

Variation in Carbonate Chemistry throughout the San Juan Archipelago

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Abstract

The absorption of carbon dioxide into the ocean acidifies the waters and has the potential to drastically alter the chemistry upon which organisms and ecosystems depend. This effect, however, is expected to vary between water masses that already differ in terms of their existing carbonate chemistry. The San Juan Archipelago is an ever-changing, complex estuarine ecosystem with little published literature regarding spatial and temporal variation in its carbonate chemistry. After measuring DIC and TA between the neap and spring tide at nine locations throughout the archipelago, we found that the water differs through space and time – both throughout the monthly tidal cycle as well as the daily tidal cycle. Measurements for six parameters – salinity, temperature, DIC, TA, pCO₂ and pH – were analyzed to further understand how areas that experience low, medium and high amounts of flushing over the tidal cycle may differ in their water chemistry. Due to few replicates and insufficient sampling days, we were only able to conclude that the Fraser River, tides and likely biology all impact the carbonate chemistry of the region. We hope that further studies will be conducted in the region to better quantify how well it will withstand increasing ocean acidification.

Keywords: ocean acidification, tidal cycles, CO₂

Introduction

The San Juan Archipelago is a complex, dynamic marine ecosystem with estuarine circulation driven primarily from discharge from the Fraser River, winds and tides (Klinger et al. 2006). Many students and scientists travel to the area to study the biology and oceanography of the region in order to better understand this highly variable system. While global warming is not a new phenomenon, a related effect of increased carbon dioxide in the atmosphere, ocean acidification, is gaining attention as to how it can alter individual organisms, ecosystems and oceanic processes. In order to measure possible effects of ocean acidification on the region, there is a need for measurements of the local carbonate chemistry.

The establishment of an analytical chemistry laboratory at Friday Harbor Labs and the later addition of equipment that can measure carbonate chemistry in June 2011

were big steps in initiating ocean acidification studies of the local water ecosystems. Ocean acidification results from increased carbon dioxide in the atmosphere that dissolves into the ocean, alters the chemistry and causes the pH to become more acidic. Evaluating the carbonate chemistry requires measuring values for two of the following four parameters – total alkalinity (TA), dissolved inorganic carbon (DIC), pH or the partial pressure of carbon dioxide ($p\text{CO}_2$). Because sophisticated equipment and knowledgeable technicians are needed to measure these parameters, the possibility of conducting a local study was only recently made an option.

The aim of our study was to gather baseline data for studying variability in carbonate chemistry over time and space in the archipelago. Specifically, we questioned how the chemistry would differ between areas of differing flushing rates. It is unknown whether organisms in this varied environment will suffer less from ocean acidification due to an enhanced ability to handle stress or whether they will suffer more because they are living on the edge of their threshold. Hopefully, our results will initiate ecologically relevant studies that can further characterize the region.

Methods

Environmental sampling procedure

We sampled over approximately the neap to spring tide 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. Samples were collected from a Niskin at 10 meters depth as close as possible to the slack low tides as given by the nearest current buoys. Schott Duran glass bottles were rinsed with the same sample water from the Niskin, the stopper was greased to form an airtight seal, and poisoned with 100 μl of mercuric chloride (HgCl_2) immediately upon collection. To ensure proper water sampling and collection protocol, recommended standard operating procedures (SOPs) were rigorously followed (Dickson et al. 2007).

The locations were initially chosen based upon areas that were thought to have high, intermediate and low flushing rates (Figure 1). On July 9 and 11, three replicates were taken at Kellett Bluff, three in San Juan Channel parallel with Yellow Island, and three at the head of East Sound. On day three and day four, July 13 and 15 respectively,

the number of sites was expanded to nine, and only salinity replicates at the original three sites were taken. Our original sampling plan was modified in order to better characterize the area and determine if carbonate chemistry was more variable across these nine sites than the predicted high and low flushing sites due to estuarine circulation, the physical oceanographic setting, and geography of the San Juan Archipelago.

In addition, four samples were collected over one tidal cycle to gain a better understanding of the diurnal oscillations in carbonate chemistry. Water samples were collected in the same manner as the earlier samples, but at a more accessible site, parallel to the Friday Harbor Laboratories pumping and weather station in the base of the San Juan Channel. We initiated this data collection on July 17 at the following tide phases: Slack low (2:20 PM), slack high (8:30 PM), slack low (3:49 AM), slack high (7:25 AM).

