Variation in Carbonate Chemistry throughout the San Juan Archipelago

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Abstract

Due to the dynamic nature of the water masses in the San Juan archipelago, the carbonate chemistry has not yet been well defined in space and time. For this short-term study during a neap to spring tidal cycle in mid July 2011, we analyzed water samples as far west as Kellett Bluff and as far east as East Sound for dissolved inorganic carbon (DIC), total alkalinity (TA), temperature, and salinity at depths of 10 meters. As expected, we found variability across space and time that may be in part explained by a freshwater signal from the Fraser River, differences in flow and flushing rates, the physical geography and the resultant estuarine and ocean circulation. With continued and more expansive sampling, this data will have pertinence for the larger and future dialogue about ocean acidification in coastal environments.

Keywords: carbonate chemistry, East Sound, Haro Strait, ocean acidification San Juan Channel

Introduction

With this preliminary study, we aim to initiate a long-term sampling program of the water chemistry of different sites within the San Juan archipelago. In order to accurately and robustly characterize the carbonate chemistry of these water masses, we analyzed water samples as far west as Kellett bluff and as far east as East Sound for dissolved inorganic carbon (DIC) and total alkalinity (TA) and used CO_2calc to calculate pH and pCO_2 (Robbins *et al.* 2010). We hypothesized that due to the predicted variable rates of flushing, physical mixing, and retention at our selected sites, the carbonate chemistry parameters would vary significantly in space and time over our chosen neap-spring tidal sampling regime. We suspected that flushing would cause more variability in the high flow areas, such as our western locations in Haro Strait and San Juan Channel locations as opposed to our East Sound sites which are typically more retentive.

The San Juan archipelago is forced oceanographically by the eastern Strait of Juan de Fuca and the southern Strait of Georgia and is bounded by Haro Strait and Rosario Strait to the west and east, respectively (Klinger *et al.* 2006). The circulation of the interior waters of the archipelago is influenced by sills and freshwater discharge which is the abundant in May and June (Klinger *et al.* 2006). This region is influenced by variable rates of flushing and retention, strong tidal currents that drive strong vertical mixing, and freshwater inputs, predominantly from the Fraser River. For example, Haro Strait is bounded by regions of intense mixing which result in strong tidal currents (Griffin & LeBlond 1990).

The Strait of Juan de Fuca is the main linkage between the Pacific Ocean and the Puget Sound-Georgia Basin System with flow at the surface reflecting river-influenced outflow and flow at depth reflecting ocean influenced inflow (Thomson 1994). Variation in the characteristics of these water masses could be characterized by off-shore oceanic signals or estuarine signals (Newton *et al.* 2003). Given this unique and complex oceanographic setting, the carbonate chemistry parameters the of the San Juan Islands have not been thoroughly and consistently characterized, yet such work will be increasingly relevant for future ocean acidification research in dynamic coastal ecosystems.

Methods

Environmental sampling procedure

We sampled over approximately the neap tide (July 8) to spring tide (July 14) 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 a depth of 10 meters 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. Temperatures were taken as the sample water was overflowing from the glass bottles. To ensure the most precise 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. 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 (Table 1). 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 a 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 (Dickson *et al.* 2007), 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 slack low tide (2:20 PM), and sampled again at the slack high (8:30 PM), slack low (3:49 AM), and slack high (7:25 AM) (Table 2).

Data measurement and Analysis

DIC and TA were analyzed following Dickson *et al.* 2007 in the analytical chemistry laboratory at Friday Harbor Laboratories. These two parameters were chosen because there is less room for operator error and while measurements of pH can be precise, they are not as accurate and reliable. Descriptive figures and tables were created to highlight any trends or deviations in space and time.

Results

Our results for sites 1 (Kellett Bluff/Haro Strait), 4 (San Juan Channel), and 9 (East Sound) over the sampling period converge for TA, DIC, and salinity (Fig. 1). Total alkalinity approximately tracks the salinity data with East Sound showing the most consistency over the sampling period and San Juan Channel showing the most variability. As expected, the pH trend is inversely related to the calculated pCO_2 data, and the temperature data stays relatively constant expect for a large spike on day two in East Sound. Over the sampling period, pCO_2 and DIC generally increases at the three sites, TA and salinity increase at sites 1 and 4, and pH decreases at the three sites and converges at a similar value (Fig. 1). pCO_2 is very variable throughout time especially at sites 1 and 9 and the minimum and maximum values seen at any site span from about 400 to slightly greater than 800 μatm. The salinity data in the San Juan Channel (site 4) on the first day of sampling is the lowest of all sites. However this low salinity seen particularly at site 4, but also somewhat exhibited at site 1, aligns with data from the Friday Harbor Laboratories weather station (Fig. 11). Based on this weather station data and historical salinity trends, we began sampling during a period of unusually low salinity.

With our expanded spatial data on sampling days three and four, we roughly grouped sites by 'West' (sites 1-2), 'San Juan Channel' (sites 3-5) and 'East' (sites 6-9) to more clearly see trends due to the physical environment. Figs. 3-5 illustrate how DIC, TA and pCO_2 change within our general geographical grouping over sampling days three to four across all nine sites. The DIC and TA values are higher across all sites on day four than day three, yet in variable magnitudes. Our sites within and near East Sound (sites 6-9) have a relatively constant DIC during each sampling day. It is important to note that since we sampled as close as possible to the low slack tide each day, we were sampling almost an hour later on day four than day three and yet DIC is higher on day four. The calculated pCO_2 shows more anomalous values over sampling days three and four, with neither consistently higher or lower values from day three to four (Fig. 5).

