Quartermaster Harbor Benthic Flux Study Quality Assurance Project Plan

A Targeted Watershed Grant under the 2008 Puget Sound Initiative

July 2010

King County

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ABSTRACT

We propose to conduct a marine benthic nutrient flux study in Quartermaster Harbor as part of a larger study – the Quartermaster Harbor Nitrogen Management Study. The expected outcomes of the benthic nutrient flux study are site specific measurements of benthic fluxes of essential nutrients that will support the development, calibration, and testing of a water quality model of the harbor that will be developed as part of the larger study. The larger study is designed to evaluate the role of nitrogen in the control of dissolved oxygen in Quartermaster Harbor, a sensitive marine embayment of Vashon-Maury Island in Puget Sound

1.0. INTRODUCTION

King County was awarded a West Coast Estuaries Initiative (WEI) grant by Region 10 of the U.S. Environmental Protection Agency (EPA) to conduct the Quartermaster Harbor Nitrogen Management Study. The goal of this study is to support the protection and restoration of Quartermaster Harbor–a high value, coastal aquatic resource on Vashon-Maury Island (VMI) in Puget Sound. Partners working with King County on this grant-funded study include the University of Washington-Tacoma (UWT), and the Washington Department of Ecology (Ecology). The WEI grant will also support the enhancement of aquatic resource protection programs in an area threatened by growth pressures. This Quality Assurance Project Plan (QAPP) describes the benthic flux study planned as part of the Quartermaster Harbor Nitrogen Management Study (King County 2009a).

1.1 Study Need

A recent study conducted by Ecology to support the development of a water quality model of South Puget Sound found that nutrient fluxes from marine sediments of shallow embayments may be significant source of nitrogen to marine waters during the critical period of low dissolved oxygen (Roberts et al. 2008). Based on the data provided in Roberts et al. (2008), the marine sediments of Quartermaster Harbor may also be a relatively significant source of nutrients to Quartermaster Harbor during the critical period of low dissolved oxygen (King County 2010). King County (2010) recommended conducting a benthic nutrient flux study in Quartermaster Harbor to confirm the rates measured in other shallow embayments of Puget Sound and provide site-specific data for use in the development of the marine water quality model of the harbor.

Generally, the predictive reliability of any particular model is based on the ability of the model to accurately reproduce specific observations under a variety of conditions (NRC 2007). In the case of a water quality model that includes water column and sediment interactions, reliable predictions (or specifications) of benthic nutrient and dissolved oxygen fluxes are critical (DiToro 2001). The ongoing marine monitoring program, including monthly water column sampling and high frequency sampling at fixed moorings described in the Quartermaster Harbor Nitrogen Management Study QAPP (King County 2009a) will provide spatial and temporal nutrient and dissolved oxygen profiles in the harbor for model calibration and testing. Demonstrating the ability of the water quality model to accurately reproduce these observations will provide measures with which to evaluate the reliability of the calibrated model. However, site specific observations of benthic fluxes will provide data that can be used to test the ability of the model to simulate sediment diagenetic processes and associated fluxes of nutrients and dissolved oxygen or to specify these measured fluxes as inputs to the model.

1.2 Description of Study Area

Quartermaster Harbor, located between Vashon and Maury Islands in Puget Sound, is sheltered from the wind and waves and receives runoff from about 40 percent of Vashon-Maury Island (Figure 1). It is a shallow, protected embayment that comprises approximately 12.1 km^2 (3,000 acres) of water surface area in an inner and outer harbor. Inner Quartermaster Harbor is especially sheltered and Judd Creek, located in the northwestern portion of the inner harbor, is the largest freshwater input. Transition zones between freshwater surface flows and the marine water within the bay include the estuaries at the mouth of Judd Creek, Fisher Creek, and Raab's Lagoon along with numerous smaller streams. Inner Quartermaster Harbor is shallow, with a greatest depth of about 5 to 6 meters and very little tidal flushing. Outer Quartermaster Harbor water depths range from about 11 to 46 meters with rapid tidal flushing. The subtidal sediments are generally dominated by silt and clay, although some shallow areas, especially in the outer harbor, are dominated by sand (University of Washington 1976, Long et al. 2002, King County 2009b, University of Washington Tacoma, unpublished data).

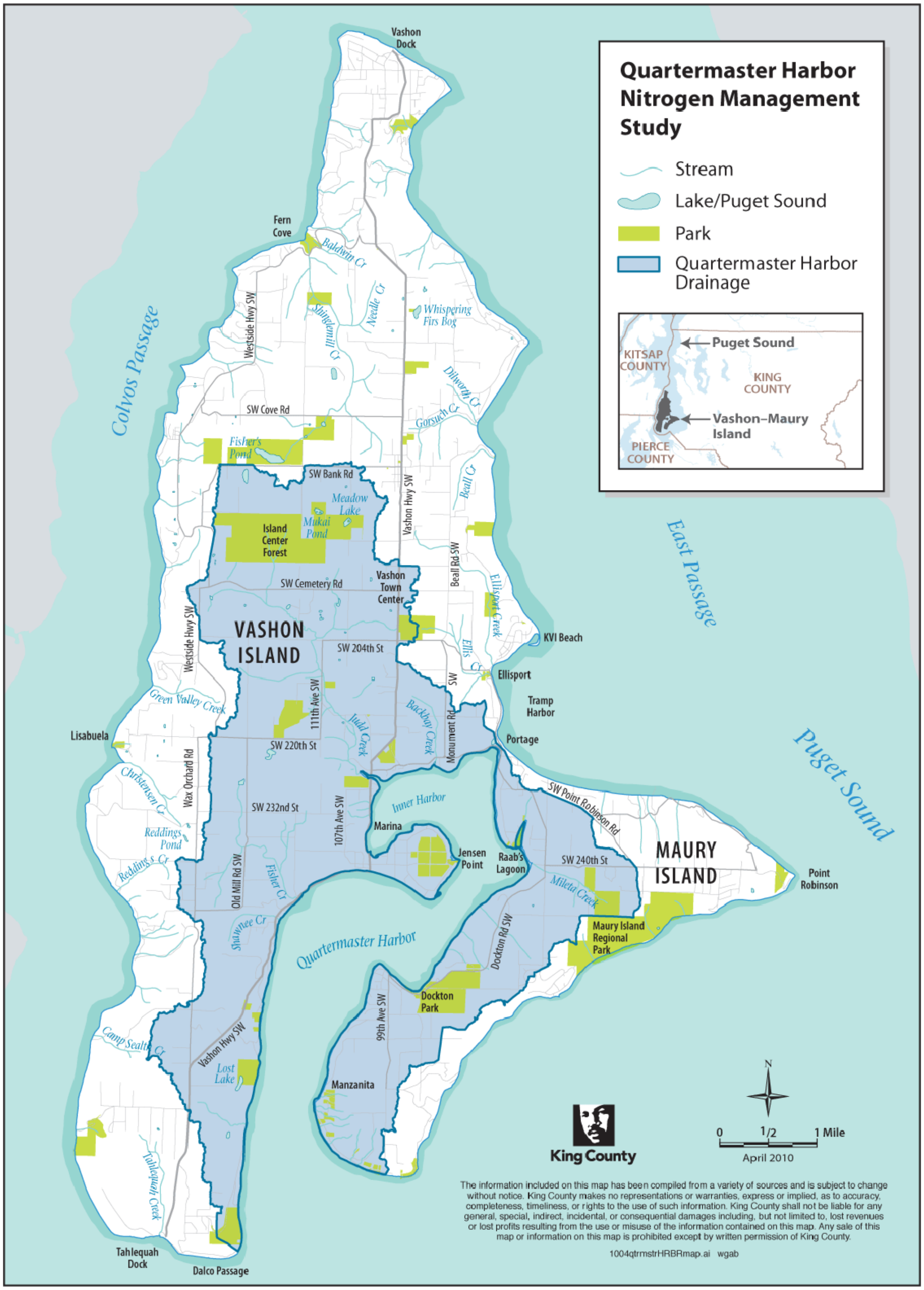

Figure 1. Map of Vashon-Maury Island highlighting the drainage area to Quartermaster Harbor.

