# Addendum #2 to

# Quality Assurance Project Plan: South Puget Sound Water Quality Study Phase 2: Dissolved Oxygen

September 2007

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### Addendum

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**Environmental Assessment Program** 

September 6, 2007

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- **THROUGH:** Karol Erickson, Unit Supervisor, Modeling and Information Support Unit Will Kendra, Section Manager, Statewide Coordination Section
- **FROM:** Mindy Roberts (Ecology) and Carol Coomes (Evans-Hamilton)

SUBJECT: ADDENDUM #2 TO THE QUALITY ASSURANCE PROJECT PLAN FOR THE SOUTH PUGET SOUND WATER QUALITY STUDY, PHASE 2: DISSOLVED OXYGEN BENTHIC FLUX SURVEYS

### PROJECT CODE: 06-509-01 PUBLICATION NO. 07-03-101ADD#2

The Washington State Department of Ecology (Ecology) began a study of low dissolved oxygen levels in South Puget Sound in August 2006 (Albertson et al., 2007). The purpose of this study is to determine how nitrogen from a variety of sources affects dissolved oxygen levels. The project includes data collection, model development and application, and a final report documenting findings.

This addendum to the Quality Assurance Project Plan summarizes additional field collection necessary to characterize nutrient and oxygen fluxes between the sediments and the water column in four inlets of South Puget Sound. Sediments likely influence the overlying water column characteristics, particularly in the shallow waters of the inlets. Therefore, this program will provide additional information with which to understand and quantify nutrient and oxygen fluxes for the water quality model under development for South Puget Sound.

### **Experimental Design**

Three benthic flux chambers will be deployed in each of four inlets in South Puget Sound (Eld, Budd, Case, and Carr Inlets). A total of six chambers will be deployed at one time so that sampling can occur at two inlets during the same 48 hours. A full description of the benthic flux chambers and associated sampling devices can be found in the Standard Operating Procedures (SOP), a draft of which is presented in Appendix A. Deployment locations for the chambers within each inlet are shown in Figure 1. These positions correspond to 5, 15, and 25 m depth along the deepest part of each inlet.

Deployment and sampling of the chambers within the four inlets will occur over four (4) consecutive days, approximately one week per month, for three months. Table 1 outlines the schedule for the deployments of the chambers. The initial shakedown cruise was originally scheduled for August but due to vessel unavailability was rescheduled for early September with Ecology permission.

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 running a few lines 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 (refer to SOP).

The benthic flux chambers will remain at each location for at least 24 hours. Once deployed, sample grabs for Winkler titration of dissolved oxygen and nutrient analysis for nitrogen and phosphorus will be performed and repeated four times per deployment. Sampling methods will be according to the SOP<sup>1</sup>. Hydrolabs with stirrers will be used to continuously measure dissolved oxygen levels within each benthic flux chamber. Table 2 lists the sampling schedule for each inlet.

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 delivered to Ecology Operations Center in Lacey at the end of each sample day, coordinating with Ecology staff.

The base of operations for the Budd/Eld Inlets' sampling will be Boston Harbor. The base of operations for Carr/Case Inlets' sampling will potentially be Wauna (Carr) and Vaughn (Case).

<sup>&</sup>lt;sup>1</sup> The SOP also describes methods for quantifying total, dissolved, and particulate carbon and particulate nitrogen, but these parameters will not be sampled in this program.

# **Analytical Laboratory**

Nutrient samples will be analyzed for total nitrogen, ammonium, nitrate plus nitrite, total phosphorus, and orthophosphate in accordance with the Joint Global Ocean Flux Study marine water methods described in the project QA Project Plan (Albertson et al., 2007). However, two separate laboratories will analyze samples.

No laboratory in the state of Washington is fully accredited for marine total and dissolved nutrient sample analyses. Dissolved and total nutrient samples from the marine data collection program (Albertson et al., 2007) are currently analyzed by the University of Washington Marine Chemistry Laboratory using specialized methods targeting low-level nutrient concentrations. However, to determine the success of the proposed sediment flux study, a reporting time of two weeks is necessary for the dissolved nutrients<sup>2</sup>. Because the current laboratory cannot achieve the short reporting time for dissolved nutrients, another laboratory is needed that can provide the same analytical techniques for marine nutrient samples.