Our alkalinity and salinity data from all sites on the four sampling days has a tight linear fit (Fig. 6). This strong relationship provides support for a salinity-TA proxy that could be used in the San Juan archipelago. A similar plot, instead with pCO_2 plotted against TA, shows a less clear relationship between these two carbonate chemistry parameters (Fig. 7). Our salinity and alkalinity over the tidal cycle (2:20PM-7:30AM) sampling similarly align (Fig. 10). In addition, during the tidal cycle, pH and pCO_2 change approximately inversely to one another with pCO_2 reaching its maximum (~960 μatm) during the last sampling point, 7:30 AM, and pH, therefore, having the lowest value at this time (Fig. 8). Somewhat similarly to pCO_2, DIC increases throughout time, but not as linearly as pCO_2 (Fig. 9).

Discussion

As expected, the carbonate chemistry of the San Juan archipelago is highly variable in space and time, but the degree of variability which we thought would align with those predicted retentive and advective sites was not clearly exhibited. San Juan Channel appeared to be the most variable during this time frame, particularly for salinity and TA, and there was not as distinct a difference in variability between the westernmost sites and East Sound as expected (Fig. 1).

In addition to these spatial characteristics, we also saw that carbonate parameters across sites converged throughout the neap-spring tidal cycle. Nearly two decades of salinity data provided by Griffin & LeBlond 1990 reveal that seaward freshwater export is greatest during neap tides. Our salinity data and the data from the FHL weather station support this theory (Figs. 1 and 11) and further show how this area is greatly dominated by estuarine circulation and discharge from the Fraser River. While little conclusions can be made with our data, the carbonate chemistry parameters converged more with the advent of the spring tide on July 14. The high exchange rates characteristic of a spring tide (Figs. 12 and 13) indicate that the various water masses throughout the archipelago may get more well mixed with this strong ebb and flood of the tides, and therefore that freshwater export during a spring tide may be dispersed more evenly and quickly.

While our main motivation was to highlight the variations in the regional carbonate chemistry with respect to differences in flow rates that are attributable to the unique physical geography, biology plays a strong role in coastal waters and it is important to identify and tease apart these biological and physical drivers. For instance, though TA followed the fluctuations in salinity almost exactly (Fig. 6), pCO_2 did not linearly increase with TA (Fig. 7) indicating that variability in pCO_2 is driven not only by the physical cycling of water masses, but also likely by a biological signal. This is also shown in our tidal cycle data in which *p*CO2 increases linearly throughout the cycle while TA roughly follows the salinity trajectory indicating there is likely a dominant diurnal signal in photosynthesis and respiration (Figs. 8 and 10).

Clearly, the San Juan archipelago is a very crucial place to study in the larger context of ocean acidification research and in part because in this ecosystem, we fail to see those ambient conditions (~380 μatm) that are often used as a baseline in ocean acidification manipulations. In addition to being higher than what is typically defined as 'ambient', our pCO_2 data oscillated across the nine sites and sampling days three and four (Fig. 5). This oscillation may be explained by the fact that pCO_2 of the water is higher than the ambient air, establishing a strong gradient for exchange. Such questions and anomalies in this preliminary dataset need to be explored with more long-term sampling and sampling at various temporal and spatial scales. Although challenging to study and confidently characterize, the San Juan archipelago is an ideal place to investigate the effects of ocean acidification in conjunction with other stressors and external pressures that typically dominate coastal environments (Johannessen & Macdonald 2009).

Acknowledgements

Many thanks to Dr. Andrew Dickson, Dr. Moose O'Donnell and Dr. Terrie Klinger for their thoughtful insight and patience. Thanks to Emma Timmins-Schiffman for her dedication, the OA class for being an amazing support group, and the rest of the FHL community.

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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).

Site	Location	Date	North coordinates	West coordinates	Collection time	Low slack at nearest current buoy
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	San Juan Channel	07/09/11	48 35.043	123 02.158	7:12 AM	6:56 AM (SP)
4-B	San Juan Channel	07/09/11	48 34.961	123 02.247	7:00 AM	6:56 AM (SP)
4-C	San Juan Channel	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)
4-A	San Juan Channel	07/11/11	48 35.186	123 02.303	8:44 AM	8:46 AM (SP)
4-B	San Juan Channel	07/11/11	48 35.004	123 02.231	8:36 AM	8:46 AM (SP)
4-C	San Juan Channel	07/11/11	48 34.917	123 02.183	8:29 AM	8:46 AM (SP)
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)
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	SJ Channel @ FHL	07/13/11	48 32.819	122 59.277	11:22 AM	11:37 AM (TR)
4	SJ Channel	07/13/11	48 35.053	123 02.314	10:16 AM	10:23 AM (SP)
3	SJ Channel 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	SJ Channel @ FHL	07/15/11	48 32.777	122 59.362	N/A	1:01 PM (TR)
4	SJ Channel	07/15/11	48 35.048	123 02.170	11:28 AM	11:45 AM (SP)
3	SJ Channel 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. 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, in this case, Turn Rock (source: Mr. Tides 3).

