Variation of environmental forcings and the potential for changes in carbonate chemistry of the San Juan Archipelago

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Abstract

The carbonate chemistry of the San Juan Archipelago is extremely varied between regions of low to high tidal flushing. Salinity seems to be a driving parameter of the carbonate system through its effects on alkalinity. Freshwater from the Fraser River may control the environmental characteristics of water moving through the archipelago. In areas of low flushing, biological effects may strongly influence the carbonate chemistry. The effects of upwelling, especially on the west side are understudied. Overall, the water of the different sounds, channels, and straits of the islands are exchanged and equilibrated by mixing during strong spring tides. It is important to understand the interplay between environmental and biological controllers of carbonate chemistry to interpret changes that may be observed with the advent of ocean acidification.

Keywords: San Juan Archipelago, Ocean Acidification, carbonate chemistry, tides

Introduction

The goal of this study was to characterize three major water masses of the San Juan Archipelago for carbonate parameters including total alkalinity, dissolved inorganic carbon, pCO_2 and pH as well as temperature and salinity. These parameters can be used to calculate the saturation state of the mineral calcium carbonate which is essential for biomineralization. Anthropogenic forcings are rapidly changing our environment through processes such as global warming and ocean acidification. It is important to describe and understand modern marine environments so we can detect the changes that are developing in the deep ocean and in coastal systems. The San Juan Archipelago is an interesting study site because of the variety of oceanic and fresh water inputs and the island geography which creates different flow regimes amongst the islands (Klinger and Ebbesmeyer 2001, Figure 1). We hypothesize that there will be differences in water chemistry around the archipelago based on the differential amount of flushing that enclosed embayments and open straits receive. Open straits are expected to be influenced by the exchange of oceanic and riverine water masses while the chemistry of sounds will be controlled more by the effects of biological activity. Throughout the tidal cycle, from neap to spring, we hypothesize that there will be increased flushing and a convergence of chemistry among sites. Oceanographically the San Juan Archipelago is understudied, not much is known about the velocity and magnitude of currents or the degree of mixing between and within different water masses. Drift card studies and ocean cruise time series have begun to describe the interconnectivity of bays and straits as well as oceanography parameters such as salinity, temperature and density throughout seasons and time (Klinger and Ebbesmeyer 2001, PRSIM cruises) This study is the first attempt to describe the variation of carbonate chemistry in both time and space around the island chain. This pilot study will serve to direct future research on ocean acidification and its potential effects on the chemistry of the San Juan Archipelago.

Methods

We sampled over the neap to spring tide in order to capture any variation in chemistry resulting from a change in the magnitude of tidal flushing. Water samples were collected every other day at low slack tide which facilitated sampling under calm current conditions. Sampling times were correlated to the predicted tides given by the nearest current buoys (Table 1). Sampling began on July 9, 2011 on a neap tide and ended on July 15, 2011 on a spring tide (Figure 2). Samples were collected from a Niskin at 10 meter depth, in order to reach below the picnocline. Schott Duran glass bottles were rinsed three times with the same sample water from the Niskin and then poisoned with 100 μl of mercuric chloride ($HgCl_2$) immediately upon collection to stop all biological activity that might change carbonate chemistry parameters. The glass stopper was greased to form an airtight seal to prevent gas exchange. To ensure proper water sampling and collection protocol, recommended standard operating procedures (SOPs) were rigorously followed (Dickson et al. 2007).

The initial sampling sites were chosen to span three flushing rates and three types of geography: a deep, highly flushed site on the west side of the archipelago (Site 1),a narrow, moderately flushed site, in San Juan Channel (Site 4), and a shallow poorly flushed site in East Sound (Site 9) (Figure 1). On the first two days of sampling, July 9th and 11th, 2011, three replicates were taken at each of three sites; Kellett Bluff (Site 1), San Juan Channel parallel with Yellow Island (Site 4), and the head of East Sound (Site 9) (Figure 1, Table 1). On the second two days of sampling, July 13th and 15th, 2011, the study was expanded to nine total sites (Figure 1, Table 1). The number of sites were extended to better characterize the variability in carbonate chemistry within and between the three hypothesized flushing regimes. On these two days, salinity replicates were made at the original three sites to continue to capture any variance within sites.

Four samples were collected over one tidal cycle to gain an understanding of the variation in carbonate chemistry in association with high and low tides. Water samples were collected as stated above at a site parallel to the Friday Harbor Laboratories pumping and weather station at the base of the San Juan Channel. We sampled at four slack tides based on the Turn Rock tide buoy (Figure 3, Table 2)

Dissolved inorganic carbon (DIC) was analyzed using a LICOR analyzer and total alkalinity (TA) was analyzed using an open cell titration following SOP3b (Dickson et al. 2007) in the analytical chemistry laboratory at Friday Harbor Laboratories, San Juan Island, Washington. These two parameters were chosen as they are the most precise to measure within the laboratory. By measuring two parameters under known conditions of salinity, temperature, and pressure, other carbonate chemistry parameters of interest including pCO_2, pH, Ω aragonite, and Ω calcite can be calculated using the free software CO2SYS. We chose to characterize the water of the San Juan Archipelago using observed values of temperature and salinity, measured values of DIC and TA, and calculated values of pCO_2 and pH.

Results

Our first analysis looked at the variation at three sites across four days of sampling (Figure 4). Temperature showed an increase on July 11th at East Sound and Kellet Bluff (Figure 4a). Overall, East Sound is the warmest site (Figure 4a). For all sites from July 9th through 15th, salinity and TA increased and converged to a range of 29-30. There was a decrease in salinity and TA on the second sampling day, July 11th. DIC and pCO_2 show the same drop on July 11th. For each site, trends in pCO_2 and pH are inversely related (Figure 4). The pCO_2 calculated for our sites was extremely variable and surprisingly higher at 850µatm than modern ambient CO_2 values of 390ppm.