Data measurement and Analysis

DIC and TA were analyzed following Dickson et al. 2007 in the analytical chemistry laboratory at Friday Harbor Laboratories. While measuring pH with a spectrophotometer is also an option, our experience using the machines at FHL demonstrated that using DIC and TA was often more reliable and consistent than any other combination of parameters. Additionally, personal communication with Andrew Dickson confirmed that DIC and TA was the most robust combination. Certified Reference Materials were analyzed with both the DIC and TA samples as an independent verification of instrument calibrations (Dickson et al 2007). Using DIC and TA, pCO₂ and pH were calculated using the software CO₂calc.

In addition to the four carbonate parameters, salinity and temperature were also recorded for each sample. Measurements were compared to nearby permanent monitoring stations – the Fraser River buoy and the Friday Harbor Labs weather station.

Results

Variation in Time and Space

Figure 2 illustrates the variation in our six parameters in the three locations used for all days during the study – East Sound, the San Juan Channel and the West side. The temperature in the San Juan Channel showed the greatest variation of the three sites and

was also warmer during most days of the sampling period. The other five parameters did not show a consistent directional trend between all three sites. However, as the days progressed from a neap to a spring tide (less exchange to greatest monthly exchange), the values obtained for total alkalinity, salinity, DIC and pCO₂ for each site converged.

Figure 3 shows the variation from west to east over the sample region, beginning with the southernmost site of Kellett Bluff and ending with the northernmost region of East Sound. The trend between days three and four was the same for all parameters except for pH and pCO₂ which changed direction in the East Sound (sites 6-9). Table three further illustrated differences between days three and four, illuminating the fact that the San Juan Channel had the greatest change for all parameters.

Further Exploration of Salinity and Total Alkalinity

Salinity was graphed against total alkalinity in order to measure how closely one can predict the other (Figure 5). Because $R^2 = 0.9862$, it was decided that salinity could be measured as a proxy for total alkalinity. Salinity data from the FHL weather station (Figure 6) was compared to our salinity data (Figure 2-b) over the same time period. Both sets of data show the same increasing trend as the days progress toward the spring tide. Total alkalinity and pCO₂ showed very little correlation (Figure 7).

24-Hour Tidal Cycle

Data gathered from the 24-hour tidal cycle near FHL showed a nice inverse relationship between pCO₂ and pH from early afternoon to morning of the next day (Figure 8-A). DIC showed an initial larger increase but overall followed a similar trend to pCO₂ (figure 9).

Discussion

After the first two days of sampling, we determined that three sites (East Sound, San Juan Channel and Kellett Bluff) with three replicates each did not give us enough geographic spread to see any spatial trends. We therefore expanded the sampling regime to 9 sites with only one sample collected at each location (Figure 1-C). In order to obtain

replicate values for alkalinity at the initial three sites, we continued to gather three samples, but only measured alkalinity. A plot of alkalinity and salinity verified that they were well correlated (Figure 5).

Over the course of the study, the transition from neap to spring tide could be seen in the converging lines of alkalinity, salinity, DIC and $p\text{CO}_2$ (Figure 2). We believe that as the tidal exchanged increased, more mixing occurred and values for all three sites began to change less from day-to-day. This is further supported by the data from the FHL weather station, which showed decreasing variation in salinity values over time (Figure 6). While the Fraser River is a large source of fresh water to the region, it is believed that it would influence water properties less during spring tide cycles (Griffin 1990). Data gathered from the Fraser River buoy at Gravesend Reach, British Columbia supported this statement (Fraser River Buoy). The low oceanic exchange (high freshwater influence) during the neap tide at the mouth of the Fraser River decreased the salinity of the body of water that was later transported to our study region. We saw this influx of low saline water in the San Juan Channel on our first day, which receives Fraser River influence most directly, followed by an increase in salinity over the remaining days (Figure 2 & Figure 6).

The variation in $p\text{CO}_2$ cannot be fully explained by the variation in alkalinity (Figure 7). Because nearly all of the variation in alkalinity is correlated with the variation in salinity, the variation in $p\text{CO}_2$ must be caused by something other than salinity. The activity of the Fraser River usually forces other systems within the islands. However, the lack of correlation between $p\text{CO}_2$ and alkalinity (in this case - salinity) indicates that perhaps biological or other physical influences are in progress.

The San Juan Channel showed the greatest variation in all parameters between days three and four (Figure 3, Table 3). We believe this is due to a large degree of mixing that occurs when multiple currents from different directions converge in the channel. The west to east trend from day three to day four remained consistent except for $p\text{CO}_2$ and pH, which changed direction for the East Sound (sites 6-9). This was surprising, because DIC did not exhibit this same change. Because we believe East Sound to be the most retentive, we thought that the difference may have been due to

biological processes occurring in the water. However, because we have no biological data to support that claim, further study of the region would be necessary.