The San Francisco State University Romberg Tiburon Center will analyze the dissolved nutrient samples collected from the benthic flux chambers using the same analytical methods as offered by the University of Washington Marine Chemistry Laboratory. For the benthic flux surveys, the absolute concentrations are less important than the trends over time that are used to calculate flux rates for the dissolved nutrients. While the laboratory will pursue accreditation, the laboratory is not currently accredited in the state of Washington. A Request for Waiver to Required Use of Accredited Laboratory has been completed with the Ecology Quality Assurance Officer.

Because the reporting time for the total nitrogen and total phosphorus samples is not as quick and because the San Francisco State University Laboratory does not currently offer these services, the total nitrogen and total phosphorus samples will be sent to the University of Washington Marine Chemistry Laboratory for analyses. This is not expected to affect the quality of the results, since the total nutrient concentration trends are also of interest but are not expected to change significantly over time. In addition, while total and dissolved concentrations are generally used to calculate organic nitrogen and organic phosphorus concentrations, these are not needed for the benthic flux study.

### **Intended Use**

Because very little information exists to quantify the fluxes of nutrients and dissolved oxygen between the sediments and the overlying water column, the data collected under this program will be used to establish ranges of fluxes under local South Puget Sound conditions. The information developed from this study will be used for two purposes. First, the fluxes will be compared among sites and over time to determine whether the fluxes are homogeneous within

 $<sup>^{2}</sup>$  In previous benthic flux studies, the concentrations of ammonium and orthophosphate increase while the concentration of nitrate plus nitrate decreases due to biological activity within the chambers. Quantifying these rates of change is the purpose of the program.

South Puget Sound or whether they vary strongly by inlet, water depth, or over time. Second, the ranges established will be used to inform water quality model development during subsequent years and to provide site-specific data with which to parameterize the boundary conditions.

# **Quality Objectives**

### **Measurement Quality Objectives**

Field measurement objectives for Hydrolab measurements are difficult to establish because of the lack of previous data collection using these methods. Replicate Hydrolab dissolved oxygen levels should meet a relative standard deviation of 25%. Rates of dissolved oxygen decrease, calculated as  $mg-O_2/L/m^2/day$ , calculated from replicate Hydrolab measurements should meet a relative standard deviation of 50%. Measurement quality will be described and re-assessed in the final project data report.

Nutrient and dissolved oxygen replicate samples will be compared using the Measurement Quality Objectives presented in the project QA Project Plan for the ambient marine samples collected during monthly cruises.

### Representativeness

This study is designed to collect data over a range of shallow waters in South Puget Sound. The four inlets were selected: (1) as having the lowest near-bottom dissolved oxygen levels during the critical fall period (Budd Inlet), (2) relatively high near-bottom dissolved oxygen levels (Eld Inlet), and (3) oxygen levels of concern (Carr and Case Inlets). Water depths were selected to encompass a range of shallow waters (<30 m) within South Puget Sound. The three field seasons focus on the time period during which the lowest near-bottom dissolved oxygen levels have been recorded.

### **Completeness**

The completeness target for this field study is 90%. Reasons why all data may not be collected include:

• Severe weather that precludes seagoing vessels from sailing.

To mitigate this, Evans-Hamilton and Ecology may modify the schedule or the program content such that the overall project schedule and objectives are met.

• Malfunctioning equipment.

To minimize risk, Ecology will ensure equipment is well maintained and will verify functionality prior to deploying in the field.

### Comparability

The same field crew, composed of two Evans-Hamilton personnel and one Ecology staff member, will conduct the surveys to maximize comparability among field days.

### **Sampling and Measurement Procedures**

Appendix A presents the Standard Operating Procedures (SOP) for the operation of the benthic flux chambers. Field personnel will report any changes from the SOP as a result of field operations. While the SOP includes methods for quantifying total, dissolved, and particulate carbon and particulate nitrogen, these parameters will not be sampled in this program.

