ELEMENTA
Science of the Anthropocene

Pelletier, G, et al. 2018 Seasonal variation in aragonite saturation in surface waters of Puget Sound – a pilot study. *Elem Sci Anth,* 6: 5. DOI: https://doi.org/10.1525/elementa.270

RESEARCH ARTICLE

Seasonal variation in aragonite saturation in surface waters of Puget Sound – a pilot study

Gregory Pelletier[*], Mindy Roberts[*,†], Mya Keyzers[*] and Simone R. Alin[‡]

A pilot study of sampling, using monthly marine flights over spatially distributed stations, was conducted with the aim to characterize the carbonate system in Puget Sound over a full year-long period. Surface waters of Puget Sound were found to be under-saturated with respect to aragonite during October–March, and super-saturated during April–September. Highest pCO_2 and lowest pH occurred during the corrosive October–March period. Lowest pCO_2 and highest pH occurred during the super-saturated April–September period. The monthly variations in pCO_2, pH, and aragonite saturation state closely followed the variations in monthly average chlorophyll *a*. Super-saturated conditions during April–September are likely strongly influenced by photosynthetic uptake of CO_2 during the phytoplankton growing season. The relationship between phytoplankton production, the carbonate system, and aragonite saturation state suggests that long-term trends in eutrophication processes may contribute to trends in ocean acidification in Puget Sound.

Keywords: Puget Sound; ocean acidification; carbonate system

Introduction

In recent years, a significant body of research has shown that increases in atmospheric CO_2 concentrations are causing ocean acidification (OA) via ocean uptake of the excess CO_2. Among other changes, OA leads to a decrease in pH, and the decrease is expected to continue into the future under various CO_2 emissions scenarios (Gattuso et al., 2015). OA also decreases the saturation state of calcium carbonate. A decrease in the saturation state of calcium carbonate has been suggested as a potential negative impact on the health of some organisms (e.g., Bednaršek et al., 2012; Waldbusser et al., 2015a). Aragonite is a metastable form of calcium carbonate that naturally occurs in the shells of many mollusk species. Aragonite has relatively rapid dissolution kinetics, and may become under-saturated in the open ocean by the year 2050 if present trends in OA continue (Orr et al., 2005). The aragonite saturation state in the surface waters of the ocean is changing rapidly with OA as a result of human activities that increase global atmospheric CO_2 (Feely et al., 2008). Aragonite under-saturation is likely to affect aragonite-shelled organisms (e.g., Hunt et al., 2008; Bednaršek et al., 2012).

The aragonite saturation state in seawater (Ω_{arag}) is the product of calcium ($[Ca^{2+}]$) and carbonate ($[CO_3^{2-}]$) ion concentrations at ambient temperature, salinity, and pressure, divided by the apparent solubility product (K_{sp}) at the ambient conditions:

$$\Omega_{arag} = \left[Ca^{2+}\right]\left[CO_3^{2-}\right]/K_{sp} \tag{1}$$

When the aragonite saturation states drop below saturation ($\Omega_{arag} < 1$), carbonate minerals in shells and skeletons may begin to dissolve (Doney et al., 2009). This condition is often described as "corrosive" (e.g., Feely et al., 2010). Recent laboratory studies indicate that impacts on sensitive species can occur at higher aragonite saturation states as organisms expend additional energy during early life stages (e.g., Thomsen et al., 2015; Waldbusser et al., 2015b).

In general, surface waters of the open ocean are typically super-saturated with respect to aragonite ($\Omega_{arag} > 1$; e.g., Feely et al., 2009). The coastal region of the Pacific Northwest is strongly influenced by seasonal upwelling of corrosive CO_2-rich offshore sub-surface water, which typically occurs during April–November. Feely et al. (2010), who sampled in February and August of 2008, found the entire water column of Puget Sound to be under-saturated with respect to aragonite in February, and super-saturated only near the surface in August.

In 2012, the governor of Washington State appointed a Blue Ribbon Panel to summarize the scientific knowledge and to recommend key early actions to address threats to the State's marine species and ecosystems (Washington

---

[*] Environmental Assessment Program, Washington State Department of Ecology, Olympia, WA, US

[†] Currently at People for Puget Sound Program, Washington Environmental Council, Seattle, WA, US

[‡] Carbon Program, NOAA Pacific Marine Environmental Laboratory, Seattle, WA, US

Corresponding author: Gregory Pelletier (greg.pelletier@ecy.wa.gov)

State Blue Ribbon Panel on Ocean Acidification, 2012). Much of the monitoring focuses on coastal areas in the Pacific Northwest, strongly influenced by the Pacific Ocean, where acidification was first recognized. A key question is the degree to which local contributions exacerbate acidification resulting from global atmospheric CO_2 levels.

Relatively little is known about the magnitudes and variability of carbonate system variables within the inland waters, including Puget Sound, of Washington State. Reum et al. (2014) presented data from five cruises between 2008 and 2011. Feely et al. (2010) presented the results of two cruises in 2008. McLaskey et al. (2016) collected samples from two stations in Hood Canal in April and June 2012. Fassbender et al. (2017) present a summary of various other published data sources of carbonate system chemistry throughout Puget Sound. The present study aims to explore the monthly variation in the carbonate system and aragonite saturation state in the surface waters of Puget Sound, by sampling a spatially distributed set of stations over a full year-long period.

Methods

Climate and physical setting

The temperate maritime climate produces strong seasonal variations in sunlight, air temperature, and precipitation. Precipitation reflects strong orographic patterns, ranging from 100 cm year^{-1} in the Puget Lowland to 380 cm year^{-1} in the Cascade Mountains and 610 cm year^{-1} in the Olympic Mountains.

Puget Sound represents one portion of the Salish Sea (**Figure 1**), which also includes the Strait of Juan de Fuca and the Strait of Georgia, both of which are shared waters with Canada. The exchange flow near the entrance to Puget Sound at the Admiralty Inlet sill is approximately 10,000 to 20,000 m^3 sec^{-1} (Sutherland et al., 2011), or about 10 to 20 times the average river flow into Puget Sound (Cokelet et al., 1990; Babson et al., 2006). Shallow sills at Admiralty Inlet, Hood Canal, and South Puget Sound restrict circulation and produce differential residence times typically ranging from about 20 to 80 days in the four major basins of Puget Sound (Sutherland et al., 2011). Rivers discharge about 1500 m^3 sec^{-1} of freshwater into Puget Sound on average. Rain-dominated river systems peak in the winter while snow-dominated systems can peak as late as June. Forested and alpine areas occupy 83% of the watershed and contribute over 90% of the freshwater input. Approximately eight million people live in the Salish Sea watershed, with over four million residents on the US side of the border. The majority is served by centralized wastewater facilities that discharge on average about 14 m^3 sec^{-1} of treated wastewater with minimal seasonal variation (Mohamedali et al., 2011).

