Quality Assurance Project Plan

Long-term, High Resolution Marine Water Quality Monitoring in Puget Sound using Profiling Buoys

2012-2013 Activities

by

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This Quality Assurance Project Plan (QAPP) is adapted from sections of the 2005 Hood Canal Dissolved Oxygen Program (HCDOP) QAPP and 2011 updates on profiling buoys. Those documents are available on the HCDOP home page at *http://www.hoodcanal.washington.edu/documents/document.jsp?id=2465*.

This document, once approved, will replace the 2011 profiling buoy QAPP that is available on the ORCA buoy home page at *http://orca.ocean.washington.edu/QAPP.html*

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Hood Canal, Lynch Cove (WA-PS-0260) – Dissolved Oxygen, pH
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Approvals

Jan Newton, Principal Investigator University of Washington Applied Physics Laboratory	Date
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Abstract

Understanding marine water quality responses to human influence within the high spatial and temporal complexity of Puget Sound requires coordination of several monitoring approaches to address the appropriate scales of variation. This project supports six profiling buoys that are essential to a comprehensive view of water, oxygen, and nutrient dynamics. The buoys provide high-resolution, near real-time, on-line and calibrated water quality data for specific locations within Puget Sound and Hood Canal. The data enhance the Puget Sound Partnership's Dashboard Indicator on oxygen by providing information on water mass dynamics allowing interpretation of oceanic influence on Puget Sound basin-scale oxygen conditions. Profiling buoy data identify oceanic intrusions, local upwelling, the thickness of a hypoxic layer, and give insights to processes contributing to eutrophication and hypoxia, thus increasing our confidence in detecting water quality change and attribution of that change. The buoys are currently located to measure oxygen dynamics at Hansville, in areas with susceptibility to hypoxia (Carr Inlet and Twanoh/Hoodsport), near King County's new sewer outfall (Pt Wells), and where the interplay between hypoxia and ocean acidification is important to Washington's premier shellfish hatchery (Dabob Bay). The buoys relay high-resolution meteorological and water property data utilized by numerical modelers. Use of the high-resolution data from these profiling buoys in concert with data from other regional monitoring approaches enhances the Partnership's ability to direct effective restoration actions.

Introduction

This project supports six profiling buoy monitoring assets that are part of a comprehensive view of Puget Sound water, oxygen, and nutrient dynamics. Fixed profiling moorings are one of the key monitoring strategies vital for understanding Puget Sound water quality (Figure 1, drawn by Dr. C. Krembs, Ecology). Understanding the response of water quality to natural and human influences in the high spatial and temporal complexity of Puget Sound requires a collaborative effort of monitoring, data quality assurance, interpretation, and thus coordination on many levels.

Located in major basins (Figure 2), the six autonomous buoys uniquely measure high-resolution dynamics of marine water focusing on vertical structure and variability with a 24h-7d-365d monitoring window. Their strength resides in diurnal (day/night) continuous resolution of the oxygen, algae biomass, and pCO_2 that is not covered by other monitoring approaches. The temporal and vertical resolution provided by the buoys reveals the response of water quality to varying levels of light, environmental disturbances (storms, rain events, unusual tides), turbidity, and vertical phytoplankton migration. Likewise, seasonal and oceanic intrusions are captured with high vertical and temporal resolution, yielding insight into the timing and extent of water transport. The buoys' unique contribution to our understanding justifies their continued support and evaluation of placement in Puget Sound under a unified strategy.

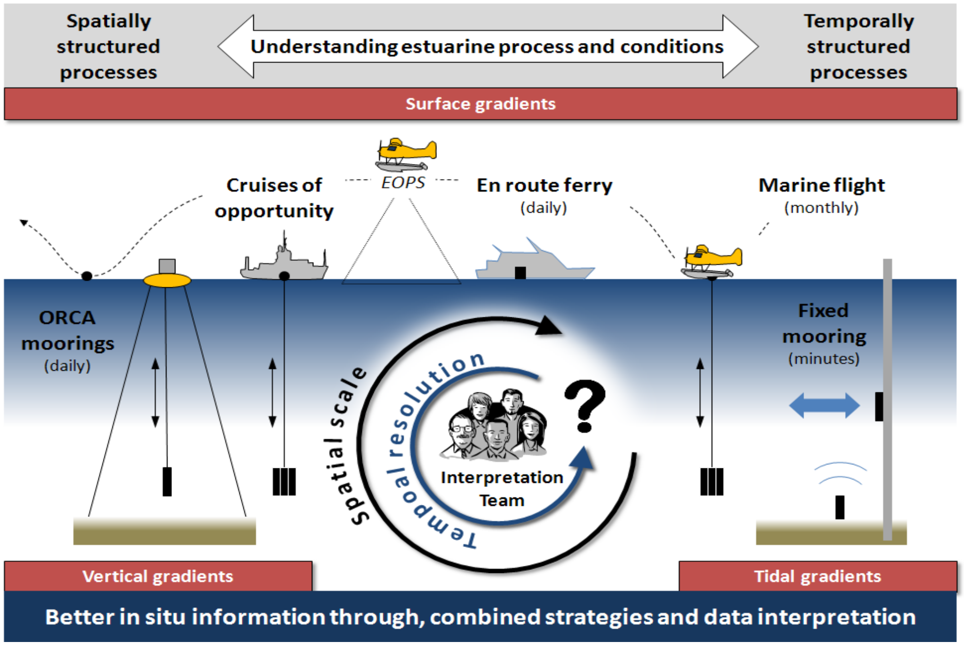

Figure 1. Conceptual model for the pillars of monitoring in Puget Sound. These in-situ assets are complemented by sea-plane and shipboard based sampling that provides the potential for calibration/validation and further context. Figure drawn by Dr. C. Krembs (Ecology).

