# Spatial and Temporal Variability in Carbonate Chemistry in San Juan Archipelago

Lydia Kapsenberg[1], Robin Elahi[2], Jenn Phillips[3], Carlie Pietsch[4], Kirk Sato[5], Chelsea Vaughn[6]

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[1]Department of Ecology Evolution and Marine Biology, University of California Santa Barbara, Santa Barbara, CA 93106
[2]Friday Harbor Laboratories, University of Washington, Friday Harbor, WA 98250
[3]Nelson Institute for Environmental Studies, University of Wisconsin Madison, WI 53715
[4]Department of Earth Sciences, University of Southern California, Los Angeles, CA 90089
[5]Scripps Institution of Oceanography, University of California, San Diego, CA 92093
[6]Department of Biology, California State University North Ridge, North Ridge, CA 91330

**Contact Information:**
Lydia Kapsenberg
Marine Science Institute
University of California Santa Barbara
lydia.kapsenberg@lifesci.ucsb.edu

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## Abstract

This is the first study that characterizes the carbonate parameters in the Salish Sea surrounding the San Juan Archipelago. Water samples were collected from 9 sites on multiple days and analyzed for total alkalinity and dissolved inorganic carbon. Results show high spatial and temporal variability in carbonated parameters. Levels of $pCO_2$ roughly fluctuated between 400 and 950 µatm. The sites are likely highly influenced by freshwater pulses and tidal exchanges. Stark differences between areas of hypothesized high and low water retention were not observed within this sampling scheme.

## Introduction

The seawater chemistry around the San Juan Islands has not yet been well characterized. Island geography, Fraser River influence from the north, and large tidal exchanges enhance the complexity and movement of water masses surrounding these islands (reviewed in Klinger *et al*, 2006). Specifically, dominating currents in Haro and Rosario Strait as well as deep island fjords likely create varying levels of water retention and flow in different areas. Haro Strait, on the west side of San Juan Islands, is likely more exposed to waters originating from the Strait of Juan de Fuca and Strait of Georgia, compared to San Juan Channel which lies between the islands. Even less exposed to strait waters is East Sound, the largest and relatively shallow fjord in the archipelago, and therefore likely has the highest level of water retention in the area. Water retention and low levels of flushing in East Sound could have profound impacts on the carbonate parameters in this area due to biological activity. Additionally, water retention and riverine input may result in spatial variations in the seawater carbonate system throughout the San Juan Islands. Therefore, variation in local carbonate chemistry may be influenced by either (1) movement water masses with different carbonate characteristics in and out of an area, (2) biological activity affecting dissolved inorganic carbon (DIC), or (3) both.

We may expect that areas of high water retention would be more influenced by biological activity than movement of water masses with different carbonate characteristics.

Although direct measurements of water mass retention and biological activity do not exist for this area, we based our sampling locations on island geography and expected currents. We hypothesize that water masses on the West side, in San Juan Channel and in East Sound will consist of different carbonate parameters, as measured by dissolved inorganic carbon (DIC) and total alkalinity (TA).

## Methods

### *Environmental sampling procedure*

Sampling occurred approximately from neap to spring tidal cycle in mid July 2011. Water samples were collected every other day at low slack tide beginning on July 9 and ending on July 15, for a total of four time points. Site locations were chosen according to island geography and expected areas of different water flow. On July 9 and 11, three replicate seawater samples were taken at Kellett Bluff (site 1), San Juan Channel (SJC site 4), and head of East Sound (site 9), see Table 1. On July 13 and 15, the original three sites were sampled without replication, and 6 additional sites (2, 3, 5, 6, 7, 8) were sampled in order to better characterize the carbonate chemistry surrounding the San Juan Island Archipelago (see Fig. 1 and Table 1). Salinity replicates at the original sites (1, 4, 9) were taken, as proxies for within site variability (data not shown).

Seawater samples were collected at a depth of 10 m using a Niskin bottle and processed according to SOP 1 (Dickson *et al*, 2007), and analyzed for salinity, DIC and TA at Friday Harbor Laboratories. Temperature of each sample was taken as the water was dispensed from the Niskin bottle into the Schott-Duran sample bottle. Sample times occurred as close as possible to low slack tides as given by nearest current buoys (see Table 1).