Our second analysis focused on two time points, July 13th and 15th and the variation between nine sites within the archipelago (Figures 1, 5-7). The nine sites were clustered into three groups for ease of analysis based on similarities in their carbonate chemistry. These groups are the west side (Site 1 and 2), San Juan Channel (Sites 3-5) and east side (Sites 6-9). Salinity and alkalinity for these nine sites were closely correlated (Figure 4b,c)so only the alkalinity analysis is shown (Figure 5). The west side shows an increase in alkalinity between sampling days and little variation between sites (Figure 5). There is also little variation between sites or between sampling days for DIC or pCO_2 (Figure 6,7). Compared to the other site groupings, the west side has the highest pCO2 (Figure 7). San Juan Channel sites show the greatest variation in total alkalinity and DIC in between sites and through time (Figure 5, 6). Alkalinity and DIC are higher in the southern sites and both show increases between July 13th and July 15th (Figure 5,6). On July 13th there is not a lot of variation between sites for pCO_2. On July 15th pCO_2 is higher in the two southern San Juan Channel sites, in correlation with the higher DIC observed there. The east side shows some variation across sites for alkalinity and overall an increase in alkalinity between sampling days (Figure 5). There is little variation in DIC between east side sites (Figure 6). The east side also has the lowest overall values for DIC and also low values for pCO_2 (Figure 6,7). Between July 13th and 15th DIC increases for all sites on the east side (Figure 6). pCO_2 drops for two sites closest to the mouth of the sound (Figure 7). Site 8 has the same pCO_2 for both days and site 9 at the head of East Sound shows an increase in pCO_2 (Figure 7).

To better understand the variation across time and between sites, we needed to look at some environmental changes that may be forcing the carbonate system. Due to the observed correlation between salinity and alkalinity (Figure 4b, c) we focused on salinity changes during our study interval. Salinity through the sampling period July 9th through July 15th shows a large pulse in low salinity water on the first day of sampling followed by a recovery to regularly observed conditions throughout the study period (Figure 8). A strong positive correlation between salinity and alkalinity is represented in our raw data (Figure 9). In Figure 5 and Figure 7 we observe a divergence between trends in alkalinity and trends in pCO_2. The relationship between salinity, represented by alkalinity, and pCO_2 are much more weakly correlated (Figure 10).

In our third analysis, we observed a single tidal cycle to see how carbonate parameters might vary. Over the course of the tidal cycle, which was measured from the afternoon of the first day to the morning of the second day, pCO_2 was shown to increase and pH decreased (Figure 11).

Discussion

Our first analysis across time showed an increase in water temperature that was associated with warm weather indicating that changes in air temperature may reach deep into the water column (10m). Salinity and therefore alkalinity showed an increase throughout the sampling period (Figure 4 b,c). On the second day the drop in salinity observed at most sites might be associated with a pulse of Fraser River water. This signal was also observed at the FHL weather station (Figure 8). By July 13th and 15th , all of the sites in the archipelago converged upon a more limited salinity and alkalinity range (Figure 4 b,c). This might be the result of greater tidal exchange during the spring tide and therefore greater mixing of water masses amongst all the sites (Figure 1,2). The isolation and low flushing hypothesized for the east side is called into question given the equilibration that this site experienced within the tidal cycle. The extremely high pCO_2 values are surprising given current knowledge on the dissolution dynamics of gasses between the atmosphere and ocean. We did not expect to calculate pCO_2 values so high above ambient CO_2.

In our second analysis we begin to better characterize the differences in our three flushing regimes. On the west side there is little variation between sites and across time (Figures 4-7). This might result from our hypothesized high flushing at these sites that could create well mixed water, resilient to transient changes from encroaching water masses, specifically low salinity Fraser River water. The geography of the archipelago also blocks direct flow from the Fraser River to these sites. The west side also has the highest pCO2 on both July 13th and 15th (Figure 7). Possible interpretations include a lack of primary productivity drawing down CO_2 or upwelling of CO_2 rich water. Greater study of the biology and oceanography of this area is needed before any conclusions can be drawn.

The sites in the San Juan Channel show a lot of variation and an overall an increase in DIC and pCO_2 for the southern sites (Figures 6, 7). Interestingly it seems that alkalinity and DIC are well correlated and that is reflected as well in the pCO_2 signal

(Figure 5-7). This is surprising considering alkalinity and DIC do not necessarily have to change in synchrony. We may have captured a water mass moving through the moderately flushed channel that carried a unique alkalinity and DIC signal. More data within the archipelago and more work characterizing the different oceanic and fresh water masses that influence the island chain are needed to interpret patterns in San Juan Channel circulation.

East Sound also showed some unexpected results. The water chemistry between East Sound and Harney Channel is similar (Figures 5-7). The lack of variation in carbonate chemistry for sites 7-9 could represent a lower degree of flushing with outside water masses and a greater importance of retention within the water mass itself (Figures 5-7). However, the east side sites do converge with salinity and alkalinity values for the channel and the west side signifying some mixing and interconnectivity between all sites (Griffen and LeBlond) (Figure 4). East Sound and Harney Channel show the lowest pCO_2 and a lack of correlation of alkalinity with pCO_2 suggesting that the salinity at this location is not the primary driver of the carbonate system (Figures 5, 7). This could be explained by a strong biological signal in this water mass which would draw down CO_2 through the process of photosynthesis. To answer this question, variation in carbonate parameters through cycles of respiration and photosynthesis need to be observed.