Frozen total nitrogen and phosphorus samples will be frozen and delivered to the University of Washington Marine Chemistry Laboratory with documentation as described in the project QA Project Plan. Frozen dissolved nitrogen and phosphorus samples will be sent via overnight delivery in a cooler filled with ice to the following address:

Julian Herndon Romberg Tiburon Center, SFSU 3150 Paradise Drive, Building 36 Tiburon, CA 94920-1205

Phone: 415-338-3708 Fax: 415 -35-7120

The list of dissolved samples will be included with the shipment and a second copy will be signed by the laboratory and returned to Ecology to verify that chain of custody has been maintained. The laboratory will note any tampering or missing samples.

Table 3 presents the tubing purge volumes that are referenced in the SOP for the 0.170-inch inner diameter tubing used for the benthic flux chambers. The purge volume will be at least 1.5 times the tubing volume.

# **Quality Control**

During four deployments (10%), replicate Hydrolab measurements will be recorded in the second of the two chambers within a vessel. Replicate nutrient grab samples will be collected during four deployments from the primary sampling chamber.

### **Data Management Procedures**

GPS coordinates and nominal depths of each chamber deployment will be reported along with any supplemental field information from field notebooks. Ecology will download and process the Hydrolab data using Standard Operating Procedures (Swanson, 2007). The laboratory will provide nutrient results electronically and Ecology field staff will upload the information into the Environmental Information Management (EIM) system.

# **Audits and Reports**

Ecology will prepare a quality assurance assessment prior to using the data for analysis and the results will be included in the final data report for the overall project, described in the project QA Project Plan.

### **Data Verification**

Field and laboratory results will be verified and validated in accordance with the project QA Project Plan.

### **Data Analysis and Use**

This program will follow the procedures for data analysis and use as outlined in the project QA Project Plan.

# **Organization**

The following responsibilities are in addition to those outlined in the project QA Project Plan:

- Mark Filippini (EPA, Contract Manager) Verify that the program is conducted in accordance with the contract.
- Laura Blake (Cadmus Group, Project Manager) Verify that the program is conducted in accordance with the contract.
- Carol Coomes (Evans-Hamilton, Inc., Technical Project Lead) Develop QA Project Plan addendum and manage technical work, arrange boat logistics, and manage Evans-Hamilton field staff.
- Maya Whitmont and Rachel Halfhill (Evans-Hamilton, Inc., Field Co-Leads) Conduct field work according to QA Project Plan addendum, deploy and retrieve benthic flux chambers, and collect nutrient and dissolved oxygen grab samples.
- Ken Peer (Ecology Marine Monitoring Unit, Field Staff) Conduct field work according to the QA Project Plan addendum; calibrate, download, and maintain Hydrolabs; maintain benthic flux chambers; and provide nutrient and dissolved oxygen sample handling and transport to the laboratory.
- Greg Pelletier (Ecology Modeling and Information Support Unit, Peer Review) Review the addendum to QA Project Plan addendum and project data.
- Mindy Roberts (Ecology Modeling and Information Support Unit, project manager) Develop QA Project Plan addendum, design program, and review data.

# **Project Deliverables and Schedules**

Evans-Hamilton, Inc., will provide a field report presenting data collected during the field sampling event (excluding laboratory data) but including field data such as GPS locations, time of sample collection, weather conditions, and purge volumes. The report shall also include copies of field notes. Interim field reports will be provided within 45 days of each sample event. The last field report can be combined with a final closeout report and shall be submitted to Ecology within 30 days of the last sample collection round but no later than November 26, 2007. If comments are received, a final data report shall be required by December 31, 2007.

Ecology will conduct data analysis and will include the results in the overall project data report, described in the project QA Project Plan for delivery in 2008.

### References

Albertson, S.L., J. Bos, K. Erickson, C. Maloy, G. Pelletier, and M. Roberts. 2007. South Puget Sound Water Quality Study Phase 2: Dissolved Oxygen, Quality Assurance Project Plan. Washington State Department of Ecology, Olympia, WA. Publication No. 07-03-101.

