A Department of Ecology Report

DEPARTMENT OF
ECOLOGY
State of Washington

Puget Sound Total Alkalinity and Dissolved Inorganic Carbon Pilot Project: Feasibility Report

Abstract

The Washington State Department of Ecology (Ecology) conducted a pilot study to:

- Test whether total alkalinity (TA) and dissolved inorganic carbon (DIC) water sampling can be incorporated into the existing long-term Marine Waters Monitoring Program.
- Provide high-quality pH data to better understand the dynamic conditions that affect the accuracy of pH measurements in Puget Sound using potentiometric electrodes for *in situ* pH sensor measurements. To accomplish this, Ecology measured TA and DIC of discrete near-surface samples to quantify pH with greater accuracy. This included calculating the saturation state of aragonite.
- Provide data that others could use to determine the range of TA, DIC, and pH at selected sites and also to assess seasonal variability in the upper water column of Puget Sound.

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Background

Ocean Acidification in the Northeastern Pacific is an important topic of recent concern, and multiple research efforts are underway to address these concerns along the coast of Washington. The Salish Sea is greatly influenced by the Pacific Ocean and upwelling processes along the coast, particularly at depth. In contrast, freshwater inputs from land influence near-surface waters in the Salish Sea. Human impacts also affect ionic composition and the unique buffering capacity of these diverse freshwater inputs that range from silty, glacier-fed systems to rain-fed rivers rich in humic substances. In order to understand the diverse ranges of the carbon system in the Salish Sea, Ecology created a small pilot study to characterize this system specifically near the freshwater-influenced surface.

Carbon dioxide (CO_2) is part of the respiration equation and naturally occurs in seawater and the atmosphere. When CO_2 is absorbed by seawater it forms a weak acid that reduces the pH of seawater, changes the carbonate ion concentration and saturation states of biologically important calcium carbonate minerals. Alkalinity plays an important part in how well seawater can buffer increases in CO_2. Typically marine waters have a great buffering capacity for CO_2. But with increased inputs of CO_2 and freshwater the overall buffering capacity of a marine system can be exceeded. The process of chemical reactions that shift the carbonate system to a lower pH are termed "ocean acidification" or "OA" for short. Varying ionic composition of coastal water, particularly at lower salinities, makes pH measurements and estimating aragonite solubility–a form of calcium crystals–challenging.

Calcium carbonate minerals, particularly aragonite, are building blocks for skeletons and shells of many juvenile marine organisms. In the upper ocean, seawater is typically supersaturated in calcium carbonate minerals. This means there are abundant building blocks for calcifying organisms to build their skeletons and shells. However, with continued ocean acidification, or reduced capacity for seawater to buffer the dissolution of CO_2 into a weak acid, marine water becomes under-saturated with calcium carbonate minerals of a specific form (aragonite). This is likely to affect the ability of some organisms to produce and maintain their shells.

Using a potentiometric electrode for measuring pH has been a standard operating procedure for water quality monitoring programs for decades. However, this approach is known to yield potentially large and variable biases from true pH values, because most electrodes do not respond well to changes in buffering capacities in water. The stated accuracy of many potentiometric pH sensors is therefore on the order of 0.1 – 0.2 pH units. Under typical field use when taking measurements within salinity gradients, pH measurements can easily become biased. This is especially problematic when there are significant differences between the measured ionic strength and composition of brackish water compared to the internal reference solution of the pH electrode. Thus, in estuarine systems with strong salinity gradients and multiple sources of freshwater with varying composition, it is challenging to ascertain the magnitude, direction, and variability of the bias in pH measurements using only potentiometric pH sensor measurements. Additionally, organic acids within estuarine systems such as humic substances can affect variables of the carbonate system, and can exacerbate these uncertainties.