Other environmental forcings may control the changes in carbonate parameters we observed, particularly pulses of low salinity Fraser River water. The connection between salinity and alkalinity shown in Figure 4 b and c and Figure 8 support this conclusion. It seems that changes in salinity dictate the alkalinity of the San Juan Archipelago. To better correlate changes in salinity with Fraser River input, we would need to better track the movement and dispersal of these water masses as they approach the San Juan Islands. We were lucky in this study to catch an interesting and anomalous pulse of low salinity water. The recovery and equilibration of the various sites to pre-salinity pulse conditions assisted in our interpretation of interconnectivity and mixing between sounds, straits, and channels of the archipelago.

With so much variation across sites we chose to look at variation in one high to low tidal cycle. Instead of observing changes associated with high and low tides, we instead observed a cycle of respiration and photosynthesis (Figure 11). Over the course of the tide cycle, pCO_2 increased as the sun set and photosynthesis was replaced by respiration releasing CO_2 into the water column. pH showed the expected inverse trend, decreasing as pCO_2 climbed (Figure 11).

Conclusions

Through this pilot study we were able to describe some interesting changes in the carbonate system of the San Juan Archipelago over only 4 days of sampling. The Fraser River may have an important effect in controlling salinity and therefore alkalinity in the island chain. However, this signal may be overpowered in some regions by the effects of biological processes such as photosynthesis and respiration. Additionally, the geography of the islands impedes the flow of water and delays the mixing of all of the region's water bodies. As expected however, increased tidal flushing with the advent of the spring tide did function to equilibrate water characteristics among the islands. More work on upwelling, current velocity and direction, and productivity is needed at all of the sites studied to better differentiate the primary drivers of the carbonate system. More locations near the Fraser River and farther south on the west side are needed to better characterize the archipelago. We hope that our carbonate parameters, especially the pCO_2 can be used by researchers on the San Juan Islands in the field and in the lab to characterize baseline chemistry. We hope in the future, that with more time points and better parameterization, the carbonate chemistry of the San Juan Archipelago can be tracked for changes associated with anthropogenic carbon release.

Acknowledgements- Thanks to my group members in the "Retentives" for an excellent two weeks of sampling and lab time and to the orcas and pirates for keeping us on our toes. Thanks also to our instructors Dr. Andrew Dickson, Dr. Michael O'Donnell, and Dr. Terrie Klinger and teaching assistants Emma Timmins-Schiffman and Robin Elahi for ideas, logistics, and assistance with graphical analysis. Thank you to my funding source Ocean Carbon and Biogeochemistry.

Tables:

Table 1. List of sample locations and site ID (Figure 1), collection date and time, associated GPS coordinates and correlated slack current timing for sampling across the archipelago. 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 ID	Location	Date	North coordinates	West coordinates	Collection time	Low slack at nearest current buoy
9	East Sound	07/09/11	48 40.08	122 53.90	6:55 AM	7:07 AM (HC)
9	East Sound	07/09/11	48 40.02	122 53.776	7:07 AM	7:07 AM (HC)
9	East Sound	07/09/11	48 39.930	122 53.755	7:15 AM	7:07 AM (HC)
4	San Juan Channel	07/09/11	48 35.043	123 02.158	7:12 AM	6:56 AM (SP)
4	San Juan Channel	07/09/11	48 34.961	123 02.247	7:00 AM	6:56 AM (SP)
4	San Juan Channel	07/09/11	48 35.003	123 02.490	6:45 AM	6:56 AM (SP)
1	Kellett Bluff	07/09/11	48 35.164	123 12.791	8:12 AM	7:40 AM (KB)
1	Kellett Bluff	07/09/11	48 35.049	123 12.759	8:04 AM	7:40 AM (KB)
1	Kellett Bluff	07/09/11	48 34.939	123 12.732	7:55 AM	7:40 AM (KB)
9	East Sound	07/11/11	48 40.22	122 53.857	8:50 AM	8:57 AM (HC)
9	East Sound	07/11/11	48 40.56	122 53.824	9:06 AM	8:57 AM (HC)
9	East Sound	07/11/11	48 39.890	122 53.789	9:20 AM	8:57 AM (HC)
1	Kellett Bluff	07/11/11	48 35.166	123 12.658	9:32 AM	9:28 AM (KB)
1	Kellett Bluff	07/11/11	48 35.022	123 12.665	9:25 AM	9:28 AM (KB)
1	Kellett Bluff	07/11/11	48 34.951	123 12.64	9:16 AM	9:28 AM (KB)
4	San Juan Channel	07/11/11	48 35.186	123 02.303	8:44 AM	8:46 AM (SP)
4	San Juan Channel	07/11/11	48 35.004	123 02.231	8:36 AM	8:46 AM (SP)
4	San Juan Channel	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	SJ Channel @ FHL	07/13/11	48 32.819	122 59.277	11:22 AM	11:37 AM (TR)
4	San Juan 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	San Juan 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 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).

Location	Date	North coordinates	West coordinates	Collection time	Slack at nearest current buoy (Turn Rock)
Offshore of FHL Pumphouse	07/17/11	48 32.664	123 00.347	2:20 PM	2:17 PM
Offshore of FHL Pumphouse	07/17/11	N/A	N/A	8:30 PM	8:25 PM
Offshore of FHL Pumphouse	07/18/11	48 32.672	123 00.446	3:49 AM	3:44 AM
Offshore of FHL Pumphouse	07/18/11	48 32.665	123 00.454	7:25 AM	7:24 AM

Figures:

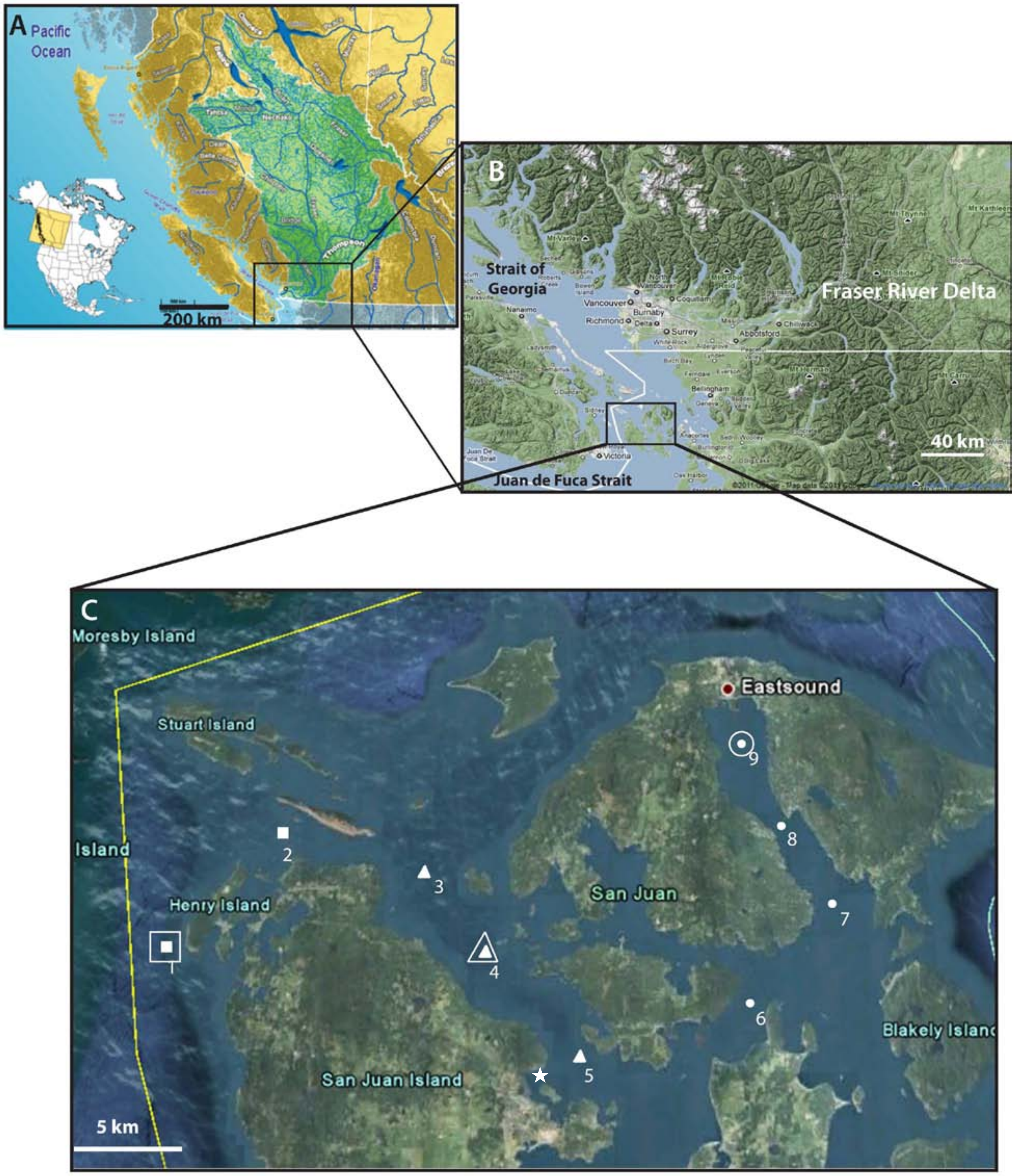

Figure 1: The location and size of the Fraser River watershed in British Columbia (A). The Fraser River Delta and its relationship to the Strait of Georgia, the Strait of Juan de

Fuca, and the San Juan Archipelago (B). Map of part of the San Juan Archipelago shows the nine sampling sites for spatial sampling (July 9th-15th 2011) and one site for tidal cycle sampling (July 17th and 18th 2011). The two western most sites (1,2) are represented by squares, three sites in the San Juan Channel (3-5) are shown as triangles, and four sites in East Sound and nearby Harney Channel (6-9) are circles. Concentric shapes represent the three sites where intra-site variance was studied. Star marks the location of the tide cycle sampling.

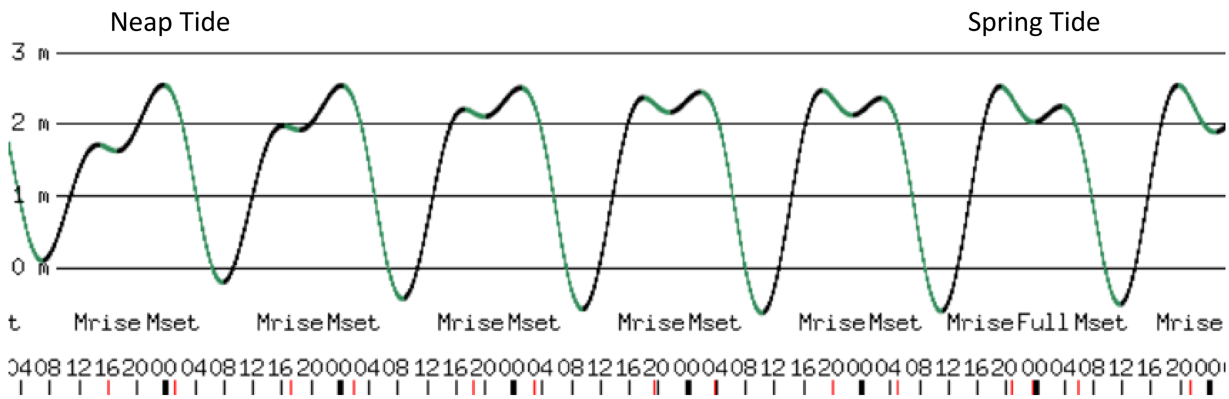

Figure2 : The tidal variation experienced on sampling days from July 9th 2011 through July 15th 2011. Source url: http://tbone.biol.sc.edu/tide/tideshow.cgi?tplotdir=horiz;type=graph;gx=640;gy=240;caltype=ndp;interval=00%3A01;glen=7;fontsize=%2B0;units=default;cleanout=1;year=2011;month=07;day=09;hour=00;min=01;tzone=local;ampm24=24;nodlines=1;notimes=1;nofill=1;colortext=black;colordatum=white;colormsl=yellow;colortics=red;colorday=white;colornight=white;colorebb=seagreen;colorflood=black;site=Friday%20Harbor%2C%20San%20Juan%20Channel%2C%20Washington%20%282%29;d_year=;d_month=Jan;d_day=01;d_hour=00;d_min=00