Swanson, T. 2007. Standard Operating Procedure (SOP) for Hydrolab® DataSonde® and MiniSonde® Multiprobes. Washington State Department of Ecology, Olympia, WA. Publication No. <u>www.ecy.wa.gov/programs/eap/qa/docs/ECY\_EAP\_SOP\_Hydrolab\_v1\_0.pdf</u>

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### **Figures and Tables**

### **Budd and Eld Inlets**



Figure 1. Proposed deployment locations for the benthic flux chambers (Latitudes and longitudes are in the projection NAD 84). Triangle is 5 m (2.7 fathoms or 16.4 ft), square is 15 m (8.2 fathoms or 49.2 ft) and open diamond is 25 m (13.6 fathoms or 82 ft).

### **Case and Carr Inlets**



Figure 1 (Continued).

Cruise	Dates	Purpose
1	September 10-13, 2007	Shakedown
2	September 24-27, 2007	Lowest DO levels
3	October 22-25, 2007	Increase in DO levels

Table 1. Schedule for Benthic Flux Chamber Deployments.

Table 2. Sampling Schedule for Benthic Flux Chambers.

Day	Time	Site	Operation	
1	AM	Budd Inlet	Deploy 3 chambers	
	AM	Budd Inlet	Sample 3 chambers	
	AM	Eld Inlet	Deploy 3 chambers	
	AM	Eld Inlet	Sample 3 chambers	
	PM	Budd Inlet	Sample 3 chambers	
	PM	Eld Inlet	Sample 3 chambers	
2	AM	Budd Inlet	Sample 3 chambers	
	AM	Eld Inlet	Sample 3 chambers	
	PM	Budd Inlet	Sample 3 chambers	
	PM	Budd Inlet	Retrieve 3 chambers	
	PM	Eld Inlet	Sample 3 chambers	
	PM	Eld Inlet	Retrieve 3 chambers	
3	AM	Carr Inlet	Deploy 3 chambers	
	AM	Carr Inlet	Sample 3 chambers	
	AM	Case Inlet	Deploy 3 chambers	
	AM	Case Inlet	Sample 3 chambers	
	PM	Carr Inlet	Sample 3 chambers	
	PM	Case Inlet	Sample 3 chambers	
4	AM	Carr Inlet	Sample 3 chambers	
	AM	Case Inlet	Sample 3 chambers	
	PM	Carr Inlet	Sample 3 chambers	
	PM	Carr Inlet	Retrieve 3 chambers	
	PM	Case Inlet	Sample 3 chambers	
	PM	Case Inlet	Retrieve 3 chambers	

Length	Tube Volume		Purge Volume (1.5*tube)		
m	m <sup>3</sup>	L	$m^3$	L	mL
1	1.46438E-05	0.015	2.2E-05	0.022	22
5	7.32192E-05	0.073	0.00011	0.110	110
10	0.000146438	0.146	0.00022	0.220	220
15	0.000219658	0.220	0.000329	0.329	329
20	0.000292877	0.293	0.000439	0.439	439
25	0.000366096	0.366	0.000549	0.549	549
30	0.000439315	0.439	0.000659	0.659	659
35	0.000512535	0.513	0.000769	0.769	769
40	0.000585754	0.586	0.000879	0.879	879
45	0.000658973	0.659	0.000988	0.988	988
50	0.000732192	0.732	0.001098	1.098	1098

Table 3. Tubing Purge Volumes to Clear Stagnant Water Prior to Collecting Nutrient and DO Samples.

# Appendix A

### Draft Standard Operating Procedures for Benthic Flux Chambers

### 1.0 Purpose and Scope

- 1.1 This document is the Environmental Assessment Program (EAP) Standard Operating Procedure (SOP) for deployment and operation of benthic flux chambers.
- 1.2 In marine and freshwaters, water quality often reflects the complex interaction with the sediments. The exchange of dissolved oxygen and nutrients, called fluxes, is necessary to understand the effect of all nutrient sources on water column dissolved oxygen levels. The term benthic flux chambers refers to equipment that isolates a portion of the water column nearest the sediment surface and allows for the quantification of dissolved oxygen and nutrient fluxes between the sediments and the lower water column.

### 2.0 Applicability

2.1 The procedure will be followed for studies quantifying the exchange of both dissolved oxygen and nutrients between sediments and the overlying water column.

