Work Plan for King County's Ocean Acidification Monitoring Program

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King County

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Table of Contents

1.0. Executive Summary 1
2.0. Background Information 3
2.1 The Chemical Basis of Ocean Acidification 3
2.2 Interactions with Upwelling, Photosynthesis, Respiration, and Mixing 3
2.3 Puget Sound Nutrient Inputs 5
2.4 Existing Monitoring in Washington 5
3.0. Goals and Objectives 8
4.0. Rationale 10
5.0. Sampling Stations 12
6.0. Sampling Design 16
6.1 Sensor Deployment 16
6.1.1 WOAC/UW – Point Wells 16
6.1.2 KC – Point Williams and Quartermaster Harbor 16
6.2 Discrete Water Sampling 17
6.2.1 WOAC/UW – Point Wells 17
6.2.2 KC – Point Williams and Quartermaster Harbor 17
6.2.3 Sample Analysis 18
7.0. Data Management 19
7.1 Sensor pH Calculation 19
7.2 KC Data Reporting 19
7.3 UW Data Reporting 20
7.4 PMEL Data Reporting 20
8.0. Schedule 21
8.1 Initial Tasks 21
8.2 Ongoing Operations 21
9.0. Budget 22
9.1 Equipment Purchase 22
9.2 Ongoing Operations 22
10.0. References 23

Figures

Figure 1. Location of ocean acidification monitoring program stations. 14

Tables

Table 1. Existing OA monitoring infrastructure on the Washington Coast and in Puget Sound. 7

Table 2. Summary of KC OA monitoring program activities, including location of SeaFET deployment and water sampling, and the sources of other data necessary for full characterization of the inorganic carbon system. 15

Appendices

Appendix A: Seafet specifications A-1

Appendix B: Storm 3 specifications A-2

Appendix C: Pump specifications.....A-4

1.0 EXECUTIVE SUMMARY

The dissolution of anthropogenic carbon dioxide (CO_2) in the ocean has decreased seawater pH and caused conditions that are increasingly corrosive to marine organisms with calcium carbonate shells. Adverse effects of this "ocean acidification" (OA) have been documented on mollusks (including commercially important shellfish), corals, echinoderms, and microscopic organisms. The corrosiveness of seawater to calcium carbonate is indicated by its calcium carbonate saturation state, where values below one are corrosive. Reductions in pH and calcium carbonate saturation state due to CO_2 emissions can be exacerbated in Puget Sound by nutrient inputs, of both natural and human origin, and local circulation patterns. King County (KC) will begin high-precision monitoring of pH and calcium carbonate saturation state to provide data for the assessment of current baseline conditions and trends in King County waters. With a better understanding of existing variation in pH and calcium carbonate saturation state, the effects of natural and anthropogenic nutrient inputs can be studied in the future.

New high-precision pH sensors will be installed on existing marine monitoring structures, including the Point Williams buoy (located in the Central Basin, south of West Seattle) and one of the moorings in Quartermaster Harbor, a location with known nutrient and low oxygen problems. KC will partner with the University of Washington (UW) and the Washington Ocean Acidification Center (WOAC) to install another pH sensor on their buoy off of Point Wells (located in the Central Basin, near Shoreline) (Figure 1, pg 13). These sensors will take measurements every 15 min, allowing the determination of pH dynamics on both short and long time-scales. The cost of this new equipment will total $60,000. This plan calls for sensors to be ordered by the end of 2014 and installed in spring of 2015. This monitoring effort will be an ongoing component of the KC ambient marine monitoring program.

Water sampling for key OA measurements (dissolved inorganic carbon and total alkalinity) will be added to normal monthly field operations at Point Williams, Quartermaster Harbor, and Point Wells (the latter conducted and funded by WOAC/UW). Analysis of these samples is not possible at the KC Environmental Laboratory (KCEL) due to the necessary addition of mercuric chloride for sample preservation, which could contaminate KCEL equipment used for ultra-low-level mercury analyses. Therefore, sample preservation and analysis will be performed by NOAA's Pacific Marine Environmental Laboratory (PMEL). These highly accurate measurements will provide for *in situ* validation of the pH sensor data as well as a complete picture of seawater inorganic carbon chemistry, in particular enabling the calculation of calcium carbonate saturation, Ω. The cost of ongoing operations will total $40,000 per year. This total includes KCEL field operations ($18,120), PMEL sample analysis ($11,880), and data management, analysis, and reporting ($10,000). Water sampling will begin in early 2015.

All data from sensors will be transmitted in real-time for public distribution via the marine mooring database web portal. These data will also be transmitted in real-time to the Northwest Association of Networked Ocean Observing Systems (NANOOS,

www.nanoos.org). Data from water sampling will also be made available on the web once a database is developed. These data are intended to be utilized by a wide variety of external entities, including UW, WOAC, NOAA, the Washington Department of Ecology (ECY), and other local OA researchers, educators, and managers. An annual summary of the analyzed data will also be produced for the KC website, and data will be included in marine water quality reports.

2.0 BACKGROUND INFORMATION

2.1 The Chemical Basis of Ocean Acidification

The uptake of anthropogenic carbon dioxide (CO_2) by the global ocean has decreased the pH of its surface waters by 0.1 units since the beginning of the industrial era (IPCC, 2013). The net effect of dissolution of CO_2 in seawater is a decrease in the concentration of carbonate ion and an increase in the concentrations of bicarbonate and hydrogen ion (the latter, by definition, lowering pH). This change in water chemistry is known as "ocean acidification" (OA). Organisms such as mollusks, corals, echinoderms, and calcified macro- and microalgae require an adequate supply of calcium and carbonate ions to build their shells and other hard parts. A growing collection of experimental studies document the adverse effects of OA on these taxonomic groups, with species-dependent reductions in abundance, survival, growth, development, and/or calcification (Kroeker et al., 2013).