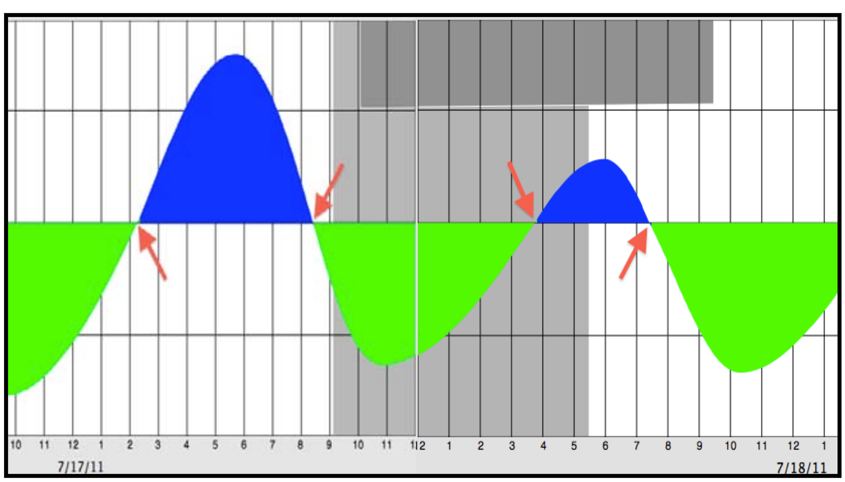

Figure 3: Tidal cycle for the 24 hour power sampling from July 17th 2011 through July 18th 2011. Red arrows indicate four slack tides that were sampled. See Table 2 for sampling and slack tide times.

