

**Carbonate chemistry of the San Juan Archipelago:
A baseline field study for future ocean acidification research**

Kirk N. Sato¹, Robin Elahi², Lydia Kapsenberg³, Jennifer C. Phillips⁴, Carlie Pietsch⁵ and
Chelsea R. Vaughn⁶

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Instructors: Dr. Moose O'Donnell² and Dr. Terrie Klinger²
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¹ Scripps Institution of Oceanography, University of California at San Diego, San Diego, CA 92093

² Friday Harbor Laboratories, University of Washington, Friday Harbor, WA 98250

³ Department of Ecology, Evolution and Marine Biology, University of California at Santa Barbara, Santa Barbara, CA 93106

⁴ Nelson Institute for Environmental Studies, University of Wisconsin at Madison, Madison, WI 53715

⁵ Department of Earth Sciences, University of Southern California, Los Angeles, CA 90089

⁶ Department of Biology, California State University North Ridge, North Ridge, CA 91330

Contact Information:

Kirk N. Sato
knsato@ucsd.edu
Scripps Institution of Oceanography
9500 Gilman Drive
La Jolla, California 92093

Abstract

Natural variability in the carbonate system is difficult to control in the lab. Furthermore, environmental carbonate chemistry data over small spatial scales is lacking. We measured discrete water samples across various flushing regimes in the San Juan Archipelago every other day during low slack tide over one neap to spring tidal transition. After analyzing these samples for temperature, salinity, total alkalinity and dissolved inorganic carbon, we plotted these variables across space and time. Our data suggest that although carbonate chemistry varies through space and time, biological processes and tidal cycles may have a significant influence on the local marine chemistry. Our study aims to inform those interested in ocean acidification research about the natural variation of various carbonate system parameters in the San Juan Archipelago.

Keywords: *acidification, carbonate chemistry, East Sound, Haro Strait, Lab 7, San Juan Channel*

Introduction

The rising concern of “ocean acidification,” defined here as the chemical perturbations in seawater due to human activities (for review, see Sabine et al. 2004), raises questions of when and where will biological organisms experience these corrosive environments (Feely et al. 2009, 2010)? Due to the alarming threat of ocean acidification on marine ecosystems, interdisciplinary teams of researchers continue to address the multiple response variables caused by these chemical changes in seawater (Gaylord et al. 2011). However, relative to the abundant number of manipulation experiments to date (Kroeker et al. 2010), there is a paucity of studies that quantify the variation of change in the environment that marine organisms experience in the field (but see Yu et al. 2011).

The complex interactions of various water masses (at the surface and at depth) within the San Juan Archipelago continue to challenge oceanographers and marine ecologists. Consisting of both oceanic water (from the Strait of Juan de Fuca and the Strait of Georgia) and freshwater input (primarily from the Fraser River, BC, Canada, but also local runoff), the upper zone of the water column throughout the San Juan Islands is difficult to characterize (Thomson 1981, Griffin and LeBlond 1990). The stratification and consequent mixing of various water masses that pass through the archipelago can be attributed to freshwater input, strong current changes, and local upwelling processes (Figure 1a; Thomson 1981, Johannessen and Macdonald 2009). Also, bathymetric features, such as depth and the location of sills can prevent deeper saline waters to reach areas within Puget Sound (Figure 1b; Thomson 1981).

While some water monitoring projects (e.g. Integrated Ocean Observing System) and research cruises (e.g. Feely et al. 2009, 2010) provide environmental data about the carbonate chemistry of surface waters and at depth, currently, no work has directly quantified the carbonate system for the San Juan Archipelago. By implementing state-of-the-art laboratory and field techniques, we measure the carbonate chemistry across various spatial and temporal scales within and around this island system. We present and analyze the first set of what we hope will become a series of data that uses the carbonate system to describe this dynamic marine environment.