The marine inorganic carbon system has four measurable variables: TA, DIC, the partial pressure of carbon dioxide (pCO_2), and pH. From any pair of measurements, all other inorganic carbon parameters can be calculated in equilibrium. This includes saturation states for the aragonite and calcite forms of calcium carbonate and concentrations of carbonate and bicarbonate ions. These calculations can be done by a program such as CO2SYS (Lewis et al., 1998). Improved pH estimates can be generated by using the selected pair of measured carbon parameters, temperature, salinity, nutrient concentrations (phosphate and silicate specifically), and the appropriate dissociation constants for the salinity range of the ecosystem (Dickson et al., 2007). Most critical to this calculation is the salinity range, because it has the largest impact on the carbonate system.

For decades, Ecology's ongoing long-term Marine Waters Monitoring Program (marine flight program) has been providing monthly full-depth profiles of estuarine state variables: temperature, salinity, pressure, and conventional electrode-based pH among other variables. Water samples for TA and DIC from this study will provide an independent and refined assessment of the magnitude, direction, and variability of pH biases in near-surface waters. In this feasibility study, we explore if adding measurements of TA and DIC in the near-surface waters allows us to effectively leverage resources to address uncertainties in the historical pH data with a variable salinity range. This would also help to delineate spatial and temporal patterns of pH in surface waters of Puget Sound with greater accuracy.

Project Description

Ecology collected 148 samples from 6 stations in Central Sound, Whidbey Basin, Hood Canal, and Totten Inlet from June 2014 to May 2015. Triplicate TA and DIC samples were taken at each station as well as a one nutrient sample. Due to space limitations of our current conductivity-temperature-depth instrument (CTD) package configuration deployed via float plane, we used methods from Bockmon and Dickson (2014). This seawater collection method allows an alternative water collection method using a peristaltic pump and extended holding time of samples suited for external batch analysis (Bockmon and Dickson, 2014). The Pacific Marine Environmental Laboratory (PMEL) Carbon Group analyzed the samples using standard operating procedures used by marine carbon scientists (Dickson et al., 2007).

Ecology's Marine Monitoring Unit will use TA and DIC data to gain a better understanding of the spatial and temporal variability of pH and other variables of the carbonate system while supporting efforts to develop specific relationships between alkalinity and salinity within Puget Sound regions. However, for this report we only assess the feasibility of collecting these samples from a floatplane, as part of the established Marine Waters Monitoring Program.

Study Area

Six stations were chosen from the 2014 long-term Marine Waters Monitoring station sampling list. Both data and logistics needs were considered when selecting stations. Two stations were located in Whidbey Basin: Saratoga Passage (SAR003) and Possession Sound (PSS019). These stations were intended to provide information on the differences in TA and DIC between the rain-fed Skagit River (SAR003) and the snowmelt-fed Snohomish River (PSS019). An Admiralty Inlet station (ADM001) provided data on water entering from north of Admiralty Reach. The northern-most Hood Canal station was chosen (HCB010) because of its close proximity to commercial oyster beds. Oakland Bay (OAK004) and Totten Inlet (TOT002) in South Sound were also chosen because of their proximity to highly productive, commercially harvested shellfish beds. For a more detailed description of the study area and complete station list see Bos et al. (2014).

Table 1. Description of Ecology's Long-term Ecology Marine Waters Monitoring stations sampled for this study.

Station	Short Description	Latitude	Longitude	Basin	WRIA	WA Level-8 HUC Boundaries
ADM001	Admiralty Inlet – Bush Pt.	48° 01.789' N	122° 37.076' W	Admiralty Inlet	06	17110019
SAR003	Saratoga Passage – East Point	48° 06.4557' N	122° 29.4925' W	Whidbey	06	17110019
PSS019	Possession Sound – Gedney Island	48° 00.6556' N	122° 18.0750' W	Whidbey	07	17110019
HCB010	Hood Canal – Send Creek, Bangor	47° 40.2000' N	122° 49.2000' W	Hood Canal	15	17110018
OAK004	Oakland Bay – Near Eagle Point	47° 12.806' N	123° 4.659' W	South	14	17110019
TOT002	Inner Totten Inlet	47° 07.2890' N	123° 01.2754' W	South	13	17110019