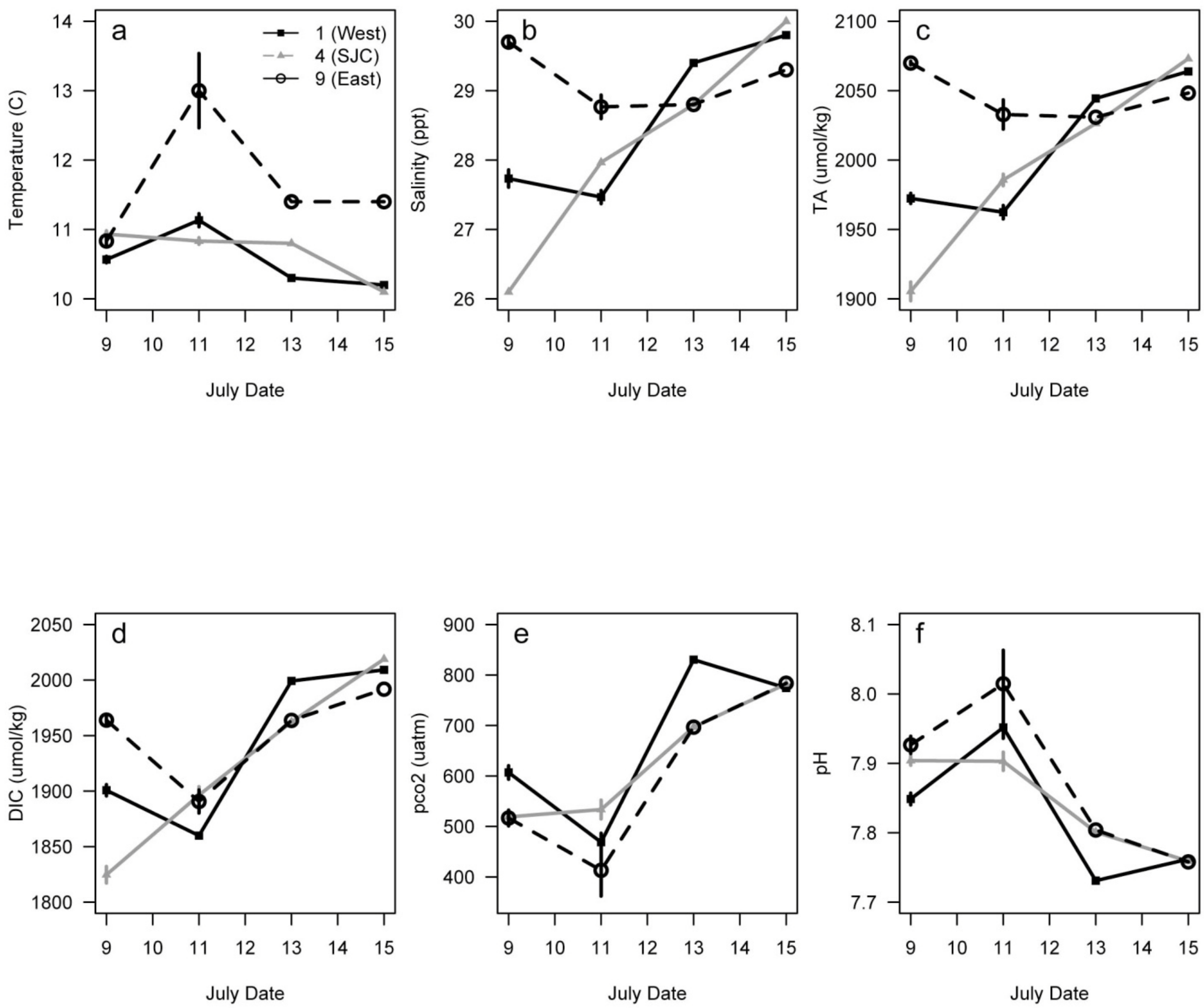

Figure 4: Shows the variation in temperature (a), salinity (b) and four of the carbonate parameters; total alkalinity (c), dissolved inorganic carbon (d), partial pressure of CO_2 (e), and pH (f). Points on July 9th and 11th represent the mean calculated value at the sampling site. Error bars represent one standard deviation from the mean. Points on July 13th and 15th represent the single sample measured from these sites. Site 1 in the west is a square connected by a black solid line, site 4 in the San Juan Channel is a triangle connected by a gray solid line, and site 9 in East Sound is a circle connected by a dashed line.

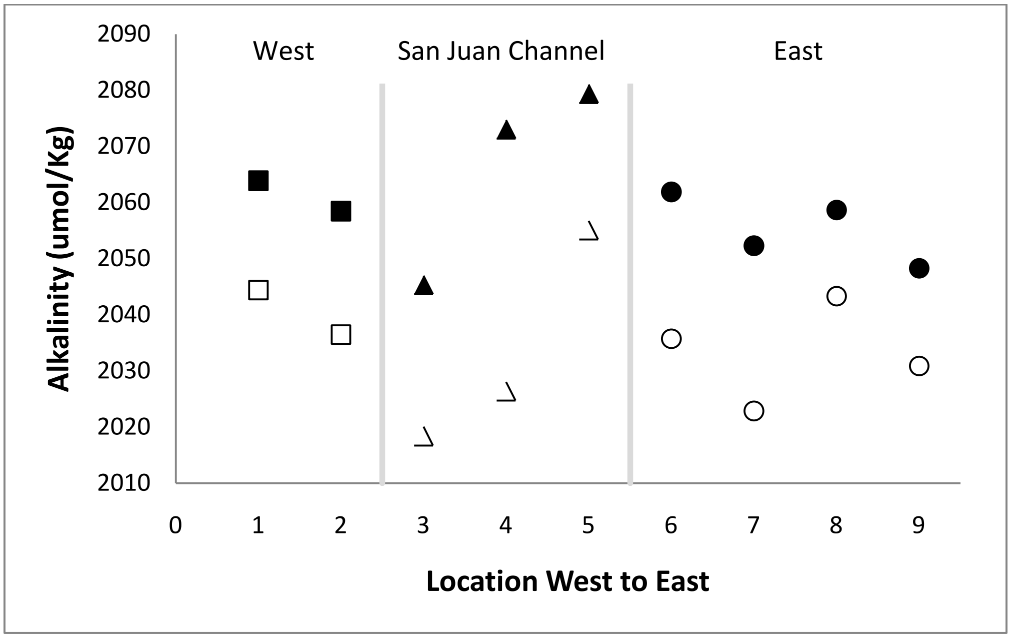

Figure 5: The variation in total alkalinity throughout the nine sampled sites (Figure 1, Table 1) over two sampling days. Sites are grouped by geographic location. The two western most sites (squares), three sites in the San Juan Channel (triangles), and four sites in East Sound and nearby Harney Channel (circles). Open circles represent samples taken on July 13th, 2011 and filled circles represent samples taken on July 15th, 2011.

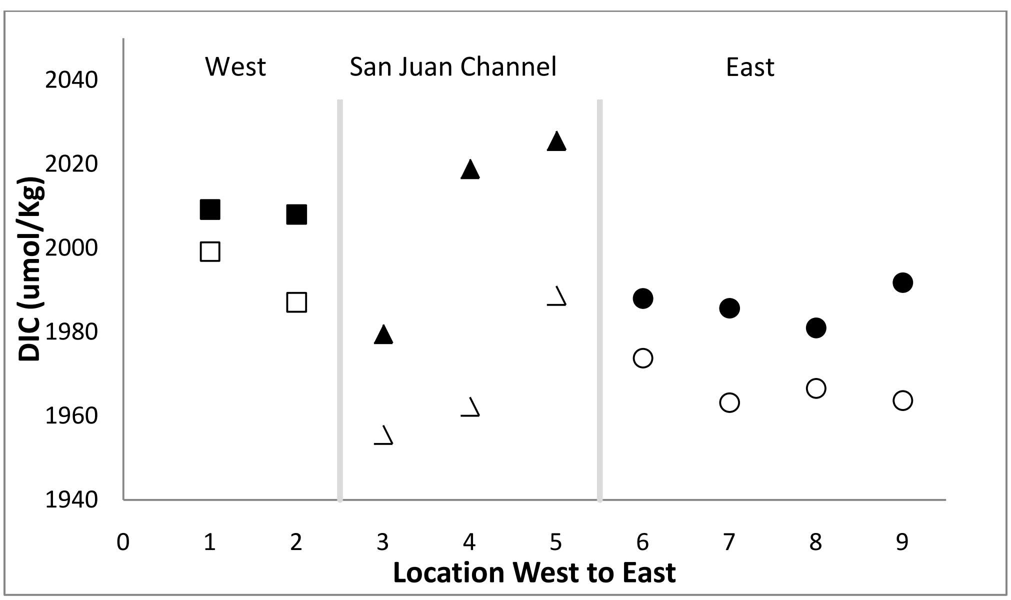

Figure 6: The variation in dissolved inorganic carbon throughout the nine sampled sites (Figure 1, Table 1) over two sampling days. Sites are grouped by geographic location. The two western most sites (squares), three sites in the San Juan Channel (triangles), and four sites in East Sound and nearby Harney Channel (circles). Open circles represent samples taken on July 13th, 2011 and filled circles represent samples taken on July 15th, 2011