*Tidal cycle sampling*

To gain a better understanding of the variation in carbonate chemistry within a tidal cycle, four samples were collected over one tidal cycle. Water samples were collected in the same manner as the earlier samples near the Friday Harbor Laboratories' pump house and weather station (Table 2). We initiated this data collection on July 17 at low slack (2:20 PM), slack high (8:30 PM), slack low (3:49 AM), slack high (7:25 AM).

**Results**

Temperature, salinity, TA, DIC, $pCO_2$, and pH are plotted in Figure 2 for site 1, 4, 9 across four sampling days. Standard deviation bars on the first two sampling days correspond with replicate samples (n=3). Temperature varied the most in East Sound (site 9). Salinity initially varied between all three sample locations, but converged toward the end of the sampling period. The largest change in salinity over time occurred in the San Juan Channel (site 4). TA follows a trend that closely tracks the salinity data. Salinity, TA, and DIC varied between sites the most on July 9 but converged toward the end of the sampling period. A similar trend is found in $pCO_2$. Fig. 1 also shows a linear increase in DIC in San Juan Channel (site 4) across the sampling period, whereas the East and West sites (1, 9) were more similar to each other than to site 4. Again, all three sites converged upon roughly the same DIC and pH value by the end of the sampling period, where Site 1 and 9 more closely matched each other than they did site 4. Unsurprisingly, there is a high correlation between the $pCO_2$ and pH (Fig. 2). Most noteworthy is that the three sites (1, 4, 9) measured over a period from neap to spring tide cycle undergo relatively large fluctuations in carbonate parameters. For example, nearly all samples had a $pCO_2$ value greater than 450 µatm, with one sample peaking above 800 µatm. It is also worth noting that this fluctuation corresponds to a pH range of ~8.0 – 7.73 over 48 hours.

In order to hone in on larger spatial variation, on July 13 and 15 six additional sample sites were included. Figure 3 shows TA, DIC, and $pCO_2$ from these samples on July 13 and 15. All sites increased in TA from July 11 to July 13, which corresponds directly with an increase in salinity observed on those days (data not shown). All sites increased in DIC over the course of the sampling period and the San Juan Channel sites (3-5) exhibit the greatest change. The East sites (6-9) exhibit relatively consistent DIC levels across sites, on both days. Changes in $pCO_2$ were more variable than the changes in TA and DIC, with some increases, decreases, and no changes between sampling days. The lowest $pCO_2$ level is 658 µatm, and the highest $pCO_2$ level is 830 µatm. It appears that the San Juan Channel sites (3-5) collectively undergo the largest changes in carbonate chemistry within this 48 hour sampling period.

Figure 4 shows the salinity overtime at the Friday Harbor Laboratories weather station. Dashed lines mark our sampling time points. This plot shows that our sampling was conducted over a pulse of low salinity waters entering the San Juan Archipelago and over time the salinity stabilized around 30. Figure 5 shows the relationship between salinity and TA. As salinity strongly influences TA, we checked to see if the observed variation in $pCO_2$ in Figure 2 and 3 could be explained by the salinity influence on TA. Figure 6 shows the TA and $pCO_2$ values for all our samples (excluding the tidal cycle sampling). Although a weak relationship might exist between TA and $pCO_2$, the correlation is not nearly as tight as between TA and salinity. Therefore, the pulse of low saline waters (Fig. 4) is not the sole contributor to the observed variation of $pCO_2$ in waters surrounding the San Juan Islands.

Figure 7 shows the change in $pCO_2$ and pH over a tidal cycle. Changes in salinity and TA were correlated (data not shown), and DIC increased throughout the sampling period (data not shown).

**Discussion**

The carbonate chemistry in the Salish Sea surrounding the San Juan Islands is complex. We hypothesized that variations in carbon parameters within sites could be contributed to either the influx of new water masses with different characteristics and/or the influence of biological processes altering DIC. Due to short sampling period, we were unable to sample on a scale that would allow us to accurately detect differences in carbonate parameters due to site geography, current exposure, and retention. Surprisingly, West and East sites (1-2 and 6-9, respectively) did not exhibit drastically different TA, DIC, and $pCO_2$ values even though these sites differ in their physical parameters such as depths and water flow. Also, San Juan Channel sites (3-5) appeared to be the most variable regarding carbonate chemistry.

