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The combined effects of ocean acidification, mixing, and respiration on pH and carbonate saturation in an urbanized estuary

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ABSTRACT

Puget Sound is a large estuary complex in the U.S. Pacific Northwest that is home to a diverse and economically important ecosystem threatened by anthropogenic impacts associated with climate change, urbanization, and ocean acidification. While ocean acidification has been studied in oceanic waters, little is known regarding its status in estuaries. Anthropogenically acidified coastal waters upwelling along the western North American continental margin can enter Puget Sound through the Strait of Juan de Fuca. In order to study the combined effects of ocean acidification and other natural and anthropogenic processes on Puget Sound waters, we made the first inorganic carbon measurements in this estuary on two survey cruises in February and August of 2008. Observed pH and aragonite saturation state values in surface and subsurface waters were substantially lower in parts of Puget Sound than would be expected from anthropogenic carbon dioxide (CO_2) uptake alone. We estimate that ocean acidification can account for 24–49% of the pH decrease in the deep waters of the Hood Canal sub-basin of Puget Sound relative to estimated pre-industrial values. The remaining change in pH between when seawater enters the sound and when it reaches this deep basin results from remineralization of organic matter due to natural or anthropogenically stimulated respiration processes within Puget Sound. Over time, however, the relative impact of ocean acidification could increase significantly, accounting for 49–82% of the pH decrease in subsurface waters for a doubling of atmospheric CO_2. These changes may have profound impacts on the Puget Sound ecosystem over the next several decades. These estimates suggest that the role ocean acidification will play in estuaries may be different from the open ocean.

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1. Introduction

Over the past two-and-a-half centuries, fossil fuel burning and land-use changes associated with human activities have caused the atmospheric CO_2 concentrations to rise from 280 ppm to about 387 ppm (Le Quéré et al., 2009). Over the same time interval, the surface oceans have absorbed more than 550 billion tons of carbon dioxide from the atmosphere, or approximately 30% of the total anthropogenic carbon dioxide emissions (Canadell et al., 2007). This absorption of CO_2 from the atmosphere has benefitted humankind significantly by reducing the greenhouse gas levels in the atmosphere (IPCC, 2007; Sabine and Feely, 2007). However, when anthropogenic CO_2 is absorbed by seawater, chemical reactions occur that reduce seawater pH, concentration of carbonate ion ($[CO_3^{2-}]$), and the saturation states of the biominerals aragonite (Ω_{arg}) and calcite (Ω_{cal}) in a process commonly referred to as ocean acidification. The in situ degree of saturation of seawater with respect to aragonite and calcite is the product of the concentrations of calcium and carbonate ions, at the in situ temperature, salinity, and pressure, divided by the apparent stoichiometric solubility product (K^*_{sp}) for those conditions:

$$\Omega_{arg} = [Ca^{2+}][CO_3^{2-}]/K^*_{sp_{arg}} \quad (1)$$

$$\Omega_{cal} = [Ca^{2+}][CO_3^{2-}]/K^*_{sp_{cal}} \quad (2)$$

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where the calcium concentration is estimated from the salinity and the carbonate ion concentration is calculated from the dissolved inorganic carbon (DIC) and total alkalinity (TA) data. Since the calcium to salinity ratio in seawater does not vary by more than a few percent, variations in the ratio of $[CO_3^{2-}]$ to the stoichiometric solubility product primarily govern the degree of saturation of seawater with respect to these minerals. In general, surface seawater is supersaturated with respect to calcium carbonate minerals (i.e. $\Omega > 1$; see Feely et al., 2009). When carbonate saturation states in seawater drop below saturation ($\Omega = 1$), whether the reason for the decline in saturation is due to ocean acidification or other natural processes, carbonate biominerals in shells and skeletons may begin to dissolve, and we describe the water as "corrosive" for this reason. We reserve the term "acidified" to refer to the oceanic conditions attributable to oceanic uptake of anthropogenic CO_2 and the associated chemical changes.

Since the beginning of the industrial era, the pH of average open-ocean surface waters has decreased by about 0.1, equivalent to an overall increase in the hydrogen ion concentration or "acidity" of about 30%. By the end of this century, surface ocean pH is expected to decline by another 0.3–0.4 pH (Feely et al., 2004, 2009; Orr et al., 2005; Doney et al., 2009; Steinacher et al., 2009). In coastal regions, ocean acidification can interact with other natural and anthropogenic environmental processes to hasten local declines in pH and carbonate mineral saturation states (Feely et al., 2008; Salisbury et al., 2008; Wootton et al., 2008). The coastal region off western North America is strongly influenced by seasonal upwelling, which typically begins in early spring when the Aleutian low-pressure system moves to the northwest and the Pacific High moves northward, causing a strengthening of the northwesterly winds (Hill et al., 1998; Pennington and Chavez, 2000; Hickey and Banas, 2003). These winds drive surface waters offshore via Ekman transport, which induces the upwelling of CO_2-rich, offshore intermediate waters onto the continental shelf from April through November (Feely et al., 2008). These acidified, oxygen-depleted waters have the potential for entering Puget Sound via the Juan de Fuca submarine canyon in the summer and fall months (Masson, 2002, 2006; Masson and Cummins, 2007; Moore et al., 2008a).