Lastly, due to our sampling occurring with tidal points, each day that we sampled occurred later in the day. In order to understand how the chemistry of the water changes over the course of a daily tidal cycle, we gathered 4 samples over a 24-hour period near FHL (Figure 8). The most notable finding was how dramatically DIC increased as the afternoon passed into the evening. This is likely due to increased respiration as photosynthesis decreased. The data for $p\text{CO}_2$ also followed this trend, but was more gradual. pH followed an inverse relationship with $p\text{CO}_2$, decreasing as $p\text{CO}_2$ increased.

Further study of the region is needed to better characterize variation throughout the archipelago and over the course of the tidal cycle. Because this area exhibits extreme fluctuation over the course of the day and month, it is challenging to draw conclusions for the area from our study covering eight days. Daily sampling over a whole month's tide cycle would be more informative. Switching from three sites to nine was a good first step; however, replication for each site would be necessary to use good statistics to analyze spatial differences. In order to incorporate possible biological influences, it would also be helpful to measure dissolved oxygen at each site. It is difficult to conclude to what extent ocean acidification might impact the region, but it is likely to vary across the archipelago.

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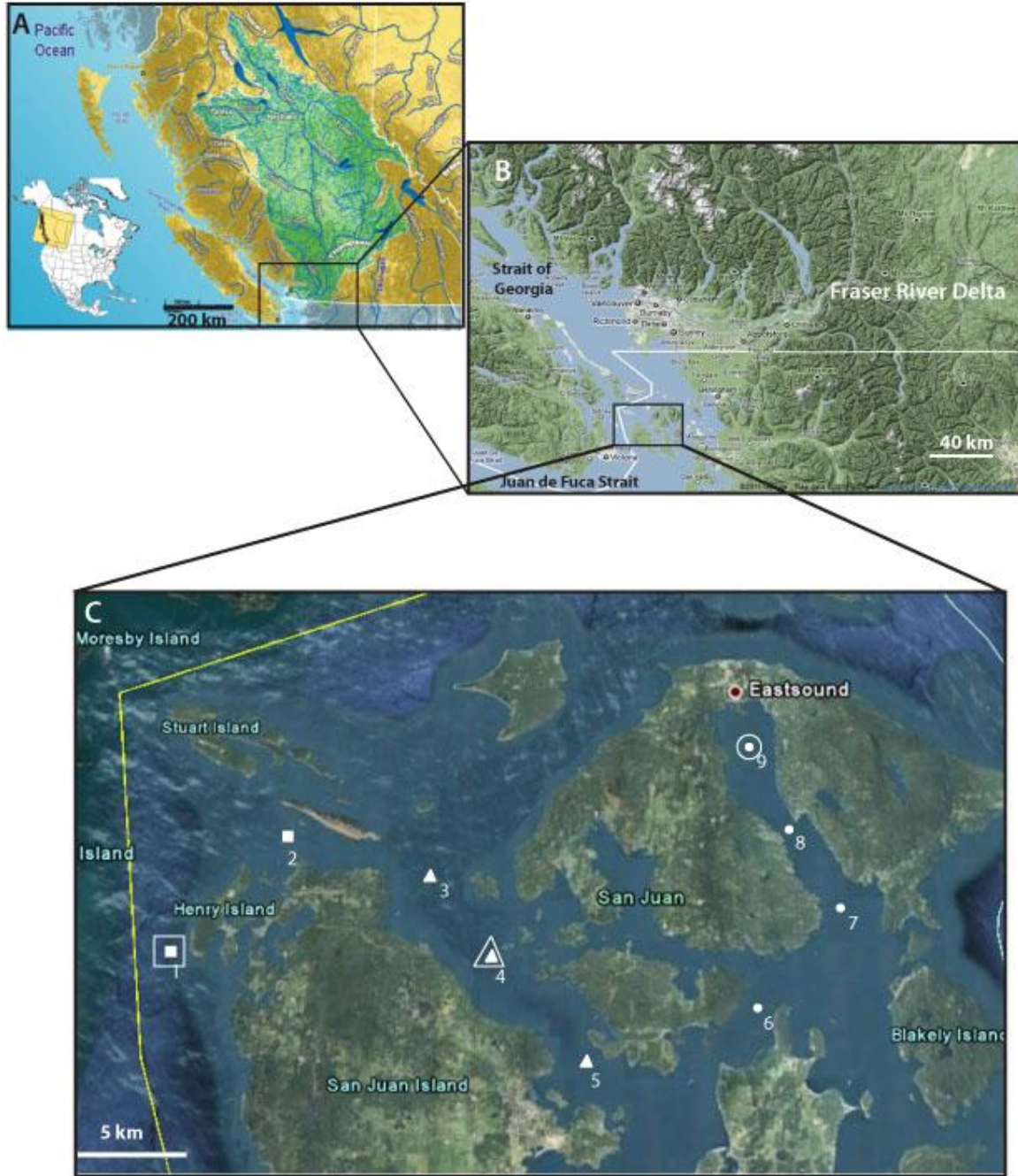