It is also noteworthy to mention that our sampling spanned a period of neap (July 8) and spring tides (July 14). Low levels of tidal exchange due to the neap tide at the beginning of our sampling dates could have contributed to the large differences observed in salinity as neap tides have been linked with periods of greatest export in freshwater in the Salish Sea (Griffin and LeBlond, 1990). Freshwater export during the neap tide would explain the pulse of low salinity waters around July 9 (Fig. 4). The period after the neap tide shows an increase and stabilization of salinity around 30. The high levels of tidal exchange around July 14 due to the spring tide may have led to higher levels of mixing and thus less variation in TA and DIC between sites.

In order to gain understanding on the changes in carbonate chemistry over a period shorter than 48 hours, 4 samples were taking in one location throughout a tidal cycle. Unsurprisingly, DIC and $pCO_2$ increased throughout the night. This may correspond to a greater amount of respiration, and thus an increase in DIC, during the night compared to the day when photosynthesis would cause a decline in DIC. To truly understand the impact of tidal exchange on the variability in carbonate parameters, more frequent sampling over a longer time period is necessary.

Overall, it appears that the carbonate chemistry surrounding the San Juan Archipelago is largely influenced by water masses with varying salinities likely originating from the Fraser River. It is possible that the variation in carbonate parameters is enhanced by complex mixing and tidal exchanges rather than biological processes. However, future studies would be required to tease apart the specific influence of biology and physical properties affecting the sites. Additionally, this study shows that the carbonate chemistry surrounding the San Juan Islands is highly variable in space and time. Specifically, $pCO_2$ values (greater than 950 µatm) are much higher than average atmospheric $CO_2$ levels (390 ppm). This highlights the importance of understanding the physical environment when studying the effects of ocean acidification on organism responses.

If this project were to be repeated in future classes, I would strongly suggest sampling our original 9 sites without replication over sampling 3 sites with replication as variation within a site appears to be low.

## Acknowledgements

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## Literature Cited

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## Tables and Figures


*Fig. 1* Map of San Juan Archipelago and sampling sites (1-9). (Squares=sites grouped as "West", triangles=sites grouped as San Juan Channel, circles=sites grouped as "East"; symbol outline=sites with replication on July 9 and 11).

*Table 1* List of sample stations, description of the location, associated GPS coordinates and time of collection. SJC=San Juan Channel. Low slack data are from nearest current buoys: Spring Passage (SP), Harney Channel (HC), Turn Rock (TR) and Kellett Bluff (KB) (source: Mr. Tides 3).