1.3 Historical Data Review

Quartermaster Harbor and the upland areas draining to the harbor have been the subject of water quality and quantity investigations beginning at least as far back as the early 1970s. Previous studies of the marine sediments of the harbor include:

- Sediment characterization conducted as part of a comprehensive study of Quartermaster Harbor in the early 1970s (University of Washington 1976)
- Chemical, physical, and biological analyses of three samples from the outer harbor as part of a larger Southern Puget Sound sediment contaminant study conducted in 1999 (Long et al 2002)
- A sample collected from the inner harbor analyzed for chemical and physical parameters in 2007 (King County 2009b)
- A survey of 24 sediment locations dispersed throughout the harbor in 2007-2008 focused on identifying the distribution of cysts of *Alexandrium catenella*, a toxin producing marine dinoflagelate (University of Washington Tacoma, unpublished data)

Based on these sources of information, the inner harbor sediments have relatively higher organic carbon content, typically greater than 5 percent total organic carbon (TOC) and consist of very fine muds. The outer harbor sediments generally become less organic (typically less than 2 percent TOC) and coarsen to sands at the harbor entrance. The marine biological component of the University of Washington (1976) study included a map that indicated that subtidal sediments were primarily mud-like, while some shallow areas along the shoreline, especially in the outer harbor were primarily sandy. This pattern of TOC and grain size is generally confirmed by the more recent data generated in the other three studies identified above (Figure 2).

Although no benthic nutrient flux measurements have previously been made in Quartermaster Harbor, as noted above, Ecology recently conducted a benthic nutrient flux study in four shallow embayments of South Puget Sound (Figure 3). Benthic flux chambers were deployed in three discrete sampling events at three depths (5, 15, and 25 m) in four South Puget Sound inlets (Budd, Carr, Case, and Eld) during September and October 2007 (Roberts et al. 2008). A range of benthic flux rates and an average rate for all sampling events were reported. The sample results are summarized along with an average of estimates from other published sources in Table 1.

The estimated dissolved inorganic nitrogen (DIN – the sum of ammonia and nitrate+nitrite nitrogen) benthic flux based on studies conducted in South Puget Sound (Roberts et al. 2008) indicates a contribution in late summer from Quartermaster Harbor sediments that could be almost 20 times higher than the largest external source (tributary streams) (Table 2). In general, streamflow and stream DIN concentrations are lowest during late summer, so the relative contributions from the other external sources are likely to be relatively more significant than indicated in this annual summary. Estimated soluble reactive phosphorus (SRP) input from benthic nutrient release from harbor sediments during late summer is estimated based on the South Puget Sound data to be potentially much larger than all other external sources–over two orders of magnitude higher (see Table 2). The estimated benthic flux of silica also suggests that sediments could be a significant source of this nutrient during late summer – potentially over an order of magnitude higher than the contribution from streams (see Table 2). The reader is referred to King County (2010) for details regarding the methods and assumptions used to develop the loading estimates discussed above.

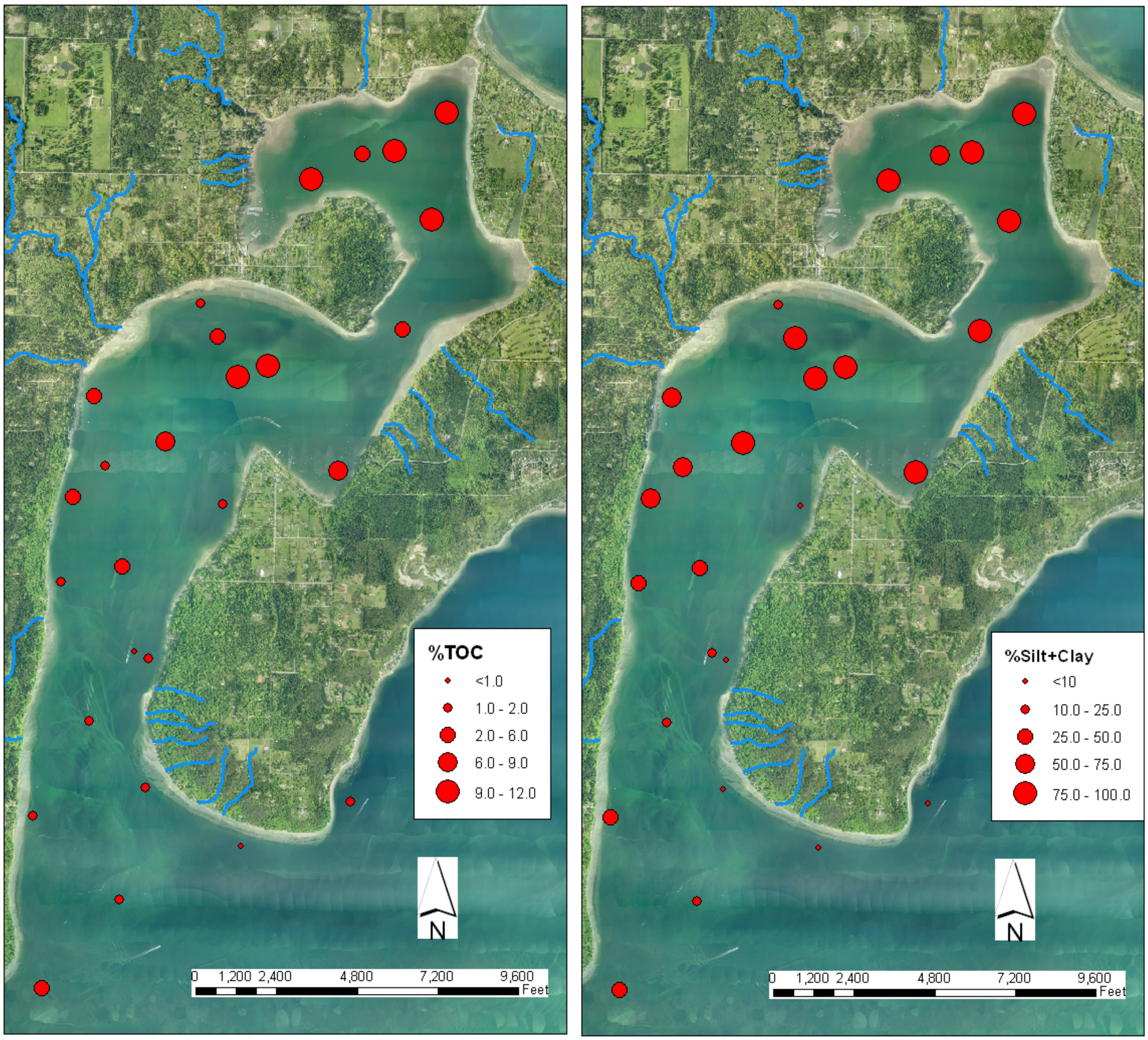

Figure 2. Map of Quartermaster Harbor showing distribution of percent total organic carbon and fine sediment (percent silt+clay).