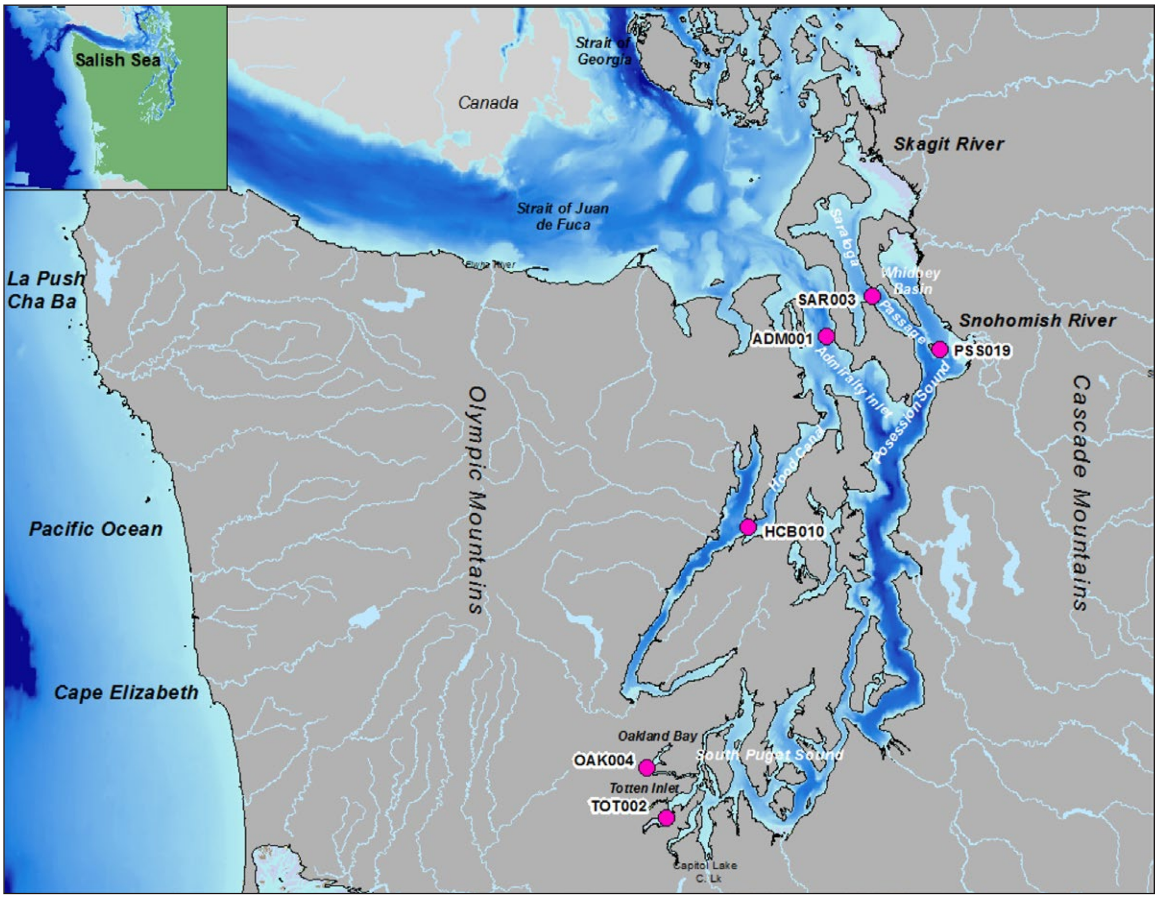

Figure 1: Locations of the six sampling stations of this pilot project in Puget Sound. The six stations (pink circles) fall within Puget Sound, which represents a portion of the Salish Sea (inset). DOI: https://doi.org/10.1525/elementa.270.f1

Sampling stations

The Washington State Department of Ecology (Ecology) collected 136 samples from six stations representing a spectrum of ocean and inland influences (**Figure 1**) monthly from June 2014 through May 2015. No samples were collected during December 2014. For a more detailed description of Ecology's marine flight study area and complete station list from which the six stations were chosen, see Keyzers and Bos (2015).

The Admiralty Inlet station (ADM001) represents water entering Puget Sound with the greatest relative influence of the Pacific Ocean. Two stations are in Whidbey Basin, which receives the largest freshwater inflows to Puget Sound: Saratoga Passage (SAR003) and Possession Sound (PSS019). Two other stations represent contrasting variability between the rain-fed Skagit River (SAR003) and the snowmelt-fed Snohomish River (PSS019). The northern-most Hood Canal station (HCB010) strongly reflects Pacific Ocean conditions and was chosen because of its close proximity to commercial oyster beds. Oakland Bay (OAK004) and Totten Inlet (TOT002) in the South Puget Sound were chosen because of their highly productive commercial shellfish beds; they also reflect inland conditions furthest from the Pacific Ocean.

Sampling methods

Total alkalinity (TA), dissolved inorganic carbon (DIC), and nutrient water samples were collected in addition to the routine marine flight sampling described in Keyzers and Bos (2015). Field staff collected triplicate water samples, which were analyzed for TA and DIC from a depth of 5 meters. The average amount of time to conduct triplicate sampling at each station was 30 minutes, including the time for the pump to pull up the water, for each sample container to be filled, and for filters to be changed between samples. Relative standard deviations of replicate samples are presented in **Table 1**. Sampling procedures specific to TA and DIC are detailed in Keyzers (2014) and were adapted from Bockman and Dickson (2014).

The marine flight CTD (SeaBird SBE25) is equipped with a temperature (SBE3F) and conductivity sensor (SBE4C). The CTD is deployed through a hatch in the belly of the plane, descends to the bottom of the water column, and then returns to the surface, collecting data at eight scans per second. Sampling procedures for all flight-based sampling are detailed in Keyzers (2014), Keyzers and Bos (2015), Bockman and Dickson (2014), and Dickson et al. (2007). CTD measurements of conductivity and temperature were used in the data analysis; we did not use results from the SeaBird SBE 18 pH sensor. The analytical methods, including instrumentation, standardization, and precision, are provided in **Table 2**. Sampling and analysis of chlorophyll *a* were performed according to Bos (2008, 2010).

To assess the quality of our nutrient data, we conducted laboratory performance and analyst proficiency tests of the analytical laboratory, using low nutrient seawater laboratory control samples of known concentrations from Ocean Scientific International Ltd. (GPO) included with every sample batch. Recovery percentage was calculated from these results and used as a measure of analytical accuracy and bias. If results fell outside of established limits, data associated with the batch were flagged as estimates. Any measurement problem that could not be resolved was given a data quality flag.

To analyze DIC and TA, a minimum of 2.5 L of water was collected to produce one 500-mL water sample. The method used a peristaltic pump and filter system to remove particulates (0.45 μm Durapore membrane filters, as in Bockman and Dickson, 2014). We used a Geofilter 350 RPMs peristaltic pump with silicone tubing. The decision to use silicone tubing was based on NOAA PMEL Standard Operating Procedures (SOP) for sampling: "3.1 Drawing tube Tygon® tubing is normally used to transfer the sample from the Niskin to the sample container; however, if dissolved organic carbon samples are being collected from the same Niskins, then it may be necessary to use silicone tubing to prevent contamination from the Tygon®" (Dickson et al. (2007). Once the TA and DIC samples were collected, the glass lids were greased and the containers capped with a rubber band and clamp. The samples were stored in the dark until they were transported back to the laboratory for addition of mercuric chloride. As the samples were collected aboard a small and unstable seaplane, post-sampling fixation was required for safety reasons. Whenever processing could not be completed within 36 hours, samples were preserved by adding 0.2 ml of saturated mercuric chloride solution (50 M) to each 500-ml sample to prevent

Table 1: Summary of relative standard deviations for replicate samples[a] of DIC and TA. DOI: https://doi.org/10.1525/elementa.270.t1

Summary statistic	Standard deviation (%)	
	DIC	TA
Minimum	0.02	0.03
25% tile	0.19	0.15
Median	0.35	0.26
75% tile	1.19	0.64
Maximum	7.15	3.68

[a] Reflecting field variability (three separate samples, not split from the same sample) in the vicinity of the station around the time they were collected.

Table 2: Description of analytical methods, including instrumentation, standardization methods, and precision. DOI: https://doi.org/10.1525/elementa.270.t2

Measurement (lab analyte)	Lab	Analytical method[a]	Expected range of results	Reporting limit	Uncertainty (%)	Instrumentation	Standardization
Nitrate	UW MCL	Armstrong et al., 1967	0.00–40.00 μM	0.15 μM	10	Technicon Auto Analyzer II	5 point standardization
Nitrite	UW MCL	Armstrong et al., 1967	0.00–2.00 μM	0.01 μM	10	Technicon Auto Analyzer II	5 point standardization
Ammonium	UW MCL	Slawyk and MacIsaac, 1972	0.00–10.00 μM	0.05 μM	10	Technicon Auto Analyzer II	5 point standardization
Orthophosphate	UW MCL	Bernhardt and Wilhelms, 1967	0.00–4.00 μM	0.02 μM	10	Technicon Auto Analyzer II	5 point standardization
Silicate	UW MCL	Armstrong et al., 1967	0.00–200.00 μM	0.21 μM	10	Technicon Auto Analyzer II	5 point standardization
Total Alkalinity	PMEL	Dickson et al. 2003, 2007 (SOP3b)	1400–2200 μmol kg^{-1}	NA[b]	±0.1	Custom instrument modeled after those made in Dr. Andrew Dickson's laboratory at Scripps Institution of Oceanography	Analytical uncertainty assessed by periodic analysis of Certified Reference Materials (CRMs) following Dickson et al. (2007)
Dissolved inorganic carbon	PMEL	Johnson et al. (1985, 1987, 1993, 1999), Johnson (1992), Dickson et al. 2007 (SOP2)	1300–2200 μmol kg^{-1}	NA	±0.1	UIC, Inc. coulometer coupled with a custom dissloved inorganic carbon extractor	Gas loop calibration, CRMs, and replicate sample analysis
Salinity	PMEL	Grasshoff et al., 1999	19.0–34.8	0.01	10	Thermosalinograph	Routine comparison with in situ CTD measurements showing agreement within ±0.07

[a] References cited provide descriptions of methods, custom instruments, and standard operating procedures (SOPs).

