

**South and West Point Wastewater Treatment Plants  
Alki, Carkeek, Elliott West, and MLK/Henderson  
Storage and CSO Treatment Plants**

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**Receiving Water Characterization Study  
King County NPDES Monitoring Program**

**Final Sampling and Analysis Plan and Quality  
Assurance Project Plan**

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Prepared for the

King County Department of Natural Resources and Parks  
Wastewater Treatment Division

and the

Washington State Department of Ecology

by the

King County Department of Natural Resources  
Marine and Sediment Assessment Group

December 2010

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December 2010

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# 1 INTRODUCTION

This sampling and analysis plan and quality assurance project plan (SAP/QAPP) presents project information, along with sampling and analytical methodologies and quality assurance procedures that will be employed to conduct a receiving water characterization study in Puget Sound, Elliott Bay, and the Duwamish River. King County is conducting this study to fulfill one requirement of its National Pollutant Discharge Elimination System (NPDES) permits for the South Wastewater Treatment Plant (WA-002958-1) and the West Point Wastewater Treatment Plant and Alki, Carkeek, Elliott West, and MLK/Henderson CSO Storage and Treatment Plants (WA-002918-1), issued by the Washington State Department of Ecology (Ecology).

King County's NPDES permits for the South and West Point Wastewater Treatment Plants (including CSO facilities) require that “. . . *the Permittee must provide data via ambient monitoring stations or collect receiving water information via field sampling necessary to determine if the effluent has a reasonable potential to cause a violation of the water quality standards. If reasonable potential exists, Ecology will use this information to calculate effluent limits. Field sampling will be required where ambient monitoring station data does not exist.*” (Ecology 2009a,b). King County will fulfill these permit requirements through a combination of existing ambient water quality data and new field sampling.

This SAP/QAPP includes a description of the project, the County's ambient water quality monitoring history, a description of the existing data that will be submitted to Ecology, the sampling design for acquiring new environmental data, sampling and analytical methodologies, quality assurance procedures, and reporting requirements. The SAP/QAPP has been prepared in accordance with *Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies* (Ecology 2004).

## 2 PROJECT DESCRIPTION

King County's Receiving Water Characterization Study will provide Ecology with ambient water quality data and new sampling and analytical data needed to evaluate whether effluent from the South and West Point treatment plants and the Alki, Carkeek, Elliott West, and MLK/Henderson CSO storage and treatment plants have a reasonable potential to cause a violation of water quality standards.

The receiving water characterizations for the South treatment plant and the West Point treatment plant and CSO facilities have different timelines in their respective permits (e.g., September 2011 and June 2010, respectively, for submittal of project quality assurance project plans). Section S11.5 of the South Treatment Plant permit also requires that sampling should occur ". . . as close as possible to the critical period." For the South treatment plant, the critical periods are July (chronic water quality criteria) and December (acute water quality criteria). Section S12.E of the West Point Treatment Plant permit requires that sampling should occur ". . . during a spring tide." Due to the sampling and analytical requirements for assessment of trace metals, the County will undertake these characterizations concurrently.

King County's Marine and Sediment Assessment Group monitors water quality in Puget Sound, Elliott Bay, and the Duwamish River both proximal to its wastewater treatment plant outfalls and CSO storage and treatment plant outfalls as well as at ambient locations outside the zone of influence of the effluent from these facilities. These stations have been sampled for numerous years and a large body of water quality data exists for these monitoring locations. The County's routine ambient monitoring program samples these stations on a monthly basis, collecting data both through *in situ* field measurements and laboratory analysis of collected samples. Data from the County's existing water quality monitoring program will be submitted to Ecology to fulfill part of the receiving water quality characterization study data requirements.

### 2.1 Existing Water Quality Monitoring

Water column monitoring at outfall and ambient sites is an important component of the County's overall water quality monitoring program and is structured to detect natural seasonal changes in the water column as well as to identify changes from anthropogenic inputs. Two of the County's Puget Sound water quality stations have been monitored continuously since 1988. General water quality parameters, including temperature, salinity, dissolved oxygen, phytopigments, nutrients, total suspended solids, and fecal bacteria are monitored on a monthly basis.

King County measures *in situ* water quality parameters at offshore monitoring stations using a SeaBird Electronics SBE 25 SEALOGGER conductivity-temperature-depth (CTD) profiler. Parameters measured by the CTD include temperature, conductivity, transmissivity, dissolved oxygen, photosynthetically active radiation (PAR), and fluorescence (an indicator of chlorophyll-*a* abundance). Salinity and density are calculated parameters, using temperature and conductivity measurements. The CTD collects a continuous water column profile on both the downcast and upcast of the instrument. Multiple 5-liter Niskin bottles are mounted onto the rosette containing the CTD profiler for collecting discrete water samples on the upcast at predetermined depths for laboratory analysis of nutrients, total suspended solids, phytopigments, and bacteria.

Figure 1 shows the location of the West Point and South treatment plant outfalls and the Carkeek, Alki, Elliott West, and MLK/Henderson storage and CSO treatment plant outfalls. The figure also shows four of King County's existing ambient monitoring stations, which will be used as the stations for the NPDES receiving water characterization study. Station KSBP01 will be the monitoring station for the West Point and Carkeek outfalls, Station LSNT01 will be the monitoring station for the South and Alki outfalls, Station LTED04 will be the monitoring station for the Elliott West outfall, and Station LTXQ01 will be the monitoring station for the MLK/Henderson outfall.

### **2.1.1 Station KSBP01**

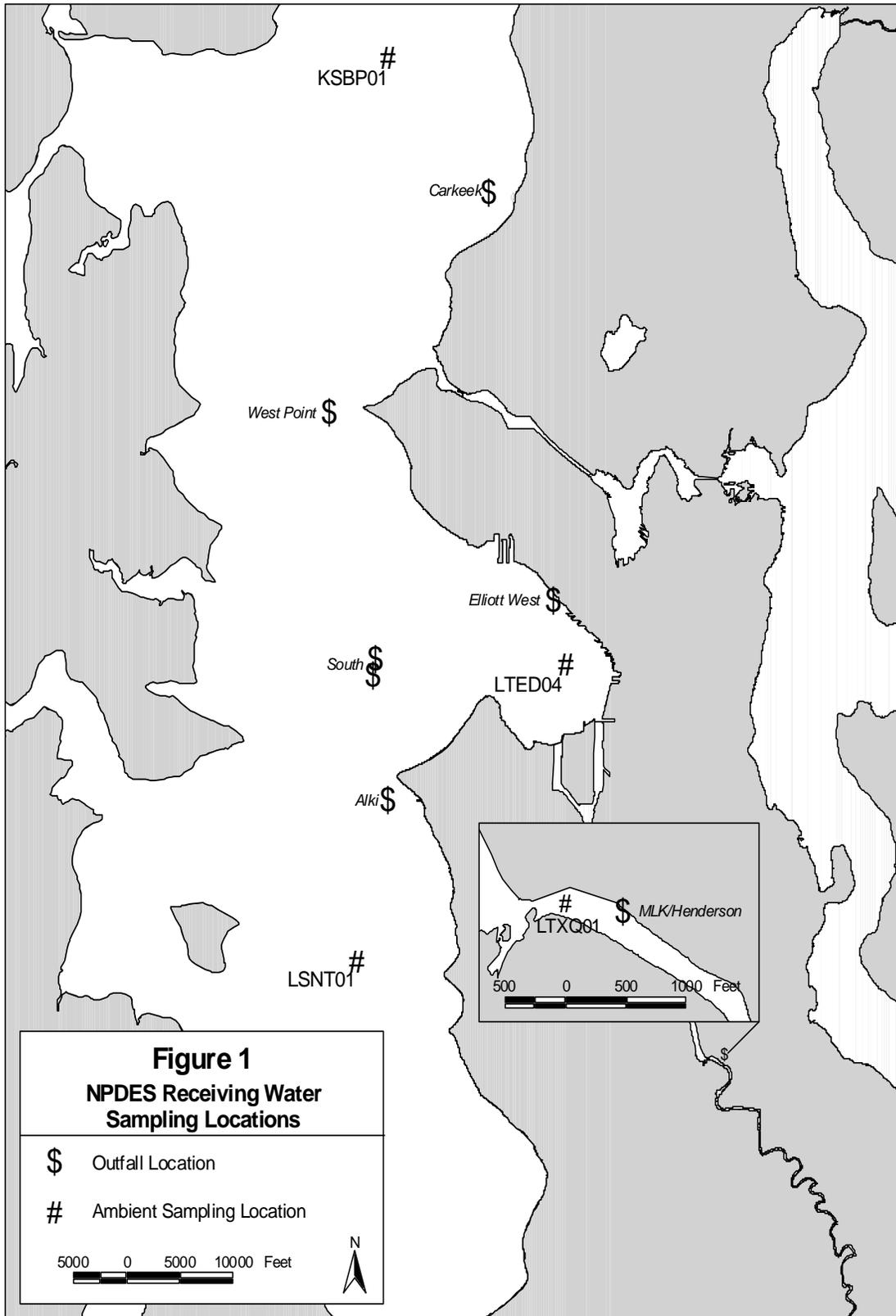
Station KSBP01 is located in the North Central Puget Sound Basin, approximately two miles from the Carkeek outfall and six miles from the West Point outfall (see Figure 1). The monitoring history for this station goes back to 1966 and, for certain parameters, it has been monitored continuously since 1988. King County currently samples this station on a monthly basis for *in situ* field measurement of temperature, dissolved oxygen, salinity, density, and transmissivity and laboratory analysis of fecal coliform and enterococcus bacteria, nutrients (ammonia, nitrate + nitrite nitrogen, silica, and total phosphorus), chlorophyll-*a* and pheophytin, and total suspended solids. Nutrient and total suspended solids samples are collected from seven depths at this station – 1, 15, 25, 35, 55, 100, and 200 meters. Chlorophyll-*a* and pheophytin samples are collected from four depths – 1, 15, 25, and 35 meters. Bacteria samples are collected from a single depth – 1 meter.

Station KSBP01 will continue to be sampled monthly as part of King County's routine ambient monitoring program. King County will submit to Ecology two years' worth of monthly data from this station for total suspended solids, dissolved oxygen, temperature, fecal coliform bacteria, and salinity (as well as future routine monitoring data, if needed) to meet the requirements of Sections S12.G and S18.I.7 of the West Point permit.

### **2.1.2 Station LSNT01**

Station LSNT01 is located in the South Central Puget Sound Basin, approximately three miles from the Alki outfall and five miles from the South outfall (see Figure 1). This station has been monitored continuously since 1988. King County currently samples this station on a monthly basis for *in situ* field measurement of temperature, dissolved oxygen, salinity, density, and transmissivity and laboratory analysis of fecal coliform and enterococcus bacteria, nutrients (ammonia, nitrate + nitrite nitrogen, silica, and total phosphorus), chlorophyll-*a* and pheophytin, and total suspended solids. Nutrient and total suspended solids samples are collected from seven depths at this station – 1, 15, 25, 35, 55, 100, and 180 meters. Chlorophyll-*a* and pheophytin samples are collected from four depths – 1, 15, 25, and 35 meters. Bacteria samples are collected from a single depth – 1 meter.

Station LSNT01 will continue to be sampled monthly as part of King County's routine ambient monitoring program. The County will submit to Ecology two years' worth of monthly data from this station for total suspended solids, dissolved oxygen, temperature, fecal coliform bacteria, and salinity (as well as future routine monitoring data, if needed) to meet the requirements of Section S11.7 of the South Treatment Plant permit and Section S18.I.7 of the West Point permit.



**Figure 1**  
**NPDES Receiving Water**  
**Sampling Locations**

\$ Outfall Location

# Ambient Sampling Location

5000 0 5000 10000 Feet

N

### **2.1.3 Station LTED04**

Station LTED04 is located in Elliott Bay, approximately one mile from the Elliott West outfall (see Figure 1). This station has been monitored continuously since 1997. King County currently samples this station on a monthly basis for *in situ* field measurement of temperature, dissolved oxygen, salinity, density, and transmissivity and laboratory analysis of fecal coliform and enterococcus bacteria, nutrients (ammonia, nitrate + nitrite nitrogen, silica, and total phosphorus), chlorophyll-*a* and pheophytin, and total suspended solids. Nutrient and total suspended solids samples are collected from six depths at this station – 1, 15, 25, 35, 55, and 75 meters. Chlorophyll-*a* and pheophytin samples are collected from four depths – 1, 15, 25, and 25 meters. Bacteria samples are collected from a single depth – 1 meter.

King County partnered with the Seattle Aquarium in November 2007 to deploy its first high-frequency, real-time, marine water quality data collection system to assess the nearshore environment in Elliott Bay. Automated, high-frequency, water quality data collection systems allow continuous measurements of physical, chemical, and biological water quality parameters as well as meteorological parameters. The data generated by these systems allow users to characterize temporal and spatial variability for multiple parameters over numerous scales (e.g., daily, seasonal, annual, inter-annual). This moored system is comprised of two YSI 6600 EDS sonde/sensor arrays that are deployed from the Aquarium's pump house at the end of Pier 59. A weighted-pulley system allows the two arrays to be deployed at fixed depths – approximately one meter and ten meters below the surface. Parameters measured include temperature, conductivity (salinity), pressure (depth), dissolved oxygen, turbidity, pH, and fluorescence (chlorophyll). Data are collected and uploaded every 15 minutes to a web interface. Data from this monitoring system may be viewed at <http://green.kingcounty.gov/marine-buoy/>.

Station LTED04 will continue to be sampled monthly as part of King County's routine ambient monitoring program. The County will submit to Ecology two years' worth of monthly data from this station for total suspended solids, dissolved oxygen, temperature, fecal coliform bacteria, and salinity (as well as future routine monitoring data, if needed) to meet the requirements of Section S18.I.7 of the West Point permit. One year of high-resolution pH, dissolved oxygen, temperature, and salinity data from the County's marine mooring in Elliott Bay will also be submitted to assess temporal variations of these parameters on a finer scale.

### **2.1.4 Station LTXQ01**

Station LTXQ01 is located in the Duwamish River, approximately 600 feet downstream of the MLK/Henderson outfall (see Figure 1). King County currently samples this station on a monthly basis for field measurement of temperature and dissolved oxygen and laboratory analysis of fecal coliform and enterococcus bacteria, nutrients (ammonia, nitrate + nitrite nitrogen, and total phosphorus), salinity, hardness, and total suspended solids. Samples are collected mid-channel from the river, using a modified, van Dorn-style sampling bottle that is lowered from a bridge. Data have been collected at this station since May 2009.

Station LTXQ01 will continue to be sampled monthly as part of King County's routine ambient monitoring program. The County will submit to Ecology two years' worth of monthly data from this station for total suspended solids, dissolved oxygen, temperature, fecal coliform bacteria, and salinity (as well as future routine monitoring data, if needed) to meet the requirements of Section S18.I.7 of the West Point permit.

## 2.2 New Water Quality Monitoring

The County's NPDES permits also require submittal of data for certain water quality parameters that have not been measured previously on a regular basis or have not been measured recently. These include trace metals and pH for all sampling locations and weak acid dissociable cyanide and alkalinity for the sampling location that will serve the South treatment plant outfall.

King County will collect a total of 12 samples from all four monitoring stations for analysis of total and dissolved metals to meet the requirements of Sections S12.H and S18.I.8 of the West Point permit and Section S11.7 of the South Treatment Plant permit. The four sampling events will be timed to occur during a spring tide in December 2010, July 2011, December 2011, and July 2012. This timing will meet the requirements of both the West Point and South Treatment Plant permits. King County previously collected monthly metals data at Stations KSBP01 and LSNT01 for 15 months during 1999 and 2000. These previous data, along with the new trace metals data collected over an 18-month period, will allow an assessment of any spatial or temporal variations in trace metals' concentrations. New sampling at Station LSNT01 will also include weak acid dissociable cyanide and alkalinity as required in the South treatment plant permit. Given the periodic excursion of the Duwamish River salt wedge into the area in which Station LTX01 is located, synoptic hardness and salinity data will also be collected along with trace metals, to allow comparison of metals' data with appropriate water quality criteria. At the three offshore stations, pH will be measured *in situ* during each sampling event in a continuous surface to bottom profile. At Station LTXQ01, pH will be measured in the field each time samples are collected for analysis of trace metals.

## 3 PROJECT ORGANIZATION AND SCHEDULE

### 3.1 Project Organization

The tasks involved in conducting the NPDES Receiving Water Characterization Study and the personnel responsible for those tasks are shown below.

- **Scott Mickelson** King County Marine and Sediment Assessment Group – (206) 296-8247 [scott.mickelson@kingcounty.gov](mailto:scott.mickelson@kingcounty.gov) Project management, study design, preparation of draft SAP/QAPP, approval of final SAP/QAPP, data validation, data analysis, and preparation of final study report.
- **Betsy Cooper** King County Wastewater Treatment Division – (206) 263-3728 [betsy.cooper@kingcounty.gov](mailto:betsy.cooper@kingcounty.gov) Internal review of study design and draft SAP/QAPP, approval of final SAP/QAPP, and internal review of final study report.
- **Mark Henley** Department of Ecology Water Quality Program – (425) 649-7103 [mahe461@ecy.wa.gov](mailto:mahe461@ecy.wa.gov) Review and approval of SAP/QAPP, review of final report and resulting data.
- **Jean Power** King County Environmental Laboratory – (206) 684-2384 [jean.power@kingcounty.gov](mailto:jean.power@kingcounty.gov) Coordination of field activities for all routine sampling events and semiannual sampling events.
- **Katherine Bourbonais** King County Environmental Laboratory – (206) 684-2382 [katherine.bourbonais@kingcounty.gov](mailto:katherine.bourbonais@kingcounty.gov) Coordination of all King County Environmental Laboratory activities, data verification, and internal data reporting.
- **Colin Elliott** King County Environmental Laboratory – (206) 684-2343 [colin.elliott@kingcounty.gov](mailto:colin.elliott@kingcounty.gov) Internal review of draft SAP/QAPP, data verification, coordination of King County Environmental Laboratory QA/QC programs.