Two forms of calcium carbonate with different crystalline structures are commonly biomineralized by calcifying organisms: aragonite and calcite, with aragonite being the more soluble. The calcium carbonate saturation state of seawater (Ω) is a measure of how favorable conditions are for calcium carbonate crystal precipitation vs. dissolution (the "corrosiveness" of seawater to calcium carbonate). This parameter is dependent upon the concentrations of calcium (relatively constant in seawater) and carbonate ions and the solubility of the particular form of calcium carbonate in question. When $\Omega > 1$, water is saturated and the precipitation of calcium carbonate is thermodynamically favorable. When $\Omega < 1$, pure calcium carbonate dissolves and its precipitation is thermodynamically unfavorable.

As anthropogenic acidification progresses over the next century, the water column will become undersaturated with aragonite sooner and shallower than with calcite due to the higher solubility of aragonite. For this reason, aragonite saturation (Ω_{arag}) is the primary focus of researchers, although Ω_{calc} will also be reduced (but will remain >1 in surface waters for much longer). Depending on an organism's protective mechanisms and the form of calcium carbonate biomineralized, different organisms will have different physiological responses to undersaturated water. However, $\Omega_{arag} = 1$ is a useful and quantifiable boundary below which the environment is generally corrosive to aragonite-forming organisms such as larval oysters (Miller et al., 2009).

2.2 Interactions with Upwelling, Photosynthesis, Respiration, and Mixing

In a complex estuary such as Puget Sound, OA is occurring over a back-drop of natural processes and other anthropogenic inputs that interact to create highly dynamic chemical conditions. One of the processes controlling pH and Ω_{arag} in Puget Sound is seasonal upwelling. In the northeastern Pacific Ocean, cold and salty waters rise to the surface after

having traveled for several decades at depth. As these waters travel through deep ocean currents, they become enriched with nutrients and CO_2 and depleted in dissolved oxygen (DO) due to the biological respiration of organic carbon. The global ocean circulation pattern and the process of respiration combine to make the aragonite saturation horizon (the depth at which $\Omega_{arag} = 1$) naturally shallowest in the northeastern Pacific Ocean. Dissolution of anthropogenic CO_2 has further decreased the Ω_{arag} of this water and shoaled the saturation horizon by 50–100 m (Feely et al., 2008; IPCC, 2013). As a result, the undersaturated water layer is now shallow enough to be upwelled onto the continental shelf (Feely et al., 2008) and to then travel into Puget Sound through the estuarine circulation process. Water upwelling on the Washington coast today carries the CO_2 signature of emissions released decades prior, when the water was last at the surface. Thus, water increasingly acidified by anthropogenic CO_2 will continue to arrive in the northeastern Pacific Ocean in coming years, even if emissions are halted today.

In addition to coastal upwelling, several other seasonal or localized processes can further contribute to the high temporal and spatial variability of pH and Ω_{arag} in Puget Sound. Local phytoplankton production (natural or stimulated by anthropogenic nutrient inputs) results in drawdown of CO_2 in surface waters. Some of this production ultimately sinks out of the euphotic zone, where bacteria and other heterotrophs remineralize the organic carbon to CO_2 while simultaneously depleting DO. In parts of Puget Sound where water exchange is restricted both vertically (due to seasonal stratification) and horizontally (due to narrow entrances and/or sills), this process can result in bottom waters that are both corrosive and hypoxic, posing a double threat to benthic organisms. In addition, Puget Sound is influenced seasonally by riverine discharges, which decrease Ω_{arag} due to the low alkalinity/buffering capacity of freshwater.

Upwelling, biological, and estuarine circulation processes combine to cause the natural variability in pH and Ω_{arag} in upwelling-zone estuaries like Puget Sound to be more extreme than almost any other marine system (Hofmann et al., 2011). This natural variability makes small long-term changes difficult to detect. However, model simulations show that pH and Ω_{arag} are already reaching levels below the pre-industrial variability envelope in the California Current System, and by ~2040 will reach levels below the current (~2011) variability envelope (SRES A2 emission scenario, Hauri et al., 2013). Feely et al. (2010) report on transects of Puget Sound in 2008 showing widespread aragonite under-saturation in subsurface waters of the Central Basin and Hood Canal, both in February and August. Highly corrosive waters with $\Omega_{arag} < 0.6$ were found as close to the surface as 50 m in Hood Canal. The authors estimate that 24–49% of the pH decrease in Hood Canal (compared to pre-industrial estimates) is due to anthropogenic carbon emissions.

The consequences of high natural variability for the responses of estuarine organisms to OA are not well understood. Because excursions to extreme low pH and Ω_{arag} already occur in their environment, estuarine species may be more adapted to handle increasingly corrosive conditions than pelagic species. However, some species may already be near their physiological tolerance, and more frequent and intense excursions to low pH and aragonite under-saturation may push them past these limits (Hofmann et al., 2011). There is evidence that the latter is true for some commercially important species. Concerns over

recent (2006–2009) failures in larval production spurred efforts to monitor pH and Ω_{arag} at several hatcheries and to investigate the effect of reduced pH and Ω_{arag} on commercially grown shellfish. For example, non-native *Crassostrea gigas* oyster larvae development and production were shown to be negatively correlated with Ω_{arag} in an Oregon hatchery (Barton et al., 2012).

2.3 Puget Sound Nutrient Inputs

In Puget Sound, nutrient availability (principally nitrogen) can act as an important control on phytoplankton production, and thus DO and inorganic carbon dynamics (see 2.2 Interactions with Upwelling, Photosynthesis, Respiration, and Mixing). Coastal upwelling naturally delivers the largest inputs of nitrogen to the system through tidal and estuarine circulation processes, making the Puget Sound in general relatively insensitive to anthropogenic nitrogen inputs. However, nitrogen limitation can occur seasonally and locally, and this condition creates the potential for phytoplankton to respond to anthropogenic inputs with increased productivity.