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

Figure 1. Map of the San Juan archipelago and our sampling locations. Outlined shapes indicate sites (1,4,9) that were sampled at all four time points and had three replicates on day 1 and 2. Similar shapes (square, triangle, circle) for sites indicate general groupings based upon similar geographical location.

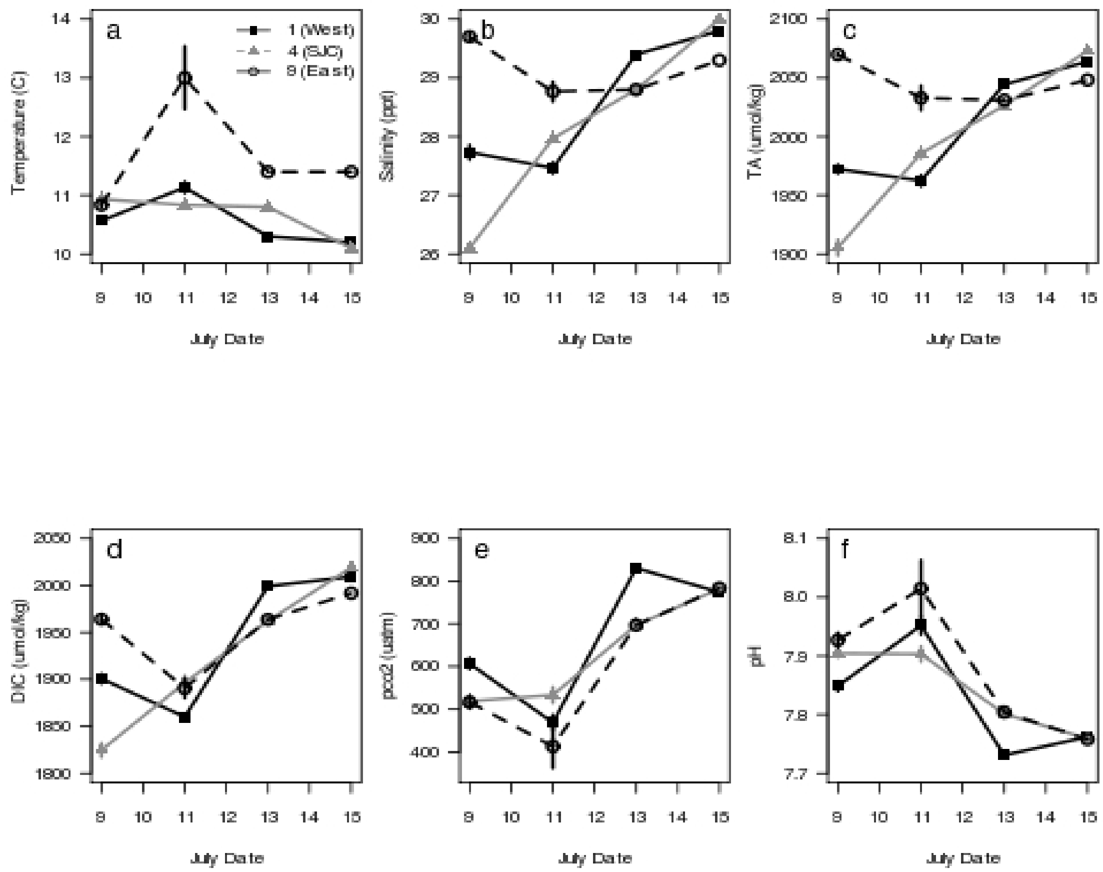

Figure 2. Plot of temperature, salinity, TA, DIC, pCO_2, pH for for sample sites 1 (Kellett Bluff), 4 (San Juan Channel), 9 (East Sound) over the neap-spring sampling. For the four time points, three replicates were taken at sites 1, 4, and 9 for sampling day 1 (July 9) and day 2 (July 11) while only one replicate was taken at those same sites for day 3 (July 13) and day 4 (July 15). Solid black line represented site 1 (Kellett Bluff), gray line represents site 4 (San Juan Channel), and dashed line represents site 9 (East Sound). The average of the replicates were plotted with +/-1 standard deviation.