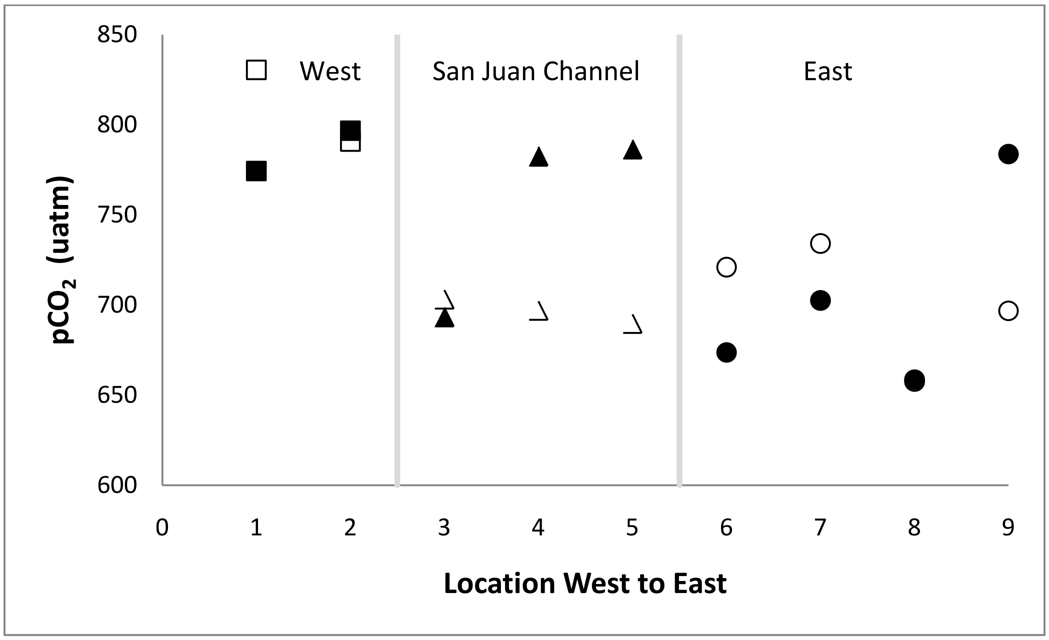

Figure 7: The variation in pCO_2 throughout the nine sampled sites (Figure 1, Table 1) over two sampling days. Sites are grouped by geographic location. The two western most sites (squares), three sites in the San Juan Channel (triangles), and four sites in East Sound and nearby Harney Channel (circles). Open circles represent samples taken on July 13th, 2011 and filled circles represent samples taken on July 15th, 2011.

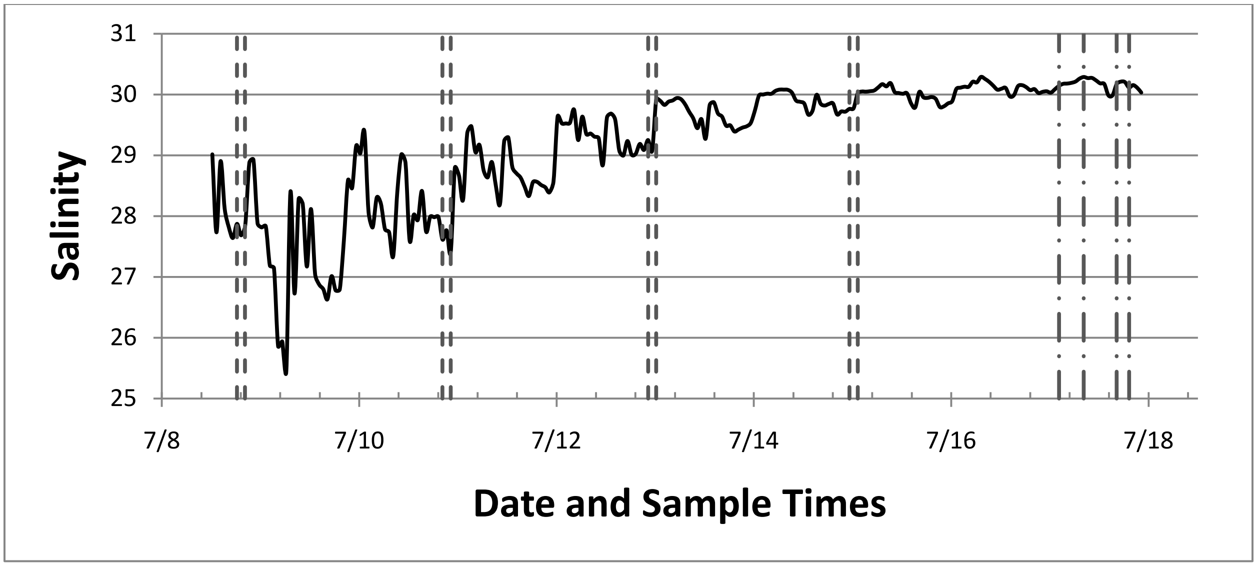

Figure 8: Salinity measured at the Friday Harbor Lab weather station across the sampling period July 8th through 16th, 2011. The four parallel pairs of vertical dashed lines represent the timing of sampling on July 9th, 11th, 13th, and 15th. The four dotted and dashed lines represent salinity during the tidal cycle from July 17th until July 18th (see below). Source: Emily Carrington, Friday Harbor Marine Lab July 2011.