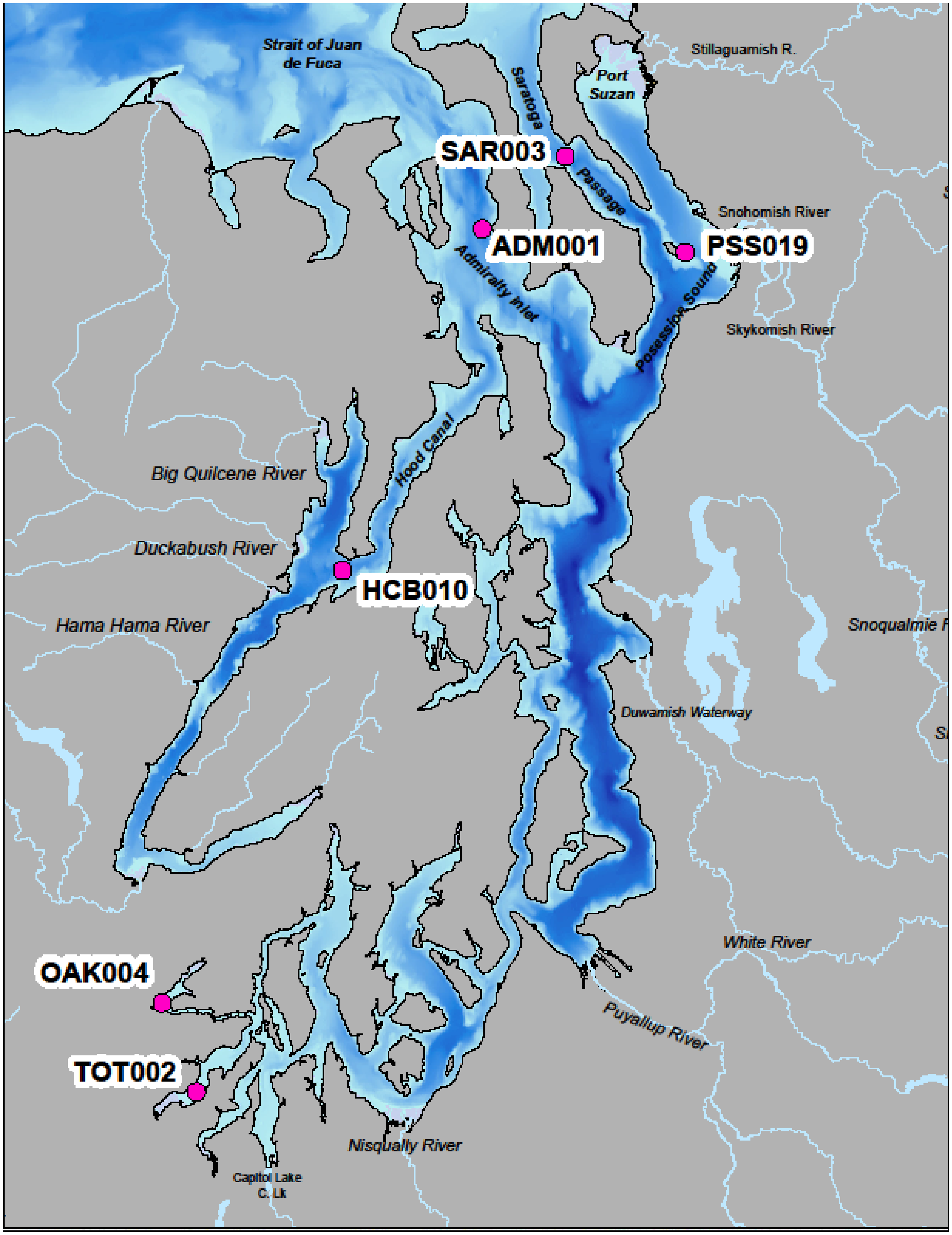

Figure 1. Ecology’s TA and DIC pilot sampling locations.

Discussion

The marine flight sampling platform is unique since it uses a DeHavilland Beaver floatplane to sample, rather than a traditional boat platform. This also presents unique challenges. Lack of space was the most challenging part of this pilot project. The instrument package is designed to fit through an 18-inch diameter hatch at the bottom of the plane cabin. To accommodate such a narrow and short space, we use four 1.7L Niskin bottles–a critical constraint on the volume of water needed to collect a 500 mL sample, which also requires rinsing and overfilling. Reducing sampling volume for DIC and TA measurements, therefore, is a critical consideration for successful implementation into this program.