Puget Sound is a deep, fjord-type, semi-enclosed estuary in northwest Washington State that is connected to the Pacific Ocean at its northern end by the Strait of Juan de Fuca (Fig. 1). Exchange of waters between the strait and the four interconnected basins of Puget Sound (Whidbey, Main, Hood Canal, and South Sound) is limited by a double sill at Admiralty Inlet (Figs. 1 and 2). In the wintertime, the winds are predominately from the south and stronger than in the summer, when weaker northwesterly winds are dominant. Associated with the seasonal change in wind direction is a corresponding change over the continental shelf from downwelling in winter to upwelling in summer. Although inflow from the strait to the sound occurs episodically throughout the seasonal cycle, the deep-water inflow tends to be warmer but saltier in the summer because of upwelling along the coast (Cannon et al., 1990; Thomson, 1994; Moore et al., 2008b). Tidal currents and vertical mixing are strongest near Admiralty Inlet, where the tidal currents range from approximately 0.5 to 1.0 m s^{-1} (e.g. Geyer and Cannon, 1982).

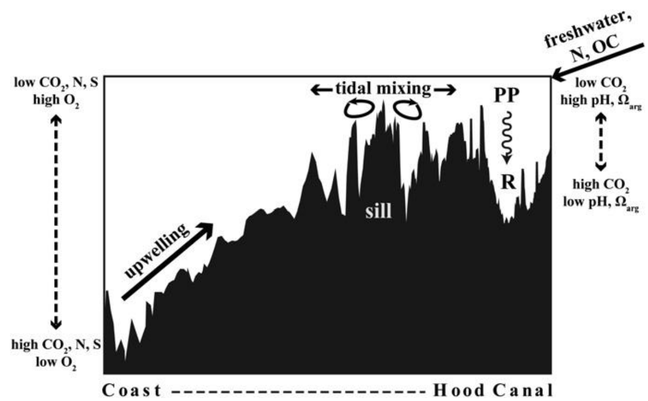

Fig. 2. Conceptual diagram illustrating processes contributing to the formation of corrosive conditions within the greater Puget Sound ecosystem. Along the coast, spring–summer upwelling brings water rich in CO_2 and nutrients (N in figure), high in salinity (S in figure), and low in O_2 close to the ocean surface and into the Strait of Juan de Fuca. Tidal mixing through the strait causes strong vertical mixing over the sills at Admiralty Inlet, where marine water flows into the Puget Sound and Hood Canal basins. Large inputs of freshwater, nutrients, and organic carbon (OC) characterize the inland portion of Puget Sound. Nutrient input stimulates primary production (PP) in surface waters. Upon sinking and decay of phytoplankton, remineralization (R) oxidizes the OC to CO_2, which in turn lowers pH and Ω_{arg}.

As an estuary with ~4000 km of shoreline, Puget Sound has an extensive land–water interface, with large fluxes of freshwater, sediments, organic matter, nutrients, and pollutants entering the sound from a variety of natural and urbanized landscapes (Emmett et al., 2000). Within Puget Sound, circulation is sluggish in many of the restricted inlets of Hood Canal and South Sound so that terrestrial inputs may have relatively localized impacts. For instance, localized inputs of nitrogenous nutrients, such as are associated with development and urbanization, have been observed to stimulate enhanced primary production in surface waters in certain parts of Puget Sound with restricted circulation and developing shorelines (Newton and Van Voorhis, 2002; Simonds et al., 2008). As phytoplankton die and sink from euphotic surface waters, the organic matter they contain is remineralized back to carbon dioxide by natural respiration processes, consuming oxygen and leading to both potential hypoxia and lower pH and Ω_{arg} values in the process. Thus, bottom waters in some areas of the sound are predisposed to the occasional formation of hypoxic, corrosive conditions because of natural physical and biological processes. In Hood Canal, for example, strong stratification, slow flushing, and restricted mixing lead to hypoxic conditions (Newton et al., 2002, 2003, 2008). While hypoxia in areas such as Hood Canal is a natural condition that fluctuates with climate forcing (Brandenberger et al., 2008), these conditions may be exacerbated by anthropogenic stressors such as

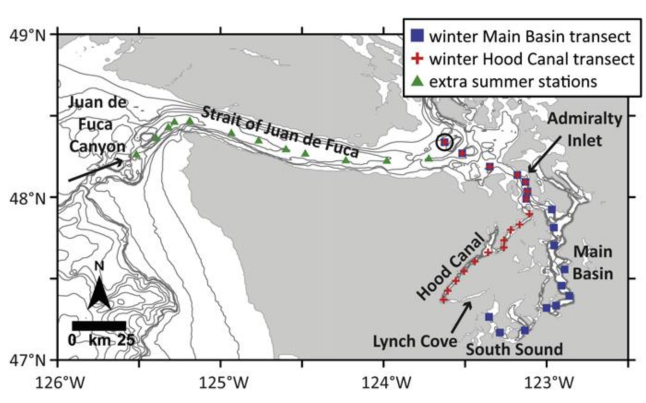

Fig. 1. Map of the study area showing the location of geographic features discussed in the text and stations used in Figs. 3 and 4. Winter 2008 transects are shown in squares and crosses. Summer 2008 transects occupied the same stations, as well as additional stations throughout the Strait of Juan de Fuca and into coastal waters, which appear as triangles. The northernmost winter station (circled in the figure) is not shown in the summer transects.