### 3.2 Project Schedule

The receiving water characterization studies for the South treatment plant and the West Point treatment plant and CSO facilities have different timelines in their respective permits. Due to the sampling and analytical requirements for trace metals, the decision was made to conduct the studies concurrently, using the earlier West Point permit timeline to create the project schedule. The following schedule for preparing draft and final SAP/QAPP documents will allow the first round of sampling to occur in July 2011:

- June 30, 2010 – Submittal of draft SAP/QAPP by King County to Department of Ecology for review and comment. This project deadline meets the reporting schedule outlined in Sections S12.A and S18.I.1 of the West Point permit
- December 16, 2010 – Submittal of comments on draft SAP/QAPP by Department of Ecology to King County for incorporation into final document.
- December 17, 2010 – Submittal of final SAP/QAPP to Department of Ecology for letter of approval.

Upon approval of the project SAP/QAPP, the following schedule will commence for the four rounds of trace metals, pH, cyanide, alkalinity, and hardness sampling:

- July 2011 (Spring Tide) – The first sampling event will be conducted during a spring tide in the month of July to meet the timing requirements of both the West Point treatment plant (spring tide) and South treatment plant (critical period) NPDES permits. Samples will be collected for analysis of trace metals at all four monitoring stations. The monitoring station proximal to the South Treatment Plant will be sampled for analysis of weak acid dissociable cyanide and alkalinity in addition to trace metals. The monitoring station proximal to the MLK/Henderson Storage and CSO Treatment Plant will be sampled for analysis of hardness in addition to trace metals. Field measurement of pH will occur at all four stations.
- December 2011 (Spring Tide) – Second sampling event for trace metals, cyanide, alkalinity, and hardness.
- July 2012 (Spring Tide) – Third sampling event for trace metals, cyanide, alkalinity, and hardness.
- December 2012 (Spring Tide) – Fourth sampling event for trace metals, cyanide, alkalinity, and hardness.

In addition to new sampling, King County will also submit to Ecology existing data from its routine monthly water column monitoring program according to the following schedule:

- June 2013 – Submittal of two years' data from four monitoring stations, to include the following parameters; total suspended solids, dissolved oxygen, temperature, fecal coliform bacteria, and salinity.
- June 2013 – Submittal of one year of high-resolution data for King County's moored water quality monitoring station in Elliott Bay for the following parameters; dissolved oxygen, temperature, salinity, and pH.
- June 2013 – Submittal of 12 months of pH data from four monitoring stations, which will have had sampling begun in January 2011.

Upon completion of all sampling and analysis, King County will prepare a final study report and data submission. The data submission will include both data collected under this SAP/QAPP, as well as trace metals data collected during a prior sampling program conducted in 1999 and 2000.

- June 30, 2013 – Submittal of study report to the Department of Ecology and submittal of study data in electronic format to the Environmental Information Management (EIM) System.

## 4 DATA QUALITY OBJECTIVES

The data quality objectives of the NPDES receiving water characterization study are to provide sufficient data of known quality to Ecology for use in their “Reasonable Potential” analysis. This section discusses both the quantity and quality of data to be collected during this study.

### 4.1 Data Quantity

The quantity of data to be collected is prescribed in the NPDES permits for both the South and West Point treatment plants (Ecology 2009 a,b). A minimum of 10 receiving water samples at each sampling location must be collected to meet the requirements of both permits. The submission of two years’ worth of existing data from the County’s monthly ambient sampling program, as discussed in Section 2, coupled with the collection of 12 new samples at each sampling location for additional trace metals and conventionals analyses will meet the requirements of the NPDES permits and provide a sufficient quantity of data for Ecology to perform their analysis.

### 4.2 Data Quality

Validation of project study data will assess whether the data collected are of sufficient quality to meet the study goals. The data quality issues of precision, accuracy, bias, representativeness, completeness, and comparability are described in the following sections.

#### 4.2.1 Precision, Accuracy, and Bias

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

- collection and analysis of field replicate samples and various field blanks such as atmosphere, bottle, filtration, and equipment blanks; and
- analysis of various laboratory QC samples such as method blanks, matrix spikes, certified reference materials, and laboratory replicates.

#### 4.2.2 Representativeness

Representativeness expresses the degree to which sample data accurately and precisely represent a characteristic of a population, parameter variations at the sampling point, or an environmental condition. Water samples for trace metals and conventional analyses will be collected from stations with predetermined coordinates and sampling depths to represent specific site locations. The collection of electronic *in situ* water column data will also be performed at stations with predetermined coordinates.

#### 4.2.3 Completeness

Completeness is defined as the total number of samples analyzed for which acceptable analytical data are generated, compared to the total number of samples submitted for analysis. Sampling at

stations with known position coordinates in favorable conditions, along with adherence to standardized sampling and testing protocols will aid in providing a complete set of data for this project. The goal for completeness is 100%. If 100% completeness is not achieved, the project team will evaluate if the data quality objectives can still be met or if additional samples may need to be collected and analyzed.

#### ***4.2.4 Comparability***

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another. This goal is achieved through using standard techniques to collect and analyze representative samples, along with standardized analytical procedures. By following the guidance of this SAP/QAPP, the goal of comparability will be achieved. Historical water quality data from King County's previous trace metals' sampling program will be compared with data generated from this study to enhance the data set. Previous data may be used since comparable sampling and analytical techniques have been employed and water samples were collected from the same locations and depths.

## 5 STUDY DESIGN FOR NEW MONITORING

The goal of the receiving water characterization study is to collect new water column data for trace metals, pH, cyanide, and alkalinity that will provide Ecology information necessary to perform their “Reasonable Potential” analysis. Both the South and West Point treatment plant permits stipulate that a minimum of 10 receiving water samples will be collected for analysis of trace metals and pH, with the additional analyses of cyanide and alkalinity required under the South treatment plant permit.

The following study design meets the requirements of both permits and, coupled with previous trace metals data collected in Puget Sound, will provide a robust data set that will meet the study goal by allowing spatial and temporal evaluations of trace metals concentrations in receiving water. The previous trace metals data were collected over 15 months in 1999 and 2000 from eight stations in Puget Sound, two of which will be revisited during this receiving water characterization study, sampling the same depths as the previous study.

The four stations shown in Figure 1 will each be sampled four times, with three samples collected from each station during each sampling event. The four sampling events will occur over an 18 month period from December 2010 to July 2012. Each sampling event will be scheduled to meet the timing requirements of both NPDES permits – sampling during the critical period (July and December) for the South treatment plant permit and during a spring tide for the West Point treatment permit.

### 5.1 Station KSBP01

A total of 12 samples will be collected from this station for analysis of total and dissolved arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc. Samples will be collected from three depths – 5, 50, and 200 meters – during each of four sampling events. The four sampling events will be timed to occur during a spring tide in December 2010, July 2011, December 2011, and July 2012. King County previously collected monthly metals data from the same three depths at Station KSBP01 for 15 months during 1999 and 2000. *In situ* measurement of pH will occur in a full water-column profile during each sampling event.

### 5.2 Station LSNT01

A total of 12 samples will be collected from this station for analysis of total and dissolved antimony, arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc. Synoptic samples will be collected for analysis of alkalinity and cyanide complete the requirements of Section S11.7 of the South Treatment Plant permit. Samples will be collected from three depths – 5, 50, and 160 meters – during each of the four sampling events occurring in December 2010, July 2011, December 2011, and July 2012. King County also previously collected monthly metals data from the same three depths at Station LSNT01 for 15 months during 1999 and 2000. *In situ* measurement of pH will occur in a full water-column profile during each sampling event.

### 5.3 Station LTED04

A total of 12 samples from this station will be collected for analysis of total and dissolved arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc. Samples will be collected from three depths – 5, 50, and 75 meters – during each of the four sampling events

occurring in December 2010, July 2011, December 2011, and July 2012. *In situ* measurement of pH will occur in a full water-column profile during each sampling event.

#### **5.4 Station LTXQ01**

A total of 12 samples will be collected from this station for analysis of total and dissolved arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc to meet the requirements of Section S18.I.8 of the West Point permit. Due to both the shallow depth of the river at this station and the resulting sampling method that will be used, samples can only be collected from a single depth – slightly below the surface. To facilitate efficient analytical batching of samples, this station will be sampled on the same schedule as the three marine stations; December 2010, July 2011, December 2011, and July 2012. This will provide two sampling events in both wet and dry seasons. To assess environmental variability, one sample will be collected on each of three successive days during each sampling event, resulting in a total of 12 samples. Given the periodic excursion of the salt wedge into this area, synoptic hardness and salinity data will also be collected, to allow comparison of metals' data with appropriate water quality criteria. Field measurement of pH will be collected synoptically with each sample collected for trace metals analysis.

## 6 SAMPLING PROCEDURES AND FIELD MEASUREMENTS

The representativeness of a data set may be enhanced by following a standard set of protocols and procedures for collecting samples and gathering field data. This section describes field methodologies and protocols for collection of representative water-column samples, as well as the electronic collection of *in situ* field data. Included in this description are the procedures that have been used to collect ongoing ambient water quality data that will be submitted to Ecology as well as the procedures for collecting new data for trace metals, cyanide, alkalinity, and pH.

Three applicable King County Environmental Laboratory Standard Operating Procedures (SOP) have been included as appendices to this SAP/QAPP. *Standard Operating Procedure for the SBE25 SeaLogger CTD (SOP #220v3)* has been included as Appendix A. *Standard Operating Procedure for Clean Sampling for Ultra Low Trace Metals using Modified Niskin Bottles (SOP #221v2)* has been included as Appendix B. *Standard Operating Procedure for Clean Surface Water Sampling for Ultra Low Trace Metals and Organics (SOP #222v2)* has been included as Appendix C.

### 6.1 Sampling Procedures for Existing Data Submission

This section describes the sampling methodologies that King County employs during routine collection of water column samples for its ambient marine monitoring program. Included in the routine monitoring program are the collection of samples for laboratory analysis of total suspended solids and fecal coliform bacteria and *in situ* measurement of dissolved oxygen, salinity, and temperature – the parameters for which King County will be submitting existing data to Ecology.

#### 6.1.1 *In Situ Measurement and Sample Collection Using a CTD*

Water quality constituents that are measured *in situ* at the three offshore marine stations – KSBP01, LSNT01, and LTED04 – employ a conductivity/temperature/depth (CTD) instrument that is deployed from King County’s research vessel *Liberty*.

The SBE 25 SEALOGGER<sup>®</sup> CTD, manufactured by SeaBird Electronics of Bellevue, Washington, is a profiling system for lake, coastal, estuarine, and deep water work. In addition to measuring conductivity, temperature, and depth, the instrument also measures dissolved oxygen, chlorophyll, light intensity (photosynthetically active radiation), and turbidity (optical backscatterance). Direct measurements are also used to calculate the parameters of salinity and density.

The CTD is deployed from the *Liberty* by hydraulic winch. The instrument is allowed to equilibrate to surface conditions for approximately five minutes before data recording begins. The CTD is lowered at a specified descent rate from the surface to approximately five meters above the sea floor (downcast). Data are recorded both on the down cast and during the instrument's return to the surface (upcast). Data are recorded to a datalogger at a frequency of eight hertz or eight recordings per second.

Upon retrieval of the instrument, data are uploaded to a laptop computer from the datalogger prior to the next cast. System software converts parameter data into surface-to-depth plots which are field-reviewed for quality control.

The thermometer, conductivity probe, turbidity probe, light intensity probes, and fluorometer are calibrated, as recommended, on an annual basis by the instrument manufacturer/distributor. The dissolved oxygen probe is calibrated by comparing samples collected and analyzed in the laboratory using Winkler titration methodology. System maintenance and calibration information are kept in instrument logbooks along with cruise-specific notes.

Samples for analysis of total suspended solids and fecal coliform bacteria are collected using Niskin sample bottles deployed on the CTD "rosette." Predetermined sampling depths are programmed into the CTD and the instrument deployed as described in the previous paragraphs. Analytical samples are collected on the upcast of the CTD. Upon retrieval of the CTD, sample aliquots are transferred from the Niskin bottles into sample containers. Total suspended solids samples are collected in 1-liter HPDE bottles and fecal coliform samples are collected in sterile 500-ml polypropylene bottles. Samples are stored in ice-filled coolers until delivery to the laboratory. Field QC samples include collection of replicate samples at the rate of one per 20 analytical samples collected.

### ***6.1.2 Collection of Samples Using Hand-Held Sampling Bottles and Meters***

Due to logistics at sampling station LTXQ01, samples at this location are collected from a bridge over the Duwamish River. Samples are collected from center channel, using a modified, van Dorn-style sampling device deployed on a sampling line from the bridge. Once the sampling device has entered the river, a sharp "tug" on the rope closes the device, capturing a discrete water sample from just below the surface. Upon retrieval of the sampling device, sample aliquots are collected for analysis of bacteria, total suspended solids, nutrients, salinity, and hardness. Another aliquot of sample is placed into a measurement cup, in which field measurements of dissolved oxygen and temperature are collected as soon as possible after sample collection. Field measurement of dissolved oxygen and temperature employs a hand-held, YSI multi-probe field meter.

## **6.2 Sampling Procedures for Acquisition of New Data**

This section describes the collection of samples for analysis of trace metals, hardness, alkalinity, cyanide, and salinity, and the field measurement of pH.

### ***6.2.1 Station Positioning***

A precise method of offshore station positioning is important for studies in which sampling stations are revisited multiple times. The receiving water characterization study will not only assess spatial differences in water column characteristics over the study area but temporal changes at each particular location as well. In order to assess both spatial differences and temporal changes in water column characteristics, the station must be revisited as precisely as possible. Reliable station positioning is crucial to be able to revisit established stations. Inaccuracies in station positioning when conducting water-column sampling in deep water can result from the action of currents and wind on the sampling vessel as well as current forces and viscous drag on the CTD and deployment line.

Station positioning for this study will be accomplished using a Furuno<sup>®</sup> Differential Global Positioning System (DGPS). Prior to the study, prescribed station coordinates (Lat/Lon coordinate system) will be loaded into the shipboard DGPS. During the sampling event, the shipboard navigational system will utilize the differential data transmissions from regional Coast

Guard base stations to automatically correct its GPS satellite data. Previous DGPS usage indicates that an average precision of one to two meters can usually be attained.

### **6.2.2 Trace Metals at Offshore Stations**

Prior to each sampling event, all sampling equipment and containers will be cleaned according to King County Environmental Laboratory SOP #630v1 (King County 2006). The sampling procedures will utilize the "clean hands/dirty hands" technique outlined in EPA Method 1669 (EPA 1995). Before arriving at the initial sampling site, sampling personnel will be designated "clean hands," "dirty hands," and "crane operator." "Clean hands" will handle all operations involving contact with the sample container and transfer of the sample from the sampling device to the sample container. "Dirty hands" is responsible for preparation of the sampling device and for all other activities that do not involve direct contact with the sample. "Crane operator" is responsible for setup and operation of the clean winch system along with backup "dirty hands" responsibilities.

All equipment will be non-metallic and sampling personnel will always wear non-powdered PVC gloves. Prior to the sampling event, a pre-deployment equipment blank will be collected and all sampling equipment will be double-bagged in zippered, plastic bags. Samples will be collected using Niskin-X bottles attached to a synthetic hydroline. A specialized, non-contaminating winch system mounted on the rear deck of the *Liberty* controls the hydroline. The skipper maneuvers the vessel in a manner that allows the hydroline to remain upwind and upcurrent of engine exhaust. The Niskin-X bottles are attached to the hydroline and lowered to the specified sampling depth. A "messenger" is released down the hydroline to trip the bottles. The Niskin-X bottles are then brought up and samples dispensed into sample containers immediately upon coming out of the water and while still attached to the hydroline. Sample containers are then double-bagged and stored in ice-filled coolers until delivery to the King County Environmental Laboratory.

### **6.2.3 Alkalinity and Cyanide Sample Collection at Station LSNT01**

Samples for the analysis of alkalinity and weak acid dissociable cyanide will be collected concurrently with the trace metals samples at Station LSNT01. Samples for both conventional parameters will be collected from the same three depths as the trace metals samples. Sample aliquots for alkalinity analysis will be placed into 500-ml, clear, high-density polyethylene (HDPE) bottles. Sample aliquots for cyanide will be placed into 500-ml, amber, HDPE bottles. Samples for analysis of cyanide will be preserved in the field by adding sodium hydroxide (NaOH) tablets to the sample bottle and measuring the pH with litmus paper until a pH of greater than 12 has been attained. Cyanide sample preservation will occur within 15 minutes of sample collection. All sample containers will be kept in ice-filled coolers until receipt at the King County Environmental Laboratory.

### **6.2.4 Field Measurement of pH at Offshore Stations**

Field measurement of pH will be added to the suite of analytes measured by the CTD, starting in January 2011, and measured for a period of 12 months. Measurement of pH will occur continuously from the surface to deepest depth measured at each station, both on the downcast and upcast of the CTD. Measurements will be averaged over 0.5-m increments for reporting purposes. The sensor used to measure pH will be a SeaBird SBE 18 pressure-balanced, glass-electrode, silver/silver chloride reference pH probe.