| Site # | Location | Date | North coordinates | West coordinates | Collection time | Low slack |
|---|---|---|---|---|---|---|
| 9-a | East Sound | 07/09/11 | 48 40.08 | 122 53.90 | 6:55 AM | 7:07 AM (HC) |
| 9-b | East Sound | 07/09/11 | 48 40.02 | 122 53.776 | 7:07 AM | 7:07 AM (HC) |
| 9-c | East Sound | 07/09/11 | 48 39.930 | 122 53.755 | 7:15 AM | 7:07 AM (HC) |
| 4-a | SJC | 07/09/11 | 48 35.043 | 123 02.158 | 7:12 AM | 6:56 AM (SP) |
| 4-b | SJC | 07/09/11 | 48 34.961 | 123 02.247 | 7:00 AM | 6:56 AM (SP) |
| 4-c | SJC | 07/09/11 | 48 35.003 | 123 02.490 | 6:45 AM | 6:56 AM (SP) |
| 1-a | Kellett Bluff | 07/09/11 | 48 35.164 | 123 12.791 | 8:12 AM | 7:40 AM (KB) |
| 1-b | Kellett Bluff | 07/09/11 | 48 35.049 | 123 12.759 | 8:04 AM | 7:40 AM (KB) |
| 1-c | Kellett Bluff | 07/09/11 | 48 34.939 | 123 12.732 | 7:55 AM | 7:40 AM (KB) |
| 9-a | East Sound | 07/11/11 | 48 40.22 | 122 53.857 | 8:50 AM | 8:57 AM (HC) |
| 9-b | East Sound | 07/11/11 | 48 40.56 | 122 53.824 | 9:06 AM | 8:57 AM (HC) |
| 9-c | East Sound | 07/11/11 | 48 39.890 | 122 53.789 | 9:20 AM | 8:57 AM (HC) |
| 1-a | Kellett Bluff | 07/11/11 | 48 35.166 | 123 12.658 | 9:32 AM | 9:28 AM (KB) |
| 1-b | Kellett Bluff | 07/11/11 | 48 35.022 | 123 12.665 | 9:25 AM | 9:28 AM (KB) |
| 1-c | Kellett Bluff | 07/11/11 | 48 34.951 | 123 12.64 | 9:16 AM | 9:28 AM (KB) |
| 4-a | SJC | 07/11/11 | 48 35.186 | 123 02.303 | 8:44 AM | 8:46 AM (SP) |
| 4-b | SJC | 07/11/11 | 48 35.004 | 123 02.231 | 8:36 AM | 8:46 AM (SP) |
| 4-c | SJC | 07/11/11 | 48 34.917 | 123 02.183 | 8:29 AM | 8:46 AM (SP) |
| 9 | East Sound | 07/13/11 | 48 40.014 | 122 53.795 | 10:07 AM | 10:34 AM (HC) |
| 8 | Rosario | 07/13/11 | 48 38.485 | 122 52.752 | 10:23 AM | 10:34 AM (HC) |
| 7 | Mouth of E. Sound | 07/13/11 | 48 36.479 | 122 51.341 | 10:40 AM | 10:34 AM (HC) |
| 6 | Upright Head | 07/13/11 | 48 34.179 | 122 34.064 | 10:57 AM | 10:34 AM (HC) |
| 5 | SJC at FHL | 07/13/11 | 48 32.819 | 122 59.277 | 11:22 AM | 11:37 AM (TR) |
| 4 | SJC | 07/13/11 | 48 35.053 | 123 02.314 | 10:16 AM | 10:23 AM (SP) |
| 3 | SJC North | 07/13/11 | 48 37.055 | 123 04.447 | 10:41 AM | 10:23 AM (SP) |
| 2 | Spieden | 07/13/11 | 48 37.960 | 123 09.473 | 11:00 AM | 11:09 AM (KB) |
| 1 | Kellett Bluff | 07/13/11 | 48 35.158 | 123 12.494 | 11:20 AM | 11:09 AM (KB) |
| 9 | East Sound | 07/15/11 | 48 40.037 | 122 53.764 | 12:10 PM | 11:56 AM (HC) |
| 8 | Rosario | 07/15/11 | 48 38.529 | 122 52.760 | 12:25 PM | 11:56 AM (HC) |
| 7 | Mouth of E. Sound | 07/15/11 | 48 36.171 | 122 51.495 | 12:36 PM | 11:56 AM (HC) |
| 6 | Upright Head | 07/15/11 | 48 34.263 | 122 54.031 | 12:50 PM | 11:56 AM (HC) |

| | | | | | | |
|---|---|---|---|---|---|---|
| 5 | SJC @ FHL | 07/15/11 | 48 32.777 | 122 59.362 | N/A | 1:01 PM (TR) |
| 4 | SJC | 07/15/11 | 48 35.048 | 123 02.170 | 11:28 AM | 11:45 AM (SP) |
| 3 | SJC North | 07/15/11 | 48 36.963 | 123 04.384 | 11:50 AM | 11:45 AM (SP) |
| 2 | Spieden | 07/15/11 | 48 37.990 | 123 09.618 | 12:10 PM | 12:37 PM (KB) |
| 1 | Kellett Bluff | 07/15/11 | 48 35.013 | 123 12.458 | 12:28 PM | 12:37 PM (KB) |

*Table 2* Tidal cycle sampling site coordinates and time of collection. Low slacks data are from nearest current buoy Turn Rock (TR) (source: Mr. Tides 3).