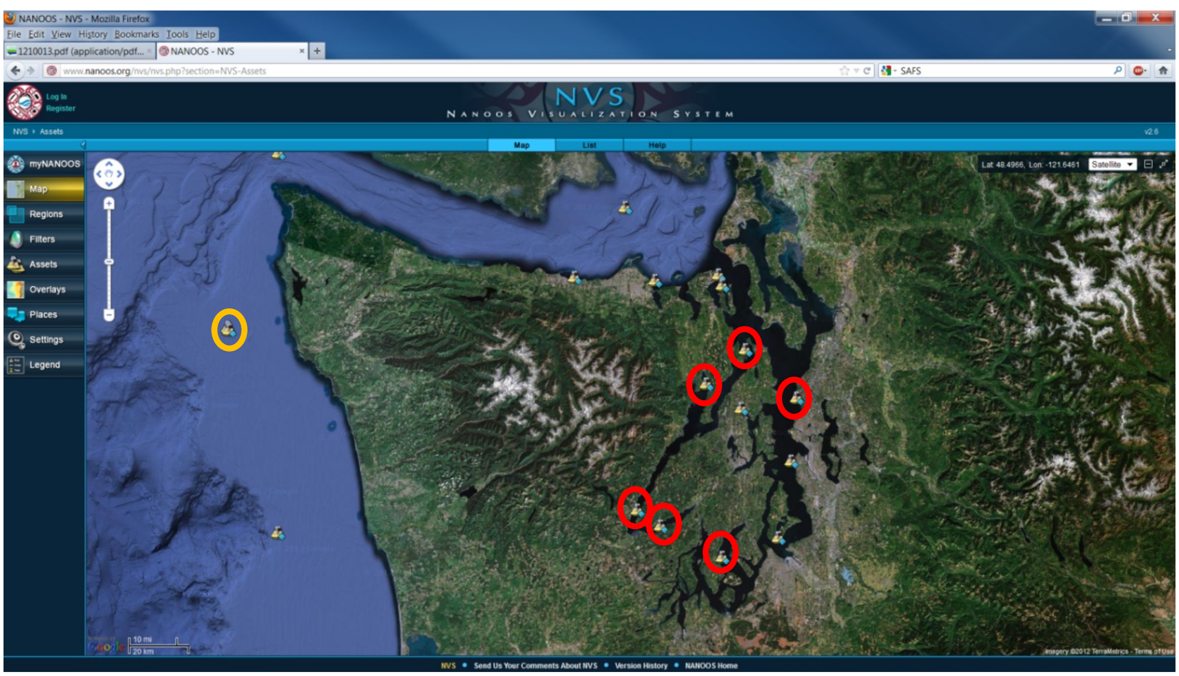

Figure 2. Map of Puget Sound from NANOOS Visualization System (NVS) screen shot showing regional monitoring assets. Locations of the six profiling buoys operated by UW are shown by red ovals. Other fixed depth shore platforms are operated by Ecology, King County, NOAA, shellfish growers and others. Orange oval denotes a profiling buoy off La Push operated by UW. Clicking on an icon results in the ability to visualize data (24 h, 7 d, 30 d) and download it to viewer's desktop. Data from NANOOS partners are a coordinated public resource for PSEMP.

Over time, interannual variation and changes in mid basin circulation patterns and water properties can be assessed in great vertical detail and data can be used to infer the net transport of water, nutrients and oxygen. The high-resolution weather and water property data are also used to feed/verify computational models. Continuous vertical water column observations in Puget Sound's major basins are indispensable to understanding processes, such as oceanic intrusion, local upwelling, the thickness of hypoxic layers and blooms, that cannot be adequately addressed with the suite of existing monitoring techniques aimed at measuring different aspects of Puget Sound's water properties at lower temporal resolution or at point locations (Figure 3).

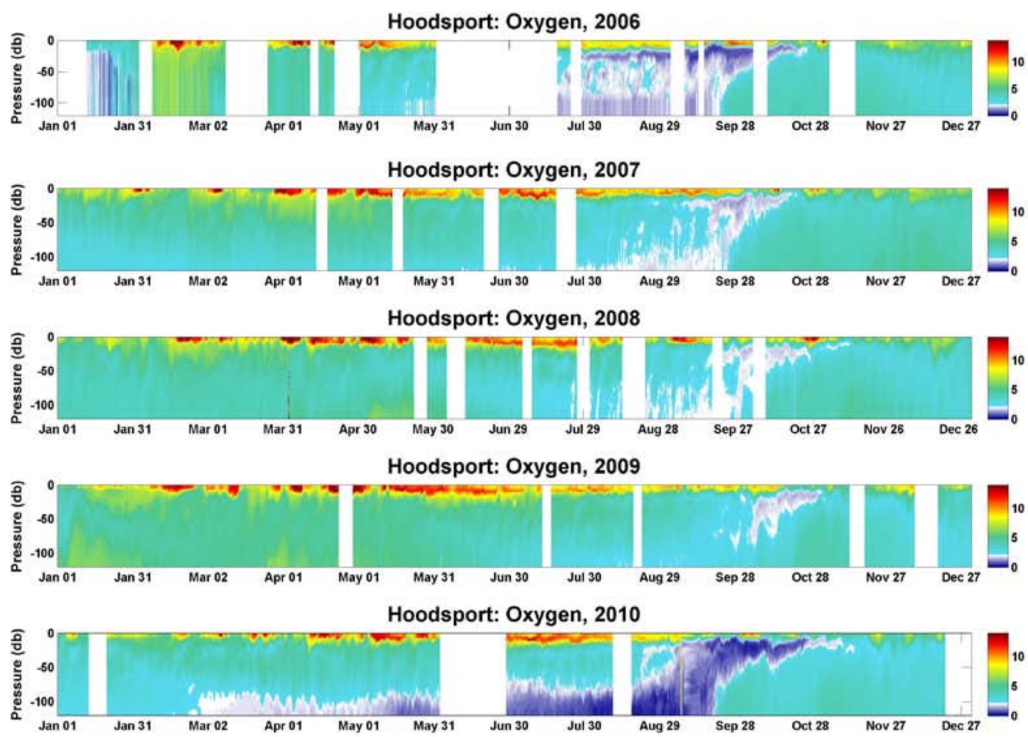

Figure 3. Hoodsport profiling buoy oxygen concentration (mg/L) time-series. An example data product from the profiling buoys is this time-series of oxygen concentration profiles (mg/L) measured at Hoodsport showing seasonal shoaling of hypoxia due to oceanic intrusion and persistence of deep hypoxia in 2010.