nutrient enrichment and ocean acidification. In Hood Canal, the late 1990s and early 2000s have seen particularly low oxygen concentrations with fish kill events occurring in three years since 2000, stimulating increased local evaluation of nutrient loading and its role in increased localized hypoxia (Newton et al., 2008). In this paper, we estimate the contribution of ocean acidification to the formation of the low pH subsurface waters undersaturated with respect to aragonite that we observed in Puget Sound.

2. Analytical methods

In February and August 2008, we collected water samples on two University of Washington (UW) Puget Sound Regional Synthesis Model (PRISM) cruises in the Strait of Juan de Fuca and throughout Puget Sound onboard the R/V *Thompson* and Environmental Protection Agency (EPA) Ocean Survey Vessel *Bold*, respectively. Full water column conductivity–temperature–depth rosette stations were occupied at specified locations along two transects, one along Hood Canal and the other through the Main Basin into South Sound (Figs. 1, 3, and 4). Water samples were collected on both cruises in modified Niskin-type bottles and analyzed in the laboratory for DIC, TA, oxygen, and nutrients. DIC was analyzed using coulometric titration (Johnson et al., 1985, 1987; DOE, 1994; Ono et al., 1998). TA was measured by the potentiometric titration method (Millero et al., 1993; DOE, 1994; Ono et al., 1998). Certified Reference Materials were analyzed with both the DIC and TA samples as an independent verification of instrument calibrations (Dickson et al., 2007). The DIC and TA data are accurate to within ~1 μmol kg^{-1} and ~2 μmol kg^{-1}, respectively.

The saturation of seawater with respect to aragonite and seawater pH (on the seawater pH scale) were calculated from the DIC and TA data using the program CO2SYS developed by Lewis and Wallace (1998), using the Mehrbach et al. (1973) carbonate constants as refit by Dickson and Millero (1987). The pressure effect on the solubility is estimated from the equation of Mucci (1983), incorporating the adjustments to the constants recommended by Millero (1995). Based on the uncertainties in the DIC and TA measurements and the thermodynamic constants, the uncertainty in the calculated aragonite saturation state is approximately ±0.02.

Oxygen analysis was done by modified Winkler titration (Carpenter, 1965), and nutrients (nitrate, nitrite, ammonium, phosphate, silicate) were analyzed using a Technicon AutoAnalyzer II (UNESCO, 1994) at the University of Washington Marine Chemistry Laboratory.

3. Results

The wintertime (February 2008) distributions of salinity, oxygen, pH, and aragonite saturation in the Strait of Juan de Fuca, Main Basin, South Sound, and Hood Canal are shown in Fig. 3. In the winter, the entire water column of the Main Basin was well mixed with only small, primarily north–south, gradients in pH (7.71–7.75). South Sound was slightly more stratified. The entire water column from the Strait of Juan de Fuca through Main Basin to South Sound was undersaturated with respect to aragonite (Ω_{arg} = 0.79–0.95). The entire water column in Hood Canal Basin was also undersaturated with respect to aragonite, but in contrast to the Main Basin was stratified with strong vertical and