**6.2.5 Sample Collection at Station LTXQ01**

Sample collection for trace metals at Station LTXQ01 will also be accomplished following EPA Method 1669. Samples will be collected at this station by lowering a single-use Teflon bailer attached to a clean rope from a bridge above the river. Two sampling staff, designated “clean hands” and “dirty hands” will accomplish all sampling. “Dirty hands” will unpack and deploy the Teflon bailer and retrieve the sample. “Clean hands” will be responsible for filling all sample containers. Samples collected in this method will include total and dissolve trace metals and hardness. An additional aliquot of water will be collected using a modified van Doren-style bottle. The salinity container will be filled from this aliquot as well as field measurement of pH. Field measurement of pH will be performed during each sampling event at this site through the use of a portable single-parameter probe or a multi-parameter such as a Hydrolab®. The single-parameter instrument is a combination electrode with a potentiometric meter and temperature probe, which automatically compensates for temperature. A two-point calibration of the meter will be performed prior to measurement. The buffers used for the two-point calibration will bracket the expected sample values.

**6.3 Sample Containers, Storage Conditions, and Holding Times**

Table 6-1 summarizes the sample containers, sampling holding conditions, and method-specific holding times for samples that will be collected during the new data acquisition effort.

**Table 6-1 Sample Containers, Storage Conditions, and Holding Times**

Analyte	Container	Storage/Preservation	Holding Time
Alkalinity	500-ml CWM HDPE	Refrigerate at 4°C	14 days
Cyanide, weak acid dissociable	500-ml AWM HDPE	Refrigerate at 4°C, NaOH to pH > 12 within 15 minutes	14 days
Salinity	125-ml CNM HPDE	Refrigerate at 4°C	28 days
Hardness	500-ml CNM HPDE	Room temperature, HNO <sub>3</sub> to pH < 2	6 months
Mercury	500-ml Teflon (hot acid-washed)	Room temperature, HCl to pH < 2	90 days
ICP-MS Metals	500-ml CNM HPDE (acid-washed)	Room temperature, HNO <sub>3</sub> to pH < 2	6 months

HDPE – high-density polyethylene

AWM – amber wide mouth

CNM – clear narrow mouth

CWM – clear wide mouth

## 7 LABORATORY ANALYTICAL METHODS

The completeness and comparability of a data set may be enhanced by following a standard set of protocols for analyzing samples. This section describes both the laboratory analytical methods currently in use for data that will be part of the existing data submission as well as those methods that will be used during the acquisition of new data. All laboratory analyses referenced in this section have been performed, or will be performed, by the King County Environmental Laboratory.

Included in the description of the analytical methodologies are the respective detection limits for each analysis. The terms MDL and RDL, used in the following subsections, refer to *method detection limit* and *reporting detection limit*, respectively. The MDL is defined as *the minimum concentration of a chemical constituent that can be detected*, while the RDL is defined as *the minimum concentration of a chemical constituent that can be reliably quantified*.

### 7.1 Summary of Methods for Existing Data Submission

The existing data submission will include three parameters for which laboratory analysis is performed – total suspended solids, fecal coliform bacteria, and salinity. Salinity is generally measured *in situ*, however, at Station LTXQ01 (Duwamish River), samples are collected and analyzed in the laboratory due to field logistics.

#### 7.1.1 Total Suspended Solids

Total suspended solids analysis is performed according to Standard Method (SM) 2540D (APHA 1998), following King County Environmental Laboratory Standard Operating Procedure (SOP) #309v3 (King County 2008). The MDL and RDL for this analysis are 0.5 and 10 mg/L, respectively. For the determination of total suspended solids, a measured volume of a well-mixed water sample is filtered through a 934AH glass fiber filter. The residue retained on the glass fiber filter is dried to a constant weight at 103 to 105°C. The resulting net weight represents the total suspended solids.

#### 7.1.2 Fecal Coliform Bacteria

Fecal coliform analysis is performed according the SM9222D (APHA 1998), following King County Environmental Laboratory SOP #506v1 (King County 2005a) . The MDL for this analysis is 1 colony forming unit per 100 milliliters (CFU/100 ml). Appropriate dilutions, if necessary, are prepared using APHA buffered water as the diluent. The sample and its dilutions are filtered through a sterile 0.45 µm nitrocellulose membrane. The membrane is then applied to an mFC agar plate. After incubation at  $44.5 \pm 0.2^\circ\text{C}$  for  $24 \pm 2$  hours, all colonies with a characteristic blue color are counted. The number of colonies per 100 mL of sample is calculated based on the colonies counted and the dilutions used per plate.

#### 7.1.3 Salinity

Salinity analysis is performed according to SM 2520B (APHA 1998), following King County Environmental Laboratory SOP #316v3 (King County 2002). The MDL and RDL for this analysis is 2.0 and 3.0 PSS (Practical Salinity Scale), respectively. Salinity is determined by measuring the conductance of an electrical current through the sample kept at constant temperature of 25 °C (set at 2°C above mean ambient room temperature) and comparing the

measurement to the conductivity of a standard sea water or reference potassium chloride (KCl) solution. The relative measurement can be displayed as conductivity ratio or Practical Salinity. The control and measurement conversion is performed by a microprocessor from the instrument to calculate salinity corrected for the bath temperature to give the equivalent salinity relative to standard sea water at 15°C.

## **7.2 Summary of Methods for Acquisition of New Data**

The acquisition of new data will include the collection of samples for analysis of both conventional and trace metal parameters. Trace metals samples will be collected from all four stations and the additional conventional samples will be collected from the station representing the South treatment plant.

### **7.2.1 Conventional**

Conventional analyses will include alkalinity and cyanide, which will be performed on the 12 samples collected from Station LSNT01, the station associated with the South Wastewater Treatment Plant outfall.

#### **7.2.1.1 Alkalinity**

As of the date this SAP/QAPP is being submitted to Ecology for review, the King County Environmental Laboratory does not have an in-house method for the analysis of alkalinity in seawater. Laboratory staff are investigating both the development of an in-house method or the possibility of contracting this analysis to an outside laboratory. Staff at Ecology will be kept apprised of the progress throughout the SAP/QAPP approval process.

#### **7.2.1.2 Cyanide**

Cyanide analysis will be performed according to SM 4500CN- I,E (APHA 1998), following King County Environmental Laboratory SOP #321v5 (King County 2005b). The MDL and RDL for this analysis are 0.005 and 0.010 mg/L, respectively.

This method is for determination of weak acid dissociable cyanide. The cyanide, as hydrogen cyanide (HCN) is released from cyanide complexes by means of a reflux-distillation using a weak acid (pH ~ 4.5) in the presence of a zinc acetate buffer. Simple and weak metal-cyano-complexes are recovered, while stronger complexes are not. The HCN is absorbed in a scrubber containing a sodium hydroxide solution. The cyanide in the scrubbing solution is determined colorimetrically. In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by the reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed by the addition of pyridine-barbituric acid reagent and the absorbance is read at 570nm using a standard 6 mm flow cell.

### **7.2.2 Trace Metals**

Analysis of trace metals will be performed on 48 samples, collected from Stations KSBP01, LSNT01, LTED04, and LTXQ01. The samples collected from Stations KSBP01, LTED04, and LTXQ01 will be analyzed for arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc. The samples collected from Station LSNT01 will be analyzed for those nine metals plus antimony. The 12 samples collected from Station LTXQ01, located in the Duwamish River, will also be analyzed for hardness.

### 7.2.2.1 Total and Dissolved Mercury

Total and dissolved mercury analysis will be performed according to EPA Method 1631E (EPA 2002), following King County Environmental Laboratory SOP #605v0 and #606v0 (King County 2003a,b). The MDL and RDL for this analysis are 0.2 and 0.5 nanograms per liter (ng/L), respectively.

- Mercury (Hg) Sample Preparation – A representative aliquot of sample is digested at room temperature for 12 hours with bromine monochloride in order to convert the organic and complex forms of mercury to the mercuric ion.
- Mercury Analysis – The sample is reduced with tin (stannous) chloride ( $\text{SnCl}_2$ ) to convert Hg(II) to volatile Hg(0). The Hg(0) is separated from solution by purging the sample with nitrogen and driving the Hg(0) onto a gold trap. The trapped mercury is thermally desorbed from the gold trap into an inert gas stream that carries the released Hg(0) into the cell of a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection. The sample is analyzed by purge and trap dual amalgamation Automated Cold Vapor Atomic Fluorescence Spectrometry using a Tekran 2600 flow-injection mercury analyzer equipped with a Model 2620 auto-sampler

### 7.2.2.2 Total and Dissolved Metals by ICP-MS

Analysis of total and dissolved metals will be performed according to EPA Method 1640 modified (EPA 1997), following King County Environmental Laboratory SOP #643v1 (King County 2010). The MDL and RDL for this study's target metals are shown Table 7-1.

**Table 7-1 Trace Metals Detection Limits**

<b>Metal</b>	<b>MDL (<math>\mu\text{g/L}</math>)</b>	<b>RDL (<math>\mu\text{g/L}</math>)</b>
Antimony	0.3	1.0
Arsenic	0.1	0.5
Cadmium	0.05	0.25
Chromium	0.2	1.0
Copper	0.4	2.0
Lead	0.1	0.5
Nickel	0.1	0.5
Silver	0.04	0.2
Zinc	0.5	2.5

- Metals Sample Preparation – Marine water samples for total metals analysis are preserved to a pH of <2 by acidification with ultrapure nitric acid. Dissolved metals samples are also preserved to a pH of <2 by the same method after being filtered through a 0.45  $\mu\text{m}$  capsule filter within 15 minutes of sample collection. Due to the inherent matrix interference of seawater on trace metals' analysis, both the total recoverable and dissolved samples will undergo reductive precipitation and preconcentration steps prior to analysis, according to American Society for Testing and Materials (ASTM) Method D6800 (ASTM 2002).
- Metals Analysis – Samples will be analyzed by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) according to EPA Method 200.8r5.4 (EPA 1994a). Aqueous samples are nebulized into a spray chamber where a stream of argon carries the sample

aerosol through a quartz torch and injects it into a plasma, where the sample is decomposed and desolvated. The ions produced are entrained in the plasma gas and by means of a water cooled, differentially pumped interface, introduced into a high-vacuum chamber that houses a quadrupole mass spectrometer. The ions are sorted according to their mass-to-charge ratio and measured with a detector.

#### 7.2.2.3 Hardness by ICP

Analysis of hardness will be performed according to SM 2340B (APHA 1998), which is a calculation based upon separately determined calcium and magnesium concentrations. Calcium and magnesium will be analyzed according to EPA Method 200.7r4.4 (EPA 1994b), following King County Environmental Laboratory SOP #612v4 (King County 2007). This method involves the simultaneous determination of multiple elements by inductively coupled plasma atomic emission spectroscopy (ICP).

## 8 PROJECT QUALITY CONTROL

This section presents field and laboratory quality control (QC) measures that will be employed to ensure data are of sufficient quality to meet the project DQOs.

### 8.1 Field Quality Control

Field QC samples are collected to assess any bias that may be introduced to an environmental sample through sampling and sample handling techniques, as well as environmental variability at a sampling location. Field QC samples will include atmosphere blanks, bottle blanks, field filtration blanks, field blanks, Niskin blanks, and field replicates.

#### 8.1.1 Atmosphere Blank

An atmosphere blank is a sample of reagent water in a laboratory-supplied container, which is left uncapped during sampling for the same amount of time that the environmental sample is exposed to the atmosphere. Analysis of atmosphere blanks is used to measure possible contamination imparted to samples from airborne sources. Atmosphere blanks are analyzed for trace metals and will be collected at the rate of one per sampling location during each sampling event.

#### 8.1.2 Bottle Blank

A bottle blank is a sample container taken from the same set used for a sampling event. The sample container is filled in the laboratory with reagent water and sent into the field with the other sample containers. Analysis of bottle blanks is used to measure and document any sample contamination that may be imparted to the samples from the sampling containers themselves. Bottle blanks are analyzed for trace metals and will be collected at the rate of one per sampling event.

#### 8.1.3 Field Blank

A field blank is a sample of reagent water supplied by the laboratory, which is transported to the field and treated as a sample in all respects – including contact with a sampling device and/or field filtration processes. Analysis of field blanks is used to measure and document any sample contamination resulting from sample handling, transport, exposure to the atmosphere or contact the sampling device(s) at the sampling location. Field blanks will be analyzed for trace metals and will be collected at the rate of one per sampling event.

#### 8.1.4 Niskin Blank

A Niskin blank is a sample of reagent water that has been used to rinse one of the Niskin bottles in the laboratory after prescribed decontamination. Analysis of the Niskin blank is used to measure and document the possible contamination of an environmental sample by the sampling equipment and to document the effectiveness of the decontamination procedure in the laboratory. An acceptable Niskin blank should be achieved before the sampling devices are deployed. Niskin blanks will be analyzed for trace metals and will be collected at the rate of one per sampling event.

### ***8.1.5 Field Replicate***

A field replicate sample consists of a second sample collected at a sampling location using the exact collection methodology that was used to obtain the first sample. The field replicate is collected at the same sampling location and as soon after the original sample as possible. The field replicate sample is generally analyzed for all the analytes for which the sample was analyzed. Analysis of the field replicate sample is used to measure and document the precision of field sampling methodologies and the environmental variability at the sample site. Field replicates will be collected at the rate of two per sampling event and will be analyzed for trace metals, alkalinity, cyanide, hardness, and salinity.

## **8.2 Laboratory Quality Control**

Laboratory QC will include the analysis of several types of QC samples that measure accuracy, precision, and bias. Laboratory QC samples will be analyzed at the rate of one per analytical batch or every 20 samples, whichever is less. Measurement of cyanide will include analysis of method blanks, spike blanks, matrix spikes, laboratory control samples, and laboratory duplicates. Measurement of alkalinity and salinity will include analysis of laboratory control samples and laboratory duplicates. Measurement of trace metals will include analysis of method blanks, spike blanks, matrix spikes, matrix spike duplicates, and laboratory duplicates. A short description of these types of laboratory QC samples is provided in the following sections.

### ***8.2.1 Method Blank***

A method blank is an aliquot of reagent water that is processed through the entire analytical procedure. Analysis of the method blank is used to evaluate the levels of contamination that might be associated with the processing and analysis of samples and any introduced bias to sample results. All method blank results should be less than the method detection limit.

### ***8.2.2 Spike Blank***

A spike blank is a second aliquot of reagent water, to which a known concentration of target analyte(s) has been added. The spiked aliquot is processed through the entire analytical procedure. Analysis of the spike blank is used as an indicator of method accuracy. The King County Environmental Laboratory has empirically-derived control limits for the percent recovery of spike blank analytes. Spike blank results should be within these control limits.

### ***8.2.3 Matrix Spike***

A matrix spike is a second aliquot of an analytical sample fortified with a known concentration of target analyte(s). The spiked sample is processed through the entire analytical procedure. Analysis of the matrix spike is used as an indicator of sample matrix effect on the recovery of target analyte(s) and any introduced bias, as a result. Both method-specified and empirically-derived control limits for the percent recovery of matrix spike analytes are used, depending on the analysis. Matrix spike results should be within these control limits.

### ***8.2.4 Matrix Spike Duplicate***

A matrix spike duplicate is a third sample aliquot fortified with a known concentration of a target analyte(s). The spiked sample is processed through the entire analytical procedure. Analysis of the matrix spike duplicate is used as an additional indicator of sample matrix effect on the recovery of target analyte(s) as well as an indicator of method precision. The relative percent

difference (RPD) between matrix spike and matrix spike duplicate results uses both method-specified and empirically-derived control limits, depending on the analysis. Both the matrix spike duplicate recovery and RPD between matrix spike and matrix spike duplicate results should be within these control limits.

### 8.2.5 Laboratory Control Sample

A laboratory control sample is a sample of known analyte concentration(s) that is prepared in the lab from a separate source of analyte(s) relative to the calibration standards. Since the laboratory control sample analysis should follow the entire analytical process, it should be stored and prepared following the same procedures as a field sample. Analysis of a laboratory control sample is used as an indicator of method accuracy and long-term analytical precision. Both method-specified and empirically-derived control limits for the percent recovery of laboratory control samples are used, depending on the analysis. Laboratory control sample results should be within these control limits.

### 8.2.6 Laboratory Duplicate

A laboratory duplicate is a second aliquot of an analytical sample, processed concurrently and in an identical manner with the original sample. Analysis of the laboratory duplicate is used as an indicator of method precision and laboratory subsampling procedures. The laboratory duplicate can also be used to provide information regarding the homogeneity of the sample matrix. The relative percent difference (RPD) between sample and laboratory duplicate results uses both method-specified and empirically-derived control limits, depending on the analysis. Laboratory duplicate results should be within these control limits.

### 8.2.7 Laboratory QC Sample Control Limits

Tables 8-1 and 8-2 provide the types of laboratory QC samples that will be analyzed for each type of analysis, along with the respective control limits.