Figure 1. The watershed of the Fraser River of British Columbia, Canada (A). The relationship of the Fraser River Delta to the Strait of Georgia, Strait of Juan de Fuca and San Juan Islands (B). The nine sampling localities around the San Juan Islands, represented by white points, with sites containing replicates (days 1 and 2) outlined (C).

Table 1. List of sample stations, description of the location, associated GPS coordinates and time of collection. Low slacks were gathered from the current buoy nearest to our sample stations. Buoys used were Spring Passage (SP), Harney Channel (HC), Turn Rock (TR) and Kellett Bluff (KB) (source: Mr. Tides 3).

Bottle ID	Location	Date	North coordinates	West coordinates	Collection time	Low slack at nearest current buoy
E001	East Sound	07/09/11	48 40.08	122 53.90	6:55 AM	7:07 AM (HC)
E002	East Sound	07/09/11	48 40.02	122 53.776	7:07 AM	7:07 AM (HC)
E003	East Sound	07/09/11	48 39.930	122 53.755	7:15 AM	7:07 AM (HC)
SJ001	San Juan Channel	07/09/11	48 35.043	123 02.158	7:12 AM	6:56 AM (SP)
SJ002	San Juan Channel	07/09/11	48 34.961	123 02.247	7:00 AM	6:56 AM (SP)
SJ003	San Juan Channel	07/09/11	48 35.003	123 02.490	6:45 AM	6:56 AM (SP)
W001	Kellett Bluff	07/09/11	48 35.164	123 12.791	8:12 AM	7:40 AM (KB)
W002	Kellett Bluff	07/09/11	48 35.049	123 12.759	8:04 AM	7:40 AM (KB)
W003	Kellett Bluff	07/09/11	48 34.939	123 12.732	7:55 AM	7:40 AM (KB)
E004	East Sound	07/11/11	48 40.22	122 53.857	8:50 AM	8:57 AM (HC)
E005	East Sound	07/11/11	48 40.56	122 53.824	9:06 AM	8:57 AM (HC)
E006	East Sound	07/11/11	48 39.890	122 53.789	9:20 AM	8:57 AM (HC)
W004	Kellett Bluff	07/11/11	48 35.166	123 12.658	9:32 AM	9:28 AM (KB)
W005	Kellett Bluff	07/11/11	48 35.022	123 12.665	9:25 AM	9:28 AM (KB)
W006	Kellett Bluff	07/11/11	48 34.951	123 12.64	9:16 AM	9:28 AM (KB)
SJ 004	San Juan Channel	07/11/11	48 35.186	123 02.303	8:44 AM	8:46 AM (SP)
SJ 005	San Juan Channel	07/11/11	48 35.004	123 02.231	8:36 AM	8:46 AM (SP)
SJ 006	San Juan Channel	07/11/11	48 34.917	123 02.183	8:29 AM	8:46 AM (SP)
EW 007	East Sound	07/13/11	48 40.014	122 53.795	10:07 AM	10:34 AM (HC)
EW 008	Rosario	07/13/11	48 38.485	122 52.752	10:23 AM	10:34 AM (HC)
EW 009	Mouth of E. Sound	07/13/11	48 36.479	122 51.341	10:40 AM	10:34 AM (HC)
EW 010	Upright Head	07/13/11	48 34.179	122 34.064	10:57 AM	10:34 AM (HC)
EW 011	SJ Channel @ FHL	07/13/11	48 32.819	122 59.277	11:22 AM	11:37 AM (TR)
EW 012	San Juan Channel	07/13/11	48 35.053	123 02.314	10:16 AM	10:23 AM (SP)
EW 013	SJ Channel North	07/13/11	48 37.055	123 04.447	10:41 AM	10:23 AM (SP)
EW 014	Spieden	07/13/11	48 37.960	123 09.473	11:00 AM	11:09 AM (KB)
EW 015	Kellett Bluff	07/13/11	48 35.158	123 12.494	11:20 AM	11:09 AM (KB)
EW 016	East Sound	07/15/11	48 40.037	122 53.764	12:10 PM	11:56 AM (HC)
EW 017	Rosario	07/15/11	48 38.529	122 52.760	12:25 PM	11:56 AM (HC)
EW 018	Mouth of E. Sound	07/15/11	48 36.171	122 51.495	12:36 PM	11:56 AM (HC)
EW 019	Upright Head	07/15/11	48 34.263	122 54.031	12:50 PM	11:56 AM (HC)
EW 020	SJ Channel @ FHL	07/15/11	48 32.777	122 59.362	N/A	1:01 PM (TR)
EW 021	San Juan Channel	07/15/11	48 35.048	123 02.170	11:28 AM	11:45 AM (SP)
EW 022	SJ Channel North	07/15/11	48 36.963	123 04.384	11:50 AM	11:45 AM (SP)
EW 023	Spieden	07/15/11	48 37.990	123 09.618	12:10 PM	12:37 PM (KB)
EW 024	Kellett Bluff	07/15/11	48 35.013	123 12.458	12:28 PM	12:37 PM (KB)