Sources: Long et al. (2002), King County (2009b), UW Tacoma (unpublished)

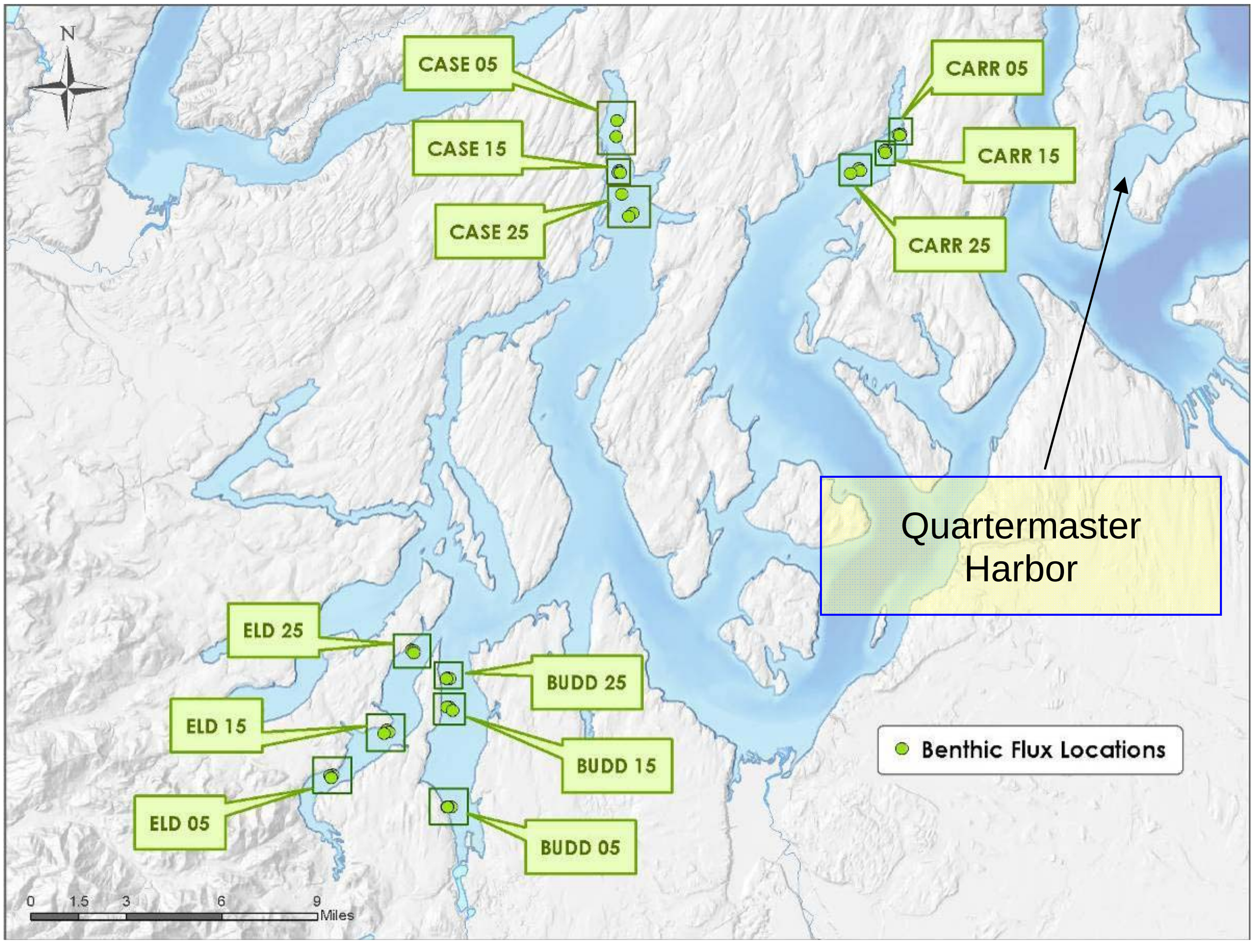

Figure 3. Map showing locations where Ecology conducted benthic nutrient flux studies in South Puget Sound.

Source: Roberts et al. (2008)

Table 1. Benthic nutrient flux rates measured by Ecology in South Puget Sound embayments and published estuarine/marine benthic nutrient flux data

Constituent	Range	Average	World Flux Database Average *
	$(g/m^2$-day)		
Ammonia Nitrogen	nr	nr	0.040
Dissolved Inorganic N	0 – 0.13	0.052	0.064
Organic Nitrogen	-0.10 – 0.34	0.038	-
Total Nitrogen	-0.07 – 0.48 (E)	0.085	-
Orthophosphate Phosphorus	-0.02 – 0.11 (E)	0.024	0.015
Total Phosphorus	-0.008 – 0.115	0.025	-
Dissolved Silica	-	-	0.200

nr – Not reported

E – Estimate derived from figures found in Appendix F of Roberts et al. (2008).

* World Flux Database – Chesapeake Biological Laboratory (Bailey and Boynton, 2007) as reported in Roberts et al. (2008), with the exception of data for dissolved silica which came from DiToro (2001) who reported a range of 0.050 to 0.300 g Si m^{-2}-day for Chesapeake Bay.

Table 2. Estimated nutrient loading to Quartermaster Harbor from the atmosphere, surface streams, groundwater, nearshore septic systems, and harbor sediments

	TN	Organic N *	DIN	NO3-N	NH3-N	TP	Organic P *	SRP	DSi
					(kg/d)				
Atmospheric	33.6	28.9	4.7	3.3	1.3	1.0	0.5	0.5	23
Stream Inputs	52.0	11.9	40.0	39.5	0.5	1.8	1.0	0.8	215
Groundwater	8.0	0.0	8.0	8.0	0.0	0.2	0.0	0.2	80
Nearshore Septics	11	0	11	0	11	2.6	0	1.9	0
Benthic Flux	1176	526	720	-	-	346	12	332	2768

TN = total nitrogen; DIN = dissolved inorganic nitrogen; NO3-N = nitrate+nitrite nitrogen; NH4-N = ammonia nitrogen; TP = total phosphorus; SRP = soluble reactive phosphorus or orthophosphate phosphorus; DSi = dissolved silica

Source: King County (2010)

2.0. STUDY GOAL AND OBJECTIVES

2.1 Study Goal

The purpose of this study is to measure benthic fluxes of dissolved oxygen and nutrients *in situ* in Quartermaster Harbor during critical conditions for dissolved oxygen in Quartermaster Harbor for use in water quality model calibration and testing. Benthic sediment fluxes of nutrients are a potentially significant source of nutrients to the harbor in late summer for which no site specific data currently exists. The expected outcomes are local benthic flux estimates from Quartermaster Harbor and increased confidence in water quality model reliability.

2.2 Project Management and Oversight

This study will be managed by King County and includes collaborators from the UWT, Ecology, and the Groundwater Protection Committee. Although no formal technical advisory committee has been formed, this QAPP and products resulting from this study will be reviewed by the project team and technical reviewers assigned by EPA Region 10, primarily the EPA Project Monitor assigned to this grant. In addition, Mindy Roberts, the Ecology lead on the South Puget Sound benthic flux study, will provide technical review of this study QAPP and provide information and recommendations for implementation of this study – several have already been incorporated into this QAPP.

3.0. STUDY DESIGN

A total of five benthic flux chambers will be deployed in Quartermaster Harbor in September 2010. September was chosen for sampling because this is the general period when maximum flux rates were observed in the Budd Inlet benthic flux study (LOTT, 1998) and it is the period when dissolved oxygen concentrations are typically lowest.

The proposed locations of the flux chambers are shown in Figure 4. Station descriptions and proposed coordinates for each sampling site are summarized in Table 3. A base of operations will be established at Dockton where a public dock is available for vessel mooring and transferring equipment and samples to and from the field vessel.

Prior to the deployment of each chamber, the vessel fathometer will be used to ensure the seabed is relatively flat with no obstructions. This will be accomplished by cruising 2 or 3 times over the proposed deployment location for each chamber. In the event that the proposed location is deemed unsuitable, areas immediately adjacent to the proposed location will be searched via the vessel fathometer for a suitable location at approximately the same water depth. Using the vessel davit, the chamber will be lowered slowly through the water column and placed on the seafloor so that the bottom sediments are disturbed as little as possible.