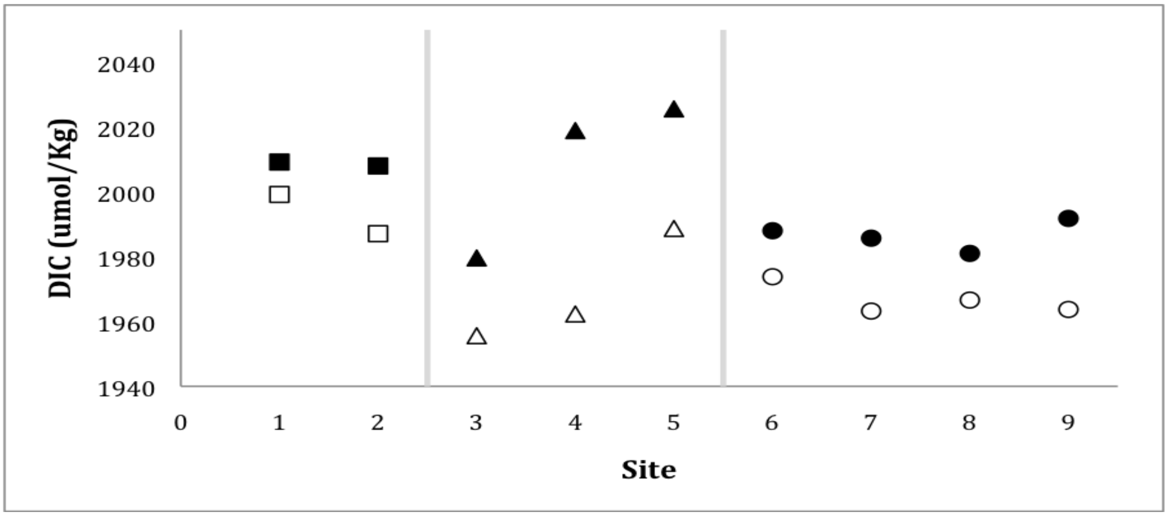

Figure 3. DIC values from sampling day 3 (July 13) and day 4 (July 15). White symbols represent day 3 values and black symbols represent day 4 data, while gray lines represent our general grouping of similar geographical sites. Sites 1-2, represented by squares, are the western most sites, sites 3-5, represented by triangles, are our sites within the San Juan Channel, and sites 6-9, represented by circles, are our eastern most sites.

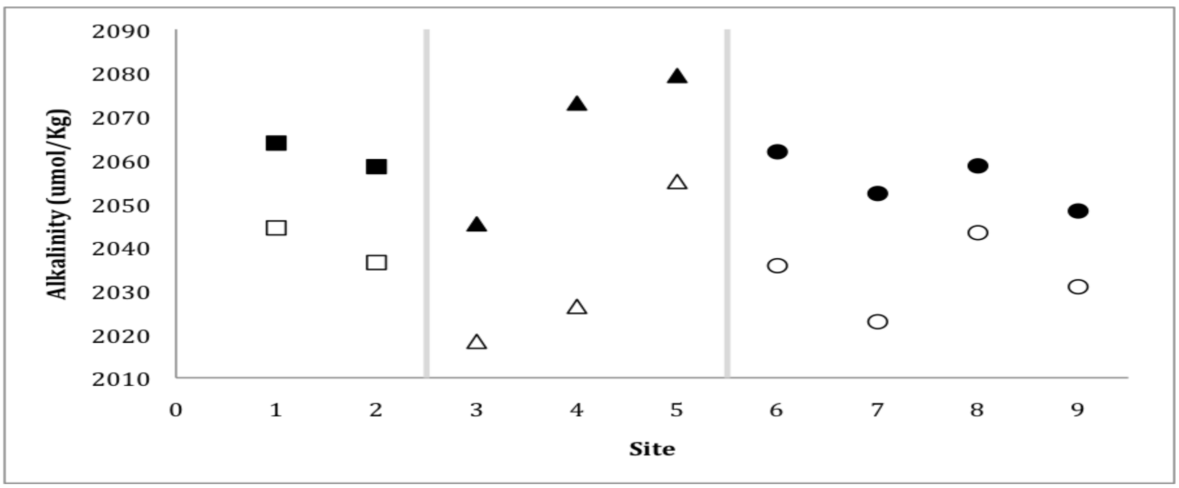

Figure 4. TA values from sampling day 3 (July 13) and day 4 (July 15). White symbols represent day 3 values and black symbols represent day 4 data, while gray lines represent our general grouping of similar geographical sites. Sites 1-2, represented by squares, are the western most sites, sites 3-5, represented by triangles, are our sites within the San Juan Channel, and sites 6-9, represented by circles, are our eastern most sites.