Vertical profiling ORCA moorings represent a fundamental component of an *in situ* sensor alliance which leverages existing assets to strategically address the large spatial and temporal dynamic and complexity of estuarine processes in Puget Sound. Individuals representing Ecology, UW, King County, NOAA, PNNL, tribes, and other entities recently formed the Marine Waters Working Group (MWWG) of the Puget Sound Environmental Monitoring Program (PSEMP) and collectively bring a suite of monitoring capabilities for Puget Sound. From a document drafted by several individuals of that group "the four proposed main pillars of the current marine water monitoring sensor network are: 1. Marine flight monitoring stations that provide a long-term historical record of monthly profiles…; 2. Fixed moorings located between basins, capturing inter-basin exchange processes, and in bays of heightened water quality concern (operated by King County, Ecology, and others); 3. En route ferry data that provide continuous real-time information of surface gradients and processes (operated by Ecology); and 4. Fixed profiling buoys, collecting data in near real-time at high frequency sampling, specifically designed to resolve the dynamic in vertical structures of mid-basin water bodies (operated by UW)".

Importantly, the buoys supply information on water mass dynamics regarding oceanic influence on hypoxia, a major issue for marine water quality assessment. Most of the data generated by the MWWG, including that of the profiling buoys, are available to the public through the NOAA-funded Northwest Association of Networked Ocean Observing Systems (NANOOS) portal (Figure 2).

While the MWWG will evaluate optimal locations for these six buoys in the coming year, buoys are currently located in four of the five major Puget Sound basins and gather data on key regional water quality features. Locations, with deployment year indicated, are: 1. Hansville (2005); 2. Pt Wells (2003-4 and 2010); 3. Carr Inlet (2000-3 and 2010); 4-5. Twanoh (2005) and Hoodsport (2005); and 6. Dabob Bay (2010). The high-resolution time-series data provide a baseline for climate change impacts assessment (e.g., temperature and salinity, which also affect density-driven circulation and thus flushing of Puget Sound). Buoys can be moved at a cost of approximately $40K for ship time, anchoring, and personnel.

Specific strengths of the profiling moorings are:
1. <u>Representative sampling</u>: Profiling buoys are important for refining accuracy of measurements from traditional monitoring strategies. Research has shown that Puget Sound waters are highly dynamic over time. Use of both autonomous sensors on remote buoys and field-collected water samples for laboratory analysis is needed in order to gain estimates of water property values that are both representative and accurate. While field-collected water samples for laboratory analysis are highly accurate, the high-frequency variation of the environment has implications for their representativeness. Figure 4 shows that an individual water property profile may vary substantially in magnitude and shape over a given month, in this case July 2008. While sensors can capture this variation so that averages of these data are representative, their accuracy may be less than water samples or point casts, due to sensor drift or other factors; using both sampling strategies allows for calibration to correct for sensor drift.

2. <u>Modular platforms for expansion</u>: The profiling buoys are modular, with possibilities for expansion of sensors as new technologies are available, such as for oil, Harmful Algal Blooms (HABs), pathogens, and optical species recognition. UW has partnered with NOAA to locate sensors for pCO_2 on two of the buoys to assess ocean acidification status in Puget Sound (Feely et al., 2010), and in the past, has partnered with NOAA/POST/WDFW for fish acoustic receivers.

3. <u>Water and weather data input to modeling</u>: The buoys relay near real-time water property data (1-6 h resolution) as well as real-time over-water weather data (1 and 10-minute resolution). Wind is particularly variable over the Puget Sound basin, yet wind data over water are sparse. Winds are an important driver of marine processes and critical to the accuracy of models. In many locations only airport reporting stations are available. Buoy meteorological data are used by numeric modelers for more accurate forcing of hydrologic and water quality models.