[b] Not available.

biological alteration. Leinweber and Gruber (2013) found that a delayed addition of mercuric chloride up to 36 hours after collection was acceptable. The maximum time between the sample collection in the field and mercuric chloride addition in the laboratory was 7 hours, considerably less than the 36 hours in Leinweber and Gruber (2013). Samples were also filtered following Bockmon and Dickson (2014) in an effort to minimize any biological activity during the time between collection and mercuric chloride addition. After preservation, the TA and DIC samples were stored in a dark walk-in cooler at 4–6°C until delivery to the NOAA Pacific Marine Environmental Laboratory (PMEL) Carbon Group for analysis. Nutrient samples were frozen and delivered to the University of Washington (UW) Marine Chemistry Laboratory (MCL) at the end of each month. All samples were analyzed within 3 months of collection.

Calculation of carbonate system variables

Carbonate system calculations were performed using CO2SYS (CO2SYS-Excel-Pelletier, described in Orr et al., 2015, and Pelletier et al., 2007). The "best practices" recommendations of Orr et al. (2015) were applied with CO2SYS for selection of equilibrium constants and use of total scale for pH. Observed TA and DIC, along with CTD salinity, temperature, and depth, and silicate and phosphate from the discrete nutrient samples, were input values used in CO2SYS. CO2SYS was used to calculate the pH, pCO_2, and aragonite saturation state for each sample. All of the carbonate system variables, which are inter-related, were calculated from the observed TA and DIC using CO2SYS.

Temperature-normalization of pCO_2

Temperature-normalization of pCO_2 was evaluated to consider whether the seasonal variations in pCO_2 could be explained by seasonal variations in temperature. The following equation was used to temperature-normalize the observed pCO_2 (Takahashi et al., 2002):

$$pCO_{2,\mathrm{Tmean}} = pCO_2 * \exp\left(0.0423\left[T_{\mathrm{mean}} - T_{\mathrm{obs}}\right]\right) \quad (2)$$

where $pCO_{2,\mathrm{Tmean}}$ is the pCO_2 normalized to the mean temperature of the observations, pCO_2 is the observed

pCO_2 at ambient temperature (estimated from CO2SYS), T_{mean} is the mean of the observed temperature data, and T_{obs} is the temperature corresponding to the observed pCO_2.

Excess DIC due to the net effect of biological activity and mixing

Excess DIC (*E*DIC) is the difference between observed DIC and DIC computed from total alkalinity and atmospheric CO_2; it provides an estimate of CO_2 outgassing if the water mass is upwelled (Borges et al., 2011). *E*DIC is also an indicator of the gain or loss of DIC due to the net effect of primary production and respiration (Clargo et al., 2015), within Puget Sound and in source waters entering Puget Sound, and mixing of waters from various locations. *E*DIC was estimated as follows (Borges et al., 2011; Burt et al., 2016; Clargo et al., 2015):

$$E\,\mathrm{DIC} = \mathrm{DIC}_{obs} - \mathrm{DIC}_{atm} \qquad (3)$$

where DIC_{obs} is the observed DIC during 2014–2015 and DIC_{atm} is the DIC that would have been present if the water were in equilibrium with the atmospheric pCO_2. Atmospheric pCO_2 during 2014–2015 was estimated to be 400 μatm (NOAA reported an average of 399.74 μatm for 2014–2015 at the Mauna Loa Earth System Research Laboratory Web site esrl.noaa.gov/gmd/ccgg/trends/global.html#global; PSEMP Marine Workgroup, 2016, reported an average of 399 μatm for 2014–2015 at the Chá bă and Cape Elizabeth stations near the coast of Washington). Average atmospheric pCO_2 reported at Mauna Loa is within a difference of about 0.5% to 2% compared with the averages of regional data from stations near the coast of Washington (PSEMP Marine Waters Workgroup, 2016).

DIC_{atm} was calculated with CO2SYS using the same inputs describe above, with the exception that, instead of using observed TA with observed DIC, we used the observed TA with pCO_2 of 400 μatm and calculated the corresponding DIC_{atm} as the output from CO2SYS.

Data availability

The data collected during this study are available to download from the Washington State Department of Ecology Web site at the following link: https://fortress.wa.gov/ecy/publications/SummaryPages/1603032.html.

Results

Summary statistics for observed temperature, salinity, and carbonate system variables were compared with published averages by Feely et al. (2010) (**Table 3**). In general the ranges of observed carbonate system variables overlap the ranges of averages reported by Feely et al. (2010). The ranges observed in our study tend to be larger than reported by Feely et al. (2010), which is likely due to several reasons: Feely et al. (2010) tabulated averages, and we are comparing their range of averages to our range of observations; our data represent more months of observation, and during 2014–2015, while their study addressed February and August of 2008; and our data include more inland station locations that may be more influenced by freshwater inflows.

The Ω_{arag} values we obtained indicated corrosive conditions (under-saturated) during the winter season (October–March; **Figure 2**). Statistically significant differences ($p < 0.05$) in Ω_{arag} between stations and months were found by a two-factor analysis of variance which was performed on a balanced subset of the data (stations ADM001, PSS019, SAR003, and HCB010 for the months of June, July, August, September, February, and April) using a commercial software package (MATLAB R2016b, The MathWorks Inc., Natick, MA). During April–September, conditions were generally super-saturated. However, stations exhibited much greater variability than in the winter months. For example, August Ω_{arag} ranged from 0.7 to 2.7,

Table 3: Summary statistics for temperature, salinity, and carbonate system variables for samples collected (n = 136) at the six stations in Puget Sound during 2014–2015 (Figure 1). DOI: https://doi.org/10.1525/elementa.270.t3

Variable (units)	Mean	Standard deviation	Coefficient of variation (%)	Minimum	Maximum	Range of averages[a] in Feely et al. (2010)
Temperature (°C)	12.3	2.6	21	8.7	19.1	NA[b]
Salinity	25.8	3.1	12	17.3	30.4	NA
TA (μmol kg^{-1})	1910	130	6.6	1510	2101	2018–2171
DIC (μmol kg^{-1})	1795	130	7.4	1431	2038	1913–2085
*E*DIC (μmol kg^{-1})[c]	5.63	76	1400	–206	156	NA
pH (total scale)	7.95	0.24	3.0	7.51	8.50	7.72–7.95
pCO_2 (μatm)	532	300	56	99.9	1417	NA
pCO_2,T_{mean} (μatm)[d]	534	300	57	103.7	1279	NA
Ω_{arag}	1.51	0.75	50	0.47	3.65	0.75–1.56

[a] For Feb 2008 and Aug 2008.

[b] Indicates not available.

[c] Excess DIC relative to equilibrium with atmospheric CO_2, an indicator of the net effect of biological activity (primary production and respiration).

[d] pCO_2 normalized to the mean temperature of the observations.

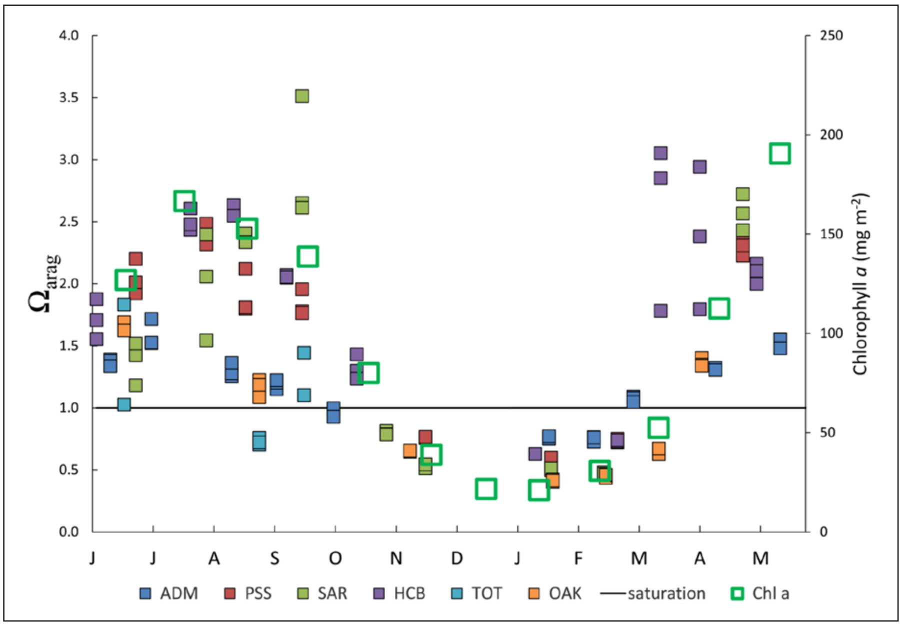

Figure 2: Aragonite saturation state, June 2014 through May 2015, and 15-year monthly averages for chlorophyll *a*. This time series of aragonite saturation state (Ω_{arag}) from June 2014 through May 2015 in surface water samples form the six stations (color-coded, with locations shown in Figure 1) shows a seasonal pattern of highest values during the phytoplankton growing season (March–September). Samples were collected monthly at a depth of 5 meters, with the exception of station HCB in March 2018 (10 meters). Long-term (15-year) monthly averages of depth-integrated (0–50 m) phytoplankton biomass measured by chlorophyll *a* over all of Puget Sound (open green squares) shows a similar seasonal pattern compared with Ω_{arag} measured during 2014–2015. The horizontal line indicates the Ω_{arag} saturation level of 1.0; values below the line are under-saturated. DOI: https://doi.org/10.1525/elementa.270.f2