If available, the King County Sheriff Marine/Dive/Rescue Unit will provide dive support during the deployment, primarily to verify and document that the chamber is seated properly on the bottom (i.e., the rim is in contact with the sediment). A tethered camera or a handheld dive camera will be used to document the position of the chamber on the sediment surface and the general character of the bottom near the chamber. A conductivity-temperature-depth (CTD) cast will also be conducted at each location, using a calibrated Seabird 19 CTD provided by UWT, at the time of deployment to characterize the water column stratification and dissolved oxygen conditions at each location.

The benthic flux chambers will remain at each location for approximately 24 hours. Once deployed, sample grabs for Winkler titration of dissolved oxygen and nutrient analysis for nitrogen, phosphorus, and silica compounds will be performed initially and repeated four more times during the deployment for a total of five sampling events per chamber. The plan is to collect water samples from each chamber at approximately 2, 4, 8, and 24 hours after initial deployment sampling. Nutrient analyses will include nitrate+nitrate, ammonia, total nitrogen, soluble reactive phosphorus (SRP also referred to as orthophosphate phosphorus or ORTHOP), total phosphorus, and dissolved silica. Calibrated Hydrolab sondes with stirrers will be used to autonomously measure dissolved oxygen levels, temperature, salinity, pH, and depth at 15 minute intervals within each benthic flux chamber during the deployment period.

Log sheets will be maintained during each sampling round noting date, time, station, position using Global Positioning System (GPS), weather, serial numbers, and notes on sample collection. All samples collected will be transferred under chain-of-custody from the Quartermaster Harbor base of operations at Dockton by King County Environmental Sampling Section (ESS) staff for transfer to the King County Environmental Laboratory (KCEL) at the end of each sample day, coordinating with ESS and KCEL staff to ensure receipt upon delivery.

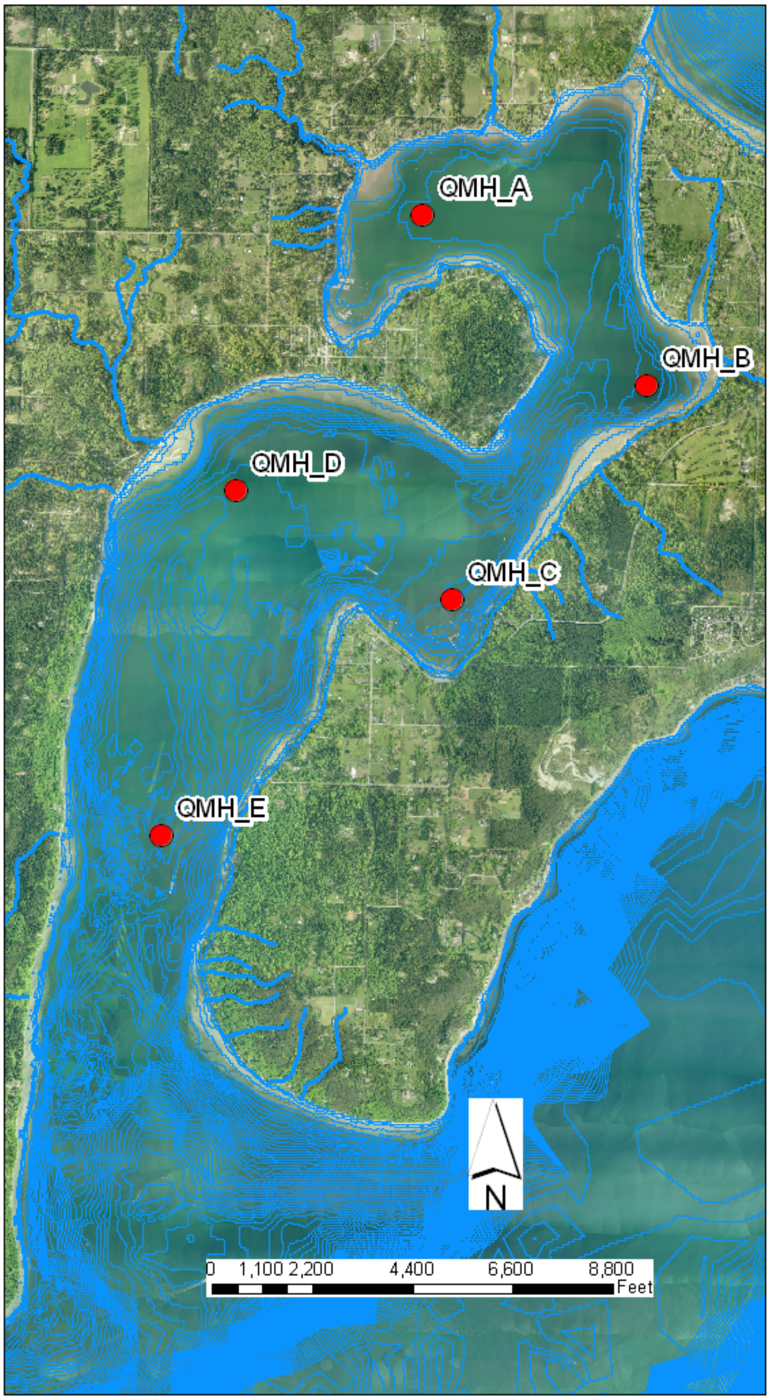

Figure 4. Map showing proposed locations of benthic nutrient flux chambers.

Note: Bathymetric contours (5-ft intervals; NAVD 1988) based on data from Finlayson (2005) are shown to illustrate expected bottom topography at each sampling station.

Table 3 Proposed station locations. Note proposed station coordinates may change slightly depending on site conditions encountered during deployment.

Station ID	Station Description	Approximate Depth in meters (feet)	Washington State Plan North Coordinates in feet (Easting/Northing)
QMH_A	Inner harbor near marina	4.0 (13.0)	1238172 / 149372
QMH_B **(replicated chamber)**	Inner harbor near Mileta	6.1 (20.0)	1243101 / 145646
QMH_C	Outer harbor near Dockton	7.6 (25.0)	1238818 / 140937
QMH_D	Outer harbor near Fisher Creek	14.0 (46.0)	1234079 / 143328
QMH_E	Outer harbor near Lost Lake Creek	16.8 (55.0)	1232421 / 135788

Note: Approximate depths relative to mean lower low water (MLLW).

King County will obtain five benthic flux chambers from Ecology that were used in the South Puget Sound Benthic Flux Study (Roberts et al. 2008). The chambers are inverted 12x12x36 inch inverted aquaria with a flange fitted around the open end of each chamber (Figure 5). The chamber is divided into two separate sub-chambers to allow for replicated sampling. The divider is constructed to support Hydrolab sondes sealed into the divide to sample each sub-chamber. The top of each sub-chamber is equipped with a one-way valve to allow replacement of chamber water with ambient water as water is withdrawn through a separate sampling port. Appropriate lengths of flexible tubing are connected to each sampling port to allow water to be drawn to the surface for sample collection using a peristaltic pump.

Prior to September 2010, the chambers will be checked to ensure that each unit has adequate lengths of flexible tubing for sampling and any chambers that are not already painted will be painted black to prevent sunlight from entering chambers placed in shallow areas. Sunlight has the potential to drive photosynthetic oxygen production, which would confound estimates of oxygen depletion during the deployment.

Pre-deployment preparation will also include calibration and testing to ensure that six Hydrolab sondes equipped with stirring mechanisms and capable of autonomous deployment in the chambers are available for this study – one sonde will serve as a backup in the event that one of the six sondes required malfunctions before deployment. Also prior to the field study in Quartermaster Harbor, at least one chamber will be tested in the Lake Washington Ship Canal next to the KCEL. Testing will be limited to verifying Hydrolab oxygen measurement and peristaltic pump sampling capability.

Within 24 hours of the field work to be conducted in Quartermaster Harbor, the seven Hydrolabs will be calibrated for measurement of salinity (specific conductance), dissolved oxygen, and pH according to KCEL SOP #205v4. The Seabird 19 CTD will be calibrated and programmed for measurement of salinity, temperature and depth according to KCEL SOP #220v3.