A report on preliminary results of the South Sound Dissolved Oxygen Model, under development by the Washington Department of Ecology (ECY), showed several areas where anthropogenic nutrients may exacerbate naturally low dissolved oxygen (DO) in Central and South Puget Sound (Ahmed et al., 2014). In these locations, the report presents evidence that anthropogenic nutrient inputs result in decreases in dissolved oxygen (DO) of more than 0.2 mg/L, which violate Washington State's water quality standard for waters where DO naturally falls below or within 0.2 mg/L of state criteria. Modeled violations were shown in several enclosed inlets in South Sound (Totten, Eld, Budd, Carr, and Case) and in East Passage (east of Maury Island) in Central Puget Sound. These DO depletions below natural conditions were modeled to be nearly entirely due to marine point-source nitrogen inputs (which primarily consist of treated wastewater, but also include stormwater, industrial waste, and construction site discharges). Field observations in East Passage agree well with model results and show low DO to be a common seasonal occurrence (unpublished data, King County).

King County (KC) is the largest discharger of treated wastewater into the Central Basin (Mohamedali et al., 2011). KC and the City of Seattle also operate multiple combined sewer overflow outfalls that periodically discharge into the Central Basin, which are additional sources of nitrogen. KC currently conducts routine monitoring of DO to assess the impact of these inputs on DO in county marine waters. For the same reason, monitoring of the inorganic carbon system, which is similarly impacted by nutrient dynamics, is a priority for King County.

2.4 Existing Monitoring in Washington

Increasing concerns over the impacts of OA in Washington State led then-Governor Christine Gregoire to convene the Washington State Ocean Acidification Blue Ribbon Panel and issue an executive order in 2012 that directed the Washington Department of Ecology

to coordinate implementation of the panel's recommendations (Executive Order 12-07). The Washington Ocean Acidification Center (WOAC), led by the College of the Environment at the University of Washington (UW), was established as a result of the Blue Ribbon Panel's recommendations. One of the goals of WOAC is to facilitate increased ocean acidification monitoring in Washington marine waters, and to coordinate these efforts with existing regional and global networks of monitoring infrastructure and activities (Adelsman and Binder, 2012). In 2013, the KC Council requested monitoring of OA parameters with the goal of providing scientifically valid information on the degree of anthropogenic acidification occurring in KC marine waters.

Monitoring of inorganic carbon system parameters on the Washington coast and in Puget Sound is essential for assessment of OA and adaptation to its impacts. Unfortunately, although pH has been historically monitored by various water quality programs, the historical data do not have the precision and accuracy necessary for assessing OA due to the small rate of change (0.002 units/year) that must be measured amid the noise of natural variability. In addition, the difficulties inherent to measuring other parameters in seawater (which has a high buffering capacity) mean that inorganic carbon system parameters other than pH have been infrequently measured until relatively recently.

There is currently a limited network of monitoring platforms and laboratories in Washington that are capable of monitoring OA parameters with the necessary precision and accuracy (Feely et al., 2012). This infrastructure is summarized in Table 1. The National Oceanographic and Atmospheric Administration's Pacific Marine Environmental Laboratory (NOAA-PMEL), WOAC, UW, ECY, and other organizations are currently collaborating to expand OA monitoring. KC will contribute to this effort by adding spatial and temporal coverage of OA parameters in the Central Basin of Puget Sound. This information will help identify the need for any local response on this emerging issue, provide present baseline data, and support KC's goal of leadership in addressing climate change. This document presents the expansion of KC's marine monitoring program to include monitoring of OA parameters.

Table 1. Existing OA monitoring infrastructure on the Washington Coast and in Puget Sound.

Location	Platform	Organization(s)	Matrix	OA Parameters[2]	Measurement method
La Push (WA coast)	*In situ* ORCA[1] profiling buoy	UW and PMEL	Surface seawater and air	CO_2	$MAPCO_2$ sensor
North Hood Canal (Dabob Bay)	*In situ* ORCA[1] profiling buoy	UW and PMEL	Surface seawater and air	CO_2	$MAPCO_2$ sensor
	Shellfish hatchery intake	Taylor Shellfish	Intake seawater	pH	SeaFET sensor
South Hood Canal (Twanoh)	*In situ* ORCA[1] profiling buoy	UW and PMEL	Surface seawater and air	CO_2	$MAPCO_2$ sensor
Lummi Bay (Bellingham)	Shellfish hatchery intake	Pacific Shellfish Institute	Intake seawater	pH	SeaFET sensor
Elliott Bay (Seattle)	Aquarium intake	Seattle Aquarium and PMEL	Intake seawater	CO_2 and pH	$MAPCO_2$ and SeaFET sensors
Throughout Puget Sound and WA coast	Oceanographic cruises	UW and PMEL	Niskin seawater	Various, including CO_2, dissolved inorganic carbon, total alkalinity, and/or pH	Laboratory analysis of discrete water samples

[1] Ocean Remote Chemical Analyzer.
[2] CO_2 is measured as partial pressure (pCO_2) in water or mole fraction (xCO_2) in air.

3.0 GOALS AND OBJECTIVES

The primary goal of this program is to expand KC's existing marine monitoring activities to include long-term monitoring of ocean acidification parameters in order to assess potential OA impacts in KC waters. In order to meet this goal, the following objectives were developed:

1. Determine the diel, seasonal, and interannual variability in surface pH (and Ω_{arag}, to the extent possible) in the Central Basin and in Quartermaster Harbor, a small, restricted-flow embayment sensitive to eutrophication and prone to hypoxia (DeGasperi, 2014). In particular, evaluate the effects of phytoplankton bloom dynamics and seasonal freshwater inputs on the inorganic carbon system in these two areas.
2. Assess data from KC's existing potentiometric pH sensors, which have been deployed *in situ* at some mooring stations since 2008 or 2009; some water column profiles of potentiometric pH are also available from 1980, 1985, 1986, and 2011. Determine whether these data may be used for estimates of at least large-scale variability (ECY is working on similar assessment of their pH dataset).
3. Work with ECY, UW, and PMEL to develop a regional relationship between total alkalinity and salinity. Similar relationships have been developed for the California Current System (Alin et al., 2012). However, the relationship is not well constrained at salinities below 29 psu or in areas of restricted circulation, both of which occur in Puget Sound. Thus, further testing and development is required to assess the utility of this approach at our monitoring locations. If such a relationship can be defined, estimation of all inorganic carbon system parameters, including Ω_{arag}, would be possible from appropriately precise salinity and pH measurements alone.
4. Make OA data readily available to support other efforts by multiple organizations and researchers. This effort will:
    a. Allow researchers to design perturbation studies of local species' tolerances in the context of existing conditions and variability (McElhany and Busch, 2012).
    b. Provide validation and context for OA models. Two major models are currently under development in Puget Sound:
        i. ECY's extension of the Salish Sea dissolved oxygen model to include ocean acidification processes and evaluate the relative contributions of natural (upwelling) vs. anthropogenic (CO_2 emissions, eutrophication) forcing.
        ii. A WOAC/UW OA forecast model to provide short-term forecasts of corrosive conditions for various users (e.g., oyster hatcheries) and allow mitigation for predicted corrosive water conditions.

5. Expand the regional network of OA monitoring assets distributing data for wide-ranging interest groups (scientists, managers, educators, shellfish growers, and the general public) via the Northwest Association of Networked Ocean Observing Systems (NANOOS, www.nanoos.org).

4.0 RATIONALE

To achieve the sampling program objectives, both *in situ* deployment of sensors on existing water quality monitoring moorings and point (discrete) sampling of water will be added to KC's existing program.

The four inorganic carbon system parameters that can be measured directly (either with sensors or laboratory analytical methods) are: pH, total alkalinity (TA), partial pressure of CO_2 (pCO_2), and dissolved inorganic carbon (DIC). From measurements of any two of these four parameters (plus temperature, salinity, and phosphate and silicate concentrations), the other two parameters can be calculated using a well-defined model such as CO2SYS (Lewis et al., 1998). With these inputs, CO2SYS can also calculate the concentrations of carbonate and bicarbonate ions and Ω.

KC will purchase four Satlantic SeaFET pH sensors, which are designed for highly accurate (±0.05 units), precise (±0.007 to ±0.015 units, Hofmann et al., 2011) and stable (±0.005 units/month) measurement of seawater pH on long-term autonomous deployments (see Appendix A for manufacturer specifications). The potentiometric pH sensors that are standard in water quality monitoring programs and in current use at KC are prone to much higher drift on shorter time-scales; these sensors are unable to monitor pH with the precision and accuracy necessary for OA research. Currently, the Satlantic SeaFET pH sensor is the most cost effective, precise, and stable OA sensor available commercially (Martz, 2010). Sensors measuring pCO_2 are also available but are significantly more expensive.

Discrete water sampling for analysis of OA parameters will take place at all SeaFET moorings for the following purposes:

1. *Sensor validation.* Frequent sensor validation is crucial for the success of this program. SeaFETs are designed for deployments of up to a year at a time, but sensor drift still occurs, with a manufacturer published rate of 0.005 pH units/month. In addition, measurement error is not well quantified but is potentially high for SeaFET deployment in dynamic estuarine environments with rapid growth of biofouling organisms. Field-collected water samples can be analyzed with high accuracy and precision, and these data can be used to determine and account for sensor drift. Finally, to satisfy the program objective of providing validated data to multiple users, data quality must be confirmed using community standard analytical methods.
2. *Calculation of all inorganic carbon system parameters.* As detailed above, pH measurements alone cannot fully describe the chemical conditions related to OA that affect organisms. Discrete water samples collected for the purpose of sensor validation can simultaneously be used to obtain snapshots of all OA parameters, including Ω_{arag}. Analysis of TA alongside salinity measurements can also be used to characterize the relationship between TA and salinity, which would ultimately allow

estimation of Ω_{arag} from continuously logged pH and salinity data at high temporal resolution.

The most robust and practical laboratory analytical methods for OA parameters are currently available for DIC and TA (Dickson et al., 2007). Advantages of sampling for these two parameters include their stability over time in storage (unlike samples for pH), and the capacity of PMEL to analyze samples collected by a wide range of partners, including KC. pH will be calculated from sample DIC and TA for the purpose of sensor validation.

5.0 SAMPLING STATIONS

Sampling stations (Figure 1, Table 2) were chosen based primarily on existing monitoring infrastructure, but also to maximize spatial coverage by including both open water Central Basin stations and a station within a poorly flushed embayment with known seasonally low dissolved oxygen. Only stations where complementary and concurrent data are already being collected were chosen. Monitoring will occur at three stations:

1. *Point Wells ORCA Buoy (WOAC/UW and PMEL)* – Chosen as a collaboration with UW and PMEL, this autonomous *in situ* monitoring buoy located south of Point Wells in the Central Basin is equipped with SeaBird instruments collecting full depth profiles of temperature, salinity, chlorophyll fluorescence, and dissolved oxygen. Profiles are collected at variable frequency dependent on solar-powered battery capacity: approximately two per day in winter and every two hours in summer. Discrete water samples are also collected for sensor validation (oxygen and chlorophyll) every 3–5 weeks (Newton and Devol, 2012). This location is ~100 m deep. Two nearby stations (JSUR01-Point Wells and KSBP01-Point Jefferson) are currently sampled by KC twice monthly. At these sites, a SeaBird CTD (Conductivity, Temperature, Depth analyzer and sampling rosette) is used to collect water column profiles of temperature, salinity, chlorophyll fluorescence, dissolved oxygen, photosynthetically active radiation (PAR), and transmissivity. Water samples for nutrients, chlorophyll-α, and total suspended solids are collected at multiple depths. At KSBP01, samples for quantitative taxonomic analysis of phytoplankton and zooplankton are also collected. Periodic cruises by WOAC/UW will also collect a suite of chemical, physical, and biological data near the ORCA buoy.
2. *Point Williams Buoy (KC)* – This autonomous *in situ* monitoring buoy (KC locator: PTWILLBUOY) located just north of Point Williams in the Central Basin is equipped with a YSI sonde at a depth of 1 m. The sonde measures salinity, temperature, chlorophyll fluorescence, dissolved oxygen, turbidity, and potentiometric pH at 15-min intervals. A Satlantic SUNA optical nitrate sensor is also deployed at 1 m and collects data at 15-min intervals. This location is ~175 m deep. Samples for dissolved oxygen, nitrate, and salinity are collected monthly for sensor validation at 1 m. The YSI sonde is also swapped out, cleaned, and calibrated monthly. A mid-basin station (LSNT01) is located ~2 km offshore of the Point Williams buoy and is sampled twice monthly. A SeaBird CTD is used to collect water column profiles of temperature, salinity, chlorophyll fluorescence, dissolved oxygen, PAR, and transmissivity. Water samples for nutrients, chlorophyll-α, and total suspended solids are collected at multiple depths. Samples for quantitative taxonomic analysis of phytoplankton and zooplankton are also collected.
3. *Quartermaster Harbor Yacht Club Mooring (KC)* – This autonomous *in situ* monitoring mooring (KC locator: MSWH01) located at the end of the Quartermaster Harbor Yacht Club floating dock is equipped with a YSI sonde at 1-m depth, which measures salinity, temperature, chlorophyll fluorescence, dissolved oxygen, and potentiometric pH. This location is ~4 m deep. Water samples for nutrients,