although the salinity range (27 to 30) was relatively less variable among the stations.

Because biological processes are important for mediating seasonal variations in aragonite saturation state in estuaries (e.g., Kim et al., 2013), we examined long-term (1999–2014) monthly averages of depth-integrated (0–50 m) chlorophyll *a* over all of Puget Sound, which showed a similar seasonal pattern compared with Ω_{arag} measured during 2014–2015 (**Figure 2**). (The data for this analysis from the following sampling stations, with their locations, are available at www.ecy.wa.gov: HCB004, SAR003, DNA001, PSS019, BUD005, NSQ002, ADM001, GOR001, SIN001, GRG002, ELB015, EAP001, ADM003, BLL009, CMB003, PSB003, ADM002, OAK004). Seasonal variations in Ω_{arag} were likely driven by seasonal variations in uptake of CO_2 by phytoplankton (e.g., Borges and Gypens, 2010; Kim et al., 2013). The monthly average Ω_{arag} across all stations sampled during 2014–2015 correlated significantly with the long-term monthly average chlorophyll *a* (Spearman's rank correlation coefficient is 0.85 for the correlation between 1999–2014 monthly average chlorophyll *a* and 2014–2015 monthly average Ω_{arag} across all stations; $p < 0.05$; Zar, 1974).

The surface waters of Puget Sound typically had greater pCO_2 than the atmosphere during October–March (**Figure 3**). The pCO_2 values were typically greatest during the winter months of October–March (up to 1417 µatm), and lowest during April–September (as low as 99.9 µatm). The seasonal depletion of pCO_2 during April–September is most likely due to uptake of CO_2 by primary production of phytoplankton during the growing season. Admiralty Inlet tended to have the highest levels of surface water pCO_2 among the stations, probably due to strong vertical mixing and higher pCO_2 at depth. PSEMP Marine Waters Workgroup (2016) reported similar variations in pCO_2 in Puget Sound.

Temperature-normalization of pCO_2 was evaluated to consider whether the seasonal variations in pCO_2 could be explained by seasonal variations in temperature. The $pCO_{2,Tmean}$ values show about the same seasonal variations (**Figure 4**) and range (**Table 3**) as the observed non-normalized pCO_2 (**Figure 3**; **Table 3**), indicating that the observed seasonal variations in pCO_2 cannot be explained by variations in temperature. Seasonal variations in pCO_2 are most likely influenced mainly by biological processes.

The lowest pH occurred during October–March (as low as 7.5), and highest pH during April–September (as high as 8.5; **Figure 5**). Seasonal variations in pH were also likely strongly influenced by variations in CO_2 uptake by phytoplankton productivity.

*E*DIC ranged from –206 to 156 µmol kg⁻¹ (**Figure 6**; **Table 3**). Positive values of *E*DIC during October–February indicate outgassing of CO_2 and an increase in ambient DIC due to release of CO_2 by respiration. Negative values of *E*DIC during March–September indicate reduction of ambient DIC due to primary production and uptake of CO_2.

DIC ranged from a low of 1431 µmol kg⁻¹ (station PSS) to a high of 2038 µmol kg⁻¹ (station ADM) (**Figure 7**). TA ranged from a low of 1510 µmol kg⁻¹ (station SAR) to a high of 2101 µmol kg⁻¹ (station ADM) (**Figure 8**).

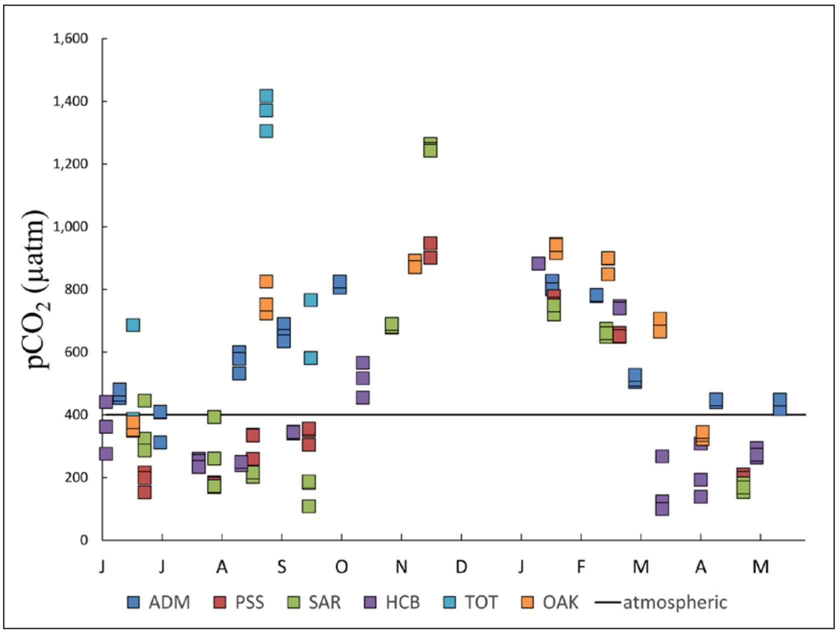

Figure 3: pCO_2 in surface water samples from June 2014 through May 2015. This time series of pCO_2 in surface water samples from the six stations (color-coded, with locations shown in Figure 1) shows the lowest values during the phytoplankton growing season (March–September). Samples were collected from a depth of 5 meters, with the exception of station HCB in March 2018 (10 meters). Atmospheric pCO_2 during 2014–2015 was estimated at 400 µatm, indicated by the horizontal line (NOAA reported an average of 399.74 µatm for 2014–2015 at the Mauna Loa Earth System Research Laboratory Web site esrl.noaa.gov/gmd/ccgg/trends/global.html#global; PSEMP Marine Workgroup, 2016, reported an average of 399 µatm for 2014–2015 at the Chá bă and Cape Elizabeth stations near the coast of Washington). Average atmospheric pCO_2 reported at Mauna Loa is within a difference of about 0.5% to 2% compared with the averages of regional data from stations near the coast of Washington (PSEMP Marine Waters Workgroup, 2016). DOI: https://doi.org/10.1525/elementa.270.f3