In the field, the chambers will be assembled at the staging area and checked to verify that the Hydrolab is firmly attached and that the stirring mechanism is working. One chamber will be set up in the inner harbor to utilize both sub-chambers with the intent of generating a replicate data set for benthic flux calculations. At each station, the chamber will be lowered into the water, initially with the open side up to remove all air bubbles. Once completely submerged, the chamber will be inverted and purged of air and lowered to the bottom with the open side down using lines attached to the chamber (see Figure 5). Care will be taken to gently lower the chamber to the bottom to minimize sediment disturbance. Care will also be taken to keep the open ends of the sample collection tubing out of the water.

Once the chamber is in place, inspection by diver or remote camera will determine if the chamber flange is adequately seated on the sediment surface. Once the field team is satisfied that the chamber position is acceptable, initial samples will be collected using the attached tubing and a battery operated peristaltic pump. To collect a sample, the tubing will be attached to the peristaltic pump and purged by 1.5 times the volume of water contained in the tubing to ensure that the sample obtained represents water from the chamber. The amount of water purged from the tubing will be measured in a graduated cylinder and discarded. The purge volumes depend on the inner diameter and length of tubing at each deployment location. As an example, purge volumes for 5 meter depth increments based on tubing with an inside diameter of 4.3 mm (0.17 in) are provided in Table 4.

Once the initial sample is collected, the pump will be disconnected from the sample tubing and the tubing will be folded over and clamped to prevent water from entering or leaving the tubing. The tubing will then be secured to a float attached by a line to the chamber so that it can be retrieved in the next sampling round.

Water collected from the chamber for Winkler dissolved oxygen analysis will be collected first to minimize oxygen exchange with the atmosphere. Samples will be drawn into 300 mL glass sample bottles without turbulence and filled to the rim and immediately fixed with 2 mL manganese chloride followed by 2 mL of alkali-iodide-azide solution. A stopper will be placed to ensure that no bubbles are trapped inside the bottle. With a finger on the stopper, the bottle will be inverted several times to mix the reagents. The labeled bottle will then be placed in a carrying case and the rim of each filled bottle will be covered with deionized water.

For unfiltered nutrient samples, water will be decanted directly into the sample bottles. For filtered nutrient samples, samples will be filtered in the field and the filtrate decanted directly into the appropriate sample container.

Following completion of the field study, the chambers will be retrieved and returned to Ecology per the instructions in the benthic flux chamber Standard Operating Procedures in Appendix A of Roberts (2007).

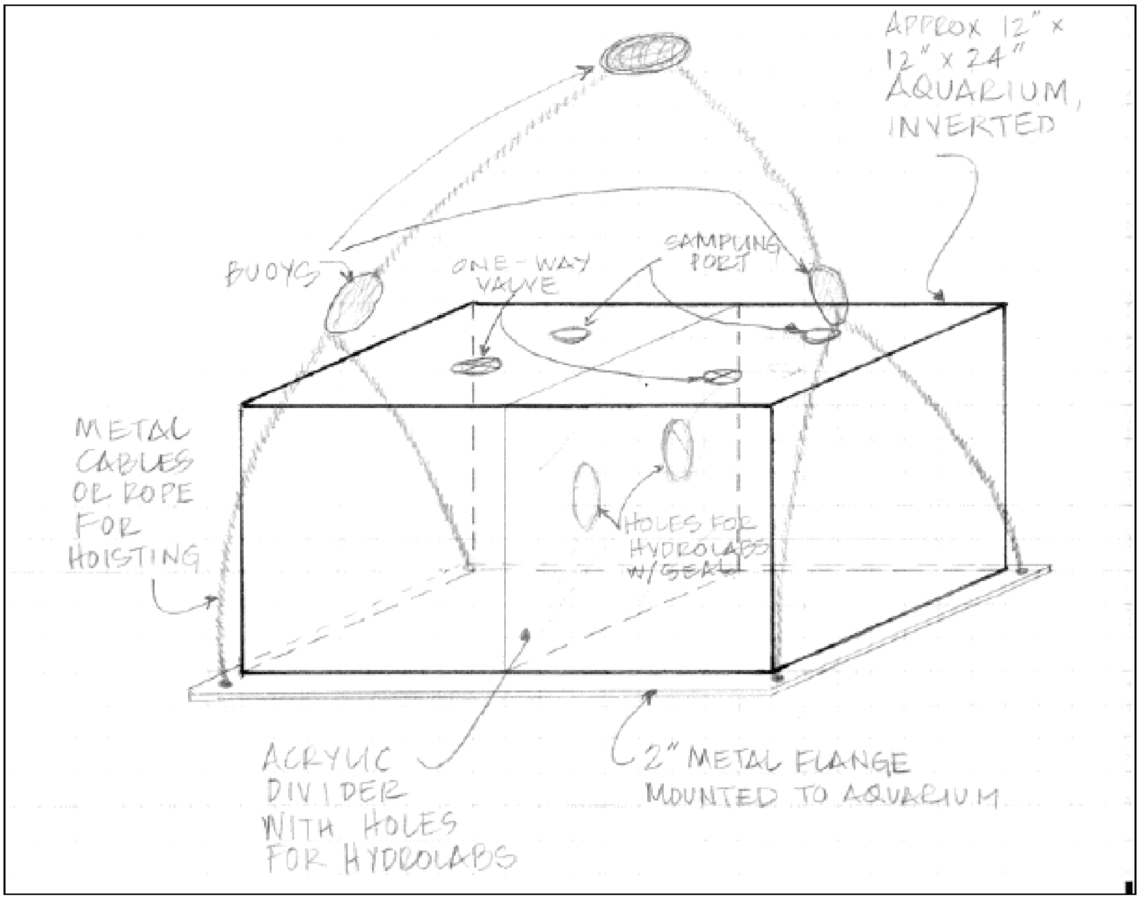

Figure 5. Schematic of the benthic flux chamber consisting of an inverted box with the open side toward the sediment.

Source: Roberts (2007).

Table 4. Tubing purge volume to clear stagnant water prior to collecting nutrient and dissolved oxygen samples based on inside tubing diameter of 4.3 mm (0.17 in).

Tubing Length	Tube Volume	Purge Volume (1.5 times tube volume) [a]
m	mL	
1	15	30
5	73	110
10	146	220
15	220	330
20	293	440
25	366	550

[a] **Rounded up to nearest 10 mL.**

Note: Volume of each chamber is approximately 1.5 cubic feet or 42,500 mL.

4.0. QUALITY OBJECTIVES

There are two types of quality objectives that need to be identified: Measurement Quality Objectives (MQOs) and Data Quality Objectives (DQOs). MQOs are "'acceptance criteria' for the quality attributes measured by project data quality indicators. They are quantitative measures of performance…" (USEPA, 2002). MQOs are the targets for precision, bias, and sensitivity against which QC results are compared. Precision is assessed from the results of replicate analyses of samples and standards. Bias is assessed from blanks and check standards and compared to their expected values. Sensitivity is related to the detection and reporting limits for the measurement method used. DQOs are needed in projects where the results are compared to a standard or used to select between two alternative conditions.

4.1 Measurement Quality Objectives

The MQOs for the field and lab measurements are presented in Table 5. Field crews and the King County Environmental Lab are responsible for adherence to objectives. King County will be responsible for verifying all MQOs are met.

Table 5 Measurement quality objectives for field and laboratory analyses.