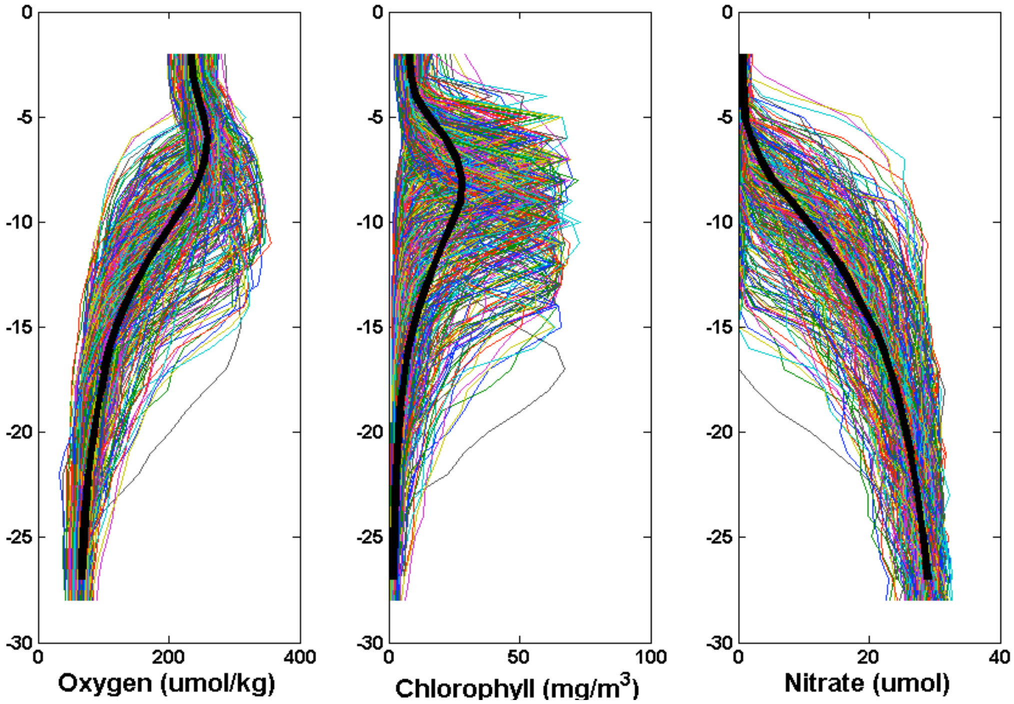

Figure 4. Representativeness of profiling buoy data over one month. Compilation of all ORCA profiles at Twanoh, Hood Canal, during July 2008, for oxygen concentration, chlorophyll fluorescence, and nitrate concentration. The thick black line is the numerical average of all 370 profiles.

Project Description

This project supports six profiling buoys that are essential to a comprehensive view of water, oxygen, and nutrient dynamics. The buoys provide high-resolution, near real-time, on-line and calibrated water quality data for Hansville, Carr Inlet, Twanoh, Pt Wells, and Dabob Bay. The data provide information on water mass dynamics allowing interpretation of oceanic influence on Puget Sound basin-scale oxygen condition. The scope of work of the project is defined by four tasks, two of which (tasks 2 and 3) are the main focus of this QAPP.

Task 1: *Project Administration and Management.* This task will be completed by the Project PIs, Newton, PI, and Devol, co-PI, who will admister this grant project, maintaining records, submitting performance items, and submit a summary of project outcomes at project completion.

Task 2: *Operation and routine maintenance of six automated buoys in the various locations within Puget Sound for one year*. APL-UW and the UW School of Oceanography will continue their collaboration to operate profiling buoys in Puget Sound, maintaining and servicing the buoys and sensors to assure high quality data streams. Operation under this QAPP updates but largely follows the Quality Assurance Project Plan (QAPP) of the HCDOP-Integrated Assessment and Modeling (IAM) project, as published by the Washington State Department of Ecology (Roberts, et al., 2005), as updated in 2011. This is important because this assures the long-term consistency of the data.

Work duties by field technicians involve fieldwork with a small boat to service and maintain buoys and all sensors, collection of calibration samples, sensor calibration and calibration sample lab analyses, and automated data processing.

Maintenance is season-dependent, but typically monthly. UW will continue field collaborations with NOAA-PMEL regarding ocean acidification monitoring equipment on the buoys at Dabob Bay and Twanoh.

An outcome of this work is the preservation of these valuable profiling buoy monitoring assets and collection of their high-resolution marine water quality monitoring data for a multitude of applications, as described above in the Introduction.

Task 3. *Data quality oversight and data dissemination.* Delivery of the near real-time data streams from these buoys will be made to websites maintained by NANOOS, NOAA-NDBC, and UW through which the data are publically available and viewable.

A technician in Devol's group at UW Oceanography will provide data quality oversight, flagging bad data streams, assure automated data processing, conduct sensor calibration revised data processing, and provide flow of data streams to the web.

The near real-time data will be available to the public for visualization and download via a variety of sources. These include the Northwest Association of Networked Ocean Observing Systems (NANOOS) Visualization System (NVS) at www.nanoos.org. The NVS shows near real-time display of buoy data and allows for visualizations and immediate data download of up to 30 days of data. In addition, near real-time and calibrated buoy data will continue to be publically available via the UW ORCA buoy site at http://orca.ocean.washington.edu, also accessible through the HCDOP website at www.hoodcanal.washington.edu. The profile plots on the ORCA buoy site are of near real-time data and the contoured plots below these profiles show calibrated data.

The profiling buoy data can also be accessed from the US IOOS webstie: http://www.ioos.gov/data/welcome.html and from the NOAA National Buoy Data Center (NDBC) website: http://www.ndbc.noaa.gov/maps/NW_Straits_Sound.shtml. The pCO_2 data (not part of this QAPP or supported by this grant) are available via the NOAA PMEL Carbon Program website: http://www.pmel.noaa.gov/co2/, also viewable at both NANOOS and UW ORCA websites.

Task 4: *Discussion of strategic role of profiling buoys within the Puget Sound Ecosystem Monitoring Program.* This task entails a discussion of the strategic role of profiling buoys within the Puget Sound Partnership's Puget Sound Ecosystem Monitoring Program (PSEMP). PI Newton is a member of the PSEMP Steering Committee. Newton and Devol are members of the PSEMP-commissioned Marine Waters Working Group (MWWG). The MWWG involves a diverse collection of federal, tribal, state, local, academic, industry, and NGO participants, both scientists and practitioners. Non-funded co-PIs on this project, Christopher Krembs (Ecology) and Kimberle Stark (King County) who lead two of Puget Sound's major monitoring programs, are both part of this Working Group and have made a specific commitment to work with Newton and Devol on this task. The MWWG is evaluating optimal use and location of the profiling buoys within a unified comprehensive monitoring plan for the marine waters of Puget Sound, as well as the broader network of Working Groups within the PSEMP, such as food webs, toxics, and others.

Newton and Devol will devote some staff time to this task.