| Sample | Date | North coordinates | West coordinates | Collection time | Low slack |
|---|---|---|---|---|---|
| 1 | 07/17/11 | 48 32.664 | 123 00.347 | 2:20 PM | 2:17 PM |
| 2 | 07/17/11 | N/A | N/A | 8:30 PM | 8:25 PM |
| 3 | 07/18/11 | 48 32.672 | 123 00.446 | 3:49 AM | 3:44 AM |
| 4 | 07/18/11 | 48 32.665 | 123 00.454 | 7:25 AM | 7:24 AM |

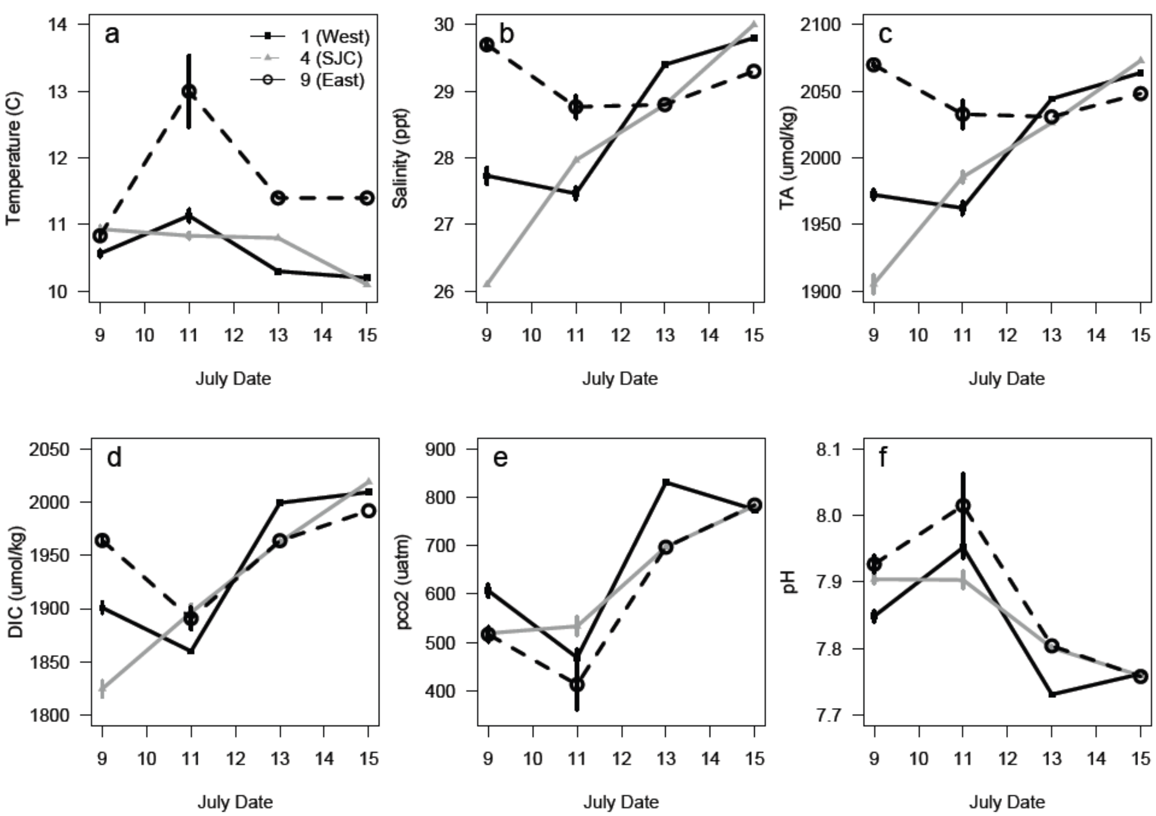


*Fig. 2* Temperature, salinity, TA, DIC, $pCO_2$, and pH for sites 1, 4, 9, over 4 sampling days.

Standard deviation bars on July 9 and 11 correspond to replicate samples (n=3). Solid line=site 1, gray line=site 4, dashed line=site 9.