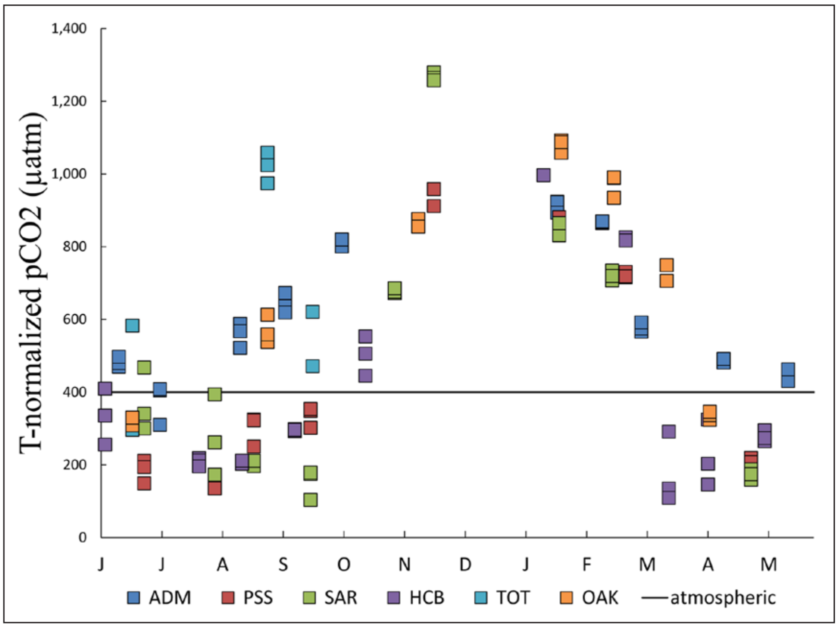

Figure 4: Temperature-normalized pCO_2 in surface water samples from June 2014 through May 2015. This time series of temperature-normalized pCO_2 in surface water samples from the six stations (color-coded, with locations shown in Figure 1) shows the same seasonal pattern of variations as non-normalized observed pCO_2. Normalization for temperature used the equation of Takahashi et al. (2002). Lowest values occurred during the phytoplankton growing season (March–September). Samples were collected from a depth of 5 meters, with the exception of station HCB in March 2018 (10 meters). Atmospheric pCO_2 is based on the 2014–2015 average from the Hawaiian Ocean Time Series. A value of 400 µatm for atmospheric pCO_2 was plotted (horizontal line) to represent the mean for 2014–2015 (NOAA reported annual averages of 398.65 in 2014 and 400.83 in 2015 for a 2014–2015 average of 399.74 µatm at Mauna Loa). DOI: https://doi.org/10.1525/elementa.270.f4

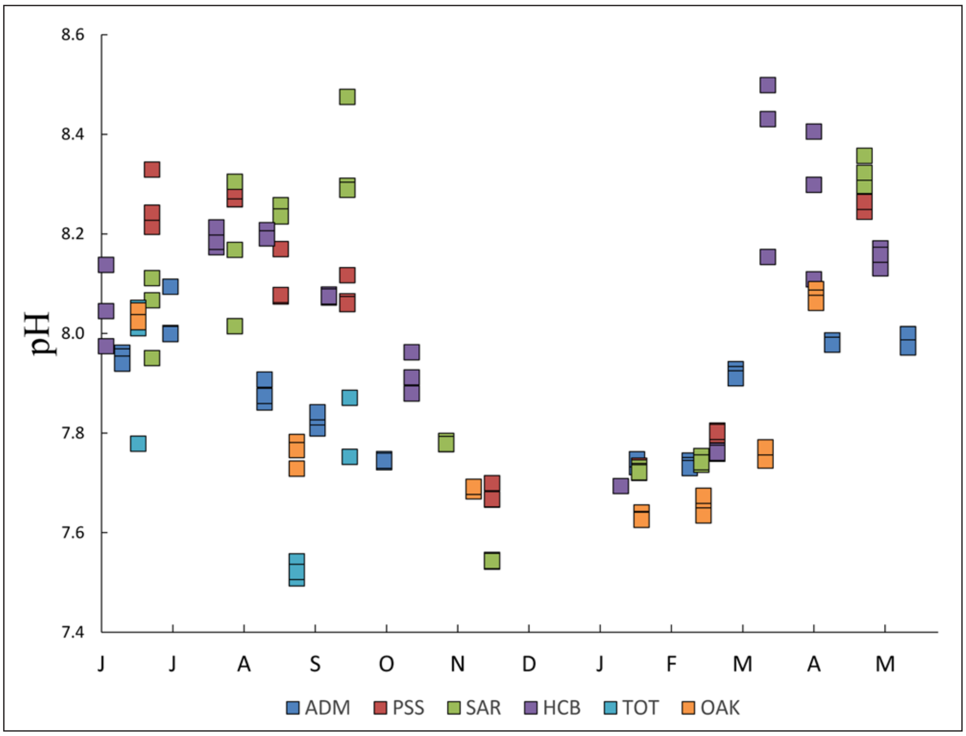

Figure 5: The pH in surface waters from June 2014 through May 2015. This time series of pH in surface water samples from the six stations (color-coded, with locations shown in Figure 1) shows the highest values during the phytoplankton growing season (March–September). Samples were collected from a depth of 5 meters, with the exception of station HCB in March 2018 (10 meters). DOI: https://doi.org/10.1525/elementa.270.f5

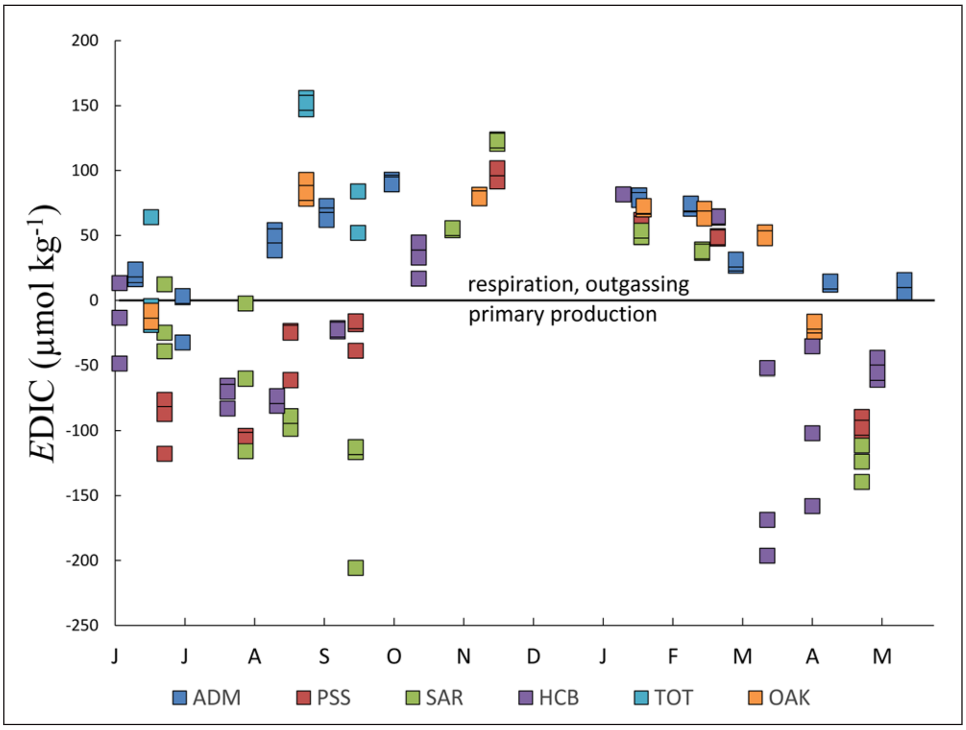

Figure 6: *E*DIC in surface waters from June 2014 through May 2015. This time series of *E*DIC in surface water samples from the six stations (color-coded, with locations shown in Figure 1) shows positive values during October–February when $pCO_2 > 400$ μatm, and negative values during March–September when $pCO_2 < 400$ μatm. Positive values of *E*DIC indicate an increase in ambient DIC relative to equilibrium with atmospheric pCO_2 (outgassing) due to respiration. Negative values of *E*DIC indicate reduction of ambient DIC due to primary production and uptake of CO_2. Values of *E*DIC range from a low of –206 μmol kg^{-1} to a high of 156 μmol kg^{-1}. DOI: https://doi.org/10.1525/elementa.270.f6