**Table 8-1 Conventional QC Samples and Control Limits**

Analysis	Method Blank Result	Spike Blank Recovery	Matrix Spike Recovery	LCS Recovery	Lab Dup. RPD
Alkalinity	--	--	--	(reserved)	(reserved)
Cyanide	<MDL	80 – 120%	70 – 130%	73 – 127%	25%
Salinity	--	--	--	99.8 – 100.2%	0.05%

**Table 8-2 Trace Metals QC Samples and Control Limits**

Analysis	Method Blank Result	Spike Blank Recovery	Matrix Spike Recovery	MS/MSD RPD	Lab Dup. RPD
Mercury	<MDL	77 – 123%	71 – 125%	24%	--
Antimony	<MDL	85 – 115%	75 – 125%	20%	--
Arsenic	<MDL	58 – 110%	58 – 110%	20%	--
Cadmium	<MDL	64 – 105%	64 – 105%	20%	--
Chromium	<MDL	85 – 115%	75 – 125%	20%	--
Copper	<MDL	77 – 109%	75 – 125%	20%	--
Lead	<MDL	62 – 129%	62 – 129%	20%	--
Nickel	<MDL	26 – 147%	26 – 147%	20%	--
Silver	<MDL	30 – 151%	30 – 151%	20%	--
Zinc	<MDL	75 – 95%	75 – 125%	20%	--
Hardness by ICP	<MDL	85 – 115%	75 – 125%	--	20%

## 9 DATA VERIFICATION AND VALIDATION

Data verification and validation are critical in the evaluation of how well analytical and field data meet project DQOs. Data verification is performed, at some level, during several steps in the process of sample collection and analysis.

All laboratory analytical data and field measurements are entered into King County's Laboratory Information Management System (LIMS). Field data, such as *in situ* data measurements or recorded environmental observations, are peer reviewed prior to entry into LIMS. Laboratory analytical data are reviewed, first by the primary analyst and then by a senior peer reviewer, prior to entry of the data into LIMS. Analytical data are reviewed for completeness and QC sample data are viewed for compliance with project and method QA/QC requirements. If there are any QC failures at this point, corrective action may be taken or qualifier flags applied to the data.

The laboratory project manager (LPM) for the receiving water characterization study will provide the next data review step, at a "per-sampling-event" level. The LPM will verify the completeness of the data set and report any QA/QC failures or anomalies. Upon completion of all sampling and analysis, the project manager (study lead) will provide a final data validation process of all data to ensure that they meet the project DQOs. Data then will be reported in a variety of formats.

All laboratory analytical data and *in situ* field measurements are maintained *in perpetuity* on LIMS. Laboratory analytical data may be stored with data qualifier flags indicating QC failures. The flag "B" is used to indicate possible laboratory contamination of a sample and is applied when the parameter of interest is also detected in the laboratory method blank. Sample results that are less than five times the concentration detected in the method blank will be qualified with a "B" flag. The flag "J" is used to indicate that the sample result is an estimate (with unknown bias) due to one or more QC failures. A "JL" flag indicates possible high-biased data and a "JG" flag indicates possible low-biased data. A "JK" flag indicates unknown bias. The flag "H" is used to indicate an analytical holding time exceedence. The "SH" flag indicates that one or more sampling criteria/conditions were not met. Handling conditions may include an improper sample container or improper preservation of the sample.

Collection of CTD data at a rate of eight readings per second generates a very large data set for each sampling event and precludes inclusion of these data on LIMS. Some CTD data that have been averaged at discrete depths will be maintained on LIMS, however, the major portion of these data will be maintained in a separate web-accessible database.

Hard copy field notes, field instrument calibration records, raw analytical data, and any other hard copy project information will be stored according to standard King County Environmental Laboratory practices for a period of ten years.

## 10 DATA REPORTING

A final study report will be prepared and submitted to Ecology no later than June 30, 2013. The report will include the following elements:

- A study narrative. The narrative will include:
  1. A summary of sampling and analytical methodologies.
  2. Maps of sampling locations.
  3. An assessment of overall data quality.
  4. Summary tables of both existing data and new data generated during the study.
- Appendices that will provide complete hard-copy data reports for both existing data and new generated during the study.
- Appendices of data validation memoranda. Project data will be validated following guidance provided in *USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review* (EPA 2004).

All data will also be submitted at that time in electronic format, which will be compatible with Ecology's EIM database.

## 11 REFERENCES

- APHA 1998. *Standard Methods for the Examination of Water and Wastewater, 20<sup>th</sup> Edition*. American Public Health Association. Washington, D.C.
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## **APPENDIX A**

**Standard Operating Procedure for the SBE25 SeaLogger CTD**

**King County Environmental Laboratory SOP #220v3**

STANDARD OPERATING PROCEDURE

for

SBE 25 SEALOGGER CTD

SOP # 220v3

Date of Implementation: February 28, 2005

Supersedes SOP: 02-02-011-002

Approved by:

Author: \_\_\_\_\_ Date: \_\_\_\_\_

Supervisor: \_\_\_\_\_ Date: \_\_\_\_\_

QA Officer: \_\_\_\_\_ Date: \_\_\_\_\_

King County Environmental Laboratory  
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## 1.0 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the use of the Seabird SBE 25 CTD and LI-COR LI-1400 DataLogger, including maintenance, calibration, routine use, sample collection, quality control, instrument programming, data upload, reporting and review. This SOP applies to attended field operations. Two CTD configurations are possible; one using the CTD independently and the second incorporating the AFM (Auto-Fire Module) to simultaneously collect water quality samples. The CTD instrument and calibration is optimized for marine work but can be utilized in fresh water for physical water sample collection. Fresh water analysis using CTD sensors is not recommended for two reasons: (1) the conductivity probe is calibrated for high salinity water bodies and does not have the dynamic range to accurately measure fresh water conductivity levels and (2) the instrument is designed to move quickly through the water column which is not conducive for accurately measuring extreme thermoclines that often occur in fresh water bodies such as Lake Washington.

## 2.0 ASSOCIATED DOCUMENTS AND SOPS

- 2.1 KCEL Sampling Methods for Marine Water Column: 02-02-002-003
- 2.2 KCEL Sampling Methods for Water Column of Lakes: 02-02-003-001
- 2.3 KCEL C-14 Study Nutrient and Chlorophyll Sampling: 02-02-010-001
- 2.4 KCEL CTD File Handling Protocol (see appendix at the end of this SOP)
- 2.5 KCEL Oxygen, Dissolved -- Winkler Titration, Azide Modification : 03-03-007-002

## 3.0 METHOD SUMMARY

The *SBE 25 SEALOGGER CTD* (referred to as CTD) is a profiling system for lake, coastal, estuarine, and deep water work. In addition to monitoring conductivity, temperature, pressure, derived salinity, density, dissolved oxygen, chlorophyll, light intensity (PAR) and light transmission, the CTD also utilizes a carousel (rosette) of sample bottles capable of collecting up to 12-five liter samples. Additional sensors can be added to analyze more or different parameters. Individual probes for the parameters to be monitored are calibrated annually at the factory or, in the case of dissolved oxygen and light transmission, monthly based on laboratory Winkler dissolved oxygen results and transmissometer calibration. The LI-1400 DataLogger is a simple data collection instrument with a remote radiation sensor attached. For both instruments, data is collected electronically and uploaded to a PC. Sample data are downloaded to LIMS. Daily logbooks are kept, along with calibration and system maintenance records.

## 4.0 DEFINITIONS

- 4.1 Conductivity, Temperature, Depth Profiler (CTD): An instrument capable of profiling conductivity, temperature, and depth (pressure) throughout a water column.
- 4.2 Auto-Fire Module (AFM): The AFM allows Carousel operation without a conducting sea-cable by firing bottles at user programmed time intervals, or when used with SBE 25 CTDs, the AFM monitors CTD pressure data and fires bottles at user-programmed depths. The AFM also records bottle number, firing confirmation, and 5 scans of CTD data for each bottle fired.
- 4.3 Fluorometer: Optical instrument used for the detection of chlorophyll and other pigments that fluoresce in the selected wavelength range.
- 4.4 Light Intensity (see PAR): Measurement of solar energy in units of  $\mu\text{mol s}^{-1} \text{m}^{-2}$ .
- 4.5 PAR: Photosynthetically Active Radiation
- 4.6 Dissolved Oxygen (DO): The concentration of oxygen dissolved in water, expressed in mg/l or as percent saturation, where saturation is the maximum amount of oxygen that can theoretically be dissolved in water at a given altitude and temperature.
- 4.7 Temperature/Conductivity (TC) Duct: Plastic duct through which an exact amount of water is pumped at a constant rate in order to produce a consistent time delay between the temperature and conductivity sensors. This time delay can then be corrected when calculating water column parameters.
- 4.8 Bottle Data: The .afm file stores the exact time each bottle is tripped. Using the Seabird Data Processing Software, CTD data can be related and compared directly to the physical water collected.

- 4.9 RO Water: Reverse osmosis water (de-ionized water).
- 4.10 Nickel-Cadmium (Nicad) Battery: 12 volts at maximum charge; CTD shuts down at 7.4 volts. Alkaline Battery: 13.5 volts fresh.
- 4.11 Transmissometer: An instrument used in the measurement of light transmission through water in units of % transmission.
- 4.12 Density is calculated from *in situ* measurements of pressure, temperature, and conductivity using the equation of state for sea water. The units are defined as kg/m<sup>3</sup>. (description and units)
- 4.13 Chlorophyll: The WETStar miniature fluorometer allows the user to measure relative chlorophyll by directly measuring the amount of fluorescence emission from a given sample of water. Specifically, it measures the fluorescence of chlorophyll-containing phytoplankton, which absorb light of wavelengths between 400 and 520 nm and emit light between 670 and 730 nm. The instrument is calibrated at the factory on an annual basis.

## 5.0 SAFETY AND HAZARDOUS MATERIALS MANAGEMENT

All sampling personnel will follow standard safety procedures while on board the sampling vessel. The vessel skipper has ultimate responsibility for safety while the vessel is underway. During deployment and retrieval of the CTD, the boom operator takes responsibility for safety on the back deck of the vessel. Sampling personnel are required to wear steel-toed footwear during deployment and retrieval of the CTD.

No hazardous materials are associated with this method of sample collection and *in-situ* analysis except for **Alkali-Iodide-Azide (AIA)**- AIA is a poisonous and caustic liquid reagent used for Winkler dissolved oxygen fixation. Contact with skin must be avoided. AIA must be stored in a well ventilated, dry, and cool area. Working reagents will be stored in a re-pipet dispenser. Always wear gloves and safety glasses when working with AIA.

## 6.0 SAMPLE CONTAINERS, PRESERVATION AND STORAGE

See appropriate method SOPs if water quality samples are to be collected and analyzed.

## 7.0 APPARATUS, EQUIPMENT, AND CONSUMABLES

- 7.1 Seabird SBE 25 Sealogger CTD
- 7.2 Seabird SBE 32 Carousel Water Sampler
- 7.3 Seabird Auto-Fire Module
- 7.4 Seabird SBE 29 Pressure Sensor
- 7.5 Seabird SBE 3 Temperature Sensor
- 7.6 Seabird SBE 4 Conductivity Sensor
- 7.7 Seabird SBE 5T Pump
- 7.8 Seabird SBE 43 Dissolved Oxygen Sensor
- 7.9 WETlabs WETStar Chlorophyll Fluorometer
- 7.10 WETlabs Seastar Transmissometer
- 7.11 LI-COR Light Intensity (PAR), LI-193-SA
- 7.12 LI-COR Surface Light Intensity (PAR), LI-190-SA-50
- 7.13 LI-COR LI-1400 Data Logger
- 7.14 Laptop computer with Microsoft Windows
- 7.15 Seabird SeaTermAF, Seasave-Win32, and SBE Data Processing-Win32 software
- 7.16 Replacement Ni-Cad Battery (PN 80256)
- 7.17 Deck crane with meter wheel
- 7.18 100 ml syringe with tube

## 8.0 PROCEDURE

### 8.1 CTD with AFM and Rosette

#### 8.1.1 Prior to the first cast of the Day

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Disconnect the dummy plug on the AFM bulkhead connector and insert the 10 meter four pin data I/O cable (801616). Connect the opposite end of the I/O cable to the 9 pin serial port on the PC. In Windows, open SeaTermAF Click on the Connect CTD Button. An S> prompt should appear. Note the connection is using a baud rate of 4800.Type st and press Enter. This will prompt you for the correct time. Type in the time using the following format; e.g. 134325 is 1:34:25 pm. Press Enter and type the date; e.g. 091006 is September 10, 2006. Press Enter. Click on the Status button. The important things to look for are the vmain (the nicad battery stops working below 7.4 volts), the vlith (this should be >5 and can be replaced only by the factory), the minimum frequency for pump turn on (3500 for salt water, 2000 for fresh water), and the correct time and date. If the main battery voltage is low, replace with either a freshly charged nicad battery or new alkaline batteries (use cc if changing battery types). If the minimum frequency for pump turn on is incorrect, use the cc command to adjust to the correct setting. The date and time should be calibrated between the AFM, CTD, and Li-Cor based on the atomic clock in the calibration room. Each of the instruments should be within one second. Switch to the AFM by clicking on the Connect AFM button. Type st as above to correct the AFM time.

### 8.1.2 Programming CTD

In Sea-TermAF, click on the Connect CTD button. If the minimum frequency to turn pump on is incorrect, adjust it according to 8.1.1. At the S> prompt, type il to initialize logging. Click on the Init Log button. This changes the ncast to 0 and prepares the instrument for the upcoming cast. Wait for about 5 seconds until a message box confirms the CTD is ready to go. . .

### 8.1.3 Programming AFM

Click on Connect AFM and the A> prompt should appear. Click on the Configure Menu and then AFM with SBE 25. Make sure the current CTD instrument configuration (.con) file is being used. Monthly, a new configuration file is created following calibration. Real time baud rate is always 4800 and radio button is either on **Close on upcast** or **Close on elapsed time, record CTD Data**. Use the latter setting only for very shallow stations that require multiple bottles tripped at the same depth.

#### 8.1.3.1 Close on Upcast

8.1.3.1.1 Option one is to close the first bottle at the bottom of the cast after it has been sitting stationary for one minute. Check the **Bottom bottle closure enabled** box, set **Pressure to Enable Upcast** to 0.5xdepth. Pressure Change to Enable upcast is 2, Stationary time on Bottom is 1 minute and Bottom Pressure Window is 3. Click on the Bottle Closure Pressures/Times tab and select the Number of Bottles to Close and type the closure pressures.

8.1.3.1.2 Option two is to close the bottom bottle with no wait at the end of the downcast. Uncheck the Bottom bottle closure enabled box, set Pressure to Enable Upcast to (0.5 x depth). Pressure Change to Enable upcast is 2. Click on the Bottle Closure Pressures/Times tab and select the Number of Bottles to Close and type the closure pressures.

#### 8.1.3.2 Close on Elapsed Time

Set the Number of bottles using the drop down box, then Bottle Closure Times to allow for time to deploy the CTD and become stationary for each bottle/depth. For very shallow sampling, allow for 3 minutes of CTD equilibration and one minute of casting prior to the first sample. Samples only need to be separated by 0.1 minutes if conducting freps or multiple bottles at one depth. Note that if you use this method, the elapsed time begins when you click the Arm button!

Click on the OK button. Click on the Program Button. Be patient-this takes about 20 seconds to complete. Click on the Arm Button.

### 8.1.4 Deployment

Cock all bottles on the carousel, tighten all air valves and close each Niskin's spigot. Communicate with the vessel's skipper to determine if deployment is OK. Detach the computer cable from the AFM and attach the dummy plug. Make sure the connection is good and that all air has been "burped out". See section 13 for info on rinsing the TC Duct. Tighten the plastic fitting. Remove the rinsing syringe and slowly slide the CTD on/off switch to the on position. Using the deck crane and a swivel shackle, lift the unit out of the vessel and place in the water so the top of the CTD package is slightly under water.. Adjust the meter wheel. Make sure the elapsed time between switching the unit on and placing it in the water is less than two minutes. After a total of five minutes from the time the switch was

turned on, begin the descent at 0.5 meters per second for the first 20 meters and then 1.5 meters per second below that. (slower rates will produce better data). If necessary, Stop the descent at the proper depth and wait for the period indicated in the Time to Hold Stationary at Bottom setting, otherwise instantly begin the upcast after the proper depth has been achieved. On the upcast, ascend at 1.5 meters per second until the top 20 meters where you slow down to less than 0.5 m/s. Once the CTD is in sight, inform the skipper and place the CTD on the deck. Immediately turn the on/off switch to off and rinse the TC duct, temperature probe, conductivity cell, DO probe, fluorometer and transmissometer with 10-100 mL of RO water.

**8.1.5 Filling Sample Bottles**

Following the CTD retrieval, water collected in each Niskin bottle is to be transferred to individual sample bottles as soon as possible. The order of bottle filling should be described in each Sampling and Analysis Plan or Sampling Procedure SOP. Prior to the next cast, the bottles must be cocked and the air vents and spouts closed.

**8.1.6 Data Upload**

Remove the dummy plug on the AFM bulkhead connector and connect the 10-meter four-pin data I/O cable with the blue label. In the SeaTermAF software, click on the Connect CTD button. Click on the status button to verify there is only one cast. If it is greater than 1, note that value minus one for the cast number and record this in the log book. Click on the Upload button. Note the ncasts value. It should be 1. If not, use that value minus one for the cast number. Type in the cast number (usually 0) and press OK. A header prompt will occur and the following information must be entered:

Ship:

Project:

Station:

Operator:

Comments: - leave this field blank under all circumstances.

Click on OK and a Save As box will display. Enter the cast ID and select the proper directory for the file. Click Save and the file will download. Following the hex file download, click on the Connect AFM button. Click on OK. Click on the Upload button and fill in the header information (again). Click on OK and a Save As box will display. Enter the cast ID (same as hex file name) and select the proper directory for the file. Click Save and the file will download.

**8.1.7 Data Evaluation**

After each cast, two evaluations are to be completed; a display of the sensors to evaluate data quality and sample bottle depth data should be checked before moving on to a new cast site.