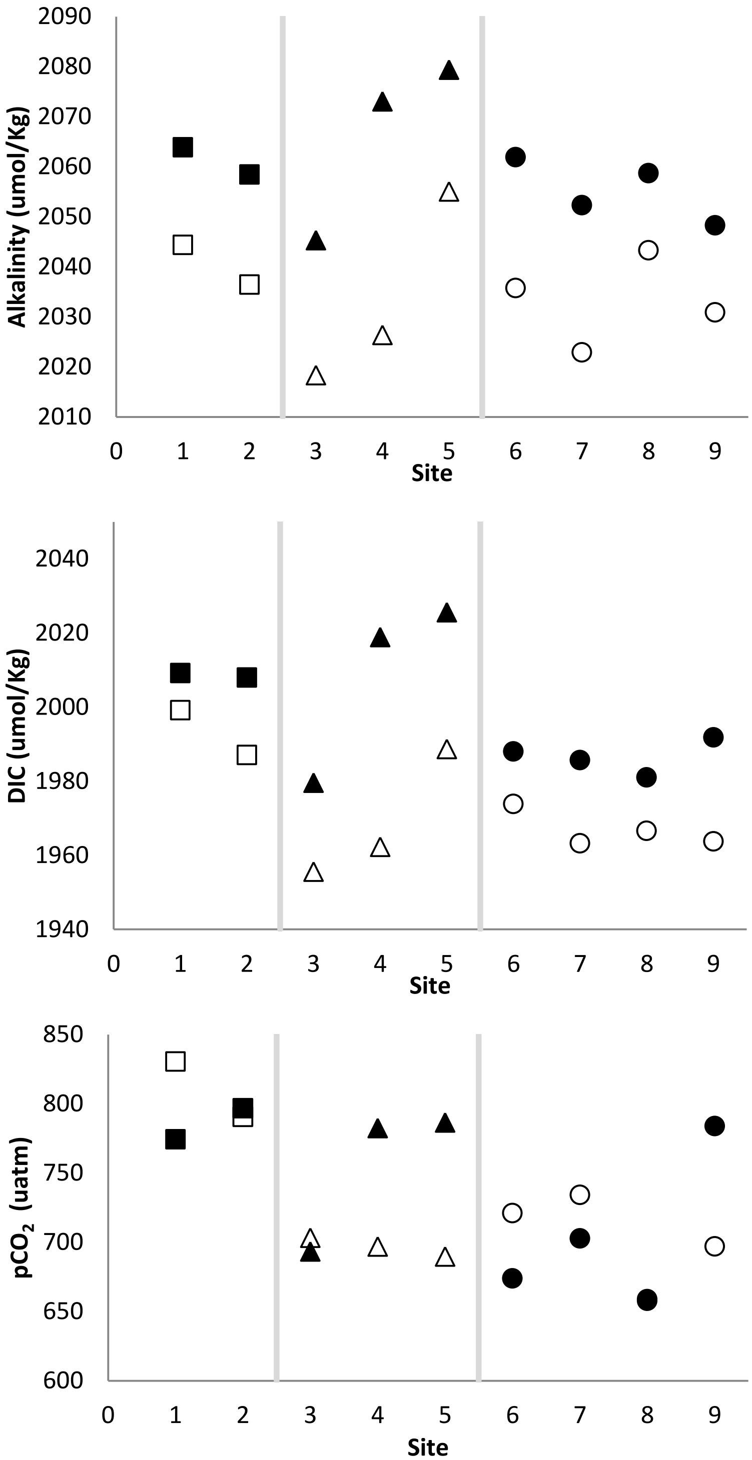


*Fig. 3* Plot of TA, DIC, and $pCO_2$ across sites (1-9). Open symbols=July 13 data, closed symbols=July 15 data; squares=sites grouped as "West", triangles=sites grouped as San Juan Channel, circles=sites grouped as "East."

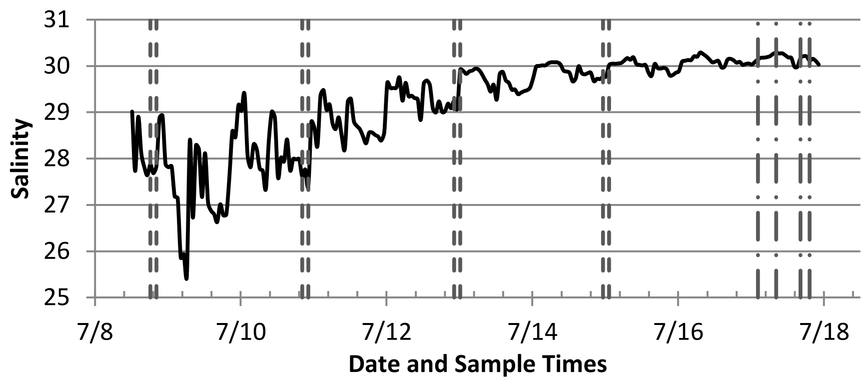


*Fig. 4* Salinity over time, recorded by Friday Harbor Laboratories weather station. Dashed lines = sampling time points.