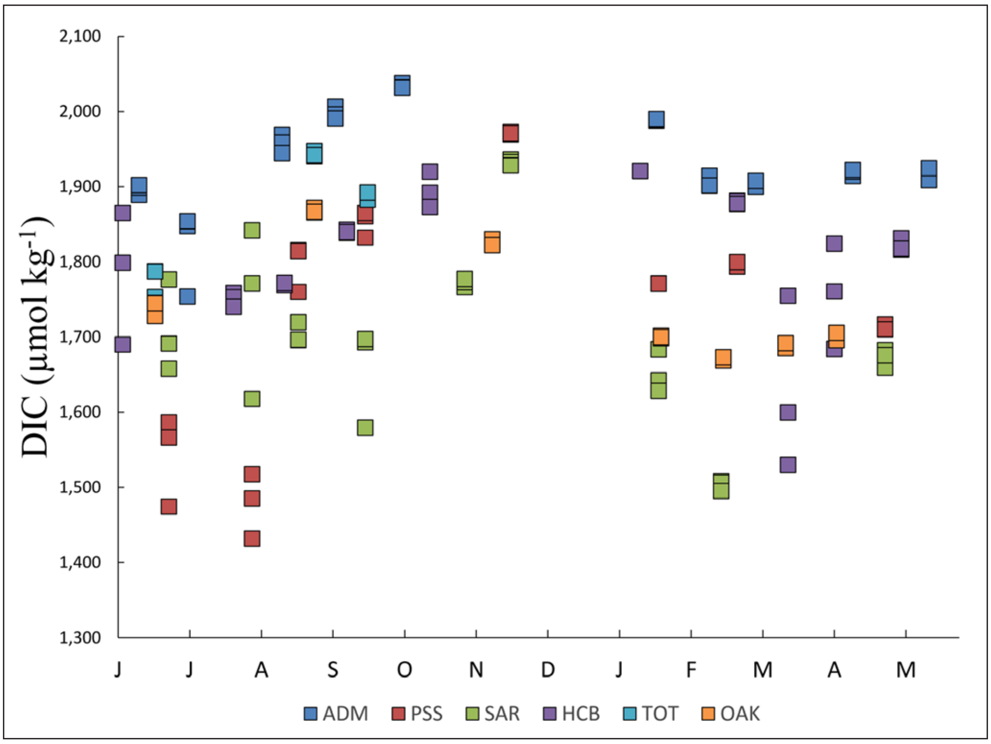

Figure 7: DIC in surface waters from June 2014 through May 2015. This time series of DIC in surface water samples from the six stations (color-coded, with locations shown in Figure 1) from June 2014 through May 2015 includes values of DIC that range from a low of 1431 µmol kg^{-1} to a high of 2038 µmol kg^{-1}. DOI: https://doi.org/10.1525/elementa.270.f7

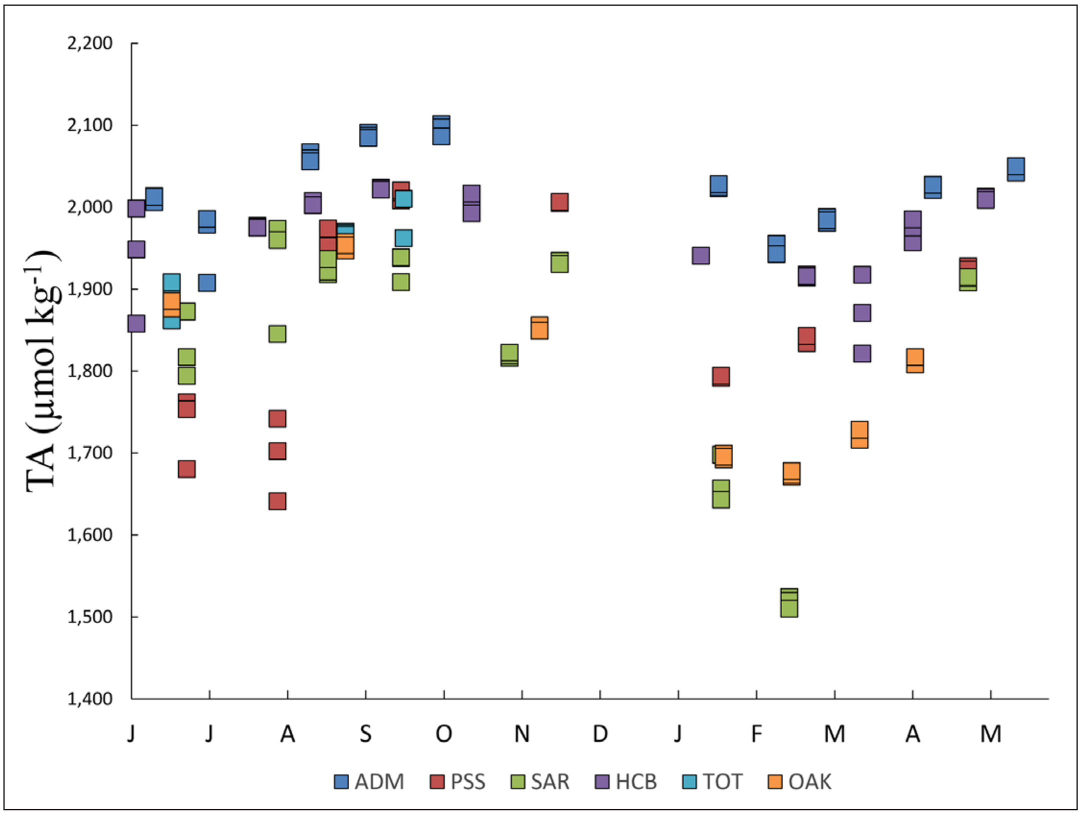

Figure 8: TA in surface waters from June 2014 through May 2015. This time series of TA in surface water samples from the six stations (color-coded, with locations shown in Figure 1) from June 2014 through May 2015 includes values of TA that range from a low of 1510 µmol kg^{-1} to a high of 2101 µmol kg^{-1}. DOI: https://doi.org/10.1525/elementa.270.f8

Discussion

Data published to date in the Pacific Northwest represent limited locations or coastal conditions that may not provide the full context for acidification levels in Puget Sound and the Salish Sea (e.g., Feely et al., 2010; Ianson et al., 2016). Though this program was designed as a limited pilot study focused on the logistics of monitoring aboard a space-constrained sea plane, the results provide a unique glimpse into both seasonal patterns and spatial variability of acidification in the surface waters of Puget Sound. Ongoing efforts will evaluate the relative influence of local human contributions through water and air pathways using circulation and biogeochemical models (Long et al., 2014; Roberts et al., 2015). Meanwhile, the results of this study provide insight into the major processes involved.

The Pacific Ocean strongly influences conditions in Puget Sound. The deep waters entering Puget Sound originate in the Pacific Ocean and represent a mix of subtropical and subarctic water masses. Upwelling varies in strength and duration, with short-term intrusions over the sill at Admiralty Inlet (Deppe et al., 2013; Khangaonkar et al, 2017). The surface layer is influenced by vertical mixing with deep waters enhanced by circulation around the sills, and also by inputs of freshwater and primary productivity within the euphotic zone. Winter conditions produce the most biologically challenging environments in terms of low Ω_{arag} and low pH.

Primary production of phytoplankton in Puget Sound is greatest in the spring and summer with optimum sunlight and intermediate water column stability and residence time (Strickland, 1983). Uptake of CO_2 by phytoplankton for photosynthesis decreases the surface water pCO_2, which increases the Ω_{arag} above corrosive conditions. Admiralty Inlet surface layer Ω_{arag} remains among the lowest of the stations because of vertical mixing with more corrosive deep waters, while Hood Canal surface waters are among the highest. However, previous studies have identified Hood Canal bottom waters as highly corrosive throughout the year (Feely et al., 2010). Thus, primary production may either improve or worsen conditions depending on the location within the water column. Uptake of CO_2 to support primary production increases Ω_{arag} in the euphotic zone, but sinking and decomposition of organic matter releases CO_2 back into the deeper water and decreases Ω_{arag} at depth below the euphotic zone. Species that exploit different depth habitats are likely to experience far different conditions.

The fundamental question is the relative importance of each of the following on the total anthropogenic influence on the CO_2 system in the Salish Sea: (1) increases in local atmospheric CO_2; (2) increases in eutrophication due to local sources of nutrient loading; and (3) increases in inorganic C inputs from the ocean due to global anthropogenic processes. Although the data from this pilot project are not sufficient to answer this over-riding question, they provide some insight on the magnitude of variability of carbonate chemistry in space and time in Puget Sound surface waters.

Washington State leaders have recognized the dominant influence of global atmospheric pCO_2 levels in the acidification of the Pacific Ocean (Washington State Blue Ribbon Panel on Ocean Acidification 2012). The surface layer of Puget Sound appears to be outgassing to the local atmosphere between October and March, as surface water pCO_2 levels were above 400 μatm throughout Puget Sound during this period (with the exception of Hood Canal in March 2015). Regional atmospheric pCO_2 values were higher in the winter than at a global marine reference location (the NOAA Earth System Research Laboratory, Mauna Loa, Hawaii) but can decline below the Hawaiian record during the growing season (PSEMP Marine Waters Workgroup, 2016). Even so, during the summer months, phytoplankton productivity likely decreases pCO_2 to the point where local atmospheric CO_2 represents a source of carbon to most inland surface waters, except Admiralty Inlet where surface layer pCO_2 remains above global and regional atmospheric pCO_2.