In the following report, we present carbonate chemistry data from various locations at depth (10 meters) throughout the San Juan Islands over one neap-spring tidal transition period in mid-summer when freshwater runoff is particularly high (Griffin and LeBlond 1990). We hypothesize that locations shown to experience varying degrees of

retention and advection will show different carbonate chemistries. We document the change in carbonate chemistry over time and hypothesize that this change will vary with time and location. The correlation between salinity and total alkalinity (one of the critical parameters used to calculate the carbonate system; Wolf-Gladrow et al. 2007) for this particular time series was also determined for the first time.

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. Two teams of scientists departed from the Friday Harbor Laboratories (FHL, N 48.546274, W -123.013315) in motorboats and arrived at each location within 30 minutes of their respective low slack (Table 1). Proper vehicle operation training was received for all scientists prior to sampling days. Slack current times were based on buoy predictions from the Apple software, Mr. Tides. We sampled from a Niskin at 10 meter depth from each site, which, for at least locations in East Sound, was below the pycnocline (Jan Newton, personal communication). 500 mL Schott Duran glass bottles were rinsed with the same sample water from the Niskin, the stopper was greased to form an airtight seal, and the sample was poisoned with 100 μ L 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). Temperatures were taken using calibrated temperature probes and salinities were measured in the laboratory. Samples were analyzed for total alkalinity (TA) and dissolved inorganic carbon (DIC) at the

Analytical Chemistry Laboratory at FHL (Lab 7). The program, CO2Calc (Robbins et al. 2011) was used to calculate pCO₂ and pH using recommended constants by Dr. Andrew Dickson (personal communication). Selected CO2Calc values are reported in Table 3.

Sampling locations

The locations were initially chosen based upon areas that were thought to have high, intermediate and low flushing rates. On July 9 and 11 (days 1 and 2, respectively), three replicate samples were taken in Haro Strait (High), three in San Juan Channel parallel with Yellow Island (Medium), and three at the head of East Sound (Low), sites 1, 4, and 9, respectively. Replicate samples on days 1 and 2 were taken ~600 ft. apart, equidistant from their respective shorelines (Figure 1c). On day 3 and day 4, July 13 and 15, respectively, the number of sites was expanded to nine (Figure 1c), 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 (Thomson 1981).

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 and took our final water sample on July 18 (see Table 2).

Autonomous Sensor Comparison

To further understand the environmental variation we anticipated observing in our discrete water samples, we sought out various water monitoring resources located throughout the San Juan Archipelago. While several these autonomous sensors have been well established throughout the Salish Sea and Strait of Georgia regions, there is a lack of such resources within the San Juan Islands that measure the carbonate system parameters. We compared salinity data from the FHL weather station with our discrete water samples.

Results

Days 1 and 2

Temperature did not vary at 10 meters on day 1 between sites, but increased on average by 2.2 degrees Celsius at SJC on day 2 (Figure 2a). Variation in salinity, TA and DIC between sites 1,4 and 9 was greatest on day 1 of all 4 days sampled (Figure 2b-d and Table 3). San Juan Channel (SJC, site 4) had the lowest average salinity (26.1 ± 0.4) on day 1. On day 2, salinity, TA and DIC varied less than on day 1, but SJC displayed the greatest standard deviation than any other site (Figure 2b-d). Calculated pCO₂ tended to decrease across all 3 sites on day 2 (Figure 2e). Analysis of results from days 1 and 2 displayed high variation between sites and inconsistent trends. However, due to the small amount of variation within a single site, we decided to reduce our replication from three to one, and expand our number of sites from three to nine (n=1 per site).

Days 3 and 4

On day 3, temperature decreased and salinity, TA and DIC increased from day 2 at sites 1, 4 and 9. On day 4, salinity, TA and DIC continued to increase, but temperature remained constant or decreased slightly for each of these three sites (Figure 2a-d). Calculated pCO₂ for sites 1, 4 and 9 on day 4 had on average increased 65% in the 48

hour time period with one time point in between (Figure 2e). Additionally, calculated pH for these three sites decreased on average by 0.2 pH units between days 2 and 4.