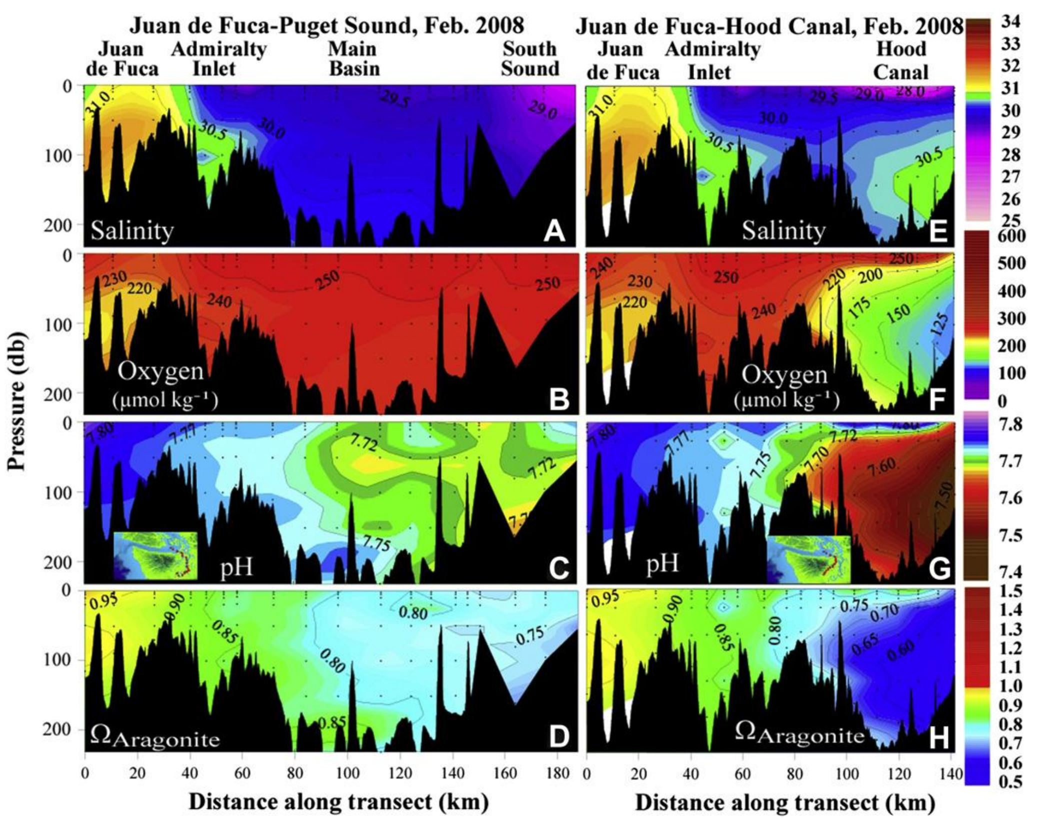

Fig. 3. Distribution of (A) salinity, (B) oxygen, (C) pH, and (D) Ω_{arg} along a transect from the Strait of Juan de Fuca through the Main Basin and into South Sound; and (E) salinity, (F) oxygen, (G) pH, and (H) Ω_{arg} from the Strait of Juan de Fuca to the southern end of Hood Canal during February 2008. Note that color scales for winter cross-sections span smaller ranges for some parameters than summer cross-sections. Black dots represent sampling depths.

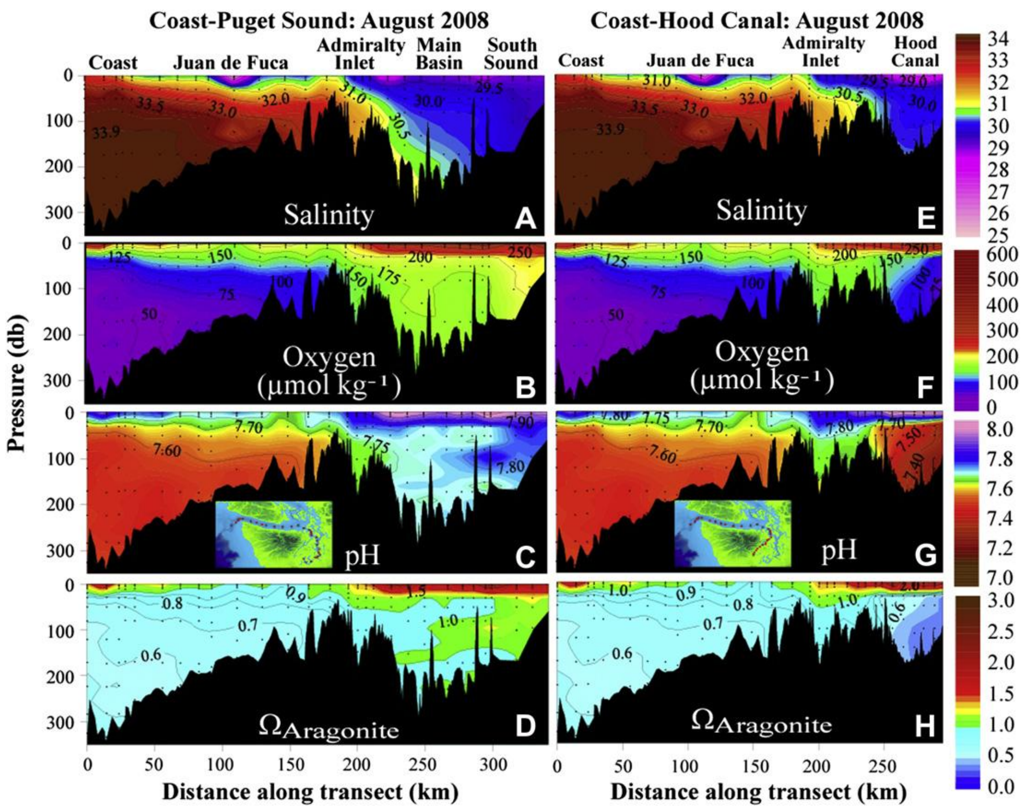

Fig. 4. Distribution of (A) salinity, (B) oxygen, (C) pH, and (D) Ω_{arg} along a transect from the coast through Puget Sound's Main Basin and into South Sound; and (E) salinity, (F) oxygen, (G) pH, and (H) Ω_{arg} on a transect from the coast to the southern end of Hood Canal during August 2008. Note that color scales for summer cross-sections span larger ranges for some parameters than winter cross-sections. Black dots represent sampling depths.