Measurement		Precision (RSD*)	Bias (% deviation from true value	Lowest Value/Range of Interest
pH	Field	0.05 SU	N/A	1 to 14 SU
Temperature	Field	0.025 °C	0.05 °C	0.1 °C
Dissolved Oxygen	Field	10%	5%	0.1 mg/L
Specific Conductance/Salinity	Field	10%	5%	1 µS/cm
Pressure / Depth	Field	5%	1%	0.1 db
Ammonia Nitrogen	Laboratory	20%	5%	0.02 mg/L
Nitrite + Nitrate Nitrogen	Laboratory	20%	5%	0.01 mg/L
Total Nitrogen	Laboratory	20%	5%	0.05 mg/L
Orthophosphate Phosphorus	Laboratory	10%	5%	0.005 mg/L
Total Phosphorus	Laboratory	10%	5%	0.005 mg/L
Silica	Laboratory	10%	5%	0.05 mg/L
Dissolved Oxygen (Winkler)	Laboratory	xx	xx	0.1 mg/L

*RSD (relative standard deviation) is calculated as the ratio of the standard deviation and the mean of several values

NA–Not Applicable.

4.2 Laboratory Data Quality Objectives

The data quality objectives (DQOs) of this study are to collect data of sufficient quantity and quality to meet the study goals. Statistical analysis of data collected for this study will be performed to evaluate whether a sufficient quantity of data has been collected to meet the study goals. Data quality issues of precision, accuracy, bias, representativeness, completeness, comparability, and sensitivity are described below

The study goals are to characterize water concentrations of various constituents at different monitoring locations and depths and to evaluate any differences between sites and depths, either spatially or temporally. Statistical analysis of data that are "undetected"; i.e., laboratory analysis results reported as "<MDL", will use binomial calculations on the probability of a sample with a detectable concentration of the specific constituent and the probability of finding two and three samples in succession with detectable values at a given site or depth. Statistical analysis of data for those constituents that are detected regularly or occasionally will be accomplished through the use of medians and interquartile ranges.

Validation of project data will assess whether the data collected are of sufficient quality to meet the study goals. The data quality components 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 analytical chemistry may be evaluated by one or more of the following quality assurance/quality control (QA/QC) procedures:

- Collection and analysis of field replicate samples. Field replicate results should exhibit a relative percent difference less than 150% in order for the evaluation of the spatial and temporal chemical concentrations to be meaningful; and
- Analysis of various laboratory QC samples such as blanks, spikes and 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. This study is designed to collect data that adequately represents the flux of nutrients from Quartermaster Harbor marine sediments at key locations during the most critical period. Benthic flux chambers will be deployed at stations with predetermined coordinates and sampling depths to represent specific site conditions, both compared to other locations and at each location over time.

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 instrument setup and calibration procedures will aid in providing a complete set of data for this project. The goal for completeness is 100%.

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 the same or very similar equipment, equipment setup, and calibration to collect representative samples, along with standardized data validation and reporting procedures. The benthic flux chambers used in the study are the same equipment used in the previous study conducted by Ecology in South Puget Sound (Roberts et al. 2008) and will be set up and calibrated following the same protocols, with the expectation that the data should be comparable. The equipment will also be set up and calibrated in a consistent manner in the proposed study to ensure comparability of the data among the sampling stations.

5.0. SAMPLING PROCEDURES

Sampling activities will be conducted as described in this QAPP and consistent with the regionally-accepted guidance found in the Puget Sound Estuary Program's (PSEP) Puget Sound Protocols (PSEP 1997, 1998).

Station positioning for the benthic flux stations will be accomplished using a shipboard Differential Global Positioning System (DGPS). Prior to the sampling event, the prescribed station coordinates will be loaded into a computer. During the sampling, 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 will be 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 obtained.

All samples will be processed within established holding times and stored frozen or refrigerated as necessary (Table 6).

Table 6. Sample Containers, preservation, and holding times for King County marine water samples.

Analysis	Container	Preservation	Holding Time
Ammonia, Nitrate+Nitrite, Orthophosphate Phosphorus	60mL HDPE, CWM	Field filter within 15 minutes and freeze	14 days @ -20 ^{o}C
Total Phosphorus , Total Nitrogen	250mL HDPE, CWM	Refrigerate, <6°C and freeze within 2 days @ -20°C	28 days @ -20 ^{o}C
Dissolved Silica (collect together with Total Phosphorus and Total Nitrogen)	250mL HDPE, CWM	Filter within 1 day	28 days @ <6 ^{o}C
Dissolved Oxygen	300mL glass Wheaton with glass stopper	MnSO4, AIA within 15 minutes of collection	8 hours at ambient temperature

CWM–Clear wide mouth

HDPE–High density polyethylene

The King County Standard Operating Procedures for Hydroloab and CTD sonde setup and deployment will also be followed (SOP #205v4 and SOP #220v3).

5.1 Chain-of-Custody

The objective of chain-of-custody (COC) procedures is to allow tracking of the possession and handling of individual samples from the time of field collection through laboratory analysis. Once a sample is collected, it becomes part of the COC process. A sample is "in custody" when:

(1) it is in someone's direct possession; (2) it is within visual proximity of that person; (3) it is not in that person's direct possession, but locked up and sealed (e.g., during transport); or (4) it is in a designated secure sample storage area. Field or laboratory staff will complete a COC form, which will accompany each batch of samples as they are transported.

When sample custody is transferred to another individual, samples must be relinquished by the present custodian and received by the new custodian. This will be recorded at the bottom of the COC form where the persons involved will sign, date and note the time of transfer.

Sampling team members will keep sample coolers in locked vehicles while not in active use or visual range. Samples are hand delivered to the laboratory for analyses.

6.0. MEASUREMENT PROCEDURES

6.1 Field Measurements

During the collection of marine water samples, field parameters temperature, pH, salinity, and dissolved oxygen will be measured. These field parameters will be measured with a Hydrolab multi parameter probe (SOP #205v4) and water column profiles of temperature, dissolved oxygen, and salinity will be conducted using a Seabird 19 CTD (SOP #220v3). The detection limits for these parameters are provided in Table 7.

6.2 Laboratory Measurements

The benthic flux chamber samples will be analyzed for the following water quality parameters: ammonium nitrogen, nitrate + nitrite nitrogen, total nitrogen, orthophosphate phosphorus, total phosphorus, dissolved silica, and Winkler dissolved oxygen (Table 7). The methods and detections limits for these parameters are presented in Table 7.

Table 7. Water quality parameter method and detection limits for Quartermaster Harbor benthic flux study sites.

Parameters		Method	Method Detection Limit
Ammonia Nitrogen	Laboratory	Kerquel & Aminot 1997	0.005 mg/L
Nitrite + Nitrate Nitrogen	Laboratory	SM4500-N03-F	0.01 mg/L
Total Nitrogen	Laboratory	SM4500-N-C	0.05 mg/L
Total Phosphorus	Laboratory	SM4500-P-B,F	0.005 mg/L
Orthophosphate Phosphorus	Laboratory	SM4500-P-F	0.005 mg/L
Dissolved Silica	Laboratory	Whitledge 1981	0.05 mg/L
Winkler Dissolved Oxygen	Laboratory	SM4500-O-C	0.1 mg/L
Temperature	Hydrolab	KC SOP 205v4	0.1 deg C
Dissolved Oxygen	Hydrolab	KC SOP 205v4	0.5 mg/L
Salinity/ Conductance	Hydrolab	KC SOP 205v4	0.01 PSU
pH	Hydrolab	KC SOP 205v4	0.1
Dissolved Oxygen	Seabird 19 CTD	Seabird CTD	0.5 mg/L
Temperature	Seabird 19 CTD	Seabird CTD	0.01 deg C
Salinity / Conductance	Seabird 19 CTD	Seabird CTD 4	0.01 PSS

"SM*" refers to Standard Methods

7.0. QUALITY ASSURANCE AND CONTROL

Quality assurance and control will be provided by project manager oversight, project staff training, and adherence to a combination of laboratory and field standard operating procedures referenced previously.