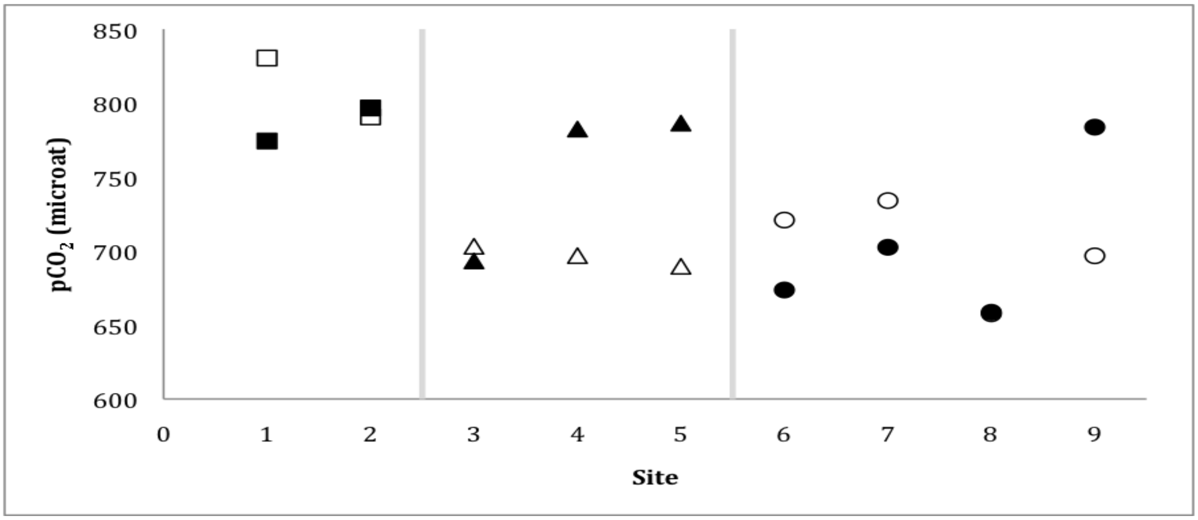

Figure 5. pCO_2 values from sampling day 3 (July 13) and day 4 (July 15). White symbols represent day 3 values and black symbols represent day 4 data, while gray lines represent our general grouping of similar geographical sites. Sites 1-2, represented by squares, are the western most sites, sites 3-5, represented by triangles, are our sites within the San Juan Channel, and sites 6-9, represented by circles, are our eastern most sites.

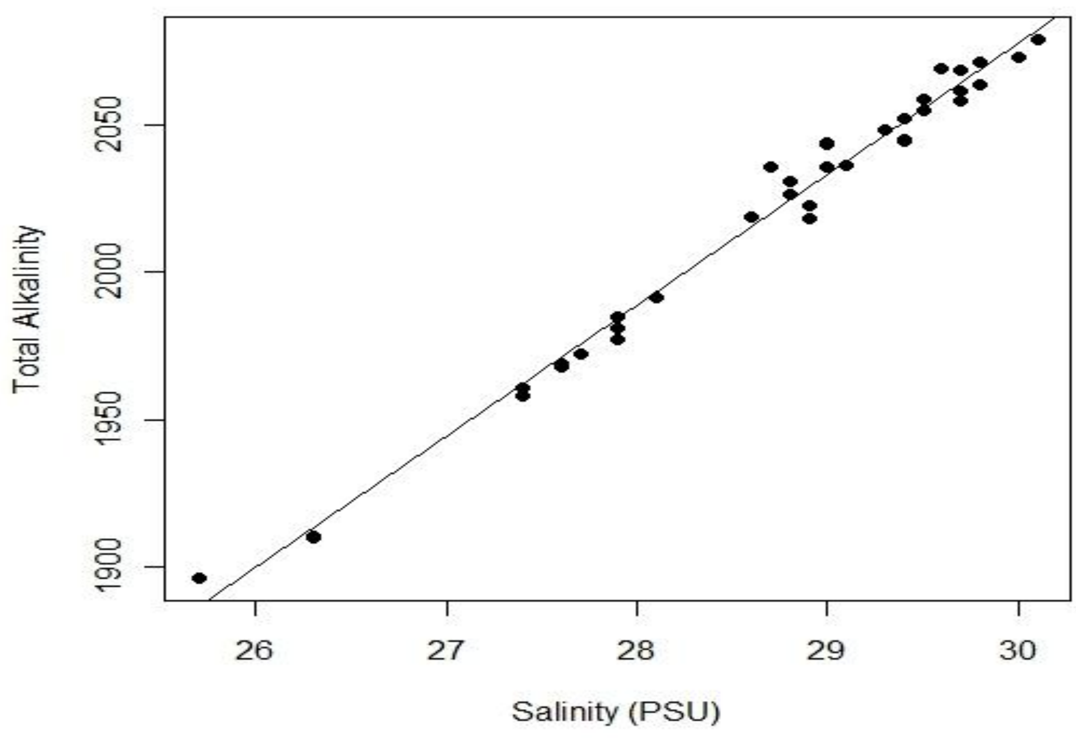

Figure 6. Plot of the linear relationship between total alkalinity (TA) and salinity for all water samples collected during the four sampling days (July 9, 11, 13, and 15).