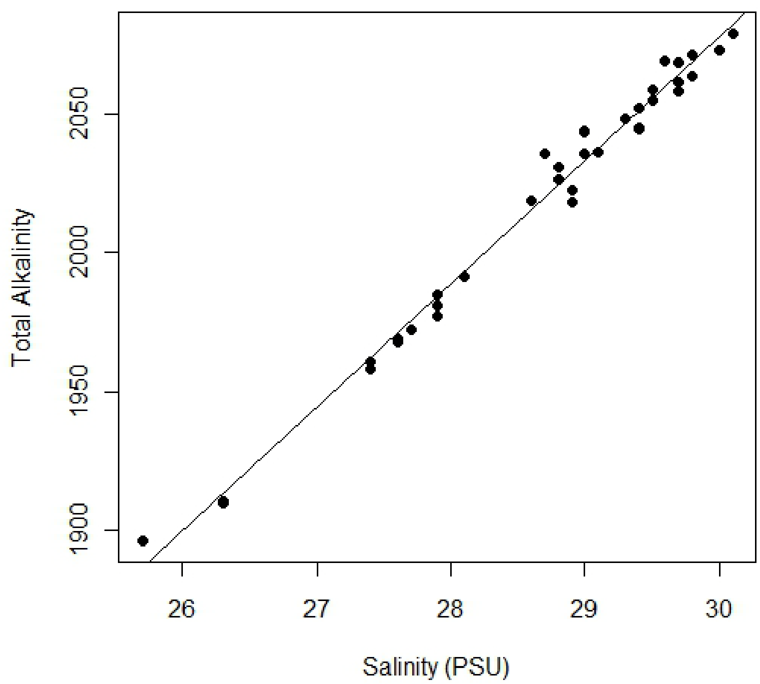

Figure 9: Shows corresponding salinity and alkalinity values for all samples measured between July 9th and July 15th, 2011. Alkalinity is in umol/kg.

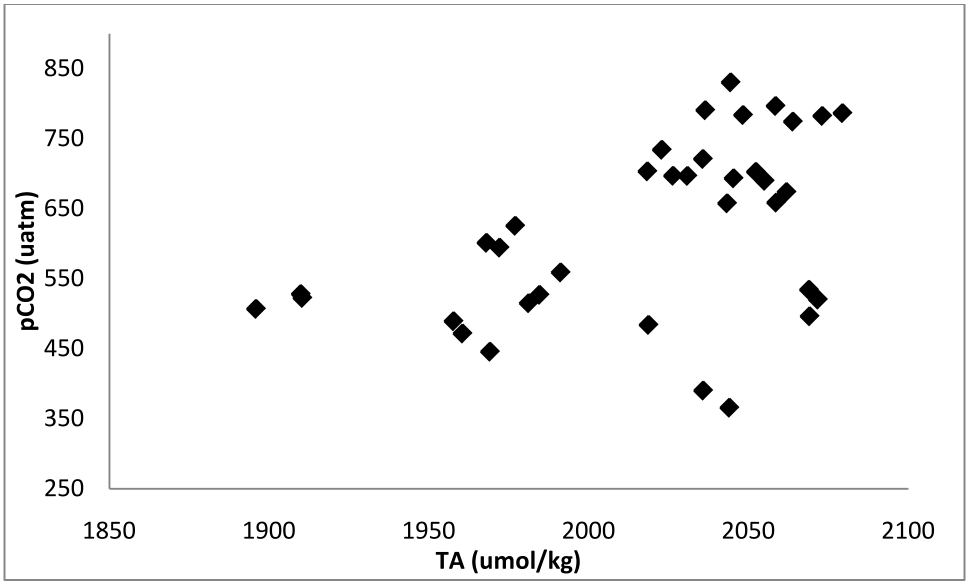

Figure 10: Shows pCO_2 and total alkalinity values for all samples measured between July 9th and 15th, 2011.

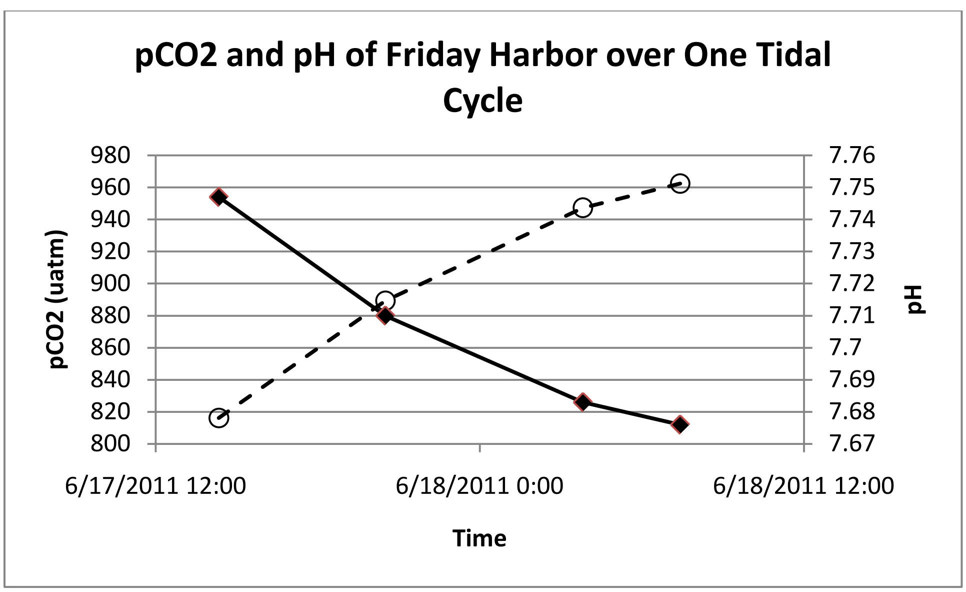

Figure 11: pCO_2 and pH over most of a tidal cycle (Figure 3) sampled at four slack tides (Table 2) from Friday Harbor (Figure 1C) from July 17th and 18th, 2011.

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