Organization and Schedule

The grant period this QAPP covers is one year, with a start date anticipated of 1 September 2012, but will be commensurate with the acceptance of this QAPP. The personnel, responsibilities and timeline for each of the Project Tasks are described below.

<u>Task 1</u>: *Project Administration and Management.* It will be the responsibility of Newton, PI, and Devol, co-PI, to administer this grant project, maintaining records, submitting performance items, and submit a summary of project outcomes at project completion.

<u>Task 2</u>: *Operation and routine maintenance of six automated buoys in the various locations within Puget Sound for one year.* Newton and Devol will jointly oversee this task, with their technicians responsible for fieldwork with a small boat to service and maintain buoys and all sensors, collection of calibration samples, sensor calibration and calibration sample lab analyses, and automated data processing. This will commence throughout the project period.

<u>Task 3</u>. *Data quality oversight and data dissemination.* Newton and Devol will jointly oversee this task. A technician in Devol's group will provide data quality oversight, assure automated data processing, conduct sensor calibration revised data processing, and provide flow of data streams to the web as well as delivery of the near real-time data streams from these buoys to websites maintained by NANOOS, NOAA-NDBC, and UW. This will commence throughout the project period.

<u>Task 4</u>: *Discussion of strategic role of profiling buoys within the Puget Sound Ecosystem Monitoring Program.* This task entails a discussion of the strategic role of profiling buoys within the Puget Sound Partnership's Puget Sound Ecosystem Monitoring Program (PSEMP). Newton and Devol will devote some staff time to this task throughout the project period.

Experimental Design

Autonomous monitoring buoys are established at six locations (Figure 2) in Puget Sound: Point Wells, Carr Inlet, Hansville, Dabob Bay, Hoodsport, and Twanoh. The details of the buoy operation are given in Dunne et al., 2002, Ruef et al 2004, and Ruef and Devol 2007, and only a brief description will be given here. Each buoy contains a winch that lowers a CTD package through the water column. Profiling is controlled by a microprocessor (BitsyX) that specifies profile times and depths. After a profile is completed the controller uploads the data from the CTD. The controller also records 10 min averaged meteorological data. At preprogrammed times the data is telemetered by cellular internet and wi-fi from the buoy to a central computer at the University of Washington; CTD files are automatically processed using sensor manufacturer procedures, graphed and posted to the internet (http://orca.ocean.washington.edu). The buoy power system consists of two 123 watt solar panels and a 24 volt battery energy storage system. Consequently profiling frequency is dependent on available solar energy. During the summer, sufficient energy is typically available to profile every 2 hours. During the winter months, solar radiation is only sufficient to support 2 profiles a day under normal working conditions at all buoys. This is entirely dependent on solar radiation levels.

The suite of sensors includes a: Sea-Bird SBE 19plus CTD to determine temperature and salinity; Sea-Bird model 43 dissolved oxygen probe; WET Labs WET Star fluorometer or WET Labs FLNTUS fluorometer and turbidity sensor; Biospherical Instruments or LiCor Biosciences PAR sensor; Satlantic ISUS-X Nitrate sensor; Nortek Aquadopp 3D current meter. Profiles are made by powering up the sensor package, equilibrating the sensors, and raising the package from a parking depth of 20 meters (chosen to minimize biofouling) to the surface. This is followed immediately by a "downcast" from the surface to the bottom profile depth, after which the package is returned to the parking depth.

The ORCA buoys are instrumented with sensors to quantify the following chemical and physical parameters (http://orca.ocean.washington.edu/sensors.html).

At all buoys the following variables are available:
- pressure (converted to depth)
- temperature
- salinity
- density (derived from the three variables above)
- chlorophyll fluorescence
- dissolved oxygen

Additionally, there are limited sensors to measure the following parameters:
- current velocity (3 sensors available; 1 currently deployed at Carr Inlet)
- nitrate (3 sensors available; 1 currently deployed at Carr Inlet)

The available sensors will be planned for deployment during this grant period and locations are to be determined with input from Ecology and PSEMP.

All buoys were designed to have meteorological sensors. Currently, due to lack of replacement funds the following sensors are working at three buoys: Carr Inlet, Dabob (except needs PAR) and Hansville (except needs PAR). The met packages at Pt Wells, Twanoh, and Hoodsport are in need of repair and the funding of this grant is not sufficient for this repair.
- barometer
- wind speed/direction
- air temperature
- solar radiation (PAR)

For this QAPP and funded project, temperature, salinity, derived density, oxygen, and chlorophyll are the intended deliverables. We will make data for nitrate, currents, and weather variables available as much as possible, but these sensors require repair funding that is outside the scope of this grant and thus these data streams are not assured.

Temperature, salinity, oxygen concentration, and chlorophyll fluorescence are measured during each profile; due to the limited number of specialized sensors, nitrate concentration and current speed and direction are not measured at every buoy. Location and timing of deployment for these sensors is dependent on season, water column properties, and open research questions. Sensors measuring nitrate concentration are typically deployed spring through fall to capture dynamics associated with phytoplankton blooms. The current meter is deployed when the buoy profiling frequency allows for enough data collection to study mean currents while averaging out the tidal signal, also typically in the spring through fall months. Ideally these sensors are deployed at 3 buoys 60% of the year. The suite of sensors also includes underwater PAR sensors, but due to lack of repair funds they are not currently deployed.

Researchers visit the buoy locations every three to five weeks (depending on season/biofouling) to collect discrete samples, as described in greater detail below under Sampling Procedures. These samples are used to calibrate the sensor readings using procedures detailed below under Measurement Procedures.

Quality Objectives

Measurement Quality Objectives

Measurement quality objectives (MQOs) refer to the performance or acceptance criteria for individual data quality indicators such as accuracy, precision, resolution, method detection limit, comparability, and completeness. MQOs provide the basis for determining the procedures that should be used for sampling and analysis.