north–south gradients in salinity (27.5–30.5), pH (7.50–7.85), and Ω_{arg} values (0.50–0.85). Oxygen concentrations throughout the Main Basin and South Sound were undersaturated (oxygen saturation at observed water densities of Puget Sound waters is ~280–321 μmol kg^{-1}; calculated as in Garcia and Gordon, 1992), but remained substantially above the hypoxic levels (~62 μmol kg^{-1} or about 2 mg O_2 L^{-1}; the common definition of hypoxia). Oxygen concentrations in Hood Canal were strongly stratified, ranged from 119 to 279 μmol kg^{-1} (3.8–8.9 mg L^{-1}), and grew increasingly undersaturated with depth and proximity to the southern end of Hood Canal, where the lowest oxygen concentrations were observed. The conditions observed in winter, when the water column should mix most deeply in all areas, reflect the water column baseline for the seasonal evolution of chemical conditions from spring to fall as rates of biological processes in surface waters increase with the warming and increased stratification of the water column.

The summertime (August 2008) distributions of salinity, oxygen, pH, and aragonite saturation in the Strait of Juan de Fuca, Main Basin, South Sound, and Hood Canal are shown in Fig. 4. Low pH (<7.75), low aragonite saturation state (Ω_{arg} = ~0.9), high salinity (>31.0) water undersaturated in oxygen enters the Strait of Juan de Fuca in the deeper waters and flows eastward toward Admiralty Inlet where it mixes upward due to strong tidal mixing (Fig. 2). A portion of this water returns to the mouth of the strait in the outflowing surface water, lowering pH and Ω_{arg} values to near saturation. The remaining fraction flows over the sill at Admiralty Inlet and spills into the deeper basins. The pH values of the deep waters flowing into Puget Sound over the sill range from 7.64 to 7.78, with Ω_{arg} values ranging from 0.77 to 1.05, and oxygen concentrations of 105–184 μmol kg^{-1}. Outflowing surface waters at the sill have higher pH values that range from 7.75 to 7.81, with Ω_{arg} values from 0.99 to 1.12, and oxygen concentrations of 168–192 μmol kg^{-1}. In the shallow surface waters (depth < 8 m) of Main Basin, South Sound, and Hood Canal, the pH ranged from 7.77 to 8.25, Ω_{arg} was saturated to supersaturated everywhere (1.01–2.79), and oxygen concentrations ranged from 192 μmol kg^{-1} to 385 μmol kg^{-1}. Below 50 m in the Main Basin and South Sound, the pH values were lower (7.71–7.91), the waters ranged from slightly supersaturated to undersaturated with respect to aragonite (Ω_{arg} = 0.86–1.35), and oxygen concentrations ranged from 142 to 217 μmol kg^{-1}. In contrast, the deep waters of Hood Canal had markedly lower pH and Ω_{arg} values and oxygen concentrations (7.32–7.75, 0.34–0.97, and 57–175 μmol kg^{-1}, respectively) than the deep waters of the Main Basin. These highly corrosive waters with pH values < 7.4 and Ω_{arg} < 0.6 reach as shallow a depth as 50 m in the southern part of the Hood Canal Basin. Within Puget Sound, only the deepest sample from the southernmost station in Hood Canal was hypoxic (57 μmol kg^{-1} = 1.9 mg L^{-1}), and surface (<2 m depth) nitrate concentrations in this area were between 0.07 and 1.36 μmol kg^{-1}, indicating strong stratification and nutrient-limited phytoplankton growth. However, we were not able to sample in Lynch Cove, the arm of Hood Canal where the most severe hypoxia has previously been observed (Fig. 1), because the ship was too large to navigate there. Thus, it is possible that more extensive hypoxic conditions were present at the time that may have affected the aragonite saturation values in that arm.

4. Discussion

4.1. The contribution of ocean acidification to the corrosiveness of Puget Sound waters

Since there are no high-quality, long-term, carbon times-series measurements in Puget Sound, it is not possible to directly determine the increase of anthropogenic CO_2 in the region. However, coastal waters, which are the source for the marine waters in the Puget Sound system, carry an anthropogenic CO_2 burden, and a corresponding pH decrease associated with ocean acidification, that can be estimated by extrapolating the open-ocean CO_2 results for the North Pacific to the coastal region (Feely et al., 2008). Sabine et al. (2004) determined that the surface waters of the North Pacific were enriched in DIC by about 55–60 μmol kg^{-1} due to the uptake of anthropogenic CO_2 since the beginning of the industrial age. This is equivalent to a pH drop of about 0.1 units. Feely et al. (2008) used the WOCE/JGOFS Global CO_2 Survey data to determine that the upwelled corrosive waters along the Pacific Northwest coast contained approximately 31 $\pm$ 4 μmol kg^{-1} anthropogenic CO_2, corresponding to a pH decrease of $\sim$0.05 units. However, Doney et al. (2007) used both data and model results to show that in coastal regions fossil fuel combustion and agricultural practices produce increased atmospheric inputs of strong acids (HNO_3 and H_2SO_4) and bases (NH_3) to the coastal ocean that can further reduce the pH by as much as an additional 50%. Based on these three studies, a reasonable estimate of the range of the present-day pH decrease in the Puget Sound region due to ocean acidification is between 0.05 and 0.15.