Table 2. List of sample stations, description of the location, associated GPS coordinates and time of collection. Low slacks were gathered from the current buoy nearest to our sample stations. Buoys used were Spring Passage (SP), Harney Channel (HC), Turn Rock (TR) and Kellett Bluff (KB) (source: Mr. Tides 3).

Bottle ID	Location	Date	North coordinates	West coordinates	Collection time	Slack at nearest current buoy
TC001	SJ Channel @ FHL	07/17/11	48 32.664	123 00.347	2:20 PM	2:17 PM
TC002	SJ Channel @ FHL	07/17/11	N/A	N/A	8:30 PM	8:25 PM
TC003	SJ Channel @ FHL	07/18/11	48 32.672	123 00.446	3:49 AM	3:44 AM
TC004	SJ Channel @ FHL	07/18/11	48 32.665	123 00.454	7:25 AM	7:24 AM

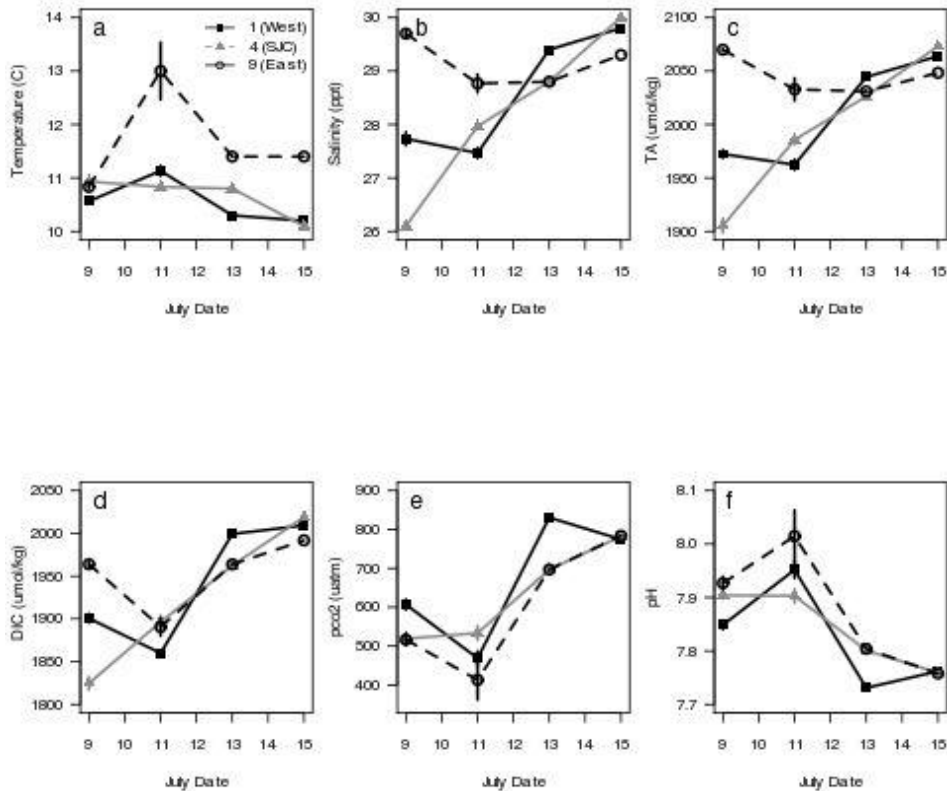


Figure 2. Variation through time at the three sites – East Sound, West side and San Juan Channel. The first sampling day was Saturday, July 9th and continued every other day until Friday, July 15th.