Field studies are designed to generate data adequate to reliably estimate the temporal and spatial variability of that parameter. Sampling, laboratory analysis, and data evaluation steps have several sources of error that should be addressed by MQOs. Accuracy in MQOs can be more easily controlled in a laboratory setting but does not address field variability. Analytical bias needs to be low and precision as high as possible in the laboratory. Sampling variability can be somewhat controlled by strictly following standard procedures and collecting quality control samples, but natural spatial and temporal variability can contribute greatly to the overall variability in the parameter value, thus representativeness is important. Resources limit the number of samples that can be taken at one site spatially or over various intervals of time.

The ORCA buoys measure a variety of parameters that are quite variable in the aquatic environment. Table 1 summarizes the measurement quality objectives for both *in situ* sensor measurements and laboratory sample values. For sensors, the MQOs for resolution and range are based on sensor capabilities published by the manufacturer; accuracies are based on factory calibrations. For laboratory measurements, the MQOs for accuracy and precision are based on the published method as implemented in the UW Lab Accreditation procedures (Krogslund, 1998).

Table 1. Measurement quality objectives (MQOs) for *in situ* values and laboratory analyses conducted by UW.

Measurement	Field Equipment	Accuracy	Sensor Resolution	Range	Unit
Buoy Measurements					
Temperature	Sea-Bird SBE 19plus	0.005 °C	0.0001 °C	-5 to 35	°C
Pressure	Sea-Bird SBE 19plus	0.1	0.002	0 to 120	db
Depth	Sea-Bird SBE 19plus	0.1	0.002	0 to 120	m
Conductivity	Sea-Bird SBE 19plus	0.0005	0.00005	0 to 9	S/m
Salinity	Sea-Bird SBE 19plus	0.005	0.0004	0 to 35	PSU
Dissolved Oxygen	Sea-Bird SBE 43	0.1	0.01	0 to 20	mg/L
Chlorophyll Fluorescence	WET Labs WET Star and FLNTUS	0.1	0.01	0 to 200	µg/L
Measurement	Laboratory Method	Accuracy	Precision	Range	Unit
Laboratory Measurements					
Dissolved Oxygen	Carpenter 1965 modification of Winkler	0.05	0.01	0 to 12	mg/L
Marine Nitrate	UNESCO 1994	0.1	0.01	0 to 40*	µM
Chlorophyll a	UNESCO 1994	0.1	~10% of value	0 to 100**	µg/L

** Detection range can be adjusted depending on expected sample range. Range listed for concentrations expected in Puget Sound.*
*** As calibrated on the TD700 fluorometer in the University of Washington Marine Chemistry Lab, using a reasonable filtration volume.*

In addition, ambient samples are split in the laboratory to isolate laboratory precision. The UW Marine Chemistry Lab analyzes laboratory control samples, or standards, as well as matrix spikes to verify that quality objectives are met (UNESCO, 1994).

An assessment of representativeness is shown in Figure 4, which presents a typical month of profiles. In practice, from studies on the Twanoh buoy in Hood Canal, sensor drift was found to vary 10% for the buoy oxygen sensors over one month. Using samples from monthly versus every 6 hours intervals was found to account for 50-300% of variation, based on Monte Carlo sub-sampling simulations of 6-h frequency data (Devol et al. 2007). Thus, the sensor data are calibrated with the analysis results from regularly sampled water samples. The resultant values are the most accurate time-averaged estimate for a specific location (<5% error for oxygen; 5-15% for nitrate) and representative possible for the strong high-frequency variation evident in Puget Sound.

Comparability is high because sensors are the same between buoys and have been that way since the buoys were deployed in 2005. This QAPP updates that of Roberts et al., (2005), which was the first QAPP to guide the operations of the ORCA buoys. For the most part, these also match those used by Ecology in their marine flight and mooring programs.

Completeness will be addressed recognizing that this grant funds only partial operation of the buoys. Additional operations and maintenance is funded through NANOOS by the U.S. Integrated Ocean Observing System (IOOS) from its federal program office at NOAA. These combined funding streams are sufficient to provide an anticipated operation of 80% of assets operational 80% of the time, an IOOS standard for real-time systems. Funding for rehabilitation of winch packages and solar panels is not sufficient at this time. When the buoys are operational, sensor measurements are available ~95% of the time.

Sampling Procedures

Researchers visit the buoy locations every three to five weeks (depending on season/biofouling) to collect discrete samples that will be used to calibrate the sensor readings following procedures described below under Measurement Procedures. Discrete samples are collected with a Niskin bottle lowered independently and simultaneously with the ORCA CTD package to a predetermined depth. Once the CTD and Niskin are at the same depth, the CTD is run for 60 seconds to equilibrate the sensors; the messenger on the Niskin line is released at 90 seconds. CTD sampling continues through 120 seconds and is then halted. The Niskin is brought on board the vessel and sampled from, starting first with dissolved oxygen samples, followed by samples collected for analysis of nutrient and chlorophyll concentrations. The CTD data are downloaded after each depth and stored in individual files.

Water samples for oxygen will be collected directly in pre-cleaned containers. Pre-cleaned syringes used for sample collection will be rinsed with ambient water three times before filtering, repeated for each sampling site and depth. Nutrient samples will be collected in a syringe and filtered into pre-cleaned containers. Water samples for chlorophyll will be collected into syringes, filtered, and the filter collected and placed in pre-cleaned tubes with 10 mL of pre-measured 90% acetone. Chlorophyll and nutrient samples are immediately placed on ice and in the dark. Oxygen samples are shaken twice with an intermediate settling, and then maintained in the dark with deionized water filling the bottle top. Samples are stored according to established protocols (Carpenter, 1965 for oxygen samples, and UNESCO 1994 for chlorophyll and nutrient samples) and described in further detail below under Quality Control Procedures. All samples are transported back to UW the same day as collection for analysis.