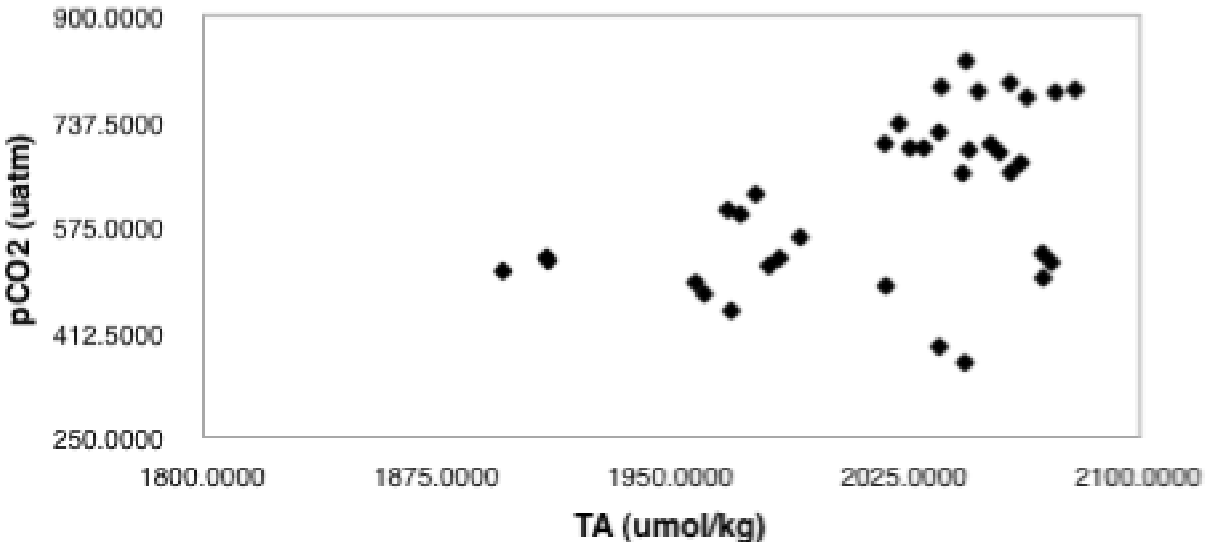

Figure 7. Relationship of pCO_2 and TA for all samples collected during the four sampling days.

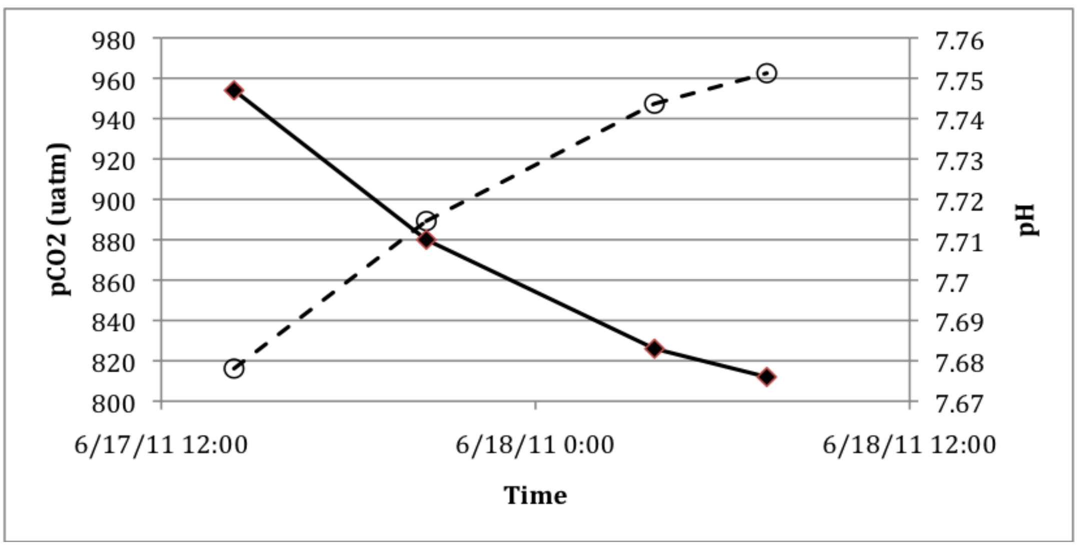

Figure 8. Trend of pCO_2 and pH in the San Juan Channel near Friday Harbor Laboratories over a tidal cycle (July 17-18). pCO_2 is represented by the dashed line while pH is represented by the black solid line.

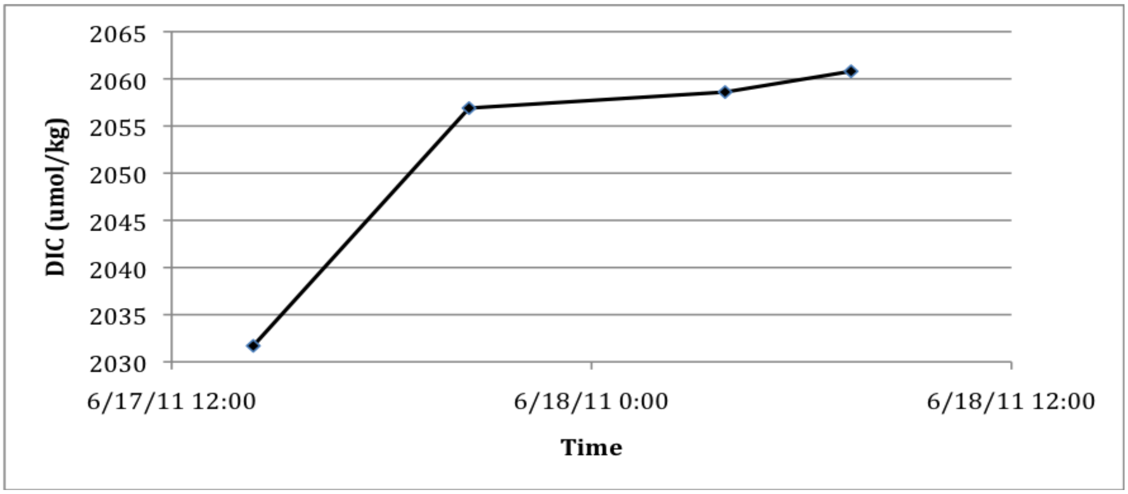

Figure 9. Trend of DIC in the San Juan Channel near Friday Harbor Laboratories over a tidal cycle (July 17-18). DIC is represented by the black solid line.