Another way to estimate the potential anthropogenic CO_2 impact on Puget Sound is to calculate how much the DIC has increased in Puget Sound, assuming that the partial pressure of CO_2 of the waters (pCO_2) has increased at the same rate as the atmosphere. Takahashi et al. (2009) examined over three million surface CO_2 observations collected over the last 40 years and found that, within the uncertainties of the estimates, surface water pCO_2 values everywhere are increasing at about the same rate as the atmosphere. Atmospheric CO_2 during the February and August 2008 Puget Sound cruises was 106 ppm and 104 ppm higher than the pre-industrial value of 280 ppm, respectively. Rising CO_2 levels do not change the total alkalinity of the waters, so a first-order estimate of the pre-industrial DIC can be made by decreasing the modern pCO_2 values by 106 or 104 ppm and calculating DIC from the TA and adjusted pCO_2 values using the CO2SYS program (Lewis and Wallace, 1998).

The estimated anthropogenic DIC increases from the pre-industrial to the present for Puget Sound surface waters ranged from 13 to 36 μmol kg^{-1} (Table 1). This is considerably less than the estimated anthropogenic DIC increases in open-ocean waters (55–60 μmol kg^{-1}) because waters in Puget Sound have very high Revelle factors (RF) (Revelle and Suess, 1957). The RF indicates how much change in DIC would be expected with a given change in pCO_2, with high RFs corresponding to smaller changes in DIC. Modern Puget Sound RF values range from 14 to 19 (Table 1), significantly higher than open-ocean RF values, which range from 8 to about 15 (Sabine et al., 2004). RF values are higher in Puget Sound than the open ocean because the DIC to TA ratio is higher (Feely et al., 2009). Although the DIC changes are relatively small, surface water changes in pH estimated using this approach indicate pH decreases of up to 0.11 in Puget Sound since the pre-industrial era. Surface Ω_{arg} values appear to have decreased since the pre-industrial era by 0.09–0.33, with larger decreases in the summer and in the Main Basin (Table 1).

Deep-water anthropogenic DIC increases within Puget Sound from the pre-industrial to the present ranged from 7–18 μmol kg^{-1} in the summer to 10–14 μmol kg^{-1} in the winter (Table 1). The corresponding pre-industrial to present decreases in pH and aragonite saturation state are 0.00–0.06 and 0.02–0.09, respectively, with larger decreases in the Main Basin (Table 1). Since deep waters enter Puget Sound through Admiralty Inlet, the net biological respiration signal can be estimated by comparing the average DIC from Admiralty Inlet to the deep DIC values within each basin. Since transit times between Admiralty Inlet and the deep parts of each basin are not known, we used the average Admiralty Inlet value across all depths and both sampling seasons (2008 average DIC_{AI} = 2068 μmol kg^{-1}). Deep DIC values in Hood

Table 1
Average and standard error values for estimated pre-industrial (PI) summer and winter and measured Feb. and Aug. 2008 carbon system conditions at the mouth of the Juan de Fuca Canyon (no Feb. 2008 data or winter PI estimate), Admiralty Inlet, and in Puget Sound's Main Basin and Hood Canal.

Location	pH		Ω_{arg}		DIC (μmol kg^{-1})		TA (μmol kg^{-1})		Revelle factor	
	Surface (0–20 m)	Deep[a]	Surface (0–20 m)	Deep[a]	Surface (0–20 m)	Deep[a]	Surface (0–20 m)	Deep[a]	Surface (0–20 m)	Deep[a]
Juan de Fuca mouth										
PI – summer	7.87	7.59	1.33	0.68	2064	2254	2171	2268	15.6	18.7
Aug. 2008	7.80 ± 0.10	7.55 ± 0.01	1.19 ± 0.34	0.61 ± 0.02	2085 ± 57	2264 ± 7	2171 ± 31	2268 ± 7	16.5	18.7
Admiralty Inlet										
PI – winter	7.84	7.83	1.03	1.03	2032	2043	2107	2117	17.3	17.3
PI – summer	7.85	7.77	1.23	1.02	2034	2093	2129	2162	16.1	17.4
Feb. 2008	7.78 ± 0.01	7.77 ± 0.01	0.90 ± 0.03	0.89 ± 0.03	2050 ± 11	2061 ± 20	2107 ± 15	2117 ± 23	18.1	18.1
Aug. 2008	7.79 ± 0.02	7.72 ± 0.06	1.07 ± 0.05	0.92 ± 0.13	2053 ± 21	2108 ± 62	2129 ± 15	2162 ± 43	17.1	18.0
Main Basin										
PI – winter	7.71	7.73	0.93	0.89	1985	1987	2041	2044	17.7	17.8
PI – summer	8.05	7.83	1.89	1.16	1884	2022	2052	2111	12.6	16.4
Feb. 2008	7.74 ± 0.02	7.73 ± 0.03	0.79 ± 0.03	0.78 ± 0.04	1998 ± 4	2001 ± 6	2041 ± 6	2044 ± 8	18.2	18.2
Aug. 2008	7.95 ± 0.09	7.77 ± 0.02	1.56 ± 0.32	1.00 ± 0.04	1920 ± 48	2040 ± 8	2052 ± 20	2111 ± 9	14.2	17.3
Hood Canal										
PI – winter	7.77	7.60	0.84	0.66	1966	2076	2018	2095	18.3	18.8
PI – summer	8.01	7.41	1.73	0.42	1881	2115	2032	2080	13.3	17.6
Feb. 2008	7.72 ± 0.07	7.56 ± 0.06	0.75 ± 0.07	0.61 ± 0.06	1981 ± 49	2086 ± 18	2018 ± 38	2095 ± 6	18.9	18.8
Aug. 2008	7.90 ± 0.20	7.39 ± 0.05	1.50 ± 0.66	0.40 ± 0.05	1913 ± 97	2122 ± 18	2032 ± 31	2080 ± 6	14.7	17.3