8.1.7.1 Reviewing the Cast Profile

Open the program entitled "Seasave-Win32". Click on Screen Display and Edit Selected Display Window. Click on Select Display (.DSO) File and select the proper file (salt.dso or fresh.dso). Click on OK.

Click on Modify Display Parameters and enter the proper maximum depth and modify any other parameters that may be appropriate. Click on OK but don't save the settings since they will remain the same until you close the program.

Click on Archived Data and No Wait. Click on Archived Data and Start. Select the appropriate data (.dat) and instrument configuration (.con) files. Click on the green Start Display button. The cast should be displayed and the operator can evaluate the data quality based on the results. This evaluation is based on experience and an understanding of historical data. The operator should look for signs of instrument anomalies such as spikes, drifts, unexpected noise and significant differences between the downcast and upcast. Also, operators should be familiar with the symptoms of a plugged air vent, hitting the bottom and plugging the TC duct and when a hose becomes detached, stopping the controlled flow of water past the sensors. If any of these problems should be identified, the cast should be discarded and done over.

8.1.7.2 Sample Bottle Depth Data Processing

After the upload, please follow these steps to determine if the Niskins tripped at the proper depth:

On the desktop in Windows, open SBE Data Processing-Win32. Under Run, open Data Conversion. Open the Program setup file DatCnv.psa Select the proper configuration file. Select the input file (the cast that was just previously uploaded with the .hex extension). The output directory should be the

same as the input directory. Output file should be the same as the input files, but without an extension. Click on Start Process. Following processing, click Cancel.

Open Bottle Summary. Open the Program setup file BottleSum.psa. Select the input file (the .ros file that was created during Data Conversion). Make sure the output directory is the same as the input directory. Name append should be blank. The Output file should be the same as the input files, but with a .bt1 extension. Click on Start Process and once the program has completed, click on Exit. Close SBE Data Processing.

Open Microsoft Excel and open the appropriate .bt1 file that was just created. Click Next. Select Space Delimiters (Tab is already selected). Click on finish, then scroll down and look at cell F49, F53, F57, F61, F65, F69, F73, etc to compare the actual sampled depth to the target depth. See section 9.6 for acceptance criteria. Corrective action would include qualifying data in LIMS and filling out a Data Anomaly Form. The DAF is electronically entered into LIMS.

### **8.1.8 Data Reduction**

See section 10.1

## **8.2 CTD without AFM**

### **8.2.1 Prior to the first cast of the Day**

Remove the dummy plug on the AFM bulkhead connector and connect the 10 meter four pin data I/O cable (801616). Connect the opposite end of the I/O cable to the 9 pin serial port on the PC. In Windows, open Open TermAF Click on the Connect CTD Button. An S> prompt should appear. Note the connection is using a baud rate of 4800. Type st and press Enter. This will prompt you for the correct time. Type in the time using the following format; e.g. 134325 is 1:34:25 pm. Press Enter and type the date; e.g. 091006 is September 10, 2006. Press Enter. Click on the Status button. The important things to look for are the vmain (the nicad battery stops working below 7.4 volts), the vlith (this should be >5 and can be replaced only by the factory), the minimum frequency for pump turn on (3500 for salt water, 2000 for fresh water), and the correct time and date. If the main battery voltage is low, replace with either a freshly charged nicad battery or new alkaline batteries (use cc if changing battery types). If the minimum frequency for pump turn on is incorrect, use the cc command to adjust to the correct setting).

### **8.2.2 Programming CTD**

In TermAF, click on the Connect CTD button. If the minimum frequency to turn pump on is incorrect, adjust it according to 8.2.1. At the S> prompt, type il to initialize logging. Click on the Init Log button. This changes the ncast to 0 and prepares the instrument for the upcoming cast. Wait for about 5 seconds until a message box confirms the CTD is ready to go. . .

### **8.2.3 Deployment**

Communicate with the vessel's skipper to determine if deployment is OK. Detach the computer cable from the CTD and attach the dummy plug. Make sure the connection is good and that all air has been "burped out". Tighten the plastic fitting. Remove the rinsing syringe and slowly slide the CTD on/off switch to the on position. Using the deck crane and a swivel shackle, lift the unit out of the vessel and place in the water so the top of the CTD package is slightly under water.. Adjust the meter wheel. Make sure the elapsed time between switching the unit on and placing it in the water is less than two minutes. After a total of five minutes from the time the switch was turned on, begin the descent at 0.5 meters per second for the first 20 meters and then 1.5 meters per second below that. (slower rates will produce better data). If necessary, Stop the descent at the proper depth and wait for the period indicated in the Time to Hold Stationary at Bottom setting, otherwise instantly begin the upcast after the proper depth has been achieved. On the upcast, ascend at 1.5 meters per second until the top 20 meters where you slow down to less than 0.5 m/s. .Once the CTD is in sight, inform the skipper and place the CTD on the deck. Immediately turn the on/off switch to off and rinse the TC duct, temperature probe, conductivity cell, DO probe, fluorometer and transmissometer with RO water.

### **8.2.4 Data Upload**

Remove the dummy plug on the CTD bulkhead connector and connect the 10-meter four-pin data I/O cable with the blue label. In the SeaTermAF software, click on the Connect CTD button. Click on the status button to verify there is only one cast. If it is greater than 1, note that value minus one for the

cast number and record this in the log book. Click on the Upload button. Note the ncasts value. It should be 1. If not, use that value minus one for the cast number. Type in the cast number (usually 0) and press OK. A header prompt will occur and the following information must be entered:

Ship:

Project:

Station:

Operator:

Comments: - leave this field blank under all circumstances.

Click on OK and a Save As box will display. Enter the cast ID and select the proper directory for the file. Click Save and the file will download.

### **8.2.5 Reviewing the Cast Profile**

Open the program entitled "Seasave-Win32". Click on Screen Display and Edit Selected Display Window. Click on Select Display (.DSO) File and select the proper file (salt.dso or fresh.dso). Click on OK.

Click on Modify Display Parameters and enter the proper maximum depth and modify any other parameters that may be appropriate. Click on OK but don't save the settings since they will remain the same until you close the program.

Click on Archived Data and No Wait. Click on Archived Data and Start. Select the appropriate data (.dat) and instrument configuration (.con) files. Click on the green Start Display button. The cast should be displayed and the operator can evaluate the data quality based on the results. This evaluation is based on experience and an understanding of historical data. The operator should look for signs of instrument anomalies such as spikes, drifts, unexpected noise and significant differences between the downcast and upcast. Also, operators should be familiar with the symptoms of a plugged air vent, hitting the bottom and plugging the TC duct and when a hose becomes detached, stopping the controlled flow of water past the sensors. If any of these problems should be identified, the cast should be discarded and done over..

### **8.2.6 Data Reduction**

See section 10.1

## **8.3 DataLogger (Surface Light Intensity)**

### **8.3.1 Preparation for Deployment: Programming the LI-1400**

Connect the sensor to the BNC setting I1. Press the On/Off button. Press the Fct button. Arrow to the right until Clear Memory appears. Press Enter. Arrow down until the display reads !Clear Mem ?NO!. Arrow right and the NO will change to YES. Press Enter and the memory will clear.

Press the Setup button and the arrow right button until SETUP LOGGING is on the screen. Press Enter. Arrow down until the cursor is on LR1. Press Enter. Type in the start time in military time and press Enter. Arrow down and type the Stop Time. Press Enter. Arrow down and type in the Smpl Per= and arrow to the right or left to choose different sampling times. Currently we are using 1 second. Arrow down to Log Per= and arrow to the right or left to choose different logging times. We are currently using 30 seconds. Press Esc. Arrow up until the cursor is under Logging=Off. Press the right arrow button for Logging=On. Monitor the new data by pressing the View button and arrowing to the right or left to choose VIEW NEW DATA. Press Enter and current Light Intensity data will appear on the screen. If sampling for more than 15 minutes, the display will turn off automatically, but logging will continue until the sampling period is over. The instrument uses an AC adapter and four alkaline "AA" batteries with a life of approximately 50 hours for backup.

### **8.3.2 Licor Data Upload**

The LI-1400 utilizes a Microsoft Windows software package. Connect the LI-1400's RS-232 port to the PC's COM1 port using a 9 pin serial cable. Open the LI-1400 software package. Open the Liberty.I14 file and click on Remote, Connect. Select Channels I1, click on Remote, then Receive data. Select the 'all' button and click on OK. Type file name (using the following format: YYMMDDpar.txt, where YY is year, MM is month and DD is date) and press Enter. At this point, the logged data will upload to the PC. When it is finished, close the LI-1400 software and open the text file with Microsoft Excel.

## **9.0 QA/QC REQUIREMENTS**

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## 9.1 Calibration

Calibration of the Thermometer, Conductivity, and Dissolved Oxygen sensors will be calibrated at Seabird on an annual basis. The SBE-43 Dissolved Oxygen sensor is post-calibrated using comparisons to Winkler DO samples. The C-Star Transmissometer is also post-calibrated in the lab.. This is done post-cruise for two reasons. One is to determine if the instrument has drifted since the last calibration and secondly, there is no other way to determine if the results are within a reasonable range since there are no conventional chemistry tests or field tests that can be done for evaluation. There are no standards to do a "check", so post-cruise calibrations are the most efficient and sensible method. The PAR sensors are sent to Li-Cor on a bi-annual basis while the C-Star Transmissometer and the Wetstar Fluorometer are sent to Wetlabs annually. The depth sensor is maintained and calibrated by Seabird every 5 years based on their recommendation.

### 9.1.1 SBE 43 Post-Cruise Calibration for Dissolved Oxygen

- 9.1.1.1 Initial DO evaluation: Using the method in section 8.1.7.2, process CTD bottle data using the LIMS datcnv.psa file and the previous month's configuration file to calculate the pre-cal CTD dissolved oxygen values. Note these values on a copy of the Conventional Chemistry Unit's Winkler analysis form for the associated samples. This will give the operator a general idea of how much the instrument has drifted since the last calibration and the general quality of the data. There are no acceptance windows, but if the differences between the Winklers and the CTD DO are greater than 1 mg/L, the instrument should be sent in for repair.
- 9.1.1.2 Seabird 64-2 Regression: Reprocess the CTD bottle data using datcnv cal 43.psa and the previous month's configuration file to obtain the following data: Pressure (db), Temperature (deg. C), Salinity (PSS), Oxygen Saturation (ml/l) and SBE 43 Output Voltage. Enter these values into the SBE43 DO Calibration Template (taken from Seabird's Application Note 64-2 Regression), along with the Conventional Chemistry Unit's Winkler values to calculate new SOC and Voffset values. Do not use the FREP samples in the SOC and BOC calculation. These samples will be used to evaluate the quality of the Winkler vs. CTD data.
- 9.1.1.3 Updating the configuration file: Enter the new SOC and Voffset values into a new configuration file with appropriate nomenclature. This configuration file is now ready to be used to reprocess the new LIMS Bottle data and the CTD database data.
- 9.1.1.4 Compare the final calculated Bottle Data DO values to the Winkler values for a final quality evaluation. Control windows have not been set for qualification.

### 9.1.2 C-Star Post-Cruise Calibration for Light Transmission

Using the C-Star Calibration Sheet, calibrate the C-Star by monitoring voltages with no blockage followed by complete blockage. This is done by first cleaning the lenses with RO water and alcohol using Kim Wipes. Disconnect the AFM-CTD cable and insert the 10 meter four pin data I/O cable (801616). Connect the opposite end of the I/O cable to the 9 pin serial port on the PC. Open TermAF, click on the Connect CTD button. Change the minimum frequency to turn pump on to 3500 using the method in 8.2.1. Following this, at the S> prompt type il to initialize logging. Click on the Init Log button. This changes the ncast to 0 and prepares the instrument for the upcoming cast. Wait for about 5 seconds until a message box confirms the CTD is ready to go. Open Seasave-Win32. Open the C-StarTransmissometer Seasave Configuration. Click on RealTimeData and Start Acquisition. Select the previous month's configuration file and uncheck Store on Disk. Make sure the COMM port configuration settings are COM1 and baud rate of 4800. Click on Start Acquire and begin monitoring the voltages. After approximately 200 scans or when the Light Transmission values become stable begin reporting the following: Scan #, CTD Temp, Volt 1, and Light %. Completely block the light pathway and record the values as "Blocked" on the calibration sheet. Compute the M and B values and enter them into the new CTD configuration file.

## 9.2 Replicate Measurements

Replicate sensor readings will be reported to LIMS once per cruise. . Both the original and replicate samples are true samples and loaded to LIMS. In order to calculate RPD values, QC replicate samples

are created in LIMS using the FREP locator and linked back to the original sample. See the table below for acceptable limits.

Parameter	DO, Field	Sal, Field	Samp Depth	Sample Temp	Light Transmission, Field
Acceptance Limits	20 % RPD	0.3 PSS	1 or 4 meters	0.3 deg C	20 % RPD

**9.3 Split Samples and Field Replicates**

For marine projects, Salinity and Dissolved Oxygen measurements will be analyzed synoptically using water samples in the Conventionals Unit. The frequency will be a minimum of 1 per cast to facilitate the dissolved oxygen post-cruise calibration. The acceptance range for field dissolved oxygen versus Winkler DO is 20% RPD. For salinity, the acceptance range is 0.3 PSS. Field replicates are analyzed at a minimum frequency of 1 per 20 samples or once per day, whichever is more frequent.

**9.4 Method Blanks**

Method Blanks are not appropriate for CTD analysis.

**9.5 Continuing Calibration Verification**

CCV's are not appropriate for CTD analysis.

**9.6 Depth Comparison**

Following the Bottle Summary calculations, each bottle trip will be compared with the intended sample depths. For samples less than 100 meters, the intended depth and the CTD depth should be within 1 meter. For depths greater than 100 meters, the difference should be no greater than 4 meters.

**10.0 DATA REDUCTION, REPORTING, REVIEW AND DOCUMENTATION**

**10.1 LIMS**

**10.1.1 Data Entry to LIMS**

After all post-calibration work and creation of a workgroup with the appropriate sample numbers and products, follow the steps in 8.1.7.2 to create the necessary .bt1 files required to extract the LIMS data. Open Excel, Click on EnvLab then ESS Data Entry. Click on the CTD Data option button then Open Data. Find the .bt1 file, select it and click OK. The macro will run and a pop-up window will ask you to Enter Sample Numbers, Surface PAR data, and then press Load to LIMS button. Click on OK. Complete these tasks and other necessary editing. Click on the Post to LIMS button. It will then ask you if you are ready to post and say Yes. The data will automatically be transferred to LIMS. Note that the values for all LIMS parameters, including sample depth, will be averaged for three seconds during the bottle trip period. Field replicates will then need to be created in Workstat and those data will be entered into LIMS electronically.

**10.1.2 LIMS Data Review**

Seedpak3 reports are to be reviewed against the \*.xls rossum files for accuracy. Following this, the data is approved and moved to EDS. Once all the laboratory analyses have been completed, an EDS report is created to compare the CTD data versus the laboratory data.

**10.1.3 Documentation and Data Reporting**

Seedpak3 reports, \*.txt transfer files, \*.xls rossum files, post-cruise calibration records and lab data comparisons are to be filed as a hard copy report. All electronic files are stored and backed up on a daily basis. Instrument calibration records done by the manufacturer, including sensor serial numbers and inclusive dates, are stored in a logbook and updated when applicable.

10.1.4 LIMS Table

Product	Parameter	Listtype	Units	MDL	RDL	Sigfig MDL	Sigfig RDL
SAMP DEPTH	Sample Depth	ESS-CTD	m	n/a	n/a	2	3
SAMP TEMP	Sample Temperature, Field	ESS-CTD	Deg. C	n/a	n/a	*	*
DO, FIELD	Dissolved Oxygen, Field	ESS-CTD	mg/L	0.5	1.0	2	3

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SAL, FIELD	Salinity, Field	ESS-CTD	PSS	n/a	n/a	5	5
DENSITY, FIELD	Density, Field	ESS-CTD	kg/m <sup>3</sup>	n/a	n/a	7	7
CHLA, FIELD	Chlorophyll	ESS-CTD	ug/L	0.06	0.12	2	3
LIGHT TRANSMISSION	Light Transmission	ESS-CTD	% light	0.01	0.01	2	3
PAR, FIELD	Light Intensity (PAR), Field	ESS-CTD	umol/sm <sup>2</sup>	n/a	n/a	*	n/a
PAR, SURF, FIELD	Surface Light Intensity (PAR), Field	ESS-FM	umol/sm <sup>2</sup>	n/a	n/a	*	*

\*= Round to 0.1

## 10.2 Full Cast File Handling

Follow the instructions in the CTD File Handling Protocol (2.5). Completed data files are reviewed, qualified and loaded to the CTD database.