#### **3.0 Definitions**

3.1DODissolved oxygenEAPEnvironmental Assessment Program of the Department of EcologyOCOperations Center, 8270 28th Court NE, Lacey, WA 98516MSDSMaterial Safety Data SheetsQAPPQuality Assurance Project Plan

### 4.0 Personnel Qualifications/Responsibilities

4.1 All field staff must comply with the requirements of the EA Safety Manual (EA Program, 2006). A full working knowledge of the procedures in Chapter 1 General Field Work is expected. If chambers are deployed in freshwater, field staff must comply with the section Working in Rivers and Streams. If chambers are deployed in marine waters, field staff must comply with the Chapter 2 section Operating Winches on Small Boats, Trailers, Vehicles, and Float Planes; all onboard staff must be familiar with Chapter 3, Boating.

The Field Lead directing deployment and sample collection must be knowledgeable of all aspects of the project's Quality Assurance Project Plan to ensure that credible and usable data are collected. All field staff should be briefed by the Field Lead or Project Manager on the sampling goals and objectives prior to arriving at the site.

### 5.0 Equipment, Reagents, and Supplies

### 5.1 <u>General Equipment and Supplies</u>

- Benthic flux chambers, with retrieval lines and floats for identification and handling and flexible tubing for sample collection (Figure 1).
- Hydrolabs or other continuous dissolved oxygen monitoring equipment with mounts to benthic flux chambers.
- Peristaltic pump and batteries, or similar equipment, for sample collection.
- Safety equipment appropriate for the sampling sites: safety vests or boating safety equipment; latex or nitrile gloves for hygienic protection; and leather gloves for handling ropes and cables.
- Coolers with ice (regular or blue).
- Field notebook and pens.
- Safety goggles (for adding reagents to dissolved oxygen samples).
- Lab Analysis Request (LAR) forms.
- Sample tags.
- Alligator clips.
- Nylon zip ties.
- Shears for cutting nylon zip ties.
- Container for purging stagnant water in tubing.
- Carrying case for miscellaneous equipment.
- Electrical tape.
- Extra bags for waste.



Figure 1. Schematic of benthic flux chamber, consisting of an inverted box with the open side toward the sediment.

#### 5.2 <u>Sample Containers</u>

- DO Samples
  - 125-mL glass flasks and stoppers for grab sample analyses of dissolved oxygen concentrations using a Winkler titration.
  - 3M manganese chloride (MnCL<sub>2</sub>). This chemical is stable for 2 years when stored in sealed plastic bottles and kept tin the dark. The MSDS can be found at <u>http://www.jtbaker.com/msds/englishhtml/M0767.htm</u>.
  - 8N sodium hydroxide-sodium iodide-sodium azide (NaOH-NAI-Azide). This chemical is stable for 2 years when stored in sealed plastic bottles and kept in the dark. Sodium azide is a suspected carcinogen and should be treated with care. The MSDS for NaOH, NaI, and NaN3 can be found at <a href="http://www.jtbaker.com/msds/englishhtml/S4034.htm">http://www.jtbaker.com/msds/englishhtml/S4034.htm</a>, <a href="http://www.jtbaker.com/msds/englishhtml/S4202.htm">http://www.jtbaker.com/msds/englishhtml/S4034.htm</a>, <a href="http://www.jtbaker.com/msds/englishhtml/S4202.htm">http://www.jtbaker.com/msds/englishhtml/S4202.htm</a>, and <a href="http://www.jtbaker.com/msds/englishhtml/S4202.htm">http://www.jtbaker.com/msds/englishhtml/S4202.htm</a>, and <a href="http://www.jtbaker.com/msds/englishhtml/S4206.htm">http://www.jtbaker.com/msds/englishhtml/S4202.htm</a>, and <a href="http://www.jtbaker.com/msds/englishhtml/S2906.htm">http://www.jtbaker.com/msds/englishhtml/S2906.htm</a>.
  - Pipettes and tips to dispense reagents for Winkler DO samples.
  - Carrying cases for bottles and reagents.