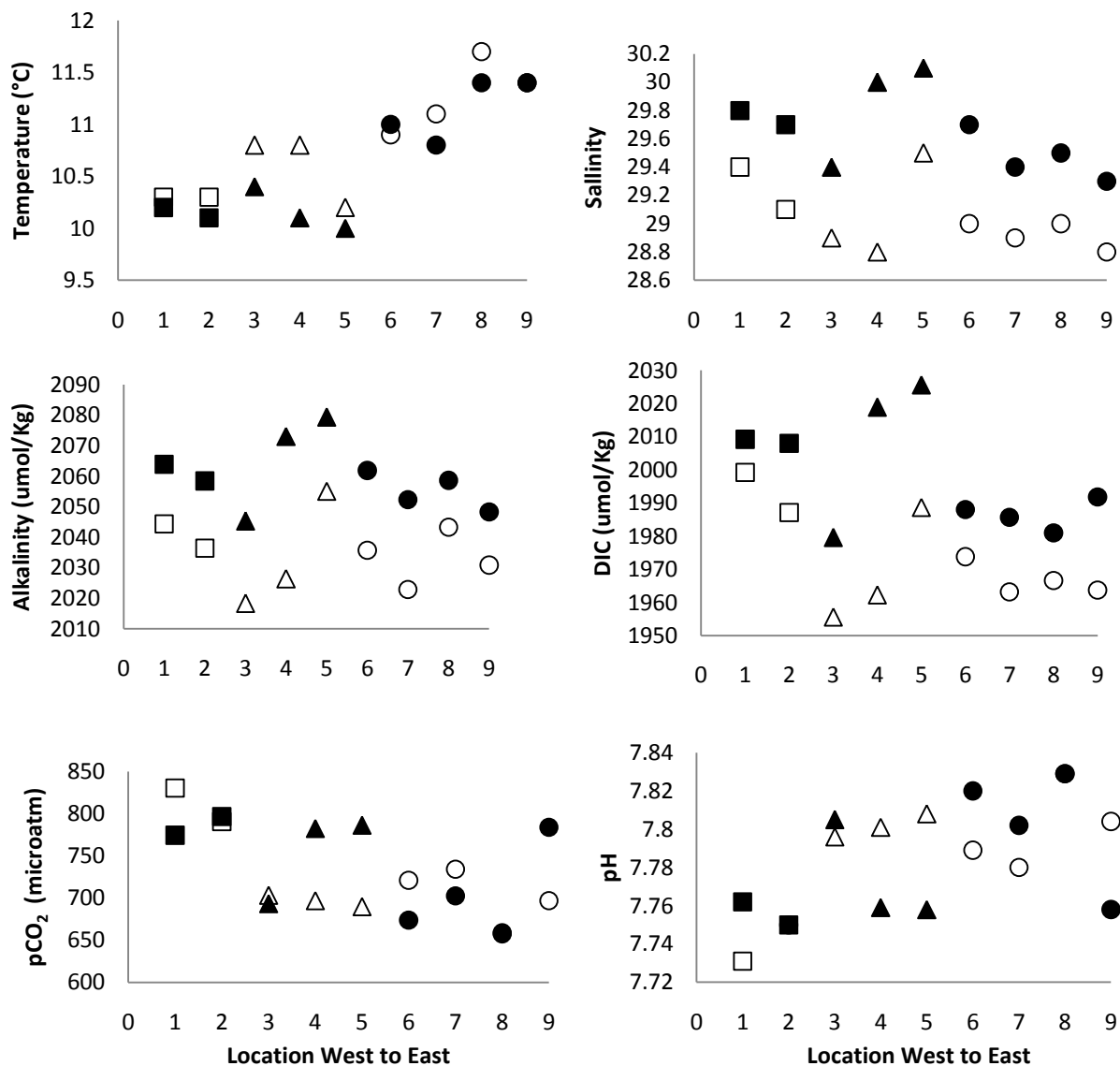


Figure 3. Variation through space and between days 3 (open shape) and 4 (shaded shape), beginning with the western most site – Kellett Bluff (1) – and ending with the northern most location within East Sound (9). These sites are then further grouped by geographical location: West side (square), San Juan Channel (triangle) and East Sound (circle).

Table 3. Change between days 3 and 4. All values are averages of the grouped sites. For all parameters, SJC showed the greatest change between those days.