chlorophyll-α, and total suspended solids are collected twice monthly at the 1-m and bottom depths. Chlorophyll-α and total suspended solid data from 1-m samples are used for monthly sensor validation. Samples for salinity are also collected monthly at 1 m for sensor validation. Samples for phytoplankton are taken twice monthly at the nearby Dockton Park station (NSAJ02). The YSI sonde is swapped out, cleaned, and calibrated monthly. Installation at a similar mooring at the Dockton Park pier was also considered, but ultimately rejected because: (1) deployment at Dockton Park is riskier because the pier has public access; (2) powering the instrument is easier with Yacht Club shore power; and (3) installation, maintenance, and data interpretation is more difficult at Dockton Park because instrument depth varies with tide state.

Figure 1. Location of ocean acidification monitoring program stations. SeaFET pH sensors will be installed at three existing monitoring stations. Discrete water sampling for dissolved inorganic carbon and total alkalinity will also occur at these stations.

Table 2. Summary of KC OA monitoring program activities, including location of SeaFET deployment and water sampling, and the sources of other data necessary for full characterization of the inorganic carbon system. Highlighting indicates new work items that will be added to existing UW and KC monitoring programs. "Sample" indicates laboratory analysis of a discrete water sample. Sampling takes place on regularly scheduled trips to moorings.

Locator	Station description	Sampling frequency	Depths	pH	DIC & TA	Temperature	Salinity	Phosphorus & silica
ORCA (UW)	Point Wells buoy, Central Basin near Shoreline	Every 3–5 weeks	1 m	SeaFET	Sample[1]	SeaFET	CTD profiler[1]	Sample[1]
PTWILLBUOY (KC)	Point Williams buoy, Central Basin south of West Seattle	1× Monthly	1 m	SeaFET	Sample	SeaFET Handheld thermometer	YSI sonde Sample	Sample
		1× Monthly	25 m	(calculated)	Sample	Handheld thermometer	Sample	Sample
MSWH01 (KC)	Quartermaster Harbor Yacht Club dock mooring	2× monthly	1 m	SeaFET	Sample	SeaFET Handheld thermometer[2]	YSI sonde Sample[2]	Sample
		2× monthly	Bottom	(calculated)	Sample	Handheld thermometer[2]	Sample[2]	Sample

[1] Activities funded and performed by UW

[2] Already occurs 1× monthly, add another sample for 2× monthly.

6.0 SAMPLING DESIGN

6.1 Sensor Deployment

KC will purchase four SeaFETs. Three of these will be deployed for continuous monitoring of pH *in situ* at 1-m depth (Table 2). A fourth will be held in reserve as a spare, to be used to replace one of the three deployed SeaFETs during maintenance or yearly Satlantic calibration on a rotating basis. With the potential for future integration with SeaBird profilers, this SeaFET could eventually also be used to collect pH profiles on the KC CTD package (although profiles would be limited to 50 m with the current SeaFET depth tolerance).

Because biofouling is an issue for coastal euphotic zone deployments (Hofmann et al., 2011), SeaFETs will be installed with copper electrode guards. These guards are not expected to interfere with the flow of seawater around the electrodes, although flow cells are available for purchase if necessary.

6.1.1 WOAC/UW – Point Wells

One SeaFET will be installed by UW on their Point Wells ORCA buoy. SeaFET maintenance and collection of validation samples at this location will be performed by UW. The SeaFET will be powered by the buoy's battery bank and data will be logged and transmitted by the ORCA data logger/telemetry system. UW will check and clean the SeaFET sensors as necessary on regularly scheduled trips to the buoy. The SeaFET sampling frequency will be every 15 min, or as determined based on buoy battery capacity. If deep deployment modifications can be made to the SeaFET (currently, the depth limit is 50 m), UW plans to eventually install the SeaFET on the profiler itself, at which time sampling frequency will be set to occur continuously (a maximum of 0.25 Hz is possible for the SeaFET) during profile events.

6.1.2 KC – Point Williams and Quartermaster Harbor

Two SeaFETs will be installed on existing KC moorings (PTWILLBUOY–Point Williams buoy and MSWH01–Quartermaster Harbor Yacht Club) by KC. The SeaFETs on the Point Williams buoy will be powered by the buoy's battery bank and the Yacht Club SeaFET will use shore power. The SeaFETs will be programmed to sample simultaneously with the YSI mooring sondes, every 15 min. KC will check and clean the KC SeaFET sensors in the field as necessary on regularly scheduled trips to swap out YSI sondes.