[a] Depth range for "deep" samples is >100 m in Main Basin, >75 m in Hood Canal, and >20 m at Admiralty Inlet. Depth cutoffs were chosen on the basis of relative depth and stratification in each location.

Canal, for example, were 54 μmol kg^{-1} higher than the average Admiralty Inlet value on the summer cruise and 18 μmol kg^{-1} higher during the winter cruise. This increase is taken to be the net modern respiration signal. If we compare this respiration signal to the total difference between the average pre-industrial Admiralty Inlet (PI average DIC_{AI} = 2051 μmol kg^{-1}) and modern deep Hood Canal DIC values, we see that ocean acidification accounts for 24% of the total increase in DIC due to the combination of acidification and respiration in summer and 49% in winter.

As CO_2 continues to rise in the atmosphere, the percentage contribution of anthropogenic CO_2 to the development of corrosive conditions in the deep waters of Puget Sound will likely increase with time. For instance, if we do the same calculations for a $2\times CO_2$ (560 ppm) world, calculating the expected anthropogenic DIC in the deep water of Hood Canal by adding 280 ppm to the pre-industrial pCO_2 values and using 2008 measured TA values, we estimate that 19–25 μmol kg^{-1} of anthropogenic CO_2 would be present in Hood Canal deep waters in summer and winter, respectively. Under this scenario, the estimated percentage contribution of ocean acidification to the corrosiveness forecasted for the southern end of Hood Canal increases to 49–82%. Of course, the uncertainty on this calculation is very high, as other changes that may occur over the intervening time were not taken into account, such as increased water temperature associated with anthropogenic climate change and its effects on biological and physical processes (e.g. Bopp et al., 2002; Hofmann and Todgham, 2010); changes in terrestrial inputs of nutrients, freshwater, and carbon linked to climate or land-use change (e.g. Borges and Gypens, 2010); or changes in marine inputs due to basin-scale changes in ocean circulation (e.g. Rykaczewski and Dunne, 2010). Nonetheless, this estimate illustrates the increased role that ocean acidification may play in a high-CO_2 world in exacerbating local or regional hotspots of corrosive conditions where the impacts of multiple stressors converge.

The calculations presented in Table 1 suggest that in pre-industrial times the waters flowing into Puget Sound at depth through Admiralty Inlet were above saturation with respect to aragonite, whereas today they are undersaturated. The deep waters of the Main Basin also experienced supersaturated waters that were not observed in the modern data. While the deep waters of Hood Canal were likely undersaturated during the pre-industrial era, the degree of undersaturation is greater today than it would have been then. However, it is difficult to estimate the uncertainty in these calculations. Coastal regions are likely to have experienced additional anthropogenic stressors compared to the open ocean, so the calculations presented here represent conservative estimates (e.g. Doney et al., 2007).

It is clear that additional measurements of the Puget Sound biogeochemistry and ecosystems are needed to document and monitor for further changes as atmospheric CO_2 continues to rise in the future. Further work is also needed to assess the role of anthropogenic nutrient inputs to generating corrosive and hypoxic conditions in Puget Sound, as previous work suggests that the effects of nutrient inputs on biological processes may be quite localized and not a significant contributor to basin-wide conditions, but that changes in the timing of inputs may be an important consideration (e.g. Simonds et al., 2008; Steinberg et al., in preparation). Previous work on the comparative effects of nutrient enrichment, eutrophication, and ocean acidification in estuaries and coastal oceans has focused on the chemical and biological effects of these processes in surface waters in regions with more significant anthropogenic nutrient loading, such as Chesapeake Bay and the Belgian coastal zone (Borges and Gypens, 2010; Waldbusser et al., in press). This study highlights the importance of considering the synergistic effects of the processes leading to hypoxia (i.e. biological and physical processes, whether natural or anthropogenically enhanced) and ocean acidification (i.e. ocean CO_2 uptake and consequent chemical transformations) in benthic waters of estuaries and coastal oceans.