The occurrence of the highest Ω_{arag} and negative *E*DIC during the phytoplankton growing season suggests that uptake of dissolved CO_2 due to primary production is a very important process to explain seasonal variations in Ω_{arag}. Uptake of CO_2 by primary production could provide a benefit by increasing Ω_{arag} (e.g., Jutterström et al., 2014). The release of dissolved CO_2 due to decay of the organic carbon produced within the Salish Sea, in addition to ocean inputs of waters rich in dissolved CO_2, contributes to the observed decreases in Ω_{arag} and positive *E*DIC during the winter months, and could also decrease Ω_{arag} in the deeper waters below the euphotic zone during the growing season.

We cannot determine whether the patterns observed in 2014–2015 were typical for Puget Sound or represent anomalously low or high Ω_{arag}, pCO_2, or pH. The monitoring period coincided with anomalous Pacific Ocean and climate conditions throughout the Pacific Northwest, but a historical baseline for the carbonate system is lacking. Compared with historical temperature data, 2015 represented extremely warm water temperatures within Puget Sound that resulted from a combination of anomalously warm waters in the Pacific Ocean and anomalously low river base flows resulting from lack of snowpack the previous winter (PSEMP Marine Waters Workgroup, 2016). If the recent decline in chlorophyll *a* since 1998 continues (PSEMP Marine Waters Workgroup, 2016), decreased phytoplankton productivity could decrease the Ω_{arag} in the surface waters. Anthropogenic nutrient sources have either declined or remained constant throughout the sampling period and thus do not explain the change in chlorophyll *a* (PSEMP Marine Waters Workgroup, 2016).

Though limited to a one-year sampling period, the resulting data illustrate important seasonal and spatial patterns in the surface waters of Puget Sound. Such distributed monthly monitoring provides a complement to continuous data collection efforts now underway but in limited areas. More information is needed to constrain the carbonate system in Puget Sound. A complementary approach that combines both continuous data of high temporal resolution and a distributed network able to capture broad spatial patterns, as demonstrated in this study, may be an ideal way to obtain the needed information.

Data Accessibility Statement

The data collected during this study are available to download from the Department of Ecology's Web site at the following link: https://fortress.wa.gov/ecy/publications/SummaryPages/1603032.html.

Acknowledgements

We appreciate the reviews by Christopher Krembs at Ecology. This is PMEL contribution number 4604.

Funding information

This work was funded by Ecology's Water Quality Program.

Competing interests

The authors have no competing interests to declare.

Author contributions

- Contributed to conception and design: GP, MR, MK
- Contributed to acquisition of data: MK, SA
- Contributed to analysis and interpretation of data: GP, MR, SA
- Drafted and/or revised the article: GP, MR, MK, SA
- Approved the submitted version for publication: GP, MR, MK, SA

References

Armstrong, FAJ, Stearns, CR and **Strickland, JDH** 1967 The measurement of upwelling and subsequent biological processes by means of the Technicon Autoanalyzer® and associated equipment. *Deep-Sea Res* **14**(3): 381–389.

Babson, AL, Kawase, M and **MacCready, P** 2006 Seasonal and interannual variability in the circulation of Puget Sound, Washington: A box model study. *Atmosphere-Ocean* **44**(1): 29–45. DOI: https://doi.org/10.3137/ao.440103

Bednaršek, N, Tarling, GA, Bakker, DCE, Fielding, S, Jones, EM, et al. 2012 Extensive dissolution of live pteropods in the southern ocean. *Nat Geosci* **5**: 881–885. DOI: https://doi.org/10.1038/ngeo1635

Bernhardt, H and **Wilhelms, A** 1967 The continuous determination of low level iron, soluble phosphate and total phosphate with the Autoanalyzer. *Technicon Symp* **I**: 386.

Bockman, EE and **Dickson, AG** 2014 A seawater filtration method suitable for total dissolved inorganic carbon and pH analyses. *Limnol Oceanogr-Meth* **12**: 191–195. DOI: https://doi.org/10.4319/lom.2014.12.191

Borges, AV 2011 Present day carbon dioxide fluxes in the coastal ocean and possible feedbacks under global change. In: Duarte, P and Santana-Casiano, JM (eds.), *Oceans and the Atmospheric Carbon Content*, 47–77. Springer Science+Business Media B.V. DOI: https://doi.org/10.1007/978-90-481-9821-4_3

Borges, AV and **Gypens, N** 2010 Carbonate chemistry in the coastal zone responds more strongly to eutrophication than to ocean acidification. *Limnol Oceanogr* **55**: 346–353. DOI: https://doi.org/10.4319/lo.2010.55.1.0346

Bos, J 2008 Standard Operating Procedure for Chlorophyll *a* Analysis. Washington State Dept of Ecology, Olympia, WA. SOP No. EAP026. http://www.ecy.wa.gov/programs/eap/qa/docs/ECY_EAP_SOP_ChlorophyllAnalysis_v_3_0EAP026.pdf.

Bos, J 2010 Standard Operating Procedure for Seawater Sampling. Washington State Dept of Ecology, Olympia, WA. SOP No. EAP025. http://www.ecy.wa.gov/programs/eap/qa/docs/ECY_EAP_SOP_SeawaterSampling_v_2_0EAP025.pdf.

Burt, WJ, Thomas, H, Hagens, M, Pätsch, J, Clargo, NM, et al. 2016 Carbon sources in the North Sea evaluated by means of radium and stable carbon isotope tracers. *Limnol Oceanogr* **61**(2): 666–683. DOI: https://doi.org/10.1002/lno.10243

Clargo, NM, Salt, LA, Thomas, H and **de Baar, HJW** 2015 Rapid increase of observed DIC and pCO$_2$ in the surface waters of the North Sea in the 2001–2011 decade ascribed to climate change superimposed by biological processes. *Mar Chem* **177**: 566–581. DOI: https://doi.org/10.1016/j.marchem.2015.08.010

Cokelet, ED, Stewart, RJ and **Ebbesmeyer, CC** 1990 The annual mean transport in Puget Sound. NOAA Technical Memorandum, ERL-PMEL-92.

Deppe, RW, Thomson, J, Polagye, B and **Krembs, C** 2013 Hypoxic intrusions to Puget Sound from the Ocean, Oceans 2013 MTS/IEEE, San Diego, CA. https://depts.washington.edu/nnmrec/docs/20130430_DeppeW_pres_Hypoxia.pdf.

Dickson, AG, Afghan, JD and **Anderson, GC** 2003 Reference materials for oceanic CO$_2$ analysis: a method for the certification of total alkalinity. *Mar Chem* **80**: 185–197. DOI: https://doi.org/10.1016/S0304-4203(02)00133-0

Dickson, AG, Sabine, CL and **Christian, JR** (eds.) 2007 Guide to Best Practices for Ocean CO$_2$ Measurements. PICES Special Publication **3**: 191.

Doney, SC, Fabry, VJ, Feely, RA and **Kleypas, JA** 2009 Ocean acidification: the other CO$_2$ problem. *Annu Rev Mar Sci* **1**: 169–192. DOI: https://doi.org/10.1146/annurev.marine.010908.163834

Fassbender, AJ, Alin, SR, Feely, RA, Sutton, AJ, Newton, JA, et al. 2017 Estimating total alkalinity in the Washington State coastal zone: complexities and surprising utility for ocean acidification research. *Estuar Coasts* **40**(2): 404–418. DOI: https://doi.org/10.1007/s12237-016-0168-z

Feely, RA, Alin, SR, Newton, J, Sabine, CL, Warner, M, et al. 2010 The combined effects of ocean acidification, mixing, and respiration on pH and carbonate saturation in an urbanized estuary. *Estuar Coast Shelf Sci* **88:** 442–449. DOI: https://doi.org/10.1016/j.ecss.2010.05.004

Feely, RA, Doney, SC and **Cooley, SR** 2009 Ocean acidification: present conditions and future changes in a high-CO$_2$ world. *Oceanography* **22**(4): 36e47. DOI: https://doi.org/10.5670/oceanog.2009.95

Feely, RA, Sabine, CL, Hernandez-Ayon, JM, Ianson, D and **Hales, B** 2008 Evidence for upwelling of corrosive 'acidified' water onto the continental shelf. *Science* **320**: 1490–1492. DOI: https://doi.org/10.1126/science.1155676

Gattuso, J-P, Magnan, A, Billé, R, Cheung, WWL, Howes, EL, et al. 2015 Contrasting futures for ocean and society from different anthropogenic CO_2 emissions scenarios. *Science* **349**: aac4722. DOI: https://doi.org/10.1126/science.aac4722

Grasshoff, K, Kremling, K and **Ehrhardt, M** 1999 Methods of seawater analysis. Third edition. Verlag Chemie GmbH, Weinheim, 600. DOI: https://doi.org/10.1002/9783527613984

Hunt, BPV, Pakhomov, EA, Hosie, GW, Siegel, V, Ward, P, et al. 2008 Pteropods in Southern Ocean ecosystems. *Prog Oceanogr* **78**: 193–221. DOI: https://doi.org/10.1016/j.pocean.2008.06.001

Ianson, D, Allen, SE, Moore-Maley, BL, Johannessen, SC and **Macdonald, RW** 2016 Vulnerability of a semi enclosed estuarine sea to ocean acidification in contrast with hypoxia. *Geophys Res Lett* **43**: 5793–5801. DOI: https://doi.org/10.1002/2016GL068996

Johnson, KM, King, AE and **Sieburth, JMcN** 1985 Coulometric TCO_2 analyses for marine studies: An introduction. *Mar Chem* **16**: 61–82. DOI: https://doi.org/10.1016/0304-4203(85)90028-3

Johnson, KM, Sieburth, JMcN, Williams, PJleB and **Brändström, L** 1987 Coulometric total carbon dioxide analysis for marine studies: Automation and calibration. *Mar Chem* **21**: 117–33.