Measurement Procedures

Laboratory Measurements

University of Washington Marine Chemistry Laboratory

Krogslund (1998) details lab standard operating procedures, including quality control activities. Table 2 lists measurement procedures by parameter.

Table 2. UW laboratory measurement procedures.

Analyte	Sample Matrix	Laboratory Analytical Method	Method detection limit	Hold Time	Preservation Method	Expected Range of Results
Nitrate	water	UNESCO (1994)	0.08 µM	28 days	Filter and freeze	0-40 µM
Oxygen	water	Carpenter (1965)	0.01 mg/L	28 days	Chemical	0-15 mg/L
Chlorophyll	filter	UNESCO (1994)	0.02 µg/L	7 days	Filter and freeze	0-100 µg/L

In situ Measurements

UW Oceanic Remote Chemical Analyzer (ORCA) Buoys

Underwater sensors are calibrated at the factory prior to deployment, and every 1-2 years during deployment, as current funding allows. Field check samples are taken for the oxygen, chlorophyll, and nitrate sensors. The anemometer speed was calibrated in the NOAA-PMEL Sand Point wind tunnel facility; direction was calibrated in the field.

Discrete samples are taken with a Niskin water sampling bottle at each buoy every 3 to 5 weeks (depending on biofouling potential) throughout the deployment and processed for oxygen, chlorophyll, and nutrient (phosphate, silicate, nitrate, nitrite, ammonium) concentrations using established standard protocols. Oxygen samples are analyzed by Winkler titration (Carpenter, 1965) and chlorophyll samples are analyzed using a modification of the UNESCO (1994) Protocols for the Joint Global Ocean Flux Study (JGOFS), which are detailed in Newton et al. (2002). Nutrient samples are sent to the Marine Chemistry Lab at the University of Washington for analysis of nitrate, nitrite, ammonium, phosphate and silicate, where they are processed using modified methods based on UNESCO (1994). We note that the nutrient analysis procedure as implemented by UW results in analysis of all five nutrient species at once, while nitrate is the only variable measured on the buoys.

Oxygen sensor data are calibrated and corrected for drift by performing a linear regression for each sensor between all discrete samples and sensor readings, using an assumption that drift has been linear. Data are then corrected by applying the slope and offset of the regression to all data points for that particular sensor. We are just adopting now the procedure recommended by Sea-Bird, which uses discrete samples to recalculate the sensor coefficients.

Nitrate sensor data are calibrated by performing a simple linear regression between the discrete samples and sensor readings. Another linear regression is performed to correct for drift between discrete sample times, using the assumption that drift has been linear.

Due to high temporal and spatial variability, as well as variability in species population and biological response, fluorometers are notoriously hard to calibrate with discrete water samples. We have been in touch with the sensor manufacturer WET Labs over the years regarding this issue, and it is an open research question we are continuing to investigate. Currently, the fluorometer data are not calibrated beyond the factory calibrations. A known problem in the chlorophyll fluorescence data is the offset between the two models of fluorometers that are used. The WET Labs FLNTUS, an open-faced fluorometer, produces readings that are approximately 3-4 times lower than the WET Labs WET Star, a traditional flow-through fluorometer. This is likely due to different sensitivities of the models; the open-faced model is typically more sensitive to large particles, and the closed-cell fluorometer is more sensitive to smaller particles (personal communication, WET Labs engineers). The different fluorometer models are not deployed simultaneously at the same buoy. We make every effort to keep a single type of fluorometer at a particular buoy. In order to produce an inter-comparable time series of chlorophyll data, a scale factor between the two models was determined using cross comparison and linear correlations of profiles sampled using both models of fluorometers on one CTD package. As the data collected with the WET Star fluorometer more closely correlated with discrete chlorophyll samples, the FLNTUS data were corrected using the calculated scale factor of 3. The scale factor is not a calibration, nor a long-term solution; it is only a means to create an internally consistent time-series that can be compared with itself and other ORCA buoy time-series using WET Labs WET Stars and FLNTUS fluorometers.

Quality Control Procedures

Quality control procedures refer to the routine application of statistical procedures to evaluate and control the accuracy of measurement data. The results for quality control samples determine whether the MQOs have been met. Krogslund (1998) describes lab standard operating procedures, including quality control procedures. Table 3 details laboratory quality control procedures for the ORCA buoy relevant measurements.

Table 3. Laboratory quality control samples.

Analysis	Field Replicates	Lab Check Standard	Lab Method Blank	Lab Duplicate	Matrix Spikes
Dissolved Oxygen	3 per depth at 5 depths	3/analysis session	3/run	N/A	N/A
Chlorophyll *a*	2 per depth at 4 depths	N/A	1/run	N/A	N/A
Nitrate	1 per depth at 5 depths	1/analysis session	1/run	1/10 samples*	1/20 samples*

*or at least one per run

For oxygen, blanks (3) and standards (3) are run each time samples are titrated, per Carpenter (1965), to track contamination and determine accuracy. In the field, triplicate water samples are taken at each of 5 depths, concomitantly with the CTD sensor. For chlorophyll, water samples are only taken in the top 50 m, where phytoplankton are typically found. The fluorometer is calibrated against Sigma chlorophyll *a* standard annually as per UNESCO (1994) and a blank is run each time. For nutrient QC procedures, see Krogslund (1998) which uses UNESCO (1994).

Collecting and analyzing replicate samples is used to assess total variation for field sampling and laboratory analysis. Other field sampling and measurements will follow quality control protocols described in Newton et al. (2002).

Currently, bad data streams are identified through daily (excluding weekends) visual inspection and rudimentary automated range checks. Once bad data are identified, they are flagged and removed from the final time-series. Sensors are verified and calibrated using the discrete sample results, as described above under *In Situ* Measurements.