To overcome volume constraints set by the CTD package configuration, we chose a peristaltic pump. Inspired by and in accordance with Bockmon and Dickson (2014), we collected water using a peristaltic pump and paired it with a Pall Life Sciences 47 mm Polycarbonate In-Line Filter Holder (1119). This screw-type filter holder allowed us to use replaceable 0.45 µm Durapore Membrane Filters. The pump and intake tube did limit how deep we could pull samples. The plane's cabin floor is ~2 m above the water. We deployed ~7 m of silicone tubing weighted with custom lead weights aiming for a water intake at 5 m depth.

The plane has very limited space for gear and limited maneuverability for sampling while on station. These conditions, combined with the hazardous nature of mercuric chloride required to fix the sample, motivated us to follow an alternative method for sample preservation by Leinweber and Gruber (2013). This method showed no significant problem with delay of adding mercuric chloride at the end of the day in a controlled lab environment as long as the samples were filtered through 0.2 micrometer filters.

Another challenge for data collection and interpretation was the spatial and temporal mismatch of TA/DIC sample collection and CTD measurements collected in conditions when the plane drifted at the surface or when collecting shallow stations where the CTD deployment rate was much faster than the time to fill three replicate samples by pump. Routine deployment of the CTD was much faster than the significant time needed for setup and operation of TA/DIC sampling equipment.

At deeper stations, ADM001, SAR003, and PSS019, the CTD cast took about the same amount of time as setting up and collecting triplicate TA/DIC samples. On windy days, the plane drifted up to 0.5 mile before sampling was completed. Drifting caused the intake line to be, at best, at 5 m depth. Samples taken here also contained water taken over a much larger area. In those situations we could not be certain that pH sensor data from the CTD and TA/DIC sample results were collected from the same water mass in space and time. In addition, drifting also meant that the 3 replicate TA/DIC samples came from slightly different locations along the drift track. We concluded that pumping water samples, therefore, will not be suited to complement continuous CTD profile data in the future, due to unknown, potentially large spatial and temporal mismatch of the different data collection types.

With the sampling methods and equipment in place, we were left with how to work with the small footprint of the floatplane. We tried several different setups but none were found to be sustainable for long-term marine monitoring, due to large and considerable effects of field conditions (weather, sea state) on sample collection equipment setup. Again, we concluded that pumping water to collect samples will not be suited for sampling by plane, due to space constraints.

The pilot project, however, allowed us to realistically test and develop chain of custody sample tracking, supply procurement, sample delivery, and invoicing. Setting up all those details was one of the great outcomes and advantages of this pilot project, paving the way for developing realistic cost and resource estimates for future DIC and TA sampling.

Figure 2. Three versions of TA/DIC sampling setups in the floatplane.

Figure 3. Bottle labeling and sample storage.

Conclusions and Recommendations

The primary goal of this pilot project was to test the feasibility of adding TA and DIC sampling to our routine long-term monitoring work via floatplane using a sample pumping method. As long as the sample volume remains at 500 mL for TA and DIC, we conclude that it is not feasible to add this sampling to our routine long-term monitoring using the pump method.

If standard lab procedures require less sample volume (200-250 mL) we would be able to collect the water from our existing CTD using the Niskin bottles and thus eliminate the need for pumping water. This would also create the possibility for sampling different depths, and reduce spatial and temporal uncertainty with the pumped sample method effects on DIC and alkalinity.

This study pushed the limits of an already maximized sampling program. Significantly more staff time would be required to carry this field work forward and implement this additional monitoring effort as part of the long-term Marine Waters Monitoring Program. Sample processing, data analysis, routine quality control, data management, reporting, and communication would require a full-time staff position. This additional work cannot be absorbed by the current staff on a sustainable basis.

The pilot study produced interesting data and information that support initial pH water quality model explorations. Future funding for measurements that refine Puget Sound carbonate system information would allow us to leverage the existing and continuing pH data set. Environmental managers need a robust dataset of ocean acidification parameters in order to detect trends and make informed decisions about ocean acidification in Puget Sound.