For sites 1-9, analysis of water samples showed an increase in TA and DIC for all sites on day 4 (Figure 3a,b). Temperature, on average decreased across all sites on day 4 (Figure 3c). While the magnitude of change in TA and DIC on day 4 was similar across all sites, SJC (site 4) showed the greatest increase in salinity, TA, and DIC, as well as the greatest decrease in temperature. Calculated pCO₂ for days 3 and 4 was highly variable between days 3 and 4 for all sites, reaching 830 µatm in Haro Strait (Figure 3d). We compared our salinity data to the salinity reported by the FHL weather station for the entire course of our study (Figure 4). While no statistical analysis was carried out, the results from the weather station tend to match with our salinity results at SJC and Haro Strait (Figure 2b).

Neap to Spring Transition

Data from the Environment Canada buoy at the Fraser River measures salinity in addition to the magnitude of tides. We plotted each variable and detected the neap to spring tide transition, indicated by the increasing amplitude of tidal heights (Figure 5). Specific conductivity (a measure of salinity) also increases during this time period, which is consistent with our results.

Salinity –Total Alkalinity Proxy

We compared salinity and total alkalinity values for all samples (except the 4 samples on July 17-18). Linear regression analysis results show that salinity and TA are highly correlated ($R^2 = 0.986$; Figure 6).

24-Tidal Cycle Sampling

Calculated pH values decreased with time and pCO₂ values increased with time (Figure 8). During flood tides, DIC and TA tended to increase. Conversely, during ebb tide, carbonate parameters decreased or remained constant (Figures 9 and 10). It is important to note that one sample was taken at low slack in darkness whereas all other samples were taken in daylight.

Discussion

Our results from day 1, which are highly variable between sites, are also consistent with the real-time data from FHL. The low salinity we observed at site 4 on day 1 indicates that we had sampled a mass of freshwater in the San Juan Channel. We presume this signal to be from the Fraser River, which has high flow rates during the summer months (Griffin and LeBlond 1990). We sampled consistently during low slack tides throughout a neap to spring transition and found salinity increases over this period in the San Juan Channel and in Haro Strait (Figures 4 and 5). Griffin and LeBlond (1990) describe the influence of the lunar tidal cycle on Fraser River movement in Haro Strait. They show that during a neap tide, when the exchange rate between ebb and flood tide is weakest, freshwater movement is greater than during a spring tide, when tidal flushing is greatest. Tidal current velocities between slack tides display an increase in flushing over sampling days (Figure 11a-f). Our data suggest that the lunar cycle may have a profound influence on the carbonate chemistry in Haro Strait and the San Juan Channel, but perhaps not in East Sound.

Our results also show an increase in pCO₂ and a decrease in pH between our first two and last two sampling days (Figures 2e,f). Furthermore our calculated pCO₂ was variable across all sites on days 3 and 4, despite an average increase in TA and DIC

across all sites. While biological processes (i.e. photosynthesis and respiration) unarguably influence multiple carbonate chemistry parameters, we assume observed differences in salinity largely reflect independent water masses. Therefore, the changes in the carbonate system due to biological processes would have little effect on salinity. Based on the strong correlation between salinity and total alkalinity, if the variability in $p\text{CO}_2$ were to be explained by physical processes (i.e. upwelling; Feely et al. 2009), we would expect a strong correlation between the measured total alkalinity and calculated $p\text{CO}_2$. However, when we plot the two, we see no strong correlation (Figure 7). Although temperature strongly influences the carbonate system, we consider the likely possibility that biological processes contribute to the rise in calculated $p\text{CO}_2$.

Finally, the change in carbonate chemistry over a 24-hour tide cycle was considered and measured. We show that during a flood tide, an increase in salinity, TA, and DIC result in a $p\text{CO}_2$ rise that is much higher than current atmospheric concentration of CO_2 . Since the observed rise in $p\text{CO}_2$ occurred mainly throughout the night, we hypothesize that this change is due to respiration. While this part of our study was minor, it revealed interesting trends at depth that could be reproduced in future studies. Our results provide baseline data for future oceanographic studies and future ocean acidification experiments that aim to represent the natural variability of carbonate chemistry parameters in a controlled environment. We acknowledge the potentially large effect biological processes may have on the chemistry in shallow waters. Future studies that incorporate biological and nutrient data may reveal important mechanisms for large shifts in the carbonate system that we report.