## 11.0 STANDARDS AND REAGENTS

- 11.1** Triton X100 cleansing solution: Add 10 ml of solution to 1 liter of RO water. Prepare fresh monthly. Use this reagent very sparingly and rinse extremely thoroughly with RO water following the use. It can foul the dissolved oxygen membrane.
- 11.2** RO Water: Reverse-osmosis water produced at the laboratory and retrieved from an RO water tap. This reagent can be disposed of down the drain or overboard. ASTM Type I or equivalent. It is stored in a 2 liter HDPE bottle and replaced monthly.
- 11.3 Alkali-Iodide-Azide (AIA)**- AIA is a poisonous and caustic reagent used for Winkler dissolved oxygen fixation. Contact with skin must be avoided. AIA must stored in a well ventilated, dry, and cool area. Working reagents will be stored in a re-pipet dispenser. Always wear gloves and goggles when working with AIA. AIA is purchased by the Conventional Chemistry Unit and dispensed by a small re-pipet dispenser on the Liberty.
- 11.4 Manganous Sulfate (MnSO<sub>4</sub>)**. A reagent used for Winkler dissolved oxygen fixation. **Avoid contact with skin. Store in a well ventilated, dry and cool area in a re-pipet dispenser. Always wear gloves and safety glasses when working with MnSO<sub>4</sub>. MnSO<sub>4</sub> is purchased by the Conventional Chemistry Unit and dispensed by a small re-pipet dispenser on the Liberty.**

## 12.0 CONTAMINATION

Oil and grease can coat sensors and hoses and can destroy the on-line pump. Airborne contaminants can affect conductivity results if allowed to enter and dry in cell. Any material capable of fluorescing at or near 676 nm can affect the chlorophyll analysis. In addition, high turbidity may create a high bias with respect to chlorophyll values. Particles caught in the inverted 'Y' fitting can stop air from exiting, thus not allowing the pump to prime or causing poor readings throughout the instrument. Dirty transmissometer lenses can reduce light transmission values.

## 13.0 PREVENTATIVE MAINTENANCE

The TC duct, temperature probe, conductivity cell, DO probe, and fluorometer must be rinsed with RO water prior to and immediately following each cast. Rinse with a full 60cc syringe and a connecting tube (7/16" Tygon) on the end of the TC duct. All other parts of the CTD and carousel must be rinsed thoroughly with fresh water following each cruise. Store the CTD with the conductivity cell full of RO water between cruises. Use a 1% TritonX solution to clean the sensors if oil or grease has been encountered. Rinse thoroughly with RO water following the Triton cleaning. Use a dilute sodium hypochlorite solution (1% bleach) to kill biological growth if absolutely necessary. Rinse immediately with RO water (5 minutes minimum) following the bleach cleaning.

For storage, The DO cell should remain free of water, but the high humidity from the RO water in the conductivity cell will keep the DO sensor fresh.

The DO sensor membrane should be replaced at least every year by Seabird. Clean the transmissometer lenses with alcohol, RO water and Kim Wipes before and after each cruise.

Maintenance must be recorded in the maintenance logbook.

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**14.0 TRAINING**

New analysts must successfully perform maintenance, field measurements and data reduction/review under the direct supervision of an experienced analyst following review of this document.

**15.0 REFERENCES**

SBE 25 Sealogger CTD Operating Manual

CTD Data Acquisition software: Seasoft

Model LI-1400 Datalogger Instruction Manual

Li-Cor Surface PAR Data Acquisition software: LI-1400.

## 16.0 APPENDIX

### King County Environmental Lab CTD File Handling Protocol

#### Datcnv

- Process scans until end of file
- Scans to skip over = 1100
- Use ascii output
- Convert Data from Upcast and Downcast
- Create converted (.CNV) file only
- Output Variables (in this order) = scan count, pressure (strain gauge db), depth (salt water, meters), temperature ITS-90, conductivity (S/m), oxygen voltage (SBE 43), PAR/irradiance biospheric Licor, Fluorescence (wetlab wetstar mg/m<sup>3</sup>), Beam Transmission (Chelsea/Seatech/Wetlab).
- Do not output water bottle data, this will be done by the environmental laboratory and stored on LIMS for later retrieval.
- Creates a file with the same name and a .cnv file extension.

#### Alignctd

##### Advance Values

- Primary Conductivity alignment = 0.11 seconds
- Oxygen alignment = 2.0 seconds
- Fluorescence alignment = 4.0 seconds
- Everything else = 0
- Overwrite .cnv file

#### Cell Thermal Mass

- Alpha = 0.04
- 1/beta = 8.0
- Corrects for cell thermal mass
- Overwrite .cnv file

#### Derive

- Variables to be Derived = salinity, oxygen mg/L, potential temperature, density kg/m<sup>3</sup>, sigma-theta, descent rate.
- Variable Coefficients (oxygen, descent rate) = 2 seconds (for both coefficients)
- Overwrite .cnv file

#### Binavg

- Arrange into depth bins, no interpolation
- Bins are 0.5 meters in size
- Include number of scans per bin in output file
- Exclude bad scans (marked with Loopedit)
- Skip 0 scans
- Process upcast and downcast
- Don't include surface bin
- Overwrite new .cnv file

## **APPENDIX B**

**Standard Operating Procedure for Clean Sampling for  
Ultra Low Trace Metals using Modified Niskin Bottles**

**King County Environmental Laboratory SOP #221v2**

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## STANDARD OPERATING PROCEDURE

for

**Clean Sampling for Ultra Low Trace Metals using Modified Niskin Bottles**

**SOP #221v2**

**Implemented: December, 2004**

**Supersedes SOP: #02-02-12-001**

**Approved by:**

**Author:** \_\_\_\_\_ **Date:** \_\_\_\_\_  
**Supervisor:** \_\_\_\_\_ **Date:** \_\_\_\_\_  
**QA Officer:** \_\_\_\_\_ **Date:** \_\_\_\_\_

**King County Environmental Laboratory  
322 West Ewing Street  
Seattle, Washington 98119-1507  
(206) 684-2300**

### **1. Scope and Application**

This standard operating procedure (SOP) applies specifically to the collection of marine and fresh water samples for analysis of ultra low trace metals in the range of ng/L (parts per trillion). The purpose of this SOP is to describe the method of collecting ultra low

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level metals at depths up to 250 meters. This method is not intended for the collection of samples found at industrial facilities or in areas of known high metals concentrations. Sampling at depths less than 20 meters may be done more efficiently using the peristaltic pumping procedure, SOP #02-02-005-002 or by collection of surface grabs, SOP #02-02-013-001. For further information regarding historical trace metals collection methods, contamination sources and control, or other ultra-trace metals issues, refer to section 15: References.

## **2. Associated Documents and SOPs**

- 2.1 Reductive Precipitation Preparation of Seawater Samples (06-03-006-000)
- 2.2 Equipment Cleaning For Clean Sampling of Ultra Trace Metals Utilizing the Niskin-X (06-05-005-000)
- 2.3 Clean Sampling for Ultra Low Trace Metals by Peristaltic Pump (SOP #02-02-005-002)
- 2.4 Sampling Methods for Marine Water Column (02-02-003)
- 2.5 Trace Metal Unit's Labware and Equipment Cleaning Procedures (SOP #06-05-002-000).

## **3. Method Summary**

Prior to the sampling event, all sampling equipment and containers are cleaned according to the SOP titled "Equipment Cleaning for Clean Sampling of Ultra Trace Metals using the Niskin-X (SOP#06-05-005-000). The sampling procedure will utilize the "clean hands/dirty hands" technique. Prior to arrival at the sampling site, members of the sampling team will be designated as "clean hands", "dirty hands", and "crane operator". "Clean hands" handles all operations involving contact with the sample bottle and transfer of the sample from the sample collection device to the sample bottle. "Dirty hands" is responsible for preparation of the sampling device (except the sample container itself) and for all other activities that do not involve direct contact with the sample. "Crane operator" is responsible for setup and operation of the clean winch system, along with backup dirty-hands responsibilities.

All equipment is non-metallic and sampling staff will always wear non-powder, PVC gloves. Prior to leaving the laboratory, a pre-deployment equipment blank is collected from one Niskin. All sample containers are double-bagged, Niskin bottles are single-bagged and they are all placed on the research vessel.

Samples are collected using Niskin-X bottles attached to a synthetic hydroline. A specialized winch system mounted on the rear deck of the vessel controls the hydroline. The skipper maneuvers the vessel in a manner that allows the hydroline to remain upwind and upcurrent. The Niskin-X bottles are attached to the hydroline and lowered to the correct depth. A teflon-coated messenger is sent down the hydroline to trip the bottles. The Niskin-X bottles are then brought up and placed in a special plastic rack, where the samples are dispensed into sample containers. Finally, sample containers are double-bagged and placed on ice for transport to the laboratory.

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#### 4. Definitions

- 4.1 **Ambient Water:** Waters in the natural environment (e.g., rivers, lakes, streams, Puget Sound).
- 4.2 **Apparatus:** The sample containers, sampling devices, instrumentation, and all other materials and devices used in sample collection. (See 7.5). All original o-rings are replaced with Viton o-rings.
- 4.3 **Clean Winch System:** This is a custom built system for low level metals sampling. It consists of a plastic box that contains an enclosed hydraulic motor that runs a Teflon drum. The drum contains 1000 feet of synthetic hydroline and utilizes an electronic line-measuring device. The system is bolted to the deck and can be removed for cleaning.
- 4.4 **Niskin-X Bottle: (Sample Collection Device):** A specialized sampling bottle designed to collect water samples for low-level metals at discrete depths. These bottles have been modified using Teflon coating on the inside of the bottle and plastic/silicon coating over exposed metal on the outside.
- 4.5 **Sample Container:** HDPE or Teflon Bottles used to collect the sample from the Niskin-X for transport and storage at the lab.
- 4.6 **Ultra Low Trace Metals Samples:** Samples that will be analyzed for metals in the ng/L (parts per trillion) range. These include the following LIMS products: HG-CVAF-UL, HG-CVAF-UL, DISS and all ICPMS products using the Reductive Precipitation preparation methodology.
- 4.7 **Atmosphere blank:** A sample of analyte-free water in a lab-supplied container which is left uncapped during sampling. The analysis of the atmosphere blank is used to measure possible contamination from airborne sources.
- 4.8 **Carboy Blank:** Reagent water that is used for the Field Blank is sampled to evaluate contamination by the reagent water from the carboy. This sample is collected from the carboy just prior to the Field Blank.
- 4.9 **Pre-deployment Equipment Blank:** A sample of analyte-free water that has been processed through the sampling equipment **in the laboratory** after prescribed decontamination. The collection of the equipment blank should follow the same techniques used to collect field samples (i.e. Clean Hands / Dirty Hands). The equipment blank may be analyzed for any or all of the analytes for which the samples are being analyzed. Analysis of the equipment blank is used to measure and document the possible contamination by sampling equipment and the effectiveness of decontamination. An acceptable equipment blank should be achieved before sampling devices are used for sample collection.
- 4.10 **Field Blank:** A field blank is a sample of analyte-free water that is supplied by the laboratory, shipped to the field, and treated as a sample in all respects including contact with the sampling device following field decontamination. The field blank may be analyzed for any or all of the analytes for which the samples are being analyzed. Analysis of the field blank is used to measure and

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document any sample contamination resulting from transport, exposure to the atmosphere or contact with the sampling device at the sampling location.

- 4.11 **Reagent Water:** Reverse-Osmosis water collected from the Trace Metals Clean Room and demonstrated to be free from (or as low as possible) the metals of interest and potentially interfering substances. This water is equivalent to ASTM Type I water (ASTM D 1193).
- 4.12 **Field Replicate:** A field replicate sample consists of a second sample collected at a sampling location using the exact collection methodology as was used to obtain the first sample and as soon after the original sample as possible. The field replicate sample is generally analyzed for all the analytes for which the sample was analyzed. Analysis of the field replicate sample is used to measure and document the precision of field sampling methodologies and the homogeneity of the sample site.

## 5. Safety and Hazardous Materials Management

All sampling personnel will follow standard safety procedures while on board the sampling vessel. The vessel skipper has ultimate responsibility for safety while the vessel is underway. During operation of the sampling device, the crane operator has ultimate responsibility for safety on the back deck of the vessel. Sampling personnel are required to wear steel-toed footwear and hard hats during operation of the sampling device. Recommended equipment includes foul-weather gear and eye protection.

## 6. Sample Containers, Preservation, and Storage

- 6.1 One set of double polypropylene-bagged, acid washed and pre-labeled HDPE 500 ml bottles with lids for ICPMS using reductive precipitation preparation technique..
- 6.2 One set of double polypropylene-bagged (bags pre-labeled), acid washed Teflon 500 ml bottles with lids (HG-CVAF-UL or HG-CVAF-UL, DISS).
- 6.3 Store double-bagged sample bottles on ice for delivery to the lab. Once samples have been logged in at the lab, Trace Metals staff preserve (filter and preserve dissolved fraction) the samples in a “clean laboratory”.

## 7. Apparatus, Equipment, and Consumables

- 7.1 Carboy, 50 liter, pre-cleaned polyethylene, filled with reagent water for field blanks.
- 7.2 PVC non-powder gloves (VWR Catalog #32916-53x)
- 7.3 Non-metallic ice chest with ice and plastic barrier.

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- 7.4 Field Sheets
- 7.5 Niskin-X Bottles (General Oceanics Model 101005X; modified with Viton O-rings (fluoroelastomer 75 durometer Gardico Large; AS568-336, Medium; AS568-312, Small; AS568-012), and shrink-wrap covers on metal fittings. (See 12.2.1 for retrofit procedure).
- 7.6 Nylon coated weight; Pre-cleaned and bagged.
- 7.7 Polypropylene bags, 18"x42"x3.0 mil; John T. Vlasick
- 7.8 Visquene, clean, colorless
- 7.9 Specialized winch system with synthetic hydroline (single braid, 12 strand ¼” Spectra)
- 7.10 Teflon coated messengers, pre-cleaned and bagged.
- 7.11 Custom Niskin bottle rack with plastic interior.

## **8. Procedure**

### **8.1 In Lab Preparation**

- 8.1.1 Cleaning Equipment: The Environmental Services Unit is responsible for arranging to have all sampling apparatus cleaned. Trace Metals Lab Assistants can provide cleaning services. See Section 15: References and (Section 2.3) Equipment Cleaning For Clean Sampling of Ultra Trace Metals Utilizing the Niskin-X (06-05-005-000) The Environmental Services Unit is responsible for the proper deployment and maintenance of the sampling equipment including Niskin-X bottles, O-rings, etc.
- 8.1.2 Clean sample containers and Niskin-X bottles (packaged into plastic bags) are placed into plastic boxes. Sample coolers are filled with ice, which is covered with a plastic barrier. All sampling apparatus is transported to the vessel the morning of the sampling event. All sample containers, sampling collection devices, and other “clean” materials are stored in the cabin until the individual pieces are needed. The Clean Winch System is bolted to the deck of the vessel and covered with plastic prior to leaving the laboratory. All sampling apparatus is organized to enhance efficiency and cleanliness once on the sampling site.

### **8.2 On-Site Procedures**

- 8.2.1 Roles of Sampling Team: Dirty Hands, Clean Hands
  - 8.2.1.1 Summary of Skipper’s Responsibilities:
    - Ultimate responsibility for the vessel and the safety of the crew.
    - Maneuvers the vessel in a manner which reduces self-contamination.
    - Communicates with the Dirty Hands and Clean Hands.
  - 8.2.1.2 Summary of Crane Operator’s Responsibilities:
    - Responsible for safety and overseeing activities on the back deck.
    - Operates Crane.

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- Communicates with all back deck staff and skipper.
- Never touches cleaned plastic or Teflon-coated equipment.
- Data entry to the field sheets.

#### 8.2.1.3 Summary of Clean Hand's Responsibilities:

- Opens inner sealed bags
- Fills all lab sample containers
- Prepares atmosphere, field, and carboy blanks

#### 8.2.1.4 Summary of Dirty Hand's responsibilities:

- Opens outer sealed bags.
- Operates Niskin stopcock during filling of the sample container.
- Never comes in contact with lab sample containers.
- Attaches Niskin bottles to Hydroline.
- Cocks Niskin bottles.
- Responsible for weight, synthetic line, and deployment of messengers.

8.2.2 Station Positioning: In order to assess temporal changes in water column characteristics, the station must be revisited as precisely as possible. Station positioning for sampling will be accomplished using a Trimble Differential Global Positioning System (DGPS). Prior to the study, prescribed station coordinates (State Plane NAD83 coordinate system) are loaded into the shipboard DGPS. During the sampling event, the shipboard navigational system will utilize the differential data transmissions from regional Coast Guard base stations to automatically correct its GPS satellite data. The GPS antenna is boom-mounted above the sampler descent line to achieve a more accurate coordinate fix above the sampling point. Previous DGPS usage indicates that an average precision of one to two meters can usually be attained. Water column samples will be collected only when the DGPS coordinates are within 100 ft of the station target coordinates (King County, Jan 2003). In order to minimize contamination, the skipper will maneuver the vessel so that the Niskin-X bottles are deployed upwind and upcurrent from the exhaust of the engines, while at the same time remaining within the 100 ft window.

#### 8.2.3 Niskin-X Deployment

After arriving on station:

- 8.2.3.1 Skipper maneuvers the vessel so that the sampling will occur upwind and upcurrent.
- 8.2.3.2 Dirty Hands and crane operator don PVC gloves. Hint; using multiple gloves and removing dirty ones can increase efficiency.
- 8.2.3.3 Dirty Hands covers the safety rail with plastic.
- 8.2.3.4 Crane Operator sets up the clean winch system and Skipper provides hydraulic power.