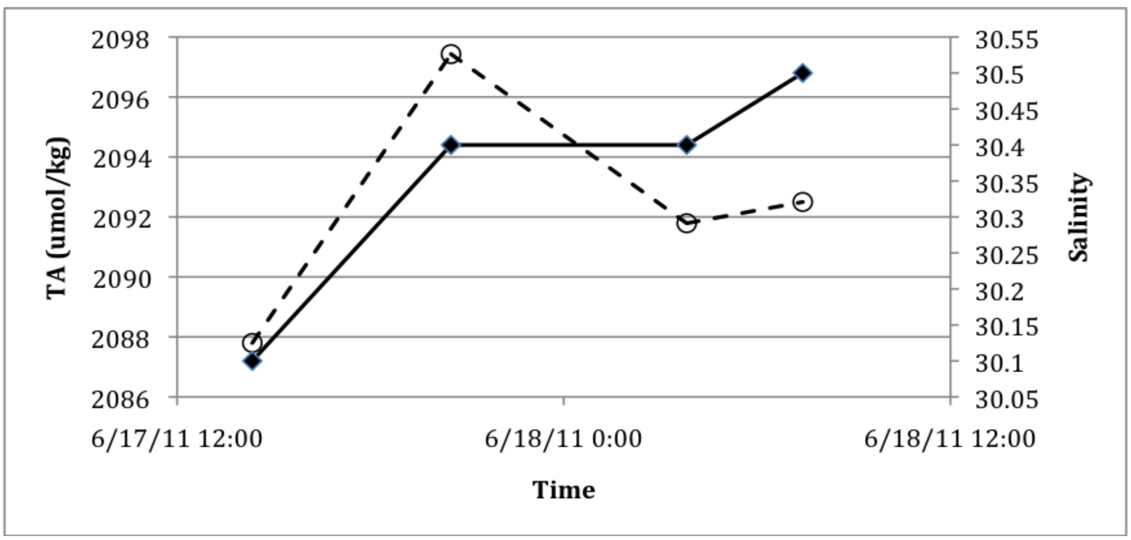

Figure 10. Trend of TA and Salinity in the San Juan Channel near Friday Harbor Laboratories over a tidal cycle (July 17-18). TA is represented by the dashed line and salinity is represented by the solid black line.

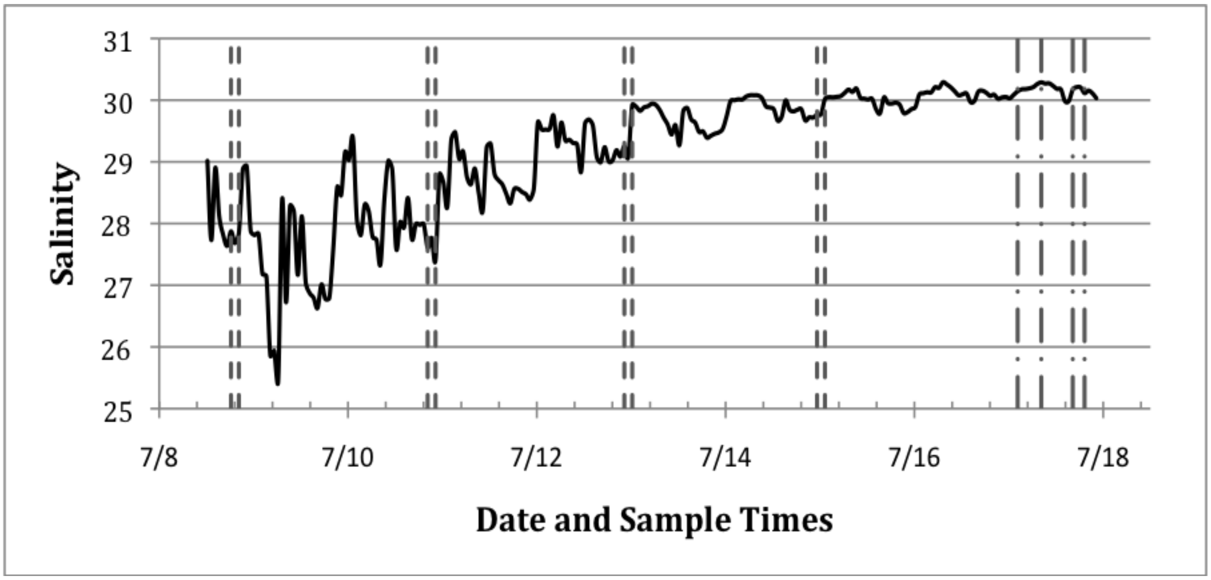

Figure 11. Salinity data from the Friday Harbor Laboratory weather station over our sampling period (July 8-July 18). Dashed lines on July 9, 11, 13, and 15 show our approximately two-hour sampling window, while dashed and dotted lines show our sampling points of the tidal cycle in San Juan Channel near FHL (source: http://depts.washington.edu/fhl/fhl_wx.html).