- o Deionized water.
- Nitrogen and Phosphorus Samples
  - Large polypropylene bottles, 1 L, that has been acid washed and rinsed, if using an interim container for nutrient sample collection.
  - Total nitrogen and phosphorus sample bottles (60-mL polypropylene), acid washed and rinsed.
  - Dissolved nitrogen and phosphorus sample bottles (175-mL square polypropylene), acid washed and rinsed.
  - o 60-mL plastic syringes, obtained from the laboratory.
  - 20-mL graduated cylinders, obtained from the laboratory, if not using syringe to measure total nitrogen and phosphorus sample.
  - 25-mm, 0.45-micron disk filters for the syringes, obtained from the laboratory.
- Carbon Samples
  - Pre-muffled 25-mm, 0.45-micron Whatman glass fiber filters (GF/F), obtained from the laboratory.
  - Filter forceps—stainless steel, straight, flat, smooth tip, obtained from the laboratory.
  - 25-mm polycarbonate filter holders for 0.20-micron GF/F filters, obtained from the laboratory.
  - Petri dish for particulate carbon samples, obtained from the laboratory.
  - o 40-mL glass vials for DOC samples, obtained from the laboratory.

#### 6.0 Summary of Procedure

### 6.1 <u>Pre-sampling Equipment Preparation</u>

EAP will prepare six benthic flux chambers that may be used in either freshwater or marine waters (Figure 1). Sampling apparatus will include flexible tubing for each unit. EAP will provide two peristaltic pumps and charged batteries at the onset of the field season, with flexible tubing and a connector with the sample tubing. If using a staging area other than the EAP Operations Center, transport chambers to field staging area.

If benthic flux chambers, peristaltic pumps, batteries, or battery chargers are used by another organization without EAP staff, the organization must complete the EAP Equipment Loan form (<u>http://aww.ecology/programs/eap/forms/index.html</u>).

If using EAP Hydrolabs for continuous DO measurements within the chambers, complete pre-deployment maintenance and calibration according to SOP outlined

in Swanson (2007). If using other equipment, complete pre-deployment and maintenance and calibration in accordance with the QAPP. Oxygen measurements must be conducted in a continuously stirred vessel to avoid stratification within the chamber.

If Hydrolabs and stirrers are deployed by another organization without EAP staff, the organization must complete the EAP Equipment Loan form (http://aww.ecology/programs/eap/forms/index.html).

#### 6.2 <u>Benthic Flux Chamber Deployment</u>

Refer to the QAPP for deployment locations, water depth, duration, and frequency of continuous and grab sample collection.

Transport chambers to each sampling location. Verify that Hydrolab or other DO sample recording equipment is firmly attached to benthic flux chambers and turn on the stirrer. Lower the chamber into the water column, initially with the open side up to remove all air bubbles. Invert the chamber near the bottom depth so that the open side faces down. Be careful to fill the chamber with water from near the bottom of the water column and prevent the chamber from disturbing the sediment. Slowly lower the chamber into position using the chamber retrieval lines. Keep the sample collection tubing attached to the chamber with the open end out of the water. Avoid locations where the lower flanges are not in complete contact with the sediment, and avoid stirring up large volumes of sediment as the chamber is lowered into position. Collect the initial samples using methods described in Section 6.3. Following sample collection, disconnect the pump from the sample tubing, fold over the tubing and clamp to avoid contamination, and secure the end of the sample tubing to a float where it can be retrieved easily during the next sample round. Verify that all floats are functional before leaving the site.

### 6.3 <u>Collecting Water Samples from Within Benthic Flux Chambers</u>

#### 6.3.1 Withdrawing Samples Using Peristaltic Pump

Refer to the QAPP for the sample collection schedule, including frequency and duration. The QAPP should specify the approximate length and inner diameter of tubing for each sample location, and the approximate volume necessary to clear the water from the tubing such that the tubing contains water from within the chamber for sample collection.

At each monitoring location, locate chamber tubing float. Carefully remove clamp from chamber tubing and attach to peristaltic pump or similar apparatus. Clear 1.5 times the inner volume of the tubing using a peristaltic pump or similar apparatus by pumping into a graduated container to verify volume pumped. Discard the cleared water.

If using an intermediate sampling container, rinse 1-L bottle three times with water cleared from the tubing, then continue to pump approximately 1 liter of sample water into the 1-L bottle for nutrient sampling.

Turn off the pump, disconnect the pump from the chamber tubing, fold the chamber tubing over and clamp to avoid contaminating water within tube, and reconnect chamber tubing to float to secure.