Data Management Procedures

Data from all ORCA buoys are archived on the ORCA server. All files including raw sensor data, processed data, calibration data and objectively mapped time-series are archived. Data are viewable for the current and all casts from the ORCA website which can be accessed from the HCDOP IAM website (www.hoodcanal.washington.edu). As indicated on the site, the near-real time depth profile plots are of raw unverified and uncalibrated data. The contoured time-series plots below these profiles show verified and calibrated data, with the newest data (the last 30 days) being preliminarily verified and calibrated. The fully verified and calibrated data are maintained in the ORCA database.

Data are downloadable from the ORCA website (www.orca.ocean.washington.edu) after obtaining a password (see ORCA website for instructions; there are no restrictions on obtaining a password) or the data are immediately downloadable for the last 30 days from the NANOOS Visualization System (NVS, www.nanoos.org/nvs).

The data and information management requirements for ORCA are met in collaboration and partnership with Northwest Association of Networked Ocean Observing Systems (NANOOS). This replaces and builds on partnerships begun through the Puget Sound Regional Synthesis Model (PRISM-UW) and Puget Sound Marine Ecosystem Modeling (PSMEM) projects.

All post-processed profile data are automatically harvested by NANOOS for ingestion and archival into the NANOOS-APL Data Assembly Center (DAC) database (Mayorga et al, 2010) soon after the data files have been updated. This database integrates ORCA data with other regional marine datasets and serves as a distribution point for access via the NANOOS NVS and also the US IOOS network.

Near real-time ORCA data for the previous month are available for visualization and direct download via NVS (Mayorga et al, 2010) immediately after ingestion into the NANOOS-APL DAC database. From NVS, ORCA data are also made available for automatic harvesting by the NANOOS Shellfish Water Quality application (www.nanoos-shellfish.org) in partnership with the Coastal Training Program, Washington State Department of Ecology, Padilla Bay National Estuarine Research Reserve, which is part of the NOAA National Estuarine Research Reserve System.

The NANOOS-APL DAC database is a relational database running on PostgreSQL and taking advantage of the PostgreSQL PostGIS geospatial add-on. It is hosted at APL-UW in a robust server with automatic daily and staggered database dumps and backups. This system is regularly analyzed and enhanced in support of NANOOS' operational and data-archival mission. Data-access enhancements that are currently being explored include access via OpenDAP to support the oceanographic community; and via Open Geospatial Consortium (OGC) web services to support the geospatial community. NANOOS already supports OGC web services (WMS and WFS) for some datasets, using the GeoServer software.

In summary, the near real-time data will be available to the public for visualization and download via a variety of sources. These include the Northwest Association of Networked Ocean Observing Systems (NANOOS) Visualization System (NVS) at www.nanoos.org. The NVS shows near real-time display of buoy data and allows for visualizations and immediate data download. In addition, near real-time and calibrated buoy data will continue to be publically available via the UW ORCA buoy site at http://orca.ocean.washington.edu, also accessible through the HCDOP website at www.hoodcanal.washington.edu. The web page has a note that: "PLEASE NOTE: Data shown here are preliminary, only partially calibrated and definitely not final!" to notify users that near real-time data are preliminary. The profiling buoy data can also be accessed from the US IOOS webstie: http://www.ioos.gov/data/welcome.html and from the NOAA National Buoy Data Center (NDBC) website: http://www.ndbc.noaa.gov/maps/NW_Straits_Sound.shtml. The pCO_2 data are available via NOAA PMEL Carbon Program website: http://www.pmel.noaa.gov/co2/, also viewable at both NANOOS and UW ORCA websites.

Audits and Reporting

The UW lab is audited as part of Washington State Laboratory Accreditation. UW will maintain, and supply upon request, all field logs, maintenance records, discrete sample logs and results, sensor deployment records, and calibration records. Data are available as described above in Data Management Procedures. The important environmental patterns of the buoy data have been and will be reported in the Puget Sound Environmental Monitoring Program's Marine Waters Working Group's annual document: Puget Sound Marine Waters: 2011 Overview (PSEMP Marine Waters Workgroup, 2012).

Data Verification, Validation, and Usability Assessment

UW will be responsible for conducting data verification and validation of ORCA data, housed at the University of Washington. Procedures for verifying laboratory data have been established by the University of Washington laboratory staff, which is a Washington State Accredited Lab (Krogslund, 1998). Procedures for verifying field data by field personnel are outlined in the field sampling text above. Verification of field and lab data will include checking for missing results, reviewing field samples and determining if adjustment is indicated based on field calibration samples, and examining potential outliers.

Validation of field and lab measurements will include comparing results to the quantitative targets for acceptability following the MQOs listed in Table 1. Marine water quality data validation procedures for datasets will be followed, as described above in the Sampling, Measurements, and Quality Control Procedures sections.

Overall usability of the data will be assessed by how well the data match the MQOs, whether calibration, verification, and validation procedures have been implemented. The objective of this project is to provide on-going marine water profile data of verified and validated quality.

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Appendix

List of Acronyms

APL	Applied Physics Laboratory
CTD	Conductivity-Temperature-Depth meter
DO	Dissolved oxygen
HCDOP	Hood Canal Dissolved Oxygen Program
IAM	Integrated Assessment and Modeling (study of the HCDOP)
MWWG	Marine Waters Working Group (of the PSEMP)
NANOOS	Northwest Association of Networked Ocean Observing Systems
NOAA	National Oceanic and Atmospheric Administration
ORCA	Oceanic Remote Chemical Analyzer
PMEL	Pacific Marine Environmental Laboratories (of NOAA)
PSEMP	Puget Sound Ecosystem Monitoring Program (of the Puget Sound Partnership)
UW	University of Washington