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- 8.2.3.5 Crane Operator orients the boom to the starboard side of the *Liberty* and attaches a nylon block to the crane.
  - 8.2.3.6 Dirty Hands opens the plastic bag containing the nylon coated weight and attaches the weight to the synthetic hydroline.
  - 8.2.3.7 Dirty Hands lifts the synthetic hydroline and places it through the nylon block.
  - 8.2.3.8 Crane Operator operates the winch so the nylon coated weight is moved over the side of the *Liberty* and under the surface of the water.
  - 8.2.3.9 Dirty Hands changes gloves.
  - 8.2.3.10 Dirty Hands opens the box containing the Niskin-X bottles and removes the first (greatest depth) bottle.
  - 8.2.3.11 Dirty Hands unzips the outer plastic bag, removes the Niskin-X bottle and attaches it to the hydroline. The first Niskin-X bottle should be attached just above the nylon weight.
  - 8.2.3.12 Dirty Hands cocks the Niskin-X.
  - 8.2.3.13 Crane Operator zeros the line metering device and lowers the hydroline until the correct length of line for attaching the second bottle is displayed on the line metering device.
  - 8.2.3.14 Dirty Hands opens the box containing the Niskin-X bottles and removes the second bottle.
  - 8.2.3.15 Dirty Hands opens the outer plastic bag and pulls out the second Niskin-X bottle and attaches it to the hydroline.
  - 8.2.3.16 Dirty Hands cocks the bottle.
  - 8.2.3.17 Dirty Hands removes a cleaned and bagged Teflon coated messenger from the box and unzips the bag. This messenger will be used to trip the bottom bottle.
  - 8.2.3.18 Dirty Hands clips it to the synthetic hydroline and attaches the release strap to the Niskin bottle.
  - 8.2.3.19 If necessary, Crane Operator lowers the hydroline until the correct length of line for attaching the third bottle is displayed on the line metering device and the procedure is repeated.
  - 8.2.3.20 Once the bottles are at the correct depth, Dirty Hands sends a Teflon coated messenger down the hydroline to trip the bottles.
  - 8.2.3.21 The trip time is noted on the fieldsheet.
  - 8.2.3.22 The serial numbers of each Niskin-X must be added to the appropriate sample on the fieldsheet.
- 8.2.4 Sample Collection from Niskin Bottles
- 8.2.4.1 Dirty hands changes gloves and clean hands dons gloves.
  - 8.2.4.2 After all bottles have tripped, Crane Operator operates the winch system and brings the top bottle above the surface of the water and adjacent to the side of the *Liberty*.

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- 8.2.4.3 The Niskin bottles are removed from the hydroline and placed in the sample rack.
- 8.2.4.4 The Crane Operator, with the help of Dirty Hands, brings the weight onto the *Liberty* and stows it in a plastic bag. Dirty Hands prepares the sampling apparatus for transport to the next station.
- 8.2.4.5 At this point, Liberty may get underway during container filling to minimize contamination.
- 8.2.4.6 Clean Hands opens the air vent at the top and the outlet nipple at the bottom of the Niskin-X bottle to begin draining sample water. Approximately 100 ml of sample water should be drained out and discarded.
- 8.2.4.7 While this is happening, dirty hands removes the first sample container from the bottle kit and unzips the outer plastic bag.
- 8.2.4.8 Clean hands reaches into the outer bag, opens the inner bag, and removes the container.
- 8.2.4.9 Clean Hands takes the sample bottle to the Niskin-X, removes the cap, and immediately begins rinsing the container. Following three rinses of the sample container and cap, the container is filled and capped. During this process, atmospheric exposure should be kept to a minimum.
- 8.2.4.10 Once the sample container is filled, clean hands replaces the cap on the sample container, places it back into the inner bag, closes the bag, and puts it in the outer bag. Dirty hands closes the outer bag and places it into the cooler filled with ice. All sample bottles for this depth are filled using the same method.
- 8.2.4.11 Dirty hands places the bottle/bag back into the original box.
- 8.2.4.12 Clean hands and Dirty Hands will again change gloves.
- 8.2.4.13 The process is repeated until all sample bottles are filled.

### **8.3 Sample Login Procedures**

Samples are to be delivered to Trace Metals for filtration and preservation. The samples should be logged in according to Chain of Custody or standard procedures, depending upon project requirements. After login, subcontracted samples must either be sent to the subcontract lab immediately following the cruise, or placed in a cooler at 4 degrees C and sent out the following morning. Mercury samples must be filtered and preserved within 48 hours of collection (EPA method 1631).

## **9. QA/QC Requirements**

The QC practices defined in this section are subject to change for specific projects. Project-specific QC requirements that differ from this SOP should be defined in a Sampling and Analysis Plan prepared for each project.

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### 9.1 Initial Validation

Initial method validation was conducted by comparing the metals results of 10 samples collected using the Niskin-X bottles with samples collected simultaneously at the same depth using the pumping system (SOP # 02-02-005-002). The results of this comparison verified that the methods were comparable. Changes to this procedure, which might bias the results, must be validated by repeating the simultaneous collection of 10 samples with the pumping system and the modified version of this method.

### 9.2 Continuing Quality Control

To ensure continuing quality control, the following QA/QC protocols will be followed, using Clean Hands/Dirty Hands methodology throughout. “Clean hands” will prepare the atmosphere, carboy, and field blanks.

- 9.2.1 **Field Replicates:** A minimum of two field replicates will be collected per sampling event. If more than 20 field samples are collected, a minimum frequency of 10% is required. (See 4.12). Replicates are collected using a separate Niskin mounted as close as possible to the original on the hydrowire.
- 9.2.2 **Atmosphere Blanks:** Two atmosphere blanks will be collected per sampling event. These samples will be collected at the first station of the cruise, prior to collecting ambient samples, and at the last station, following collection of the ambient samples. The collection is done by opening the cap (of the previously filled Atmosphere Blank) for the equivalent time and at the same physical space that a sample container would be filled. (See 4.7).
- 9.2.3 **Field Blanks:** A minimum of two field blanks will be collected per sampling event. If more than 20 field samples are collected, a minimum frequency of 10% is required. These blanks will be collected at the first and last stations of each cruise. (See 4.10). The field blank is typically prepared by filling a previously-rinsed Niskin-X with reagent water via a tube from the carboy. After filling the Niskin-X, the field blank is collected like a field sample.
- 9.2.4 **Carboy Blanks:** A minimum of two carboy blanks will be collected per sampling event. If more than 20 field samples are collected, a minimum frequency of 10% is required. These are collected by simply pouring the carboy water into the carboy blank sampling bottles, immediately after the collection of the field blank. (See 4.8).
- 9.2.5 **Pre-deployment Blank:** See SOP #06-05-004-000. This is done by the Trace Metals Staff prior to cruise.

Each set of blanks and replicates are all collected at the same site. If multiple sets are required, they are typically collected at the first and last stations of the day.

### 9.3 Acceptance Limits

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The results of each blank analysis should be less than the MDL. If results of a particular blank are above the MDL, the data will be evaluated against results of other field and method blanks, and measured concentrations in the field samples. The samples and blanks may be re-analyzed if the source of the contamination is identified as a laboratory contaminant. The Relative Percent Different (RPD) of each set of field replicates will be calculated. The acceptance limits will be project-specific. It is understood that the carboy reagent water will become contaminated with mercury from the atmosphere during the sampling event. It is therefore expected that the field blanks and carboy blanks will be greater than the method detection limit. An acceptable field blank for mercury should not contain significantly greater levels of mercury than the carboy blank.

## **10. Data Reduction, Reporting, Review and Documentation**

Field sheet data for each sample will include:

- client locator – a unique sample identifier;
- sample depth – may be entered prior to sampling event
- time and date of sample collection
- field observations that could affect the quality of the samples and blanks
- precipitation-none, light, medium, or heavy
- serial numbers of Niskin-X bottles associated with each sample

These field sheet data will be entered into LIMS for each sample.

## **11. Standards and Reagents**

This section is not applicable to this specific field sampling method.

## **12. Contamination**

### **12.1 Background and Suggestions**

12.1.1 EPA method 1669 states that the greatest challenge faced in trace metals determination, including the sampling portion, is preventing the samples from becoming contaminated. Routes of contamination include metal-containing sampling equipment, containers, reagent water, improperly cleaned and stored equipment, atmospheric inputs such as engine exhaust, and even human contact. The goal will be to eliminate contamination by ensuring that any object that contacts the sample is nonmetallic and free from potential metal contamination. Observe the following during the sample collection process:

*Printed on 12/17/10. Document may now be obsolete*

- 12.1.2 Minimize atmospheric exposure. Airborne particulate matter such as dust, dirt, exhaust, smoke, nearby corroded metallic material, and human breath (Hg cavity fillings) can contaminate samples.
- 12.1.3 Wear clean, non-powdered gloves at all times. When gloves touch any potential contaminant, change them immediately.
- 12.1.4 Use metal-free sampling equipment and containers. Materials such as FEP, PTFE, polyethylene, polycarbonate, polysulfone, polypropylene, and ultrapure quartz are free of contaminants when properly cleaned. FEP and PTFE must be used if for mercury determination.
- 12.1.5 Mark and record serial numbers on all equipment.
- 12.1.6 Pre-clean all sampling equipment using a verified cleaning procedure. Avoid carryover by rinsing equipment between sampling and by completely avoiding highly contaminated sampling sites. Alternative sampling methods may be used in these areas.
- 12.1.7 Sampling vessel should be positioned downwind and downstream from the sampling point during collection.

## 12.2 **Decontamination Procedure**

### 12.2.1 Niskin-X Bottle Retrofit

- 8.2.1.1 The following steps were taken to reduce metal exposure and potential contamination from the standard Niskin-X sampling bottles.
- 8.2.2.1 All brass crimps were replaced with stainless steel crimps and covered with plastic shrink tubing.
- 8.2.3.1 The brass clips that keep the bottles cocked were replaced with nylon clips.
- 8.2.4.1 All rubber o-rings were replaced with Viton o-rings.
- 8.2.5.1 Silicon adhesive was used to cover all exposed screw heads and other exposed metal. Note: The stainless steel bolts and wingnuts that attach the Niskin-X to the hydroline cannot be replaced or coated.

### 12.2.2 Pre-Cruise Cleaning Procedure

The Trace Metals Unit is responsible for cleaning all sample containers and sample collection devices. The Environmental Services Unit is responsible for the proper deployment and maintenance of the sampling equipment. Niskin-X bottles will be thoroughly rinsed with ambient water prior to sampling. The number of Niskin-X bottles to be cleaned is dependent on the sampling plan. There should be  $N + 2$  Niskin-X bottles cleaned, where  $N$  is the maximum number of depths at any one station. This will provide enough bottles for each depth, plus a field replicate and a spare.

### 12.2.3 Intra-Cruise Cleaning Procedure

Sampling equipment is reused and therefore cleaned between stations with copious quantities of in-situ ambient water. This process is done in the process of deployment by lowering the bottles, in an open position, to their respective sampling depths.

### **13. Preventative Maintenance**

The ultra low-level metals winch, along with all other sampling apparatus, must be kept covered to avoid possible contamination during storage. Niskin-X bottles must be regularly maintained so they will be in good operating condition at all times. If contamination has been suspected, the Trace Metals laboratory will clean the Niskin-X bottles. All broken or worn parts will be replaced upon completion of the previous cruise.

### **14. Training Outline**

The skipper and crane operator must be fully trained and experienced using this method. They must also be briefed on all of the details of the cruise. Clean Hands and Dirty Hands must go through a training process specific to this sampling method and be supervised by an experienced lead. This training process will include use of all sampling equipment and a summary of issues associated with clean sampling and ultra trace metals analysis. This includes familiarization with the SOP and references 1, 3, 4, 5, and 6. Results from field QC samples will be used to determine the effectiveness of this training.

### **15. References**

Method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels. Draft 1994. USEPA.

Method 1640: Determination of Trace Elements in Ambient Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma-Mass Spectrometry. Draft 1996. USEPA.

Stewart, R. E. (1997) Collection of Freshwaters and Wastewaters for the Determination of Trace Elements. *Virginia Department of Environmental Quality SOP*.

Hunter, Craig N. et. al. (1996) A Rosette System for the Collection of Trace Metal Clean Seawater. *Limnol. Oceanogr.*, **41(6)**, 1367-1372.

Bewers, J.M. and H.L. Windom (1982) Comparison of Sampling Devices for Trace Metal Determinations in Seawater. *Marine Chemistry*, **11**, 71-86.

Nolting, R. F. and J. T. M. de Jong (1994) Sampling and Analytical Methods for the Determination of Trace Metals in Surface Seawater. *Intern. J. Environ. Anal. Chem.*, **57**, 189-196.

*Printed on 12/17/10. Document may now be obsolete*

In Field Sampling Protocol-Dip Method from Rubber Inflatable Boat. UCSC.  
Date and author unknown.

Ultra Low Level Metals Sampling at Depth Validation Document. King County  
Environmental Laboratory, 1999.

Method 1631: Mercury in water by Oxidation, Purge and Trap, and CVAFS.  
Revision C, March 2001. USEPA.

## **APPENDIX C**

### **Standard Operating Procedure for Clean Surface Water Sampling for Ultra Low Trace Metals and Organics**

**King County Environmental Laboratory SOP #222v2**

STANDARD OPERATING PROCEDURE

for

**Clean Surface Water Sampling for Ultra Low Trace Metals and Organics**

SOP #: 222v2

Implemented: January 2008

Supersedes SOP #: 02-02-13-001

Approved by:

Author: \_\_\_\_\_ Date: \_\_\_\_\_

Supervisor: \_\_\_\_\_ Date: \_\_\_\_\_

QA Officer: \_\_\_\_\_ Date: \_\_\_\_\_

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## 1. SCOPE AND APPLICATION

This standard operating procedure (SOP) applies to the collection by grab sampling of surface water samples for the analysis of ultra low level metals in the range of ng/L (parts per trillion) using the “clean hands/dirty hands” grab methodology. It also covers non-ultra low trace metals and trace organics sampling. The purpose of this SOP is to describe the method of collecting surface grab samples including, but not limited to, streams, lakes, inter-tidal, offshore, and other surface waters. The “clean hands/dirty hands” portion of this method is not intended for the collection of samples found at industrial facilities or in areas of known high metals or organics concentrations. For further information regarding historical trace metals collection methods, contamination sources and control, or other ultra low trace metals issues, refer to section 15. REFERENCES.

## 2. ASSOCIATED DOCUMENTS AND SOPS

- Labware and Equipment Cleaning Procedures (SOP # 630v1)
- Clean Sampling for Ultra Trace Metals by Peristaltic Pump (SOP #215v2)
- Clean Sampling for Ultra Trace Metals using Modified Niskin Bottles (SOP #221v2)
- Clean Sampling for Trace Metals and Trace Organics using Modified Automated Samplers (SOP #223v2)
- Sampling Methods for Stream and River Water (SOP # 214v3)
- Lakes Water Column Sampling (SOP #213v2)

## 3. METHOD SUMMARY

When analyzing for the dissolvable trace metals constituents (except mercury) in surface water, it is necessary to filter samples within 15 minutes of collection. This constraint requires that all metals samples be filtered while in the field. Field filtration is not required when collecting trace organics samples. Samples for dissolved mercury by CVAF are filtered in the lab.

Metals sampling of surface water can be either for ultra low level analysis where special clean-handling techniques are required, or for routine (non-ultra) low level analysis using the more standard sampling methodologies (see SOP # 214v3).

### 3.1. Ultra Low Trace Metals

Prior to the sampling event, all sampling containers are cleaned according to Trace Metals SOP # 630v1. The sampling procedure for Trace Metals samples will utilize the “clean hands/dirty hands” technique. Prior to arrival at the sampling site, members of the sampling team will be designated as “clean hands” and “dirty hands”. “Clean hands” handles all operations involving contact with the sample bottle. “Dirty hands” is responsible for all other activities that do not involve direct contact with the sample. All equipment is non-metallic and sampling staff will always wear extra long, non-powder, PVC gloves. Prior to leaving the laboratory, bottles are filled for atmosphere blanks and sample containers are double-bagged with plastic zip-lock type bags. Samples are collected using the dip method (Sections 8.2.2. and 3.2.3). Samples containers are then double-bagged and placed on ice for transport to the laboratory.

### 3.2. Non-Ultra Low Trace Metals

Samples are collected using the dip method using PVC gloves. Samples are not bagged, but are placed in a cooler with ice for transport to the laboratory (see SOP # 214v3).

### 3.3. Trace Organics

Samples are collected using the dip method. Special mid-size mouth, one-liter glass bottles will be used for non-volatile parameters. Care must be taken to minimize atmospheric contamination. The preference is for sampling staff to not use gloves, but if staff is more comfortable wearing gloves, purple Nitrile surgical gloves are acceptable. Samples are placed in a cooler with ice for transport to the laboratory.

## 4. DEFINITIONS

- **Ambient Water** - Waters in the natural environment (e.g., rivers, lakes, streams, Puget Sound).
- **Sample Container** - Bottles used to collect the sample for transport and storage to the Lab.
- **Ultra Low Trace Metals Samples** - Samples that will be analyzed for metals in the ng/L (parts per trillion) range. These include the following LIMS products: HG-CVAF-UL, HG-CVAF-UL, DISS and all ICPMS-UL products.
- **Atmosphere Blank** - a sample of analyte-free water in a lab-supplied container which is left uncapped during sampling. The analysis of the atmosphere blank is used measure possible contamination from airborne sources.
- **Reagent Water** - Reverse-Osmosis water collected from the Trace Metals Clean Room and demonstrated to be free (or as low as possible) from the analytical parameters of interest and potentially interfering substances. This water is equivalent to ASTM Type I water (ASTM D 1193). (Note: this water is not considered sterile.)
- **Field Replicate Sample** - A field replicate sample consists of a second sample collected right after the first sample at the same sampling location using identical collection methodology. Both the field replicate and the first sample are generally analyzed for identical parameters. The purpose of the field replicate sample is to measure and document the precision of field sampling methodologies and the homogeneity of the sample site.
- **Field Filtration Blank** - a sample of analyte-free water in a lab-supplied container which is filtered in the field using the same equipment and process used for filtration of field samples.