The current YSI EcoNet data logger/telemetry systems on all KC mooring stations (including NSAJ02–Quartermaster Harbor Dockton Park and SEAQYSI–Seattle Aquarium) will be replaced with Xylem Storm 3 data logger/telemetry systems (see Appendix B for specifications), which will log and transmit data from the SeaFETs and other sensors in real-time to the moorings database. This update is necessary because the SeaFET uses the RS-232 communication mode; this mode is not compatible with the current EcoNet system,

which uses SDI-12. In addition, YSI is no longer offering support for the old EcoNet system. Installation at stations not currently chosen for SeaFET installation is necessary in order to simplify mooring database design and management, as well as to allow the flexibility to move SeaFETs to other stations at a later date.

6.2 Discrete Water Sampling

6.2.1 WOAC/UW – Point Wells

WOAC/UW will add sample collection for DIC, TA, and nutrients to scheduled trips to their Point Wells buoy (every 3–5 weeks). Samples will be taken according to PMEL's sampling procedure (Alin, 2010) and Dickson et al. (2007). In brief, water will be collected with a 5-L Niskin bottle as close to the SeaFET sensor as possible to minimize error due to spatial heterogeneity. A 500-ml sample bottle will be flushed to overflowing with two full exchanges of water from the Niskin before being filled completely, leaving an approximate 1% headspace. (From each 500-ml sample, both DIC and TA will be analyzed.) Duplicate samples from separate water grabs for estimation of sampling variability will also be taken approximately once every 3 months or more frequently if possible. Samples will be immediately poisoned with mercuric chloride, which is necessary for sample stability in systems with high biological activity. The necessary measurements of salinity (from the buoy CTD profiler) and samples for orthophosphate phosphorus and silica analysis (from the same Niskin grab) will also be taken.

6.2.2 KC – Point Williams and Quartermaster Harbor

KC will add sample collection for DIC and TA to scheduled trips to KC mooring stations. PMEL will advise KC on a method for DIC/TA sampling that does not require immediate poisoning with mercuric chloride. Preservation of samples with mercuric chloride, which could contaminate KCEL equipment used to collect and analyze samples for ultra-low-level mercury analyses, is not viable for KCEL. Therefore, sample preservation and analysis will be performed by NOAA's Pacific Marine Environmental Laboratory (PMEL).

KC will follow sample collection methods based on Bockmon and Dickson (2014). Water will be collected with a hand-held 5-L Scott bottle as close to the SeaFET sensor as possible. Seawater will be pumped from the Scott bottle by a peristaltic pump (see Appendix C for specifications) through an in-line 0.45 µm filter (flow rate 0.8 L min^{-1}, depending on particle load), and into a 500-ml sample bottle provided by PMEL. Bottles will be flushed with at least two full exchanges of water; about 2 L total is necessary for flushing the bottle and collecting a 500 ml sample. This process removes almost all biological activity and should allow samples (kept in the dark and on ice) to be transported via courier to PMEL the same day for mercuric chloride poisoning by PMEL staff. Although the standard protocol for DIC/TA sampling in coastal waters requires mercuric chloride poisoning (Dickson et al., 2007), R. Woosley reports analyzing open ocean (low biological activity) samples 6–12 hours after collection without poisoning (pers. comm., 2014), and Leinweber and Gruber (2013) waited as long as 36 hours to poison samples from the Coastal California Current. Once developed, KC's protocol will need to be verified with at least one

set of replicate samples taken simultaneously with WOAC/UW sampling at the Point Wells SeaFET, which may necessitate a separate cruise or an excursion from the normal KC cruise route/schedule.

In addition to the above outlined minimum sampling required for sensor validation, additional DIC/TA sampling will be conducted as the budget allows (see 9.0 Budget). Priority will be to increase depth coverage by sampling from the bottom at the Quartermaster Harbor Yacht club station and from 25 m at Point Williams buoy. Duplicate water grabs at both depths will be sampled approximately every three months or more frequently if possible, alternating between Point Williams and Quartermaster Harbor.

Table 2 outlines what additional sampling (nutrients and salinity) will be added for full characterization of the inorganic carbon system. Nutrient and salinity samples will be taken from the same water grab as the DIC/TA samples. Note: salinity measurements made by YSI sondes are not currently accurate enough for the purposes of pH calculation. See 7.1 Sensor pH Calculation for details on how this problem will be addressed.

6.2.3 Sample Analysis

Samples taken by UW and KC for DIC and TA will be delivered to either PMEL or UW's Friday Harbor Laboratory for analysis. PMEL is a global leader in OA research, and currently analyzes samples for a wide variety of partners using rigorous analytical methods that are the community accepted standard (Dickson et al., 2007). The new (2011) Ocean Acidification Environmental Laboratory at Friday Harbor is also ramping up capacity to run DIC and TA samples for external partners using the same standard protocols. KC and UW will each determine where to send samples for analysis based on (1) logistics, (2) cost, and (3) the laboratory's capacity. Due to its proximity to KCEL, KC samples will be analyzed at PMEL. Samples will be analyzed coulometrically for DIC and using potentiometric titration for TA. The precision and accuracy of PMEL's analyses are on the order of ±1 and ±2 μmol kg^{-1} for DIC and TA, respectively. Certified reference materials, i.e. seawater with sufficiently well-established inorganic carbon properties (provided by A. Dickson at Scripps Institution of Oceanography) are analyzed at least once per analysis day by both labs for DIC/TA measurement quality assessment.

7.0 DATA MANAGEMENT

The agency maintaining the instruments or analyzing the samples (KC, UW, or PMEL) will be responsible for the validation/verification, quality control, and reporting of the resulting data.