For measurements involving meters, maintenance schedules, calibration schedules and deployment, instructions will be followed for all meters and sensors. All laboratory data will be reviewed, rated for accuracy, and approved by the KCEL laboratory supervisor before being submitted as a final product.

7.1 Field QC Procedures

Field QC includes proper documentation of field activities and sampling/handling procedures, as described in previous sections.

7.1.1 Field QC Samples

Field QC samples will consist of the following:

- One replicate sub-chamber, to be analyzed for the entire suite of laboratory analyses.
- One field filtration blank per sampling day, to be analyzed for all filtered parameters (ammonium, nitrate+nitrite and orthophosphate phosphorus).
- Field equipment blank for samples collected by pump, one per sampling day for all lab parameters, except Winkler Dissolved Oxygen.

7.1.2 Calibration and Use of Meters

Before use, field equipment must be cleaned and checked for malfunctions. Meters must be calibrated each morning before use in the field, following manufacturers' procedures. All field monitoring equipment will be calibrated consistent with manufacturers' procedures using instrument calibration standards prepared according to the manufacture's specifications. In all cases, proper documentation of all calibration procedures must be completed for each sampling event, including calibration methodology (one- or two-point calibration, difference, standard concentration and expiration date).

Logbooks should be maintained for all field meters. The logbooks must contain the same information as those for permanent laboratory instruments (serial number, name and model of meter, year purchased, etc.). The books also must contain QC results, maintenance performed by the factory, and calibration notes for each day the equipment is used. Instruments used to measure pH, dissolved oxygen and electrical conductivity should be calibrated at least once each day of sampling. Temperature-measuring devices should be calibrated against a standardized laboratory thermometer at a frequency recommended by the manufacturer. Field instruments used to measure other parameters, e.g., turbidity, should be calibrated in accordance with manufacturer recommendations and documented.

7.1.3 Replicate Samples

Field replicates are used to evaluate consistency of field measurements, sample collection procedures and analytical results from a given sample point. Replicate samples are collected in the field using a matching set of laboratory-supplied sample containers. Each replicate will be sampled after the initial sample has been taken, repeating the process for sample collection. The source where the replicate is collected must be identified on the field sampling data sheet. Once a replicate is collected, it is handled and shipped in the same manner as the rest of the samples. Replicate results will be reported by the laboratory as separate samples.

7.1.4 Field Blanks

Field blanks are used to detect contamination that may be introduced in the field or from the sampling equipment. Field equipment blanks will be prepared in the field by pumping laboratory reagent-quality water through new or pre-cleaned tubing and into the field equipment blank bottles. The chamber at which the equipment blank is prepared must be identified on the field sampling data sheet. Field blank results will be reported in the laboratory results as separate samples. The field filtration blank for dissolved nutrients will be collected by filtering a portion of lab reagent water through a clean filter into the field filtration bottle.

7.2 Lab QC requirements

In general and at minimum, laboratory QC will consist of the following:

- One matrix spike (MS) per 20 samples
- One matrix spike duplicate (MSD) or lab duplicate (LD) per 20 samples

Method-specific QA/QC samples may include the following, and are discussed as follows:

- Method blanks. A method blank is an aliquot of a clean reference matrix, such as deionized, distilled water for water samples, which is processed through the entire analytical procedure. Method blank results are used to evaluate the levels of contamination that might be associated with the processing and analysis of samples. Method blank results should be “less than the MDL” for all target analytes.
- Matrix spike samples. A matrix spike (MS) is a known concentration of one or more target analytes, introduced into a second aliquot from one analytical sample. The spiked sample is processed through the entire analytical procedure. Analysis of the MS is used as an indicator of sample matrix effect on the recovery of target analytes. Control limits are based on the percent recovery of the spiked compounds.
- Matrix spike duplicate and lab duplicate samples. A matrix spike duplicate (MSD) is a known concentration (same as the MS) of target analytes, which is introduced into a third aliquot of the same analytical sample. The spiked sample is processed through the entire

analytical procedure. Analysis of the MSD is used as an indicator of sample matrix effect on the recovery of target analytes as well as method precision. The relative percent difference (RPD) between the MS and MSD results is calculated; however, control limits are not maintained. The RPD for MS/MSD results is, instead, reviewed during the data validation and analysis process to evaluate potential data quality issues arising from questions of analytical precision. A lab duplicate (LD) is a second aliquot removed from one analytical sample, processed through the entire analytical procedure as a separate sample. The RPD between the original sample and the LD is used as an indicator of method precision and sample homogeneity.

- Spiked blank samples. A spiked blank (SB) is an aliquot of clean reference matrix, such as deionized distilled water for water samples, to which a known concentration of one or more target analytes has been added. The spiked aliquot is processed through the entire analytical procedure. SB analysis is used as an indicator of method performance and can be used in conjunction with matrix spike results as an indicator of sample matrix effects. Control limits are based on the percent recovery of the spiked compounds.
- Laboratory control samples. A laboratory control sample (LCS) 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 LCS analysis should follow the entire analytical process, it should be stored and prepared following the same procedures as a field sample. Analysis of a LCS is used as an indicator of method accuracy and long-term analytical precision.
- Performance Evaluation (PE) samples. KCEL participates twice annually in the Water Pollution and annually in Water Supply Performance Evaluation programs. These programs were designed by the EPA to evaluate lab performance for testing associated with the Clean Water Act and the Safe Drinking Water Act, respectively. PE samples are single-blind samples supplied to the lab through vendors approved by the Washington Department of Ecology Lab Accreditation Program.

QC sample results that exceed control limits will be evaluated to determine appropriate corrective actions. Samples will typically be reanalyzed if unacceptable QC results indicate a systematic problem with the overall analysis. Unacceptable QC results caused by a particular sample or matrix will not require reanalysis unless an allowed method modification would improve the results. Analytical results that are outside of QC control limits for some QC sample types will be qualified and flagged according to procedures outlined in Section 7.2.3.

7.2.1 Conventionals QC Parameters

Laboratory QC samples for conventionals analyses and associated control limits are summarized in Table 8. These QC samples will be analyzed at a frequency of one per analytical batch of 20 or fewer samples.

Table 8. Laboratory QC Requirements

Analysis	Method Blank	Duplicate RPD (%)	Positive Control % Recovery	Matrix Spike % Recovery
Ammonia Nitrogen	<MDL	20	85-115	75-125
Nitrate+Nitrite Nitrogen	<MDL	20	85-115	75-125
Orthophosphate Phosphorus	<MDL	20	85-115	75-125
Silica	<MDL	20	85-115	65-120
Dissolved Oxygen (Winkler)	NA	NA	NA	NA
Total Phosphorus	<MDL	20	85-115	75-125
Total Nitrogen	<MDL	20	85-115	75-125

RPD = Relative Percent Difference

7.2.2 Laboratory Data Review and Analysis

Data evaluation will include checking holding times, method blank results, surrogate recovery results, field and laboratory duplicate results, completeness, detection limits, laboratory control sample results and COC forms. After the data has been checked, it may be entered into a project database with any assigned data qualifiers. Data evaluation is critical for evaluating how well analytical data meet project DQOs, and is performed, at some level, during several steps in the process of sample collection and analysis.

All analytical data are entered into KCEL's Laboratory Information Management System (LIMS). LIMS may perform additional calculations such as conversion of concentrations measured directly by laboratory instrumentation to final sample results. Automatic calculation of QC results is also performed within LIMS, as well as comparison to acceptance limits.

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.

A laboratory project manager (LPM) will provide the next data review step, at a project level. The LPM will verify the completeness of an entire data set (multiple parameters for a particular sampling event) and report any QC failures or anomalies. An internal King County project data validator may provide a final review of the data to ensure they meet the project DQOs. Data may then be reported in a variety of formats, depending on project needs.