Jutterström, S, Andersson, HC, Omstedt, A and **Malmaeus, JM** 2014 Multiple stressors threatening the future of the Baltic Sea-Kattegat marine ecosystem: implications for policy and management actions. *Mar Pollut Bull* **86:** 468–480. DOI: https://doi.org/10.1016/j.marpolbul.2014.06.027

Keyzers, M 2014 Quality Assurance Project Plan: Puget Sound total alkalinity and dissolved inorganic carbon pilot project. Washington Department of Ecology, Olympia, Washington. Publication no. 14-03-116.

Keyzers, M and **Bos, J** 2015 Addendum to Quality Assurance Monitoring Plan: Long-term marine waters monitoring, water column program. Washington Department of Ecology, Olympia, Washington. Publication no. 15-03-102.

Khangaonkar, T, Long, W and **Xu, W** 2017 Assessment of circulation and inter-basin transport in the Salish Sea including Johnstone Strait and Discovery Islands pathways. *Ocean Modell* **109**: 11–32. DOI: https://doi.org/10.1016/j.ocemod.2016.11.004

Kim, D, Choi, S-H, Yang, E-J, Kim, K-H, Jeong, J-H, et al. 2013 Biologically mediated seasonality of aragonite saturation states in Jinhae Bay, Korea. *J Coast Res* **29**(6): 1420–1426. DOI: https://doi.org/10.2112/JCOASTRES-D-12-00205.1

Leinweber, A and **Gruber, N** 2013 Variability and trends of ocean acidification in the Southern California Current System: a time series from Santa Monica Bay. *J Geophys Res Oceans* **118**(7): 3622–3633. DOI: https://doi.org/10.1002/jgrc.20259

Long, W, Khangaonkar, T, Roberts, M and **Pelletier, G** 2014 Approach for simulating acidification and the carbon cycle in the Salish Sea to distinguish regional source impacts. Washington Department of Ecology, Olympia, Washington. Publication no. 14-03-002.

McLaskey, AK, Keister, JE, McElhany, P, Olson, MB, Shallin, BD, et al. 2016 Development of *Euphausia pacifica* (krill) larvae is impaired under pCO_2 levels currently observed in the Northeast Pacific. *Mar Ecol Prog Ser* **555**: 65–78. DOI: https://doi.org/10.3354/meps11839

Mohamedali, T, Roberts, M, Sackmann, B and **Kolosseus, A** 2011 Puget Sound dissolved oxygen model nutrient load summary for 1999–2008. Washington Department of Ecology, Olympia, Washington. Publication no. 11-03-057.

Orr, JC, Epitalon, J-M and **Gattuso, J-P** 2015 Comparison of ten packages that compute ocean carbonate chemistry. *Biogeosciences* **12**: 1483–1510. DOI: https://doi.org/10.5194/bg-12-1483-2015

Orr, JC, Fabry, VJ, Aumont, O, Bopp, L, Doney, SC, et al. 2005. Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature* **437**: 681–686. DOI: https://doi.org/10.1038/nature04095

Pelletier, G, Lewis, E and **Wallace, D** 2007 CO2SYS.XLS: A calculator for the CO_2 system in seawater for Microsoft Excel/VBA, Washington State Dept of Ecology/Brookhaven National Laboratory, Olympia, WA/Upton, NY, USA. http://www.ecy.wa.gov/programs/eap/models.html.

PSEMP Marine Waters Workgroup 2016 Puget Sound marine waters: 2015 overview. Moore, SK, Wold, R, Stark, K, Bos, J, Williams, P, et al. (eds.). URL: www.psp.wa.gov/PSEMP/PSmarinewatersoverview.php.

Reum, JCP, Alin, SR, Feely, RA, Newton, J, Warner, M, et al. 2014 Seasonal carbonate chemistry covariation with temperature, oxygen, and salinity in a fjord estuary: Implications for the design of ocean acidification experiments. *PLoS ONE* **9**(2): e89619. DOI: https://doi.org/10.1371/journal.pone.0089619

Roberts, M, Pelletier, G, Khangaonkar, T, Long, W and **Bianucci, L** 2015 Quality Assurance Project Plan: Salish Sea acidification model development. Washington Department of Ecology, Olympia, Washington. Publication no. 15-03-109.

Slawyk, G and **MacIsaak, JJ** 1972 Comparison of two automated ammonium methods in a region of coastal upwelling. *Deep-Sea Res* **19**: 521–524. DOI: https://doi.org/10.1016/0011-7471(72)90019-8

Strickland, RM 1983 The fertile fjord. Washington Sea Grant Program, University of Washington Press.

Sutherland, DA, MacCready, P, Banas, NE and **Smedstad, LF** 2011 A model study of the Salish Sea estuarine circulation. *J Phys Oceanogr* **41**:

1125–1143. DOI: https://doi.org/10.1175/2011JPO4540.1

Takahashi, T, Sutherland, SC, Sweeney, C, Poisson, A, Metzl, N, et al. 2002 Global sea–air CO_2 flux based on climatological surface ocean pCO_2, and seasonal biological and temperature effects. *Deep-Sea Res II* **49**: 1601–1622. DOI: https://doi.org/10.1016/S0967-0645(02)00003-6

Thomsen, J, Haynert, K, Wegner, KM and **Melzner, F** 2015. Impact of seawater carbonate chemistry on the calcification of marine bivalves. *Biogeosciences* **12**: 4209–4220. DOI: https://doi.org/10.5194/bg-12-4209-2015

Waldbusser, GG, Hales, B, Langdon, CJ, Haley, BA, Schrader, P, et al. 2015a Saturation-state sensitivity of marine bivalve larvae to ocean acidification. *Nat Clim Change* **5**: 273–280. DOI: https://doi.org/10.1038/nclimate2479

Waldbusser, GG, Hales, B, Langdon, CJ, Haley, BA, Schrader, P, et al. 2015b Ocean acidification has multiple modes of action on bivalve larvae. *PLoS ONE* **10**(6): e0128376. DOI: https://doi.org/10.1371/journal.pone.0128376

Washington State Blue Ribbon Panel on Ocean Acidification 2012 Ocean Acidification: From Knowledge to Action, Washington State's Strategic Response. Adelsman, H and Whitely Binder, L (eds.). Washington Department of Ecology, Olympia, Washington. Publication no. 12-01-015.

Zar, JH 1974 Biostatistical analysis. Prentice-Hall, Inc. Englewood Cliffs, NJ.

How to cite this article: Pelletier, G, Roberts, M, Keyzers, M and Alin, SR 2018 Seasonal variation in aragonite saturation in surface waters of Puget Sound – a pilot study. *Elem Sci Anth,* 6: 5. DOI: https://doi.org/10.1525/elementa.270

Domain Editor-in-Chief: Jody W. Deming, University of Washington, US

Associate Editor: Lisa A. Miller, Fisheries and Oceans Canada, CA

Knowledge Domain: Ocean Science

Part of an *Elementa* Special Feature: Advances in Ocean Acidification Research

Submitted: 27 June 2017 **Accepted:** 06 December 2017 **Published:** 16 January 2018

ELEMENTA
Science of the Anthropocene

Elem Sci Anth is a peer-reviewed open access journal published by University of California Press.

OPEN ACCESS