-4 (DUD034)	208785	1266933
DD-5 (DUD039)	208606	1266844
KI-1	208552	1266651
KI-2	208274	1266665
KI-3	208216	1266675
KI-4	207755	1266615



King County:55-1521-27(07) 1/99

Figure E-1.
Benthic Assessment Station Locations

ANALYTICAL PROCEDURES

Benthic Samples

The University of Washington will sort, identify, and enumerate the benthic samples following the PSEP recommended protocols for sampling and analyzing benthic macroinvertebrate assemblages (Tetra Tech 1987). Benthic samples will first be sorted into major taxonomic groups (annelida, arthropoda, mollusca, echinodermata, and miscellaneous phyla), then identified to the lowest possible taxon, usually to the species level, and finally counted. After completing identifications and counting, all organisms will be placed in vials containing 70 percent alcohol. All vials from a single sample will be stored in a common jar and immersed in 70 percent alcohol. Each vial will contain an internal label with the following information: survey name, station number, replicate number, collection gear, water depth, and data of collection. All data will be recorded in a permanent notebook and on a sample data sheet. The completed data sheets will be copied and the original transferred to Peter Striplin of Striplin Environmental Associates. A copy will be retained by the University of Washington.

Sediment Samples

Sediment samples will be analyzed using the analytical procedures and detection limits appropriate to PSEP studies. These are listed in Table E-5. All results (except total solids) will be reported on a dry weight basis and non-ionizable organic compounds will be normalized using the TOC results for each sample. Particle size distribution (PSD) will be subcontracted to outside laboratories. All other parameters will be analyzed at KCEL.

Table E-5. Laboratory Analysis Summary

Parameter	Reference	Nominal Method Detection Limit*	Units
BNAs			
1,2,4-trichlorobenzene	EPA 8270 (SIM)	1.4	µg/Kg
1,2-dichlorobenzene	EPA 8270 (SIM)	1.4	µg/Kg
1,2-diphenylhydrazine	EPA 8270	110	µg/Kg
1,3-dichlorobenzene	EPA 8270 (SIM)	1.4	µg/Kg
1,4-dichlorobenzene	EPA 8270 (SIM)	1.4	µg/Kg
2,4,5-trichlorophenol	EPA 8270	220	µg/Kg
2,4,6-trichlorophenol	EPA 8270	220	µg/Kg

Table E-5. Laboratory Analysis Summary (continued)

Parameter	Reference	Nominal Method Detection Limit*	Units
2,4-dichlorophenol	EPA 8270	54	µg/Kg
2,4-dimethylphenol	EPA 8270	54	µg/Kg
2,4-dinitrophenol	EPA 8270	110	µg/Kg
2,4-dinitrotoluene	EPA 8270	22	µg/Kg
2,6-dinitrotoluene	EPA 8270	22	µg/Kg
2-chloronaphthalene	EPA 8270	32	µg/Kg
2-chlorophenol	EPA 8270	110	µg/Kg
2-methylnaphthalene	EPA 8270	85	µg/Kg
2-methylphenol	EPA 8270	54	µg/Kg
2-nitroaniline	EPA 8270	220	µg/Kg
3,3'-dichlorobenzidine	EPA 8270	54	µg/Kg
3-nitroaniline	EPA 8270	220	µg/Kg
4,6-dinitro-o-cresol	EPA 8270	110	µg/Kg
4-bromophenyl phenyl ether	EPA 8270	22	µg/Kg
4-chloro-3-methylphenol	EPA 8270	110	µg/Kg
4-chloroaniline	EPA 8270	110	µg/Kg
4-chlorophenyl phenyl ether	EPA 8270	32	µg/Kg
4-methylphenol	EPA 8270	54	µg/Kg
4-nitroaniline	EPA 8270	220	µg/Kg
4-nitrophenol	EPA 8270	110	µg/Kg
Acenaphthene	EPA 8270	22	µg/Kg
Acenaphthylene	EPA 8270	32	µg/Kg
Aniline	EPA 8270	110	µg/Kg
Anthracene	EPA 8270	32	µg/Kg

Table E-5. Laboratory Analysis Summary (continued)