## 5. SAFETY AND HAZARDOUS MATERIALS MANAGEMENT

Grab sampling often appears docile, but there are many dangers that must be taken into account. Some of these dangers include the following:

- rolling beach logs and other debris
- wave action
- unstable surface

- Potentially toxic water
- winter cold issues
- broken glass, including sample containers
- fast currents, floods

All sampling personnel will follow standard safety procedures while on a sampling run. Recommended equipment includes foul weather gear, appropriate safety gloves, and eye protection. Personnel can choose to wear personal flotation devices.

## 6. SAMPLE CONTAINERS, PRESERVATION, AND STORAGE

- Double polypropylene-bagged, acid washed and pre-labeled HDPE 500 ml bottles with lids for ICPMS UL Trace Metals analysis.
- Double polypropylene-bagged (bags pre-labeled), acid washed Teflon™ (FEP) 500 ml bottles with lids for CVAF-analyzed Hg samples.
- One set of glass, 1 liter medium-mouth bottles for Trace Organics analysis.
- One set of glass VOA bottles.

## 7. APPARATUS, EQUIPMENT, AND CONSUMABLES

- PVC non-powder gloves (Extra Long) (VWR Catalog #32916-53x).
- Purple Nitrile Gloves (VWR #40101-34x).
- Clean non-metallic ice chest with ice.
- Field sheets.
- Reagent Water (collected from Trace Metals Clean room by “Clean Hands” personnel in Trace Metals sample containers). Two sets are required if both an atmosphere blank and field filter blank are to be collected.
- Reagent Water (collected in Trace Organics bottles) for atmosphere blanks.
- Peristaltic pump with tubing and battery power supplied.
- Cleaned Nalgene 500 ml filtration apparatuses with 0.45 micron filters for dissolved metals sampling. A separate unit is required for each sample.

## 8. PROCEDURES

### 8.1. In-Lab Preparation

#### *8.1.1. Pre-Event Cleaning Procedure*

The Environmental Services Unit (ESS) is responsible for either cleaning or arranging to have all sampling apparatus cleaned. Trace Metals Lab scientists provide cleaned filtering apparatus for dissolved metals and acid-washed sample bottles. ESS is responsible for the proper deployment and maintenance of the rest of the sampling equipment.

#### *8.1.2. Final Preparation*

Clean sample containers are placed into boxes. Trace Metals sample containers are packaged into double plastic bags. Trace Organics sample containers should be kept separate from the

plastic bags. Sample coolers are filled with plastic bags containing ice. All sampling apparatus are transported to a vehicle the morning of the sampling event. It is organized to enhance efficiency and cleanliness once on the sampling site.

### **8.1.3. Atmosphere and Filter Blanks**

A sample container for each appropriate parameter is filled with reagent water at the Lab and transported into the field with the other sample containers. Separate bottles, each filled with reagent water, must be prepared if both an atmosphere and field filter blank are to be collected.

## **8.2. On-Site Procedures**

### **8.2.1. Roles of the Ultra Low Trace Metals Sampling Team: ‘Clean Hands/Dirty Hands’**

#### **8.2.1.1. Summary of Clean Hand’s Responsibilities**

- Opens inner sealed bags.
- Fills all lab sample containers.
- Filters dissolved samples and prepares field blanks.

#### **8.2.1.2. Summary of Dirty Hand’s Responsibilities**

- Opens outer sealed bags.
- Never comes in contact with lab sample containers.
- Enters data on the field sheets.
- Sets up the filtration apparatus and pump

### **8.2.2. Field Filter Blanks**

After the sampling personnel have reached the first sampling location of the day, but before taking the first sample, the filtering equipment is tested for contamination.

1. Dirty Hands sets up the peristaltic pump and attaches the battery.
2. Wearing clean PVC gloves, Dirty Hands opens the outer bag of the double bagged pre-cleaned filter apparatus.
3. Clean Hands opens the inner bag and removes the filter apparatus.
4. Dirty Hands attaches the suction side of the pump tubing to the filter suction port.
5. Dirty Hands opens the outer bag containing the filter blank bottle filled with reagent water.
6. Wearing clean PVC gloves, Clean Hands opens the inner bag and extracts the filter blank bottle.
7. Clean Hands opens the filter lid and blank bottle lid and pours the contents of the blank bottle into the filter apparatus and closes the lid.
8. Dirty Hands turns on the peristaltic pump. When the blank water has filtered, Dirty Hands turns off the pump and removes the tubing from the port.
9. Clean Hands removes the label from the original field filter blank bottle and attaches it to the bottom of the filtering apparatus which holds the filtrate.

10. Clean Hands unscrews the filter top from the filtrate bottom and caps the filtrate bottle. Clean Hands puts the filtrate bottle into the inner bag and closes the bag.
11. Dirty Hands closes the outer bag and stores the double-bagged field filter sample on ice in the same cooler that the samples will be stored in.

### ***8.2.3. Atmosphere Blank Collection***

#### ***8.2.3.1. Ultra Low Trace Metals***

The atmosphere blank will have been prepared in the Lab using the procedure described in Section '8.1.3. Atmosphere Blanks'. Once on-site and just before sample collection begins:

1. Dirty Hands opens the outer bag of the double bagged atmosphere blank bottle.
2. Clean Hands opens the inner bag, pulls the bottle out and removes the cap.
3. The bottle remains open for the same length of time that the samples are typically exposed to the atmosphere.
4. Clean Hands replaces the cap, puts the bottle back into the inner bag and re-seals.
5. Dirty Hands closes the outer bag and places it into the cooler filled with ice.

#### ***8.2.3.2. Non-Ultra Low Trace Metals and Trace Organics***

This is not a Clean Hands/Dirty Hands operation. The atmosphere blank bottle will have been previously filled with reagent water in the Trace Organics laboratory. Once on-site and just before sample collection begins:

1. The sampler removes the cap of the atmosphere blank.
2. The bottle remains open for the same length of time that the samples are typically exposed to the atmosphere.
3. The sampler replaces the cap and puts the bottle into the cooler filled with ice.

### ***8.2.4. Clean Sample Collection: Ultra Low Trace Metals using the Grab Technique***

Sample collection can start after the field filter blank has been collected and the atmosphere blank cap has been removed, initiating blank sample exposure to the atmosphere (refer to sections 8.2.2. and 8.2.3.).

Dissolved metals samples are collected in a 500 ml bottle and then filtered into and stored in the bottom portion of the filtering apparatus. Note that dissolved metals samples (except ultra low level mercury) must be filtered within 15 minutes of sample collection. Dissolved Mercury samples are typically filtered in the lab but a portion of the ICP or ICPMS filtrate can also be used if split in the field into a 500 ml FEP bottle. Total ICP and ICPMS metals samples are collected in a second 500 ml bottle, while mercury samples are collected in a separate 500ml FEP bottle. Total metals and mercury samples do not require field filtration.

Each trace metals bottle is rinsed prior to sample collection. The rinsing procedure consists of removing the cap, partially filling the bottle with ambient water, replacing the cap, inverting

three times, then pouring out the water. This is repeated three times for complete rinsing. When collecting, do not fill bottles above shoulder. This headspace is used for mixing and adding preservative.

1. Prior to entering the water, the team determines the direction of current and effects of wave action, and if it is safe to enter.
2. The team enters the water down-current from the collection site and wades in a manner to avoid disturbing the water with sediment disruption.
3. Wearing clean PVC gloves, Dirty Hands removes the first sample packet from the bottle kit and unzips the outer plastic bag.
4. Wearing clean PVC gloves, Clean Hands opens the inner bag, and removes the sample container.
5. Facing upstream, Clean Hands removes the cap, tips the sample container downward at a 45 degree angle and plunges the container in so that the mouth is approximately 5 inches below the surface. In the same motion, the sample container is then turned upward so it begins filling with ambient water. The container must remain below the surface until it is full.
6. Once the sample container is filled, Clean Hands lifts the sample container out of the water and immediately replaces the cap.
7. Clean Hands then places the sample container back into the inner bag, and reseals it.
8. Dirty Hands closes the outer bag, then both return to the van.
9. If dissolved metals are required, Dirty Hands sets up the peristaltic pump and attaches the battery.
10. Wearing clean PVC gloves, Dirty Hands opens the outer bag of the double bagged pre-cleaned filter apparatus.
11. Clean Hands opens the inner bag and removes the filter apparatus.
12. Dirty Hands attaches the suction side of the pump tubing to the filter suction port.
13. Dirty Hands opens the outer bag containing the sample container.
14. Wearing clean PVC gloves, Clean Hands opens the inner bag and extracts the sample container.
15. Clean Hands opens the filter lid and sample container lid and pours the container's contents into the filter apparatus, then closes the filter lid.
16. Dirty Hands turns on the peristaltic pump. After filtration, Dirty Hands turns off the pump and removes the tubing from the port.
17. Clean Hands removes the label from the original sample container and attaches it to the bottom of the filtering apparatus which holds the filtrate.
18. Clean Hands unscrews the filter top from the filtrate bottom and caps the filtrate bottle. Clean Hands puts the filtrate bottle into the inner bag and closes the bag.
19. Dirty Hands closes the outer bag and stores the double-bagged filtrate bottle on ice in the appropriate sample cooler.

This process is repeated until all metals sample containers for this site are filled. Clean Hands must try to avoid collecting any debris, including sticks, seaweed, leaves, feathers, etc. During this process, atmospheric exposure should be kept to a minimum. Touching anything besides the

sampling bottles is strictly prohibited. If this happens, new gloves should be donned. New gloves are also donned by both Clean Hands and Dirty Hands between sample sites.

### ***8.2.5. Standard Sample Collection: Non-Ultra Low Trace Metals and Trace Organics using the Grab Technique***

Sample collection can start after the field filter blank has been collected and the atmosphere blank cap has been removed, initiating blank sample exposure to the atmosphere (refer to sections 8.2.2. and 8.2.3.).

1. Prior to entering the water, the team determines the direction of current and effects of wave action.
2. The team enters the water down-current from the collection site and wades in a manner to avoid disturbing the water with sediment disruption.
3. The sampler opens the sample container, tips it downward at a 45 degree angle and plunges the container in so that the mouth is approximately 5 inches below the surface. In the same motion, the sample container is then turned upward so it begins filling with ambient water. The container must remain below the surface until it is full.
4. Once the sample container is filled, the sampler lifts the sample container out of the water and replaces the cap.
5. The sampling team returns to the van for the filtration step.
6. After setting up the peristaltic pump and battery and donning clean PVC gloves, the suction side of the pump tubing is attached to the filter suction port of a fresh pre-cleaned filter apparatus.
7. Both the filter lid and sample container are opened and the container's contents are poured into the filter apparatus, closing the filter lid afterwards.
8. After filtration, the label from the original sample container is removed and reattached to the bottom of the filtering apparatus which holds the filtrate.
9. The filter top is unscrewed from the filtrate bottom and the filtrate bottle is capped. The labeled filtrate bottle is then placed into the cooler filled with ice.

This process is repeated until all sample containers for this site are filled. The sampler must try to avoid collecting any debris, including sticks, seaweed, leaves, feathers, etc. During this process, atmospheric exposure should be kept to a minimum.

### ***8.2.6. Cleaning Procedure between Samples and/or Stations***

For grab sampling, no sampling equipment is used besides dedicated sample containers so cleaning is not required between samples aside from changing gloves.

## **8.3. Sample Login**

The samples should be logged in according to standard procedures. Metals samples are then delivered to the Trace Metals Lab for preservation. Subcontracted samples must either be sent to the subcontract lab immediately following the collection event, or placed in a cooler at 4 degrees C and sent out the following morning.

## **9. QA/QC REQUIREMENTS (FREQUENCY AND ACCEPTANCE LIMITS)**

The QC practices defined in this section are subject to change for specific projects. Project-specific QC requirements that differ from this SOP should be defined in a Sampling and Analysis Plan prepared for each project.

### **9.1. Initial Validation**

Validation has been completed for Clean Hands/Dirty Hands methodology. See Ultra Low Level Metals Sampling at Depth Validation Document. King County Environmental Laboratory, 1999. Since no sampling equipment is used except for sample bottles, further validation is unnecessary.

### **9.2. Continuing Quality Control**

For the ultra low trace metals and trace organics samples, field replicates and blanks (atmosphere and field filtration) will be collected at a minimum of one set for each day of the sampling event. If multiple sets are required, they are typically collected at the first and last stations of the day.

#### ***9.2.1. Field Replicates***

A minimum of one field replicate will be collected per sampling event. If more than 20 field samples are to be collected, a minimum frequency of 5% (ie, 1 replicate for every 20 samples) is required. Field replicates are collected using the same sampling method as the original sample. Gloves should be changed between sample sites.

#### ***9.2.2. Atmosphere and Field Filtration Blanks***

For ultra low trace metals and trace organics, two sets of atmosphere blanks will be collected per sampling event. These samples will be typically collected at the first station and at the last station simultaneously with the collection of ambient samples. The collection is done by opening the cap (of the previously-filled atmosphere blank) for the equivalent time and within the same physical space that a sample container is being filled.

When dissolved metals samples are to be filtered in the field, one field filtration blank must be collected to test the filtering equipment for contamination prior to collection of the first sample. The collection procedure is described in section 8.2.2.

### **9.3. Acceptance Limits**

The results of each blank analysis should be less than the MDL. If results of a particular blank are above the MDL, the data will be evaluated against results of other Field and Method Blanks, and against measured concentrations in the field samples. The samples and blanks may be re-analyzed if the source of the contamination is identified as a laboratory contaminant. The Relative Percent Different (RPD) of each set of field replicates will be calculated. The acceptance limits will be project-specific.

## 10. DATA REDUCTION, REPORTING, REVIEW, AND DOCUMENTATION

Field sheet data for each sample will include:

- Time and date of sample collection. (Note: The time recorded for each station is when the first sample is collected.)
- Sample Function (i.e., shows associations between field QC samples and a given environmental sample).
- Sample Method (refer to Sampling Methods Code).
- Precipitation (recorded as None, Light, Medium, or Heavy for ultra low trace metals).
- Sample Information (optional).
- Client locator (optional).
- Wind speed and Direction (if necessary).
- Tide Height and Condition (if necessary).

Field QC data is to be loaded to LIMS using the following locators and QC types:

- Atmosphere Blank – ATMOSBLANK locator and ATB QC type
- Field Filter Blank- FFBLANK locator, and FFB QC type
- Field Replicate- station name where collected, and FREP QC type

Quarterly, the field QC data (field blanks and field replicates) should be downloaded using the Field QC query functions in LIMSView. Results are to be reviewed for trends or consistent problems that might indicate a systematic error.

Field sheet data is entered into the Laboratory Information Management System (LIMS) for each sample. Field observations that could affect the quality of the samples (i.e., weather related and contextual commentary) are loaded to LIMS by way of the Field Observation document. When applicable, field crews note wind speed and direction, air temperature, cloud cover, and precipitation information. The TC then compiles these comments into a Word document that is entered into LIMS and linked to the field sheet data Work Group number.

## 11. STANDARDS AND REAGENTS

Not applicable.

## 12. CONTAMINATION

### 12.1. Trace Metals

EPA method 1669 states that the greatest challenge faced in trace metals determination, including the sampling portion, is preventing the samples from becoming contaminated. Routes of contamination include metal-containing sampling equipment, containers, reagent water, improperly cleaned and stored equipment, atmospheric inputs such as engine exhaust and even human contact. The goal will be to eliminate contamination by ensuring that any object that contacts the sample is nonmetallic and free from potential metal contamination.

Observe the following during the sample collection process:

- Minimize atmospheric exposure. Airborne particulate matter such as dust, dirt, exhaust, smoke, nearby corroded metallic material and human breath (Hg-containing dental amalgam) can contaminate samples.
- Wear clean, non-powdered gloves at all times. When gloves touch any potential contaminant, change them immediately.
- Use metal-free sampling equipment and containers. Materials such as fluorinated ethylene propylene (FEP), polytetrafluoroethylene (PTFE) or Teflon™, polyethylene, polycarbonate, polysulfone, polypropylene, and ultra pure quartz are free of contaminants when properly cleaned. FEP or PTFE must be used when collecting samples for ultra low or low level mercury determination.
- Pre-clean all sample bottles using a verified cleaning procedure.

## 12.2. Trace Organics

- Minimize atmospheric exposure.
- Wear clean, non-powdered gloves at all times. When gloves touch any potential contaminant, change them immediately.
- Pre-clean all sampling equipment and sample bottles using a verified cleaning procedure, or purchase pre-cleaned bottles.

## 13. PREVENTATIVE MAINTENANCE

Not applicable.

## 14. TRAINING

Clean Hands and Dirty Hands must go through a training process specific to this sampling method and be supervised by an experienced lead. The training process will include use of all sampling equipment and a summary of issues associated with ultra low trace metals data collection. This includes familiarization with all appropriate SOPs and references. Results from field blanks will be used to determine the effectiveness of this training.

## 15. REFERENCES

Method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels. July 1996. USEPA.

Method 1640: Determination of Trace Elements in Ambient Waters by On-Line Chelation Pre-concentration and Inductively Coupled Plasma-Mass Spectrometry. Draft 1996. USEPA.

Stewart, R. E. (1997) Collection of Freshwaters and Wastewaters for the Determination of Trace Elements. *Virginia Department of Environmental Quality SOP.*

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Ultra Low Level Metals Sampling at Depth Validation Document. King County Environmental Laboratory, 1999.

Method 1631: Mercury in water by Oxidation, Purge and Trap, and CVAFS. Revision E. August 2002. USEPA.