#### 6.3.2 Dissolved Oxygen Samples

DO samples must be collected from the tubing directly as soon as possible and prior to processing nutrient samples to minimize the exchange of oxygen with the atmosphere. DO samples should be drawn into glass flasks without turbulence, in accordance with SOP outlined in Ward (2007) for freshwater and Stutes and Bos (2007) Section 6.1 for marine waters. Bottles must be filled to the rim. Immediately after filling, add 1 mL of manganese chloride followed by 1 mL of sodium iodide-sodium hydroxide solution. Place the stopper on the rim and ensure that no bubbles are trapped inside. With a finger on the stopper, invert the bottle to mix the reagents multiple times, and store in carrying case. Top each sample with deionized water.

### 6.3.3 Total Nutrient Samples

For total (unfiltered) nitrogen and phosphorus samples delivered to the laboratory, follow the SOP outlined in Stutes and Bos (2007) Section 6.6. In summary, rinse 20-mL graduated cylinders 3 times with sample water and discard. Using the 20-mL graduated cylinders, measure 20 mL of sample water and transfer to 60-mL total nutrients sample bottle. Graduated cylinders can be re-used within a single field day. Alternatively, rinse syringe 3 times with sample water and discard. Use syringe to measure 20 mL of sample water into total nitrogen and phosphorus sample bottle.

For unfiltered nitrogen and phosphorus samples analyzed by other laboratories, consult with the laboratory for sample collection needs.

#### 6.3.4 Dissolved and Particulate Nutrient Samples

For dissolved (filtered) nitrogen and phosphorus samples delivered to the laboratory, follow the SOP outlined in Stutes and Bos (2007) Section 6.5. In summary, rinse 60-mL syringe 3 times with sample water and discard. Attach 0.45-micron filter to syringe, filter 2 to 5 mL to waste, then use filtered water to rinse the sample bottles 3 times and discard. Filter 100 mL of sample water directly into 175-mL dissolved nutrients sample bottle. Use one filter per sample, but syringes can be re-used within a single field day.

For dissolved organic carbon samples delivered to the laboratory, follow the SOP outlined in Stutes and Bos (2007) Section 6.4. In summary, while the particulate carbon/nitrogen sample is being filtered using the 25-mm GF/F filters, collect 20-30 mL of the filtrate in a 40-mL glass vial.

For particulate carbon/nitrogen samples delivered to the laboratory, follow the SOP outlined in Stutes and Bos (2007) Section 6.4. In summary, filter sufficient sample through the 25-mm GF/F filters using a vacuum pressure of 5 to 7 psi to ensure a dark color on the filter pad; record the volume, up to 1 L. Place filter pad in labeled Petri dish and freeze. Use a single filter pad per sample, but syringes can be re-used within a single field day.

For filtered nitrogen, filtered phosphorus, and particulate carbon/nitrogen samples analyzed by other laboratories, consult with the laboratory for sample collection needs.

#### 6.3.5 Sample Labeling, Storage, and Delivery

Each sample must be labeled immediately following collection.

DO samples should be secured upright to avoid leakage, kept in the dark, and delivered to the EAP Operations Center within 24 hours of sample collection. EAP staff will analyze samples according to the methods of Carpenter (1966), preferably within 48 hours or at least within 5 days of sample collection.

Total and dissolved nutrient samples should be kept in coolers filled with ice and delivered to the EAP Operations Center within 24 hours of sample collection. EAP staff will deliver samples to the appropriate laboratory in accordance with laboratory hold time requirements. Nutrient samples may be frozen for preservation in an upright position.

At the Operations Center, EAP staff will transfer total nitrogen and phosphorus, dissolved nitrogen and phosphorus, particulate carbon/nitrogen, and DOC samples to the freezer. EAP will deliver samples to the appropriate laboratory or transfer samples to the courier.

The QAPP will identify what laboratory will analyze the samples and what analytical methods are to be used. For nitrogen, phosphorus, and carbon samples submitted to the UW MCL, laboratory methods are described in Stutes and Bos (2007) Sections 6.4, 6.5, and 6.6.