Acknowledgements

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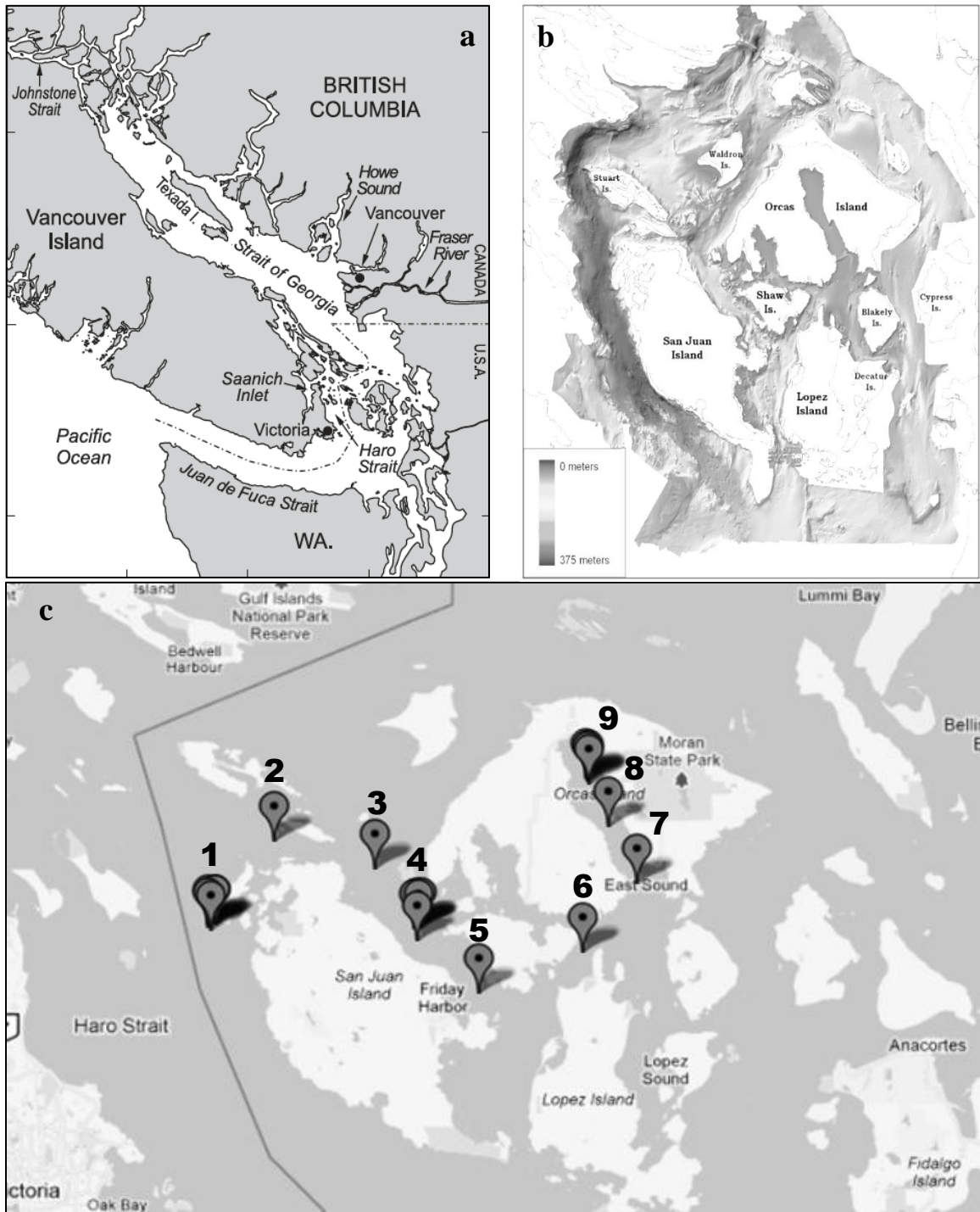


Figure 1a-c. (a) Regional map of the Pacific Northwest including the Strait of Georgia, the Fraser River, the Strait of Juan de Fuca, and the Salish Sea (from Johannessen and Macdonald 2009). (b) Bathymetric map of the San Juan Archipelago. (c) Sample sites #1-9 (1–West, 9–East). See Table 1 for GPS coordinates of exact locations.