All laboratory analytical data are maintained *in perpetuity* on LIMS. Data may be viewed on-line in LIMS by King County personnel only. Project data may also be downloaded from LIMS into a hard copy format using Microsoft Excel®. Analytical data will be reported on a routine basis in Excel® format along with an accompanying QA/QC review narrative.

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. Sample results between five and ten times the concentration detected in the method blank will be qualified with a “B3” flag. The flag “SH” is used to indicate a sample handling condition that did not meet method requirements. Handling conditions may include an improper sample container or improper preservation of the sample. The H flag will be applied when there is an exceedance of the method-specific holding time. The flag “J” may be applied to sample data at the discretion of the laboratory analyst, data reviewer, or data analyst, should control limits on one or more QC samples not be met. The flag “J” indicates that sample numerical result should be viewed as *estimated*.

Analytical results from field blanks and field replicates will be reviewed to evaluate their impact on the quality and usability of sample analytical data. Results from field QC samples will not be used to flag sample analytical data but will be taken into consideration during final data review and analysis.

8.0. DATA MANAGEMENT PROCEDURES

Except where noted otherwise, all field data and associated observations will be recorded on standardized field sheets (physical or electronic) as described above (see Sampling Procedures) and entered or transferred into one of several King County databases in a timely manner, generally within one week of collection. King County laboratory data will be stored in the King County Laboratory Information Management System. The Hydrolab sonde data will be maintained in a project specific Access database.

The Project Manager will provide supervision of all data acquisition and management activities. The Data Management Section will maintain the project database and load data. Field staff will provide all data from sondes it deploys. Project staff will enter all other data manually or download from electronic files.

9.0. AUDITS AND REPORTS

As per the EPA's contract requirements, semiannual project reports will be provided to the EPA by the Project Manager. The report will include a description of project activities and status including an overview of data collected, field and data problems encountered and solutions applied, and changes in schedule, measurements, database, and analysis. If needed, the EPA may conduct a Quality System Review on management and technical aspects of the project.

10.0. DATA VALIDATION

Data validation is critical in the evaluation of how well analytical and field data meet project DQOs. All analytical data and most 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 peer reviewer, prior to entry of the data into LIMS. Analytical data are peer reviewed for completeness and QC sample data are viewed for compliance with project and method QA/QC requirements.

Quality control results that exceed the acceptance limits will be evaluated to determine appropriate corrective actions. Samples will typically be reanalyzed if the unacceptable QC results indicate a systematic problem with the overall analysis. Unacceptable QC results caused by a particular sample or matrix will not require reanalysis unless an allowed method modification would improve the results.

11.0.DATA ANALYSIS AND USE

Data quality will be evaluated against the objectives set in this document for precision. The data will also be evaluated for obvious errors, such as incorrect units. The sum of dissolved constituents will be compared to the value found for the total constituent. The data will also be evaluated against the objectives set for representativeness and completeness.

Analysis of the benthic flux chamber data will use plots of nutrient concentrations vs. time and regression analysis to determine the rate of change of nutrient concentrations over time. The rate of change in nutrient concentration determined from this analysis divided by the sediment area within the chamber will provide an estimate of the nutrient flux in units of mass of nutrient (N, P, and Si) per unit area per time (e.g., mg m^{-2} d^{-1}).

The usability of the data will be confirmed by using it in the model and showing relationships between dissolved oxygen, nitrogen, and land use activities/best management practices.

11.1 Reconciliation with User Requirements

Reports generated for this study will include identification of any data limitations determined through application of the Data Quality Objectives described in this project plan. This information will be communicated initially through annual project reports and will be mirrored in subsequent project reports that rely on data with known limitations, including, but not limited to, modeling reports and reports containing recommended updates to decision makers that update the King County Comprehensive Plan.

12.0. ORGANIZATION AND SCHEDULE

12.1 Project Staff list and roles

The Quartermaster Harbor Nitrogen Management Study project involves staff from King County Departments of Natural Resources and Parks (DNRP, including the King County Environmental Lab, KCEL) in collaboration with the UWT Environmental Science program, Washington Dept. of Ecology's Marine Monitoring Unit and the Vashon-Maury Island Groundwater Protection Committee. Detailed roles and responsibilities for this study are:

- Benthic Flux Study project manager: Curtis DeGasperi – ensure that study is conducted in accordance with this QAPP and determine if and how deviations from the plan are made

- Ecology technical and logistic support: Mindy Roberts – provide technical review of QAPP based on previous experience conducting a similar study in South Puget Sound (Roberts et al. 2008). Provide benthic flux chambers and Hydrolab sondes equipped with stirrers and batteries capable of autonomously logging dissolved oxygen, temperature, salinity (conductance), and pH.

- Field team on field vessel: Cheryl Greengrove, Julie Masura, Curtis DeGasperi – set up and test benthic flux chambers and conduct benthic flux chamber deployment and sampling in Quartermaster Harbor

- Shore support team: 1 ESS staff person to provide logistic support, communications, and transfer samples to KCEL

- King County Sheriff Marine/Dive/Rescue Unit – inspect chamber deployment and document chamber and site conditions as part of training exercise

- King County Environmental Laboratory (KCEL) will conduct analyses described above on samples delivered to the laboratory and enter data into the laboratory information management system (LIMS).

12.2 Major Activities and Timelines

Field work will be conducted sometime during September 2010. Instruments will be calibrated and tested and flux chambers will be prepared and tested prior to field deployment. Field work will entail the deployment of five benthic flux chambers in Quartermaster Harbor at the locations specified above. The chambers will be monitored continuously (15 minute intervals) using a Hydrolab sonde calibrated for measuring dissolved oxygen, pH, temperature, and salinity. Water samples for laboratory analysis will be extracted at specified intervals over a 24-hr period for a total of 6 samples per chamber. Data will be used to calculate nutrient fluxes for each chamber deployment and summarized in a technical memo that will be reviewed in draft form and finalized by December 2010.

Quartermaster Harbor Benthic Flux Study Activities.

Activities	Timeline	Organization	Description
Benthic Flux QAPP document	Jan-Jul 2010	All	Write and approve a Benthic Flux Study Quality Assurance Project Plan (QAPP)
Collect, organize, and test equipment	May-Aug 2010	Curtis DeGasperi, Cheryl Greengrove, Julie Masura	Obtain benthic flux chamber equipment from Ecology and perform testing at KCEL to identify chambers that might not be functional and take corrective actions if feasible. KCEL personnel will be needed for this step. Access to offsite KCEL storage will also be needed.
Conduct field study	Sep 2010	Curtis DeGasperi, Cheryl Greengrove, Julie Masura, 1 ESS staff member	Perform deployment and sampling over 2 day period in September 2010 as specified in this QAPP. If available, King County Sheriff Marine/Dive/Rescue Unit will inspect and document condition of deployed chambers.
Analyze and report results	Oct-Dec 2010	Curtis DeGasperi	Analyze data to calculate nutrient fluxes for each chamber deployment and summarize in technical memo.

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Appendix A. Equipment and Supplies

Submersible camera or remotely operated camera or video camera (whose?)

Tubing (specifications: 0.17 inch diameter)

Peristaltic pump (2) and batteries for sample collection (King County)

Field notebooks and pens

Alligator clips

Nylon zip ties

Shears for cutting zip ties

Container for purging water

Electrical tape

Garbage bags for waste

Water and food for staff

Places for overnight staff to sleep

Five (5) benthic flux chambers (painted black) with retrieval lines and floats and flexible tubing for sample collection

Vessel 1: With operator. Equipped with davit, winch, fathometer, and GPS

Vessel 2: With operator. Equipped with GPS

Hydrolabs (7) with stirrers, batteries, and autonomous sampling capability

CTD (calibrated and provided by UWT)

Winkler fixing kit (ESS/KCEL)

Floats (at least 7 orange floats to mark chambers and suspend tubing)

Graduated cylinders (sizes 10, 100 and 1000 mL)