	Salinity	TA	DIC	T (C)	pH	pCO ₂	Ω _{ca}	Ω _{ar}
West	0.5	20.74	15.45	-0.15	0.016	-25.014	0.064	0.042
SJC	0.767	32.657	39.167	-0.433	-0.028	57.463	-0.069	-0.041
East	0.55	22.083	19.8	-0.125	0.002	2.305	0.033	0.022

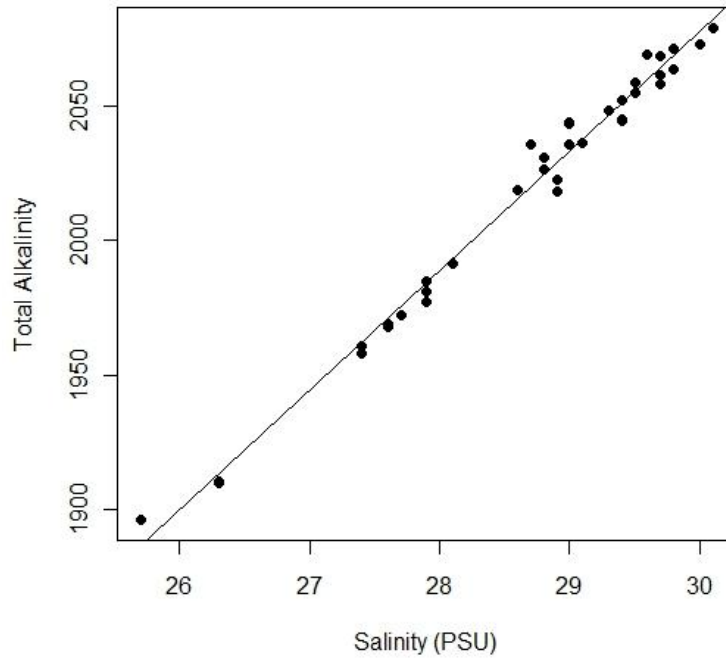


Figure 5. Measured Total Alkalinity ($\mu\text{mol kg}^{-1}$ seawater) and Salinity. All salinity measurements that were analyzed for total alkalinity were plotted. $R^2 = 0.9862$

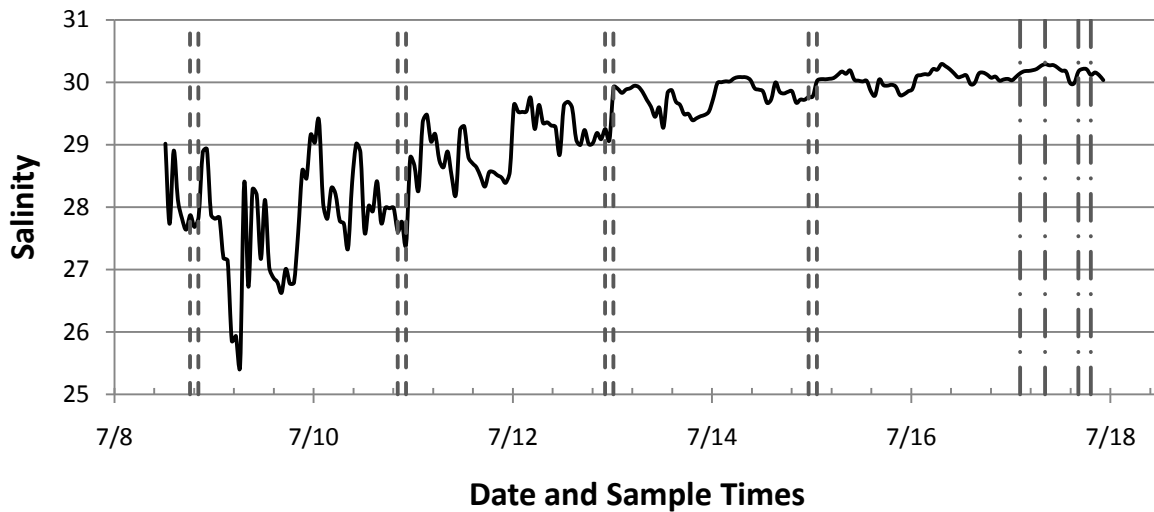


Figure 6. Measured salinity from the FHL weather station. The sample times are indicated by double, vertical, dashed lines.