7.1 Sensor pH Calculation

For every measurement logged, the SeaFET calculates pH values for the internal and external reference electrodes (see Appendix A for details) using factory calibration coefficients, temperature from the on-board thermistor, and a salinity constant (default 30 psu). The external reference electrode gives the most stable pH measurement over time; the internal reference electrode measurements will be used primarily to detect sensor drift and for other diagnostics/troubleshooting. Because the external reference electrode measures the electrical potential of the medium as the sum of the chloride and hydrogen/hydroxide ion signals, the pH (hydrogen/hydroxide ion signal alone) calculated by the SeaFET is sensitive to salinity (~0.0013 pH units salinity $^{-1}$). Measurement of salinity to an accuracy of 0.1 psu is required for most applications (Martz et al., 2010). Because salinity is variable in Puget Sound (e.g., ranging from ~23 to 31 psu in Quartermaster Harbor), pH will be recalculated from raw SeaFET voltages and ancillary salinity measurements (ancillary temperature measurements are also available for recalculating pH in case of SeaFET thermistor failure).

As detailed above (6.0 Sampling Design), salinity will be measured at Point Wells by the UW SeaBird profiler (accuracy ± 0.005 psu) and at KC stations by YSI sondes and from discrete samples. KC's YSI sonde salinity measurements have been problematic because they are prone to individual sensor bias and drift. Salinity measurements from *in situ* discrete samples (accuracy ± 0.003 psu) and pre- and post-deployment sensor calibration checks will be used to correct salinity data from YSI sondes on an approximately quarterly basis by the Marine and Sediment Assessment Group. These corrected salinity measurements will be used to recalculate SeaFET pH data in batches for internal use. However, because this manual salinity correction will be performed quarterly, SeaFET pH data in the KC marine moorings database, which is published on the web in real-time (see 7.2 KC Data Reporting), will be automatically recalculated using the real-time (uncorrected) YSI salinity data-stream and will be labeled as provisional. Efforts will be made over the first year of SeaFET deployment to improve YSI salinity measurements to an acceptable level of accuracy, or to enable archiving of past SeaFET pH data, recalculated with manually corrected salinity, in the public marine moorings database.

7.2 KC Data Reporting

KC will manage and distribute data from the SeaFETs and YSI sondes via new Storm data logger/telemetry systems. Data will be transmitted to an FTP server and automatically loaded into KC's marine moorings database every 15 minutes, and subsequently harvested

by NANOOS. All KC mooring data (as well as CTD cast data) are available for viewing and downloading in real-time at http://green.kingcounty.gov/marine. Data are viewable and downloadable for the most recent 30-day period at www.nanoos.org. KC will make data from water and plankton sampling activities available to UW and others upon request (ultimately, these data will also be made publicly available from a new database that will begin development in spring 2015).

In the KC marine moorings database, pH will be automatically recalculated using ancillary salinity data. Data in this database will be automatically flagged with appropriate qualifiers when salinity sensors fail calibration checks. Records will also be kept of all cleaning and maintenance activities and observations of environmental factors that may impact the data. Data will be manually flagged with appropriate qualifiers (on a quarterly basis by the Marine and Sediment Assessment Group) when these observations or discrete sample values indicate salinity sensor error (see the KC Marine Moorings SAP, *in prep*., for more details).

KC Marine and Sediment Assessment staff will analyze data from this program to assess temporal and spatial trends on an annual basis. Analyses will be included in marine monitoring reports (likely on a 5 year cycle). Shorter written/graphical summaries will be published on the KC website each year. The data may also be summarized in the Puget Sound Ecosystem Monitoring Program Marine Waters Work Group annual overview report.

7.3 UW Data Reporting

UW will manage and distribute data from the SeaFET in a similar manner to ORCA profiler data via the existing data logger/telemetry system. All ORCA data are automatically downloaded to and archived on the local ORCA server, where data are subsequently harvested by NANOOS. Preliminary (not calibrated or verified) data are viewable and downloadable for the most recent 30-day period via www.nanoos.org and www.orca.ocean.washington.edu in real-time. All data are available for download as MATLAB objects via www.orca.ocean.washington.edu with an account (there are no restrictions on obtaining an account); these data are calibrated and verified periodically. UW will also share with KC all field logs, discrete sample logs and results, and SeaFET maintenance, deployment, and calibration records. Relevant physical, chemical, and biological data from other periodic cruises near the buoy will also be shared with KC as available.

7.4 PMEL Data Reporting

PMEL will provide a full characterization of inorganic carbon chemistry of discrete samples collected by KC. This will include analysis of DIC/TA and calculation of pH, pCO_2, Ω_{arag}, Ω_{calc}, and concentrations of bicarbonate ion, carbonate ion, and pCO_2 using CO2SYS. PMEL will provide quality controlled and verified data from batches of DIC/TA samples as available (approximately every 3–4 months).

8.0 SCHEDULE

8.1 Initial Tasks

Date	Task	Primary personnel
February 2014 – April 2015	Preparation of draft Sampling and Analysis Plan (SAP) for sensor deployment and water sampling; equipment procurement	Amelia Kolb
December 31st, 2014	Deadline for equipment orders	Amelia Kolb
December 2014 – March 2015	Integration of mooring instruments with new data loggers, modification of KC mooring database system to automate data harvesting from new data loggers	KCEL, KCIT
February – April 2015	Development of sensor/discrete sample data and sensor validation tracking database	Amelia Kolb and/or KCIT
March – April 2015	First trials of water sampling method	KCEL
April – June 2015	SeaFET deployment at Point Williams and Quartermaster Harbor	KCEL
	SeaFET deployment at Point Wells, integration with data logger	UW
	Expand KC mooring database to include SeaFET pH data	KCIT
April 2015	Simultaneous sampling trip for validation of DIC/TA sample filtration method at Point Wells	KCEL, UW
May 2015	Incorporation of reviewer's changes and completion of final SAP	Amelia Kolb

8.2 Ongoing Operations

Date	Task	Primary personnel
2× monthly	Sample for DIC/TA, nutrients, and salinity at Quartermaster Harbor Yacht Club	KCEL
Monthly or every 3–5 weeks for UW (less in winter)	Check and clean SeaFETs at all stations; sample for DIC/TA, nutrients, and salinity at Point Wells and Point Williams	KCEL, UW
Every 3 months	Take duplicate samples for DIC/TA; data review and quality control	KCEL, UW, Amelia Kolb
Yearly	SeaFET maintenance and calibration at Satlantic	KCEL, UW
	Data analysis and web summary; update SAP as necessary	Amelia Kolb