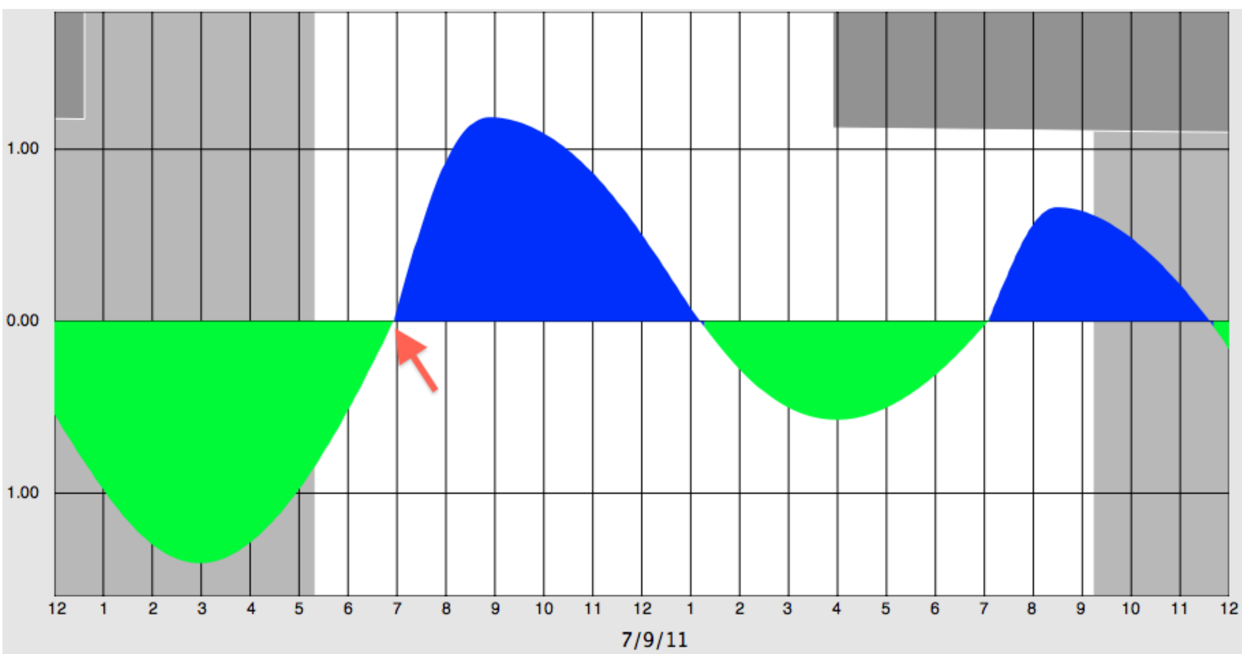

Figure 12. Low slack tide as indicated by the red arrow from the Spring Passage current buoy on the first day of sampling, July 9, 2011. The neap tide was on July 8, 2011. Source: Mr. Tides

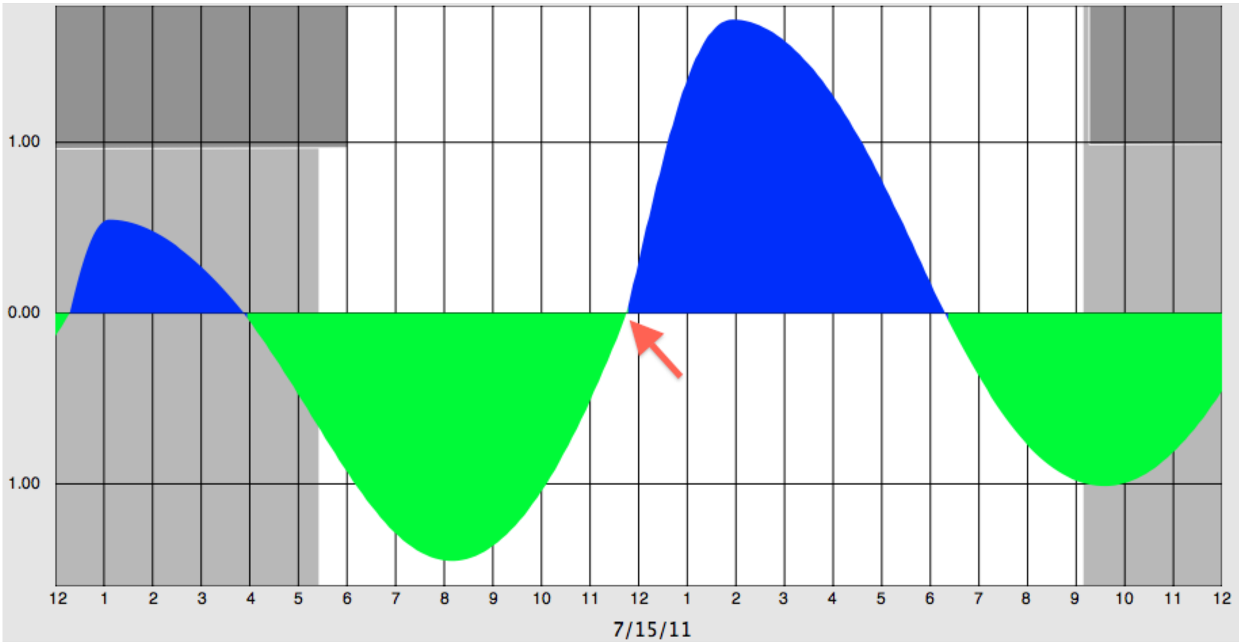

Figure 13. Low slack tide as indicated by the red arrow from the Spring Passage current buoy on the last day of sampling, July 15, 2011. The spring tide was on July 14, 2011. Source: Mr. Tides