4.2. Potential impacts on marine organisms in the Puget Sound region

At the present time, a lack of biologically meaningful, field-based information from the Puget Sound region limits our understanding of how varying exposure to waters undersaturated with respect to aragonite might affect the development and survival of larval, juvenile, and adult stages of organisms that live there. Laboratory and mesocosm experiments suggest that pH and saturation state values of the observed magnitude may impair overall calcification rates for many species of marine calcifiers, including cold water corals, coccolithophorids, foraminifera, sea urchins and pteropods (Spero et al., 1997; Riebesell et al., 2000; Engel et al., 2005; Orr et al., 2005; Guinotte et al., 2006; Kleypas et al., 2006; Fabry et al., 2008; Guinotte and Fabry, 2008; Doney et al., 2009; Ries et al., 2009). Similar decreases in calcification rates would be expected for edible mussels, clams, and oysters (Green et al., 2004; Gazeau et al., 2007; Hettinger et al., 2010). Other studies suggest that some species of juvenile fish and shellfish of economic importance to coastal regions are highly sensitive to higher-than-normal CO_2 concentrations with high mortality rates at higher CO_2 concentrations (Ishimatsu et al., 2004; Gazeau et al., 2007). Over the last four years, some oyster hatcheries in the Pacific Northwest region have experienced mass mortalities of oyster larvae in association with a combination of circumstances including unusually saline surface waters and the upwelling of cold, CO_2- and nutrient-rich waters, which contained high concentrations of the pathogenic bacteria, *Vibrio tubiashii* (Elston et al., 2008), and would also have low pH and Ω_{arg} values (e.g. Feely et al., 2008). Finally, some species of diatoms associated with harmful algal blooms are known to increase in abundance in warm, CO_2-rich coastal waters, including diatoms from the genus *Pseudonitzschia* (Moore et al., 2008c).

In Puget Sound, as may be the case for other coastal embayments and estuaries of the Pacific Northwest and elsewhere, the impacts of lowered seawater pH and hypoxia may have a synergistic or compounding impact on organisms. Locations optimal for low oxygen levels that occur normally due to natural respiration and circulation processes in subsurface waters are also where lowered seawater pH occurs. These stressful conditions may be exacerbated by combined impacts from global, regional, and local anthropogenic processes including ocean acidification, land-use change, and nutrient enrichment. The additional pH, Ω_{arg}, and O_2 decreases associated with these anthropogenic stressors may cross critical thresholds for organisms living near the edge of their physiological tolerances and may thus appear as abrupt and major changes in the health of an ecosystem (cf. Grantham et al., 2004; Chan et al., 2008). For example, the recent rapid pH decline observed by Wootton et al. (2008) at Tatoosh Island over an 8-year period in Northwest Washington State is probably explained by a combination of factors including enhanced upwelling of waters off the Washington coast resulting from changes in regional ocean circulation as well as a smaller contribution from ocean acidification. Enhanced upwelling would cause more CO_2-enriched and O_2-depleted waters to be mixed upward at Admiralty Inlet and flow into the deep basins of Puget Sound as well as to be transported at the surface back out through the Strait of Juan de Fuca to Tatoosh Island (e.g. Fig. 2). The rapid decline of the large mussel populations at Tatoosh Island and the mass mortalities of oyster larvae in the Pacific Northwest oyster hatcheries may be early indications of the kind of ecosystem changes caused by the combined effects of multiple processes and stressors interacting in a high-CO_2 world.

Estuaries face a unique status with respect to ocean acidification. The natural and anthropogenic enrichment of nutrients in estuaries may enhance the production and subsequent remineralization of organic matter leading to hypoxia and low pH waters. The input of "acidified" low pH upwelled water from the ocean combines with this process to produce very low pH conditions. Because naturally low carbonate saturation and pH levels in the North Pacific predispose the Pacific Northwest coast in general, and Puget Sound in particular, to the development of corrosive, hypoxic marine conditions, we suggest that this part of the world ocean is an important natural laboratory for studying the interactions of natural biological and physical processes with regional- to global-scale anthropogenic stressors such as urbanization and ocean acidification, respectively.

5. Conclusions

The patterns of low pH and aragonite saturation states observed in the Puget Sound estuary complex are largely the result of natural mixing, circulation, and biological processes at the present time. Ocean acidification currently plays a smaller but important role in further lowering the natural pH levels by 0.05–0.15 units, with decreases in aragonite saturation state on the order of 0.02–0.33. By the end of this century, ocean acidification may become the dominant process reducing the pH and saturation state of this large, economically important estuary. However, it may be possible to mitigate the continued development and impacts of corrosive conditions by addressing and reducing the regional-scale anthropogenic stressors that contribute to their formation, such as additional nutrient inputs associated with development and urbanization (e.g. Bricker et al., 2007; Simonds et al., 2008). While field data on the impacts of CO_2 on the local marine ecosystems of Puget Sound do not exist, laboratory and field experiments with related species of calcifying organisms suggest that there is a real cause for concern for the health of this economically important marine ecosystem. Similar processes may be causing decreases of pH and aragonite saturation states in other coastal estuaries and embayments of the Pacific Northwest and elsewhere. Further study of ocean acidification in estuaries is thus warranted because natural factors including acidic river inputs and restricted circulation can predispose these ecologically and economically important habitats toward corrosive, hypoxic conditions, and anthropogenic stressors such as nutrient enrichment may compound them.

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