9.0 BUDGET

9.1 Equipment Purchase

Item	Cost	Quantity	Total
SeaFET sensors	$8,585	4	$34,340
SeaFET biofouling guard	$676	4	$2,703
SeaFET USB programming cable	$327	4	$1,309
SeaFET RS-232 com cable, 5-m	$663	8	$2,652
SeaFET pelican shipping case	$336	4	$1,343
SeaFET shipping and tax	$4,680	-	$4680
Xylem Storm 3 datalogger with integrated modem	$1,890	4	$7,560
Datalogger cell service plan – per year	$495	4	$1,980
Storm Central data hosting – per year	$495	4	$1,980
Storm shipping and tax	$1,105	–	$1,105
Other equipment related to Storm or SeaFET	$348	–	$348
Total:			$60,000

9.2 Ongoing Operations

Item	Cost	Quantity	Total
KCEL personnel time (including courier service for sample delivery)	$18,120	–	$18,120
Marine and Sediment Assessment personnel time	$10,000	–	$10,000
DIC/TA sample analysis at PMEL[2]	$135	88	$11,880
Total:			$40,000

[2] Number of samples calculated as: two depths twice monthly + two depths once monthly (72 samples) + two duplicate samples taken quarterly (8 samples) + 8 method verification samples = 88 samples/year

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Appendix A: Seafet specifications

The Satlantic SeaFET pH sensor was developed by K. Johnson (Monterey Bay Aquarium Research Institute) and T. Martz (Scripps Institution of Oceanography) (Martz et al., 2010), and was made commercially available by Satlantic. The unit is capable of on-board data storage, has an internal battery pack, and is supplied with SeaFETCom software for configuration, data display, and data reprocessing. The primary sensor element is an ion-sensitive field effect transistor (ISFET). The SeaFET includes two ISFETs, one combined with an 'external' reference electrode (bathed in surrounding seawater) and one combined with an 'internal' reference electrode (bathed in saturated KCl solution/gel). For details of operation, see the SeaFET manual available at:

http://satlantic.com/seafet

Manufacturer Specifications

Measurement Range:	6.5 to 9.0 pH
Initial Accuracy:	0.05 pH units
Precision:	< 0.001 pH units (when averaging is applied)
Resolution:	0.0001 pH units
Stability:	0.005 pH units/month
Disk Size:	2 GB (minimum)
Data Storage:	>15 million samples, approximately 85% of storage available
Sample Rate:	~ 0.25 Hz
Internal Batteries:	10.5 V 19.8 Ah (seven alkaline D-Cells in series)
Power:	6 –18 VDC external supply 50 mA (operating) 3.2 mA (standby)
Communication:	RS-232 @ 9.6 – 115.2 kbps, USB @ 12 Mbit/s
Weight:	4.1 kg
Maximum Depth:	50 m
Salinity Range:	20 to 40 psu
Operating Temperature:	0 to 50 ºC
Storage Temperature:	2 to 55 ºC

Appendix B: Storm 3 specifications

The Xylem Strom 3 data logger transmits data via GOES satellite or CDMA cellular modem to a KC FTP server. For details, see the manual available at:

http://www.waterlog.com/productsdetail.php?Storm-3-Data-Logger-57.

Manufacturer Specifications

Analog Inputs	Channels:	4 single ended
	Resolution:	20-bit resolution
	Accuracy:	±0.025% FS
	Range:	0.001 to 4.998 V
+5.00 Volt Excitation	Type:	Switched, ratio metric with A/D
	Accuracy:	±5.0 mV overload and temperature range
	Current:	10 mA max load
Switched+12.0 Volt Excitation	Type:	Switched, unregulated based on battery voltage
	Current:	250 mA max load, protected by resettable fuse
Constant+12.0 Volt Excitation	Type:	Switched, unregulated based on battery voltage
	Current:	250 mA max load, protected by resettable fuse
Digital I/O	Channels:	4 general purpose Digital I/O's
	Modes:	Digital input Counter input Conditional output
	Input Levels:	0.0 to 5.0 V High= 3.5 V or higher Low= 0.08 V or less
	Output Levels:	High = 3.5 V min sourcing 5 mA Low = 0.4 V max sinking 5 mA
	Counter Frequency:	100 Hz max
	Counter Debounce:	Programmable up to 1 sec

SDI-12	Mode:	SDI-12 master mode V1.3 compliant
	Connector:	Three position removable screw terminal
Size:		4.37 in. L x 2.45 in. W x 7.375 in. H
Weight:		2 lbs (1 kg)
Power Requirements	Voltage Input:	10.0 to 16.0 V, reverse voltage protected
	Current:	Standby: 3.5 mA max Active: 50.0 mA typical
Connection:		Two position screw terminal
Data Storage Capacity:		300 mB
RTC Accuracy:		< .05 sec/day
RS-232	Type:	Single RS-232 configured as a DTE device
	Connector:	9 pin D connector, male
	Baud Rate:	Programmable
RS-485	Type:	Single RS-485 port
	Connector:	4 position screw terminal
USB	Type:	2 host USB-A connectors USB-A 1 device mini-B conncector
	Version:	USB version 2.0

Appendix C: Pump specifications

A peristaltic pump will be chosen that can accept Tygon tubing with 3/16" I.D. and 1/16" wall thickness (R-3603 14-169-1G) and pump water at a flow rate of at least 0.8 L min^{-1}. The pump should be similar to the Manostat Simon Varistaltic Pump model 72-310-000, which has been discontinued. A pump such as the Cole-Palmer L/S Masterflex Pump System (WU-77910-20) appears to be appropriate:

http://www.coleparmer.com/Product/L_S_Economy_Pump_System_with_Easy_Load_II_Pump_Head_115_VAC/WU-77910-20

ECY is using a Geofilter 350 RPMs peristaltic pump, available from:

http://www.geotechenv.com/peristaltic_geopump.html