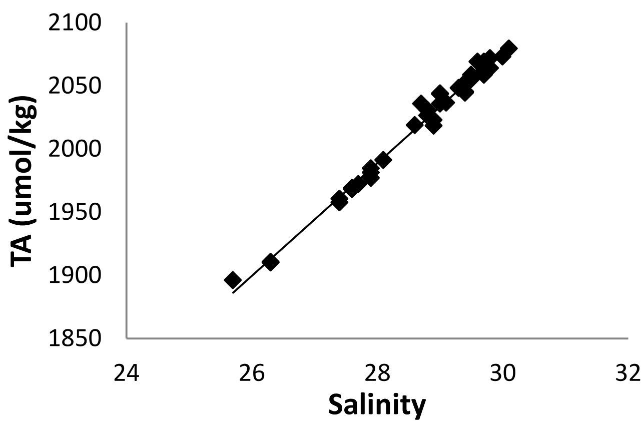


*Fig. 5* Salinity and total alkalinity (µatm/kg) for all samples (excluding tidal cycle sampling).

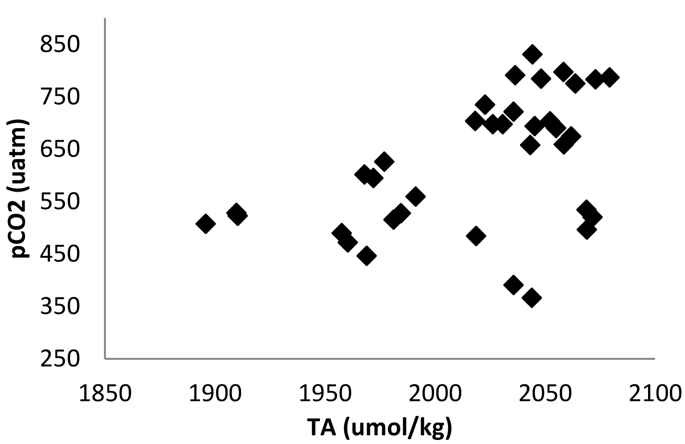

*Fig. 6* pH and $pCO_2$ over a tidal cycle. Sample points correspond to periods of high and low slack.

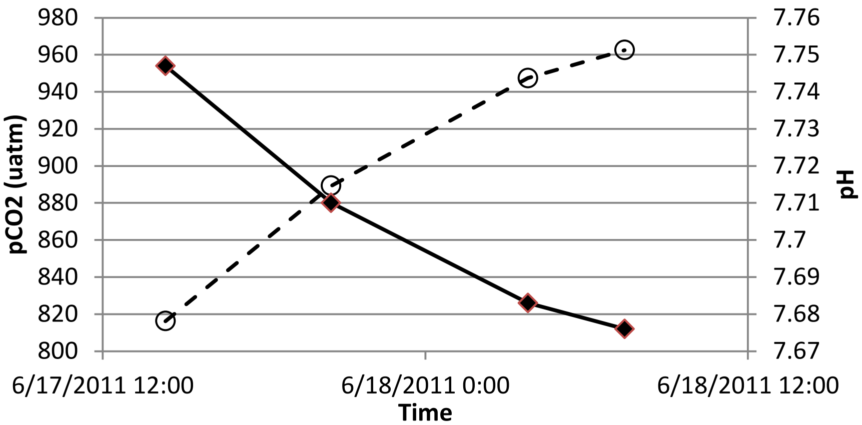


*Fig. 7* Total alkalinity (µatm) and $pCO_2$ (µatm) for all samples (excluding tidal cycle sampling). Dashed line=$pCO_2$, solid line=pH.