Table 2. Summarizing challenges and recommendations

Challenge	Recommendations
A floatplane is too small as a sampling platform.	Secure funding for TA/DIC stations to be sampled by boat, providing more space.
Pumping samples creates spatial and temporal inconsistencies between TA/DIC water samples and CTD samples.	Refine lab methods to use smaller 250ml water volume, enabling water collection from the CTD Niskins.
Sampling is limited to approximately 5m collection depth.	Work with lab to accept a 250ml water volume so we can collect water from the CTD Niskins at any depth.
Cost of sampling limits the number of stations.	Secure funding to expand the number of sampling stations.
Paper field forms and sample tracking outside of our long-term database making organization difficult.	Secure funding to integrate workflow into existing data management and workflow.
We lack timely data return and invoicing.	Build on the system Ecology and PMEL labs and purchasing departments established and set clear deliverable dates.
We lack staff resources for data analysis, quality control, and reporting.	Secure funding for more staff time.

The collected data are very valuable and provide a glimpse of the seasonal variation in aragonite saturation state for the first time in Puget Sound (Figure 4). The results show that the saturation state is below one (dissolving conditions) throughout the winter months, at least for the year 2014. Without a longer term data set, it is unknown if this is typical for Puget Sound. Clearly there are seasonal dynamics that we need to understand better. We also need more data to determine the factors responsible for these patterns, since a limited one-year study does not identify what factors influence these patterns. This kind of monitoring is needed for understanding the carbon system in Puget Sound.

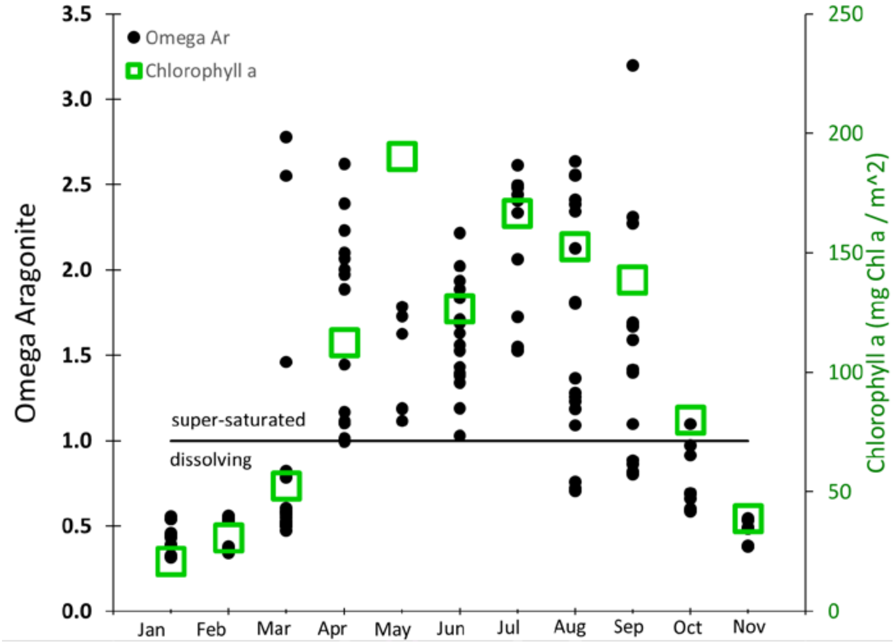

Figure 4. Provisional aragonite saturation state and monthly average chlorophyll a versus month.

If funding were available, we have four recommendations for incorporating this important work into our routine long-term marine monitoring.

1. Sample a smaller volume of water allowing the sample to be taken directly from Niskin bottles on a CTD.
2. Dedicate funding to support TA/DIC sampling at our routine water sampling depths of 0, 10, and 30 meters, and throughout our station network.
3. Dedicate a staff person to this monitoring project that includes logistical planning, sampling, and data analysis. With proper planning and support, we could collect this data at our long term-marine monitoring stations and gain insight into the Puget Sound’s carbon system.
4. Investigate the feasibility of measuring an alternative combination of variables for the CO2 system either to substitute for measurement of TA and DIC, or to add the measurement of pCO2. We suggest exploring the accuracy and cost of measurement of DIC and pCO2 compared with the measuring TA and DIC. Measurements of pCO_2 could be collected using a sensor allowing us to determine pCO2 gradients within the water column.