Parameter	Reference	Nominal Method Detection Limit*	Units
Benzo(a)anthracene	EPA 8270	32	µg/Kg
Benzo(a)pyrene	EPA 8270	54	µg/Kg
Benzo(b)fluoranthene	EPA 8270	85	µg/Kg
Benzo(k)fluoranthene	EPA 8270	85	µg/Kg
Benzoic acid	EPA 8270	220	µg/Kg
Benzyl alcohol	EPA 8270	54	µg/Kg
Benzyl butyl phthalate	EPA 8270	32	µg/Kg
Bis(2-chloroethoxy)methane	EPA 8270	54	µg/Kg
Bis(2-chloroethyl)ether	EPA 8270	32	µg/Kg
Bis(2-chloroisopropyl)ether	EPA 8270	110	µg/Kg
Bis(2-ethylhexyl)phthalate	EPA 8270	32	µg/Kg
Caffeine	EPA 8270	11	µg/Kg
Carbazole	EPA 8270	54	µg/Kg
Chrysene	EPA 8270	32	µg/Kg
Coprostanol	EPA 8270	220	µg/Kg
Di-n-butyl phthalate	EPA 8270	54	µg/Kg
Di-n-octyl phthalate	EPA 8270	32	µg/Kg
Dibenzo(a,h)anthracene	EPA 8270	85	µg/Kg
Dibenzofuran	EPA 8270	54	µg/Kg
Diethyl phthalate	EPA 8270	54	µg/Kg
Dimethyl phthalate	EPA 8270	22	µg/Kg
Fluoranthene	EPA 8270	32	µg/Kg
Fluorene	EPA 8270	32	µg/Kg

Table E-5. Laboratory Analysis Summary (continued)

Parameter	Reference	Nominal Method Detection Limit*	Units
Hexachlorobenzene	EPA 8270	1.4	µg/Kg
Hexachlorobutadiene	EPA 8270	54	µg/Kg
Hexachlorocyclopentadiene	EPA 8270	54	µg/Kg
Hexachloroethane	EPA 8270	54	µg/Kg
Indeno(1,2,3-cd)pyrene	EPA 8270	54	µg/Kg
Isophorone	EPA 8270	54	µg/Kg
N-nitrosodi-n-propylamine	EPA 8270	54	µg/Kg
N-nitrosodimethylamine	EPA 8270	220	µg/Kg
N-nitrosodiphenylamine	EPA 8270	54	µg/Kg
Phenanthrene	EPA 8270	32	µg/Kg
Phenol	EPA 8270	220	µg/Kg
Pyrene	EPA 8270	32	µg/Kg
PCBs			
Aroclor 1016	EPA 8080	26	µg/Kg
Aroclor 1221	EPA 8080	26	µg/Kg
Aroclor 1232	EPA 8080	26	µg/Kg
Aroclor 1242	EPA 8080	26	µg/Kg
Aroclor 1248	EPA 8080	26	µg/Kg
Aroclor 1254	EPA 8080	26	µg/Kg
Aroclor 1260	EPA 8080	26	µg/Kg
Butyltin			
Tri-n-Butyltin	NOAA 1989	0.17	µg/Kg
Metals			
Aluminum	EPA 6010	10	mg/Kg
Antimony	EPA 6010	3	mg/Kg

Table E-5. Laboratory Analysis Summary (continued)

Parameter	Reference	Nominal Method Detection Limit*	Units
Arsenic	EPA 6010	5	mg/Kg
Beryllium	EPA 6010	0.1	mg/Kg
Cadmium	EPA 6010	0.3	mg/Kg
Chromium	EPA 6010	0.5	mg/Kg
Copper	EPA 6010	0.4	mg/Kg
Iron	EPA 6010	5	mg/Kg
Lead	EPA 6010	3	mg/Kg
Mercury	EPA 7471	0.04	mg/Kg
Nickel	EPA 6010	2	mg/Kg
Selenium	EPA 6010	5	mg/Kg
Silver	EPA 6010	0.4	mg/Kg
Thallium	EPA 6010	20	mg/Kg
Zinc	EPA 6010	0.5	mg/Kg
Conventionals			
Particle Size Distribution	PSEP	0.1	%
Total Organic Carbon	SM 5310-B	10	mg/Kg
Total Solids	SM 2540-B	0.005	%
Ammonia Nitrogen	SM 4500-NH3 with[a]	1	mg/Kg

[a] Sediment extraction by: Methods Manual for forest soil and plant analysis. (Y.P. Kalra and D.J. Maynard 1991). NW Region Info. Report, NOR-X-319.