#### 6.4 <u>Benthic Flux Chamber Removal</u>

At the conclusion of the deployment period, collect final samples for dissolved oxygen and nutrient analyses using the procedures in Section 6.3. Using the retrieval lines with floats attached, gently pull the sampler from the sediment

surface and lift through the water column. In deeper marine waters, this may require use of a winch or other hoist. Rinse the sampler free of sediment and pour out any remaining water from the chamber. Disconnect the Hydrolab or other dissolved oxygen monitoring devices, turn off the stirrer, and return the chambers to EAP Operations Center or other field staging area for cleaning, maintenance, or storage.

#### 6.5 Benthic Flux Chamber Cleaning and Maintenance

Rinse and dry the benthic flux chambers and inspect for disconnected tubing or cracks. Inspect retrieval lines for abrasion. Replace any broken floats. Repair any leaks in the chambers. Any problems with the benthic flux chambers, peristaltic pumps, batteries, battery chargers, Hydrolabs, or stirrers must be reported to the EAP Operations Center using the Equipment Problem Report Form (http://aww.ecology/programs/eap/forms/index.html).

#### 6.6 Hydrolab Post-calibration, Downloading, Cleaning, and Maintenance

If using Hydrolabs owned by the Department of Ecology, deliver Hydrolabs to the EAP Operations Center where EAP staff will perform post-deployment Hydrolab checks, download the data, and maintain the instruments using the SOP outlined in Swanson (2007).

If using other equipment, perform similar steps. Deliver pre- and postdeployment calibration information and data collected during the deployment to EAP staff in an appropriate electronic format, as described in the QAPP.

### 7.0 Records Management

Each sample collection event will be described in the field notebook with waterproof ink. At a minimum, field staff will record the date, time, location identification, sample laboratory identification number (if samples are submitted to Manchester Environmental Laboratory), analyses to be performed, and any ancillary data. Entries will be kept neat and concise.

Sample locations will be described in enough detail to locate on a United States Geological Survey 7.5-minute quad or an Environmental Information Management (EIM) System map. In marine areas or where other locators are not available, a global positioning system (GPS) unit will be used to record an accurate location using the SOP. (Janisch, 2006). Coordinates will be recorded as per EIM requirements.

If samples are submitted to Manchester Environmental Laboratory, field staff will complete the Pre-sampling Notification form (<u>http://aww.ecologydev/programs/eap/forms/PSN2000.pdf</u>) and Sample Container Request form

(<u>http://aww.ecology/programs/eap/forms/SampleContRequestForm2006.pdf</u>) prior to sampling. Field staff must submit the Laboratory Analyses Required form to accompany samples to the laboratory.

If samples are submitted to another laboratory, field staff will document appropriate sample information and follow sample handling requirements described in the QAPP.

### 8.0 Quality Control and Quality Assurance Section

Field staff will follow Quality Assurance/Quality Control procedures described in the QAPP. Field and laboratory replicate samples will be collected as directed in the QAPP.

#### 9.0 Safety

All field staff must comply with the requirements of the EA Safety Manual (EA Program, 2006). A full working knowledge of the procedures in Chapter 1 General Field Work is expected. If chambers are deployed in freshwater, field staff must comply with the section Working in Rivers and Streams. If chambers are deployed in marine waters, field staff must comply with the Chapter 2 section Operating Winches on Small Boats, Trailers, Vehicles, and Float Planes; all onboard staff must be familiar with Chapter 3, Boating.

For further field health and safety measures, refer to the Environmental Assessment Program Safety manual.

Canvas or leather gloves will protect hands from rope burns when lowering or raising sampling equipment from boats. Latex gloves should be worn to avoid bacterial or chemical exposure when extracting samples from chambers.

#### 10.0 References

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Stutes, A. and J. Bos. 2007. Standard Operating Procedures for Seawater Sampling. Environmental Assessment Program, Washington State Department of Ecology. Olympia, WA.

Swanson, T. 2007. Standard Operating Procedures for Hydrolab Calibration and Deployment. Environmental Assessment Program, Washington State Department of Ecology. Olympia, WA. www.ecy.wa.gov/programs/eap/qa/docs/ECY\_EAP\_SOP\_Hydrolab\_v1\_0.pdf

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