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Glossary, Acronyms, and Abbreviations

Glossary

Alkalinity: Measures the ability of a solution to neutralize acids to the equivalence point of carbonate or bicarbonate. The alkalinity is equal to the stoichiometric sum of the bases in solution.

Ambient: Background or away from point sources of contamination.

Aragonite Saturation State: The saturation state of seawater with respect to aragonite can be defined as the product of the concentrations of dissolved calcium and carbonate ions in seawater divided by their product at equilibrium: ([Ca2+] × [CO3. 2-]) / [CaCO3] = Ω (Omega). Omega is commonly used to track ocean acidification because it is a measure of carbonate ion concentration. Aragonite is one of the more soluble forms of calcium carbonate and is widely used by marine calcifiers (organisms with calcium carbonate structures).

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

CTD: A set of sensors (conductivity-temperature-depth) combined into an instrument package used for collecting continuous water column profile data. The CTD is equipped with sensors to measure additional variables and a pump to draw water through the sensors. Profiles at each station are collected from the sea surface (top bin = 0.5 m) to the sea bottom. The CTD and sensors are operated and maintained according to manufacturer's recommended protocols, with factory calibration occurring annually.

Dissolved Inorganic Carbon (DIC): The sum of inorganic carbon species in a solution. The inorganic carbon species include carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate anion (HCO_3^-), and carbonate (CO_3^{2-}).

Nutrient: A substance such as carbon, nitrate, nitrite, silicate, ammonium and phosphate. These compounds are used by organisms to live and grow. Too many nutrients in the water can promote algal blooms and rob the water of oxygen vital to aquatic organisms.

Ocean Acidification (OA): The term given to the chemical changes in the ocean as a result of carbon dioxide emissions. Specifically, the ongoing decrease in the pH of the Earth's oceans, caused by the uptake of carbon dioxide (CO2) from the atmosphere. Seawater is slightly basic (meaning pH > 7), and the process in question is a shift towards less basic conditions rather than a transition to acidic conditions (pH < 7).

Parameter: A physical chemical or biological property whose values determine environmental characteristics or behavior.

Peristaltic Pump: A type of positive displacement pump used for pumping a variety of fluids. The fluid is contained within a flexible tube fitted inside a circular pump casing.

pH: The negative logarithm of the activity of the (solvated) hydronium ion, more often expressed as the measure of the hydronium ion concentration. pH is a measure of the acidity and basicity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 has ten times less hydronium ion activity than one with a pH of 7.

Potentiometric Electrodes: Potentiometry passively measures the potential of a solution between two electrodes, affecting the solution very little in the process. The potential is then related to the concentration of one or more analytes.

Acronyms and Abbreviations

CDIAC	Carbon Dioxide Information Analysis Center
CO_2	Carbon dioxide
CTD	Conductivity-temperature-depth instrument
DIC	Dissolved inorganic carbon
Ecology	Washington State Department of Ecology
et al.	And others
GPS	Global Positioning System
MQO	Measurement quality objective
OA	Ocean acidification
ORNL	Oak Ridge National Laboratory
pCO_2	Partial pressure of carbon dioxide, a measure of CO2 in water or the atmosphere
PMEL	Pacific Marine Environmental Laboratory
PSEMP	Puget Sound Ecosystem Monitoring Program
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedure
TA	Total alkalinity

Units of Measurement

m	meter
mL	milliliters
L	liters
µm	micromolar
µm/kg	micromolar per kilogram

Appendix. Total alkalinity, dissolved inorganic carbon, nutrient, and salinity data collected during this study

The Excel files for this appendix are available only online.

They are in a zip file under *View Now* on the report summary page:

https://fortress.wa.gov/ecy/publications/SummaryPages/1603032.html