* Nominal detection limits based on estimated percent solids of 50%.

DATA REDUCTION, REVIEW AND REPORTING

For sediment samples data will be loaded into LIMS, where it will be available for authorized users. A copy of the LIMS "COMP" and "QC" reports will be prepared by the lab project manager along with the narrative of the QA1 data review (see Section 8).

Peter Striplin of Striplin Environmental Associates will analyze the data for benthic invertebrates. It is envisioned that the resulting data will be organized by taxonomic group (e.g. numbers of species, numbers of dominant, pollution tolerant, or pollution sensitive species). Values of each of these variables will be obtained from the list of abundances of species provided by the University of Washington. Differences between transects or stations will be analyzed statistically employing an analysis of variance and an appropriate post *a priori* test.

QUALITY CONTROL PROCEDURES

Laboratory Quality Control Procedures

KCEL is accredited by WSDOE and participates in audits and inter-laboratory studies by WSDOE and U.S. EPA. These performance and system audits have verified the adequacy of the laboratory standard operating procedures, which include preventative maintenance and data reduction procedures.

Frequency of Lab Quality Control Samples

For samples performed at KCEL, the frequency of QC samples to be performed for this project is shown in Table E-6.

DATA ASSESSMENT PROCEDURES

Data assessment will be conducted by reviewing QC data supplied from the laboratory. Data assessment using QA1 guidelines will be summarized by the lab project manager in the format of a case narrative. Professional judgment will be used to evaluate situations where data quality objectives have not been met.

Completeness will be assured by comparing valid sample data with this QA project plan and the COC records. Completeness will be calculated by dividing the number of valid values by the total number of values.

Table E-6. Laboratory Quality Control Samples

Parameter	Blank	Replicate	Triplicate	Matrix Spike	CRM*	Surrogates
Total Organic Carbon	1 per batch	5% minimum, 1/batch	5% minimum, 1/batch	N/A	1 per batch	N/A
Total Solids	1 per batch	N/A	5% minimum, 1/batch	N/A	N/A	N/A
Ammonia Nitrogen	1 per batch	N/A	5% minimum, 1/batch	5% minimum, 1/batch	As available	N/A
Particle Size Distribution	N/A	N/A	5% minimum, 1/batch	N/A	N/A	N/A
Metals	1 per batch	5% minimum, 1/batch	N/A	5% minimum, 1/batch	1 per batch	N/A
Mercury	1 per batch	5% minimum, 1/batch	N/A	5% minimum, 1/batch	1 per batch	N/A
BNAs	1 per batch	5% minimum, 1/extraction batch	N/A	5% minimum, 1/extraction batch	1 per extraction batch	Yes
PCBs	1 per batch	5% minimum, 1/extraction batch	N/A	5% minimum, 1/extraction batch	1 per extraction batch	Yes
Tributyltin	1 per batch	5% minimum, 1/extraction batch	N/A	5% minimum, 1/extraction batch	As available	Yes

*Certified Reference Material. Blank spike may be used if CRM not available.

Note: Batch is generally defined as a set of 20 samples or less, prepared and analyzed using the same reagents and equipment and by the same analyst(s).

N/A = Not applicable

BNA = Base/neutral/acid compounds

PCBs = Polychlorinated biphenyls

REFERENCES

Puget Sound Estuarine Program (PSEP). 1987. Recommended protocols for sampling and analyzing subtidal benthic macroinvertebrate assemblages in Puget Sound. Prepared for U.S. EPA, Region 10, Office of Puget Sound, Seattle, Washington. Prepared by Tetra Tech, Inc. Bellevue, Washington.

Puget Sound Estuarine Program (PSEP). 1996. Recommended guidelines for sampling marine sediment, water column, and tissue in Puget Sound. Prepared for U.S. EPA Region 10, Office of Puget Sound, Seattle, Washington by King County Environmental Laboratory (KCEL). Seattle, Washington.

Puget Sound Ambient Monitoring Program (PSAMP). 1996. Recommended guidelines for sampling marine sediment, water column, and tissue in Puget Sound. Prepared for U.S. EPA. Region 10, Seattle, Washington and the Puget Sound Water Quality Authority, Olympia, Washington. Prepared by King County Water Pollution Control Division Environmental Laboratory (Metro Environmental Laboratory). Seattle, Washington.

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