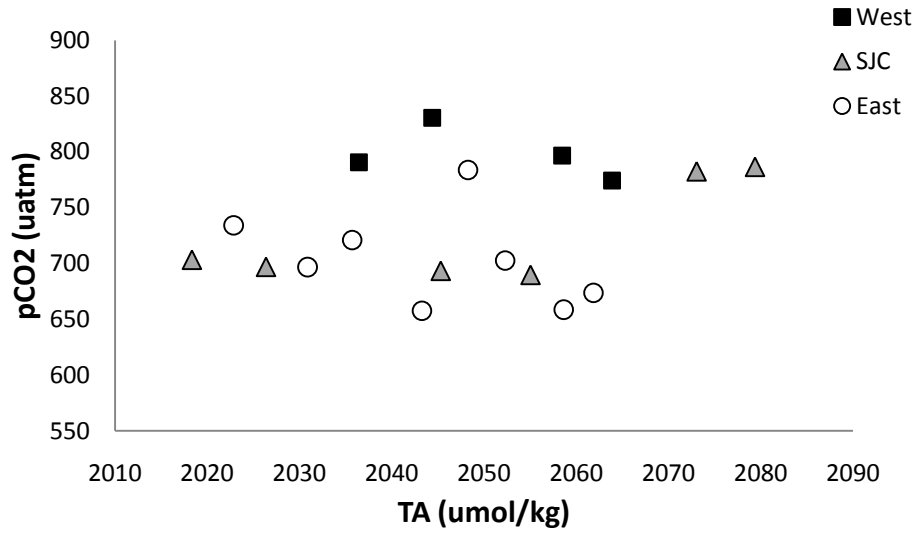


Figure 7. Relationship between measured TA and calculated pCO₂. The lack of correlation indicates that variation in pCO₂ cannot be explained by total alkalinity.

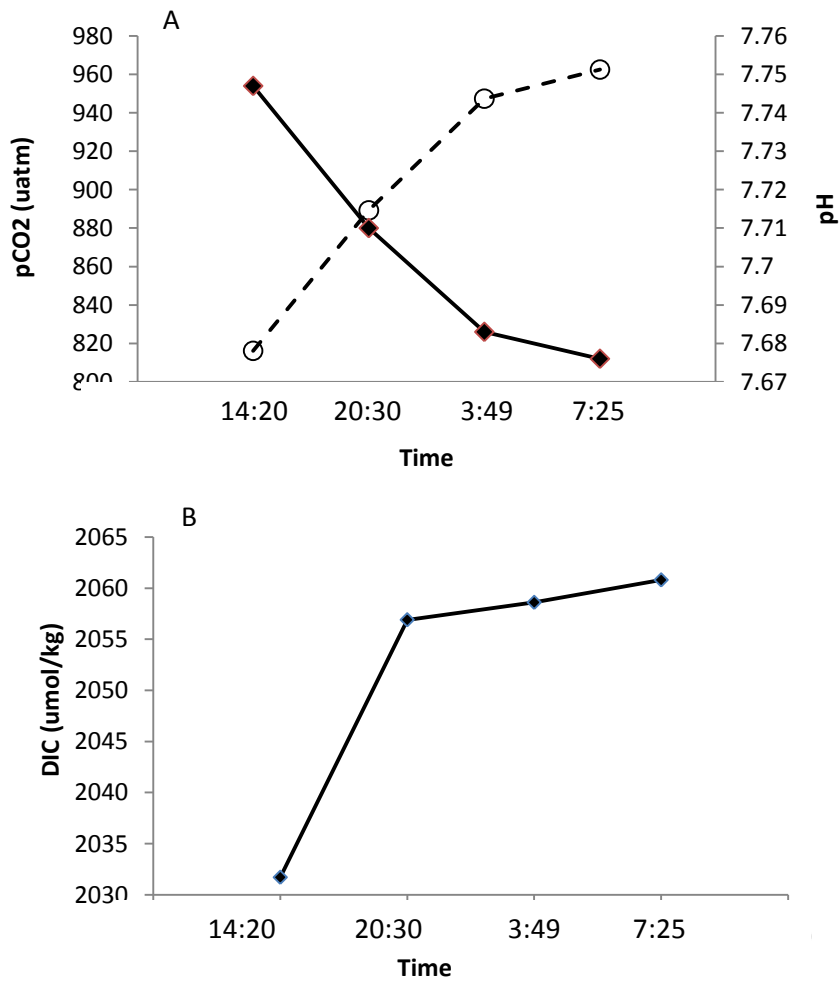


Figure 8. Variation in pCO₂ and pH (A) and DIC (B) over one tidal cycle, from the afternoon of July 17th to the morning of July 18th.