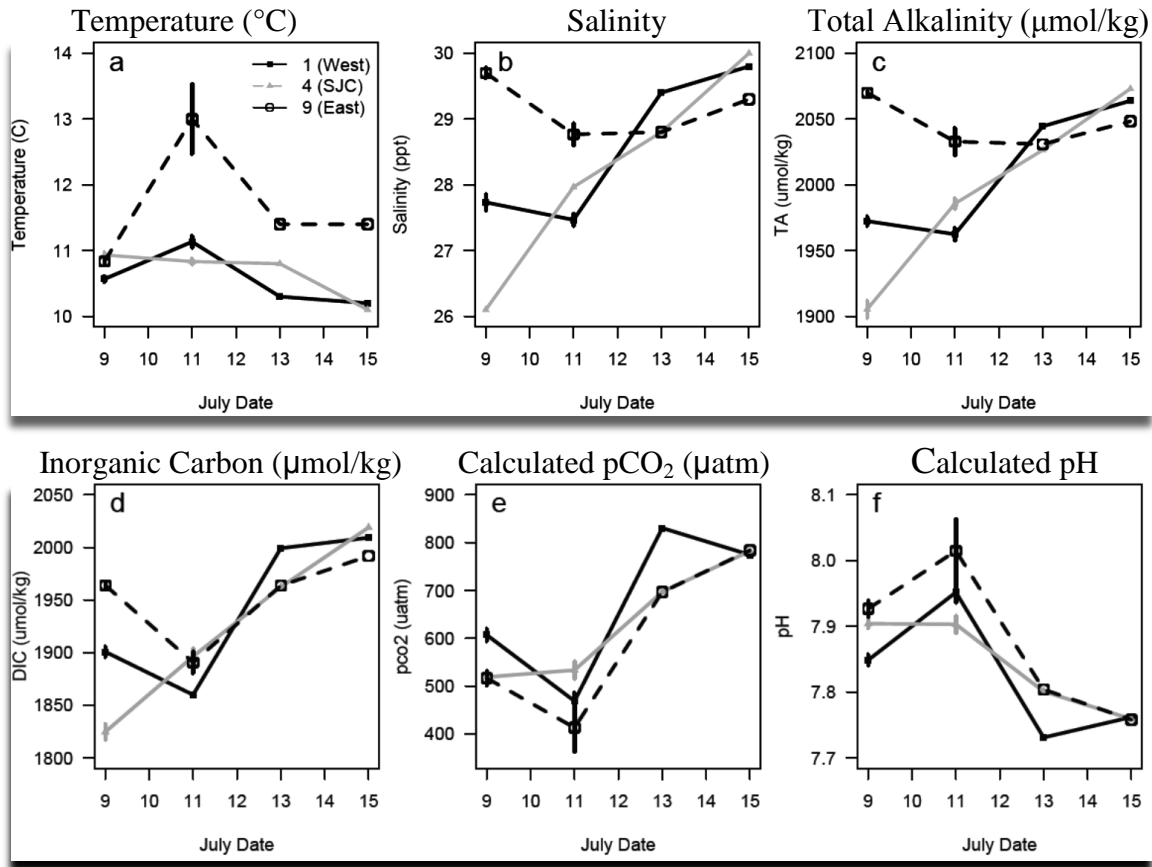


Figure 2a-f. Response variables plotted across time at three locations - sites 1 (West), 4 (SJC), and 9 (East). Site 1 (West) = Solid black line with squares. Site 4 (SJC) = Solid Grey line with triangles. Site 9 (East) = Dashed black line with open squares. \pm S.E. bars for July 9 & 11 only. pCO₂ (μatm) and pH values were calculated using CO2Calc (Robbins et al. 2010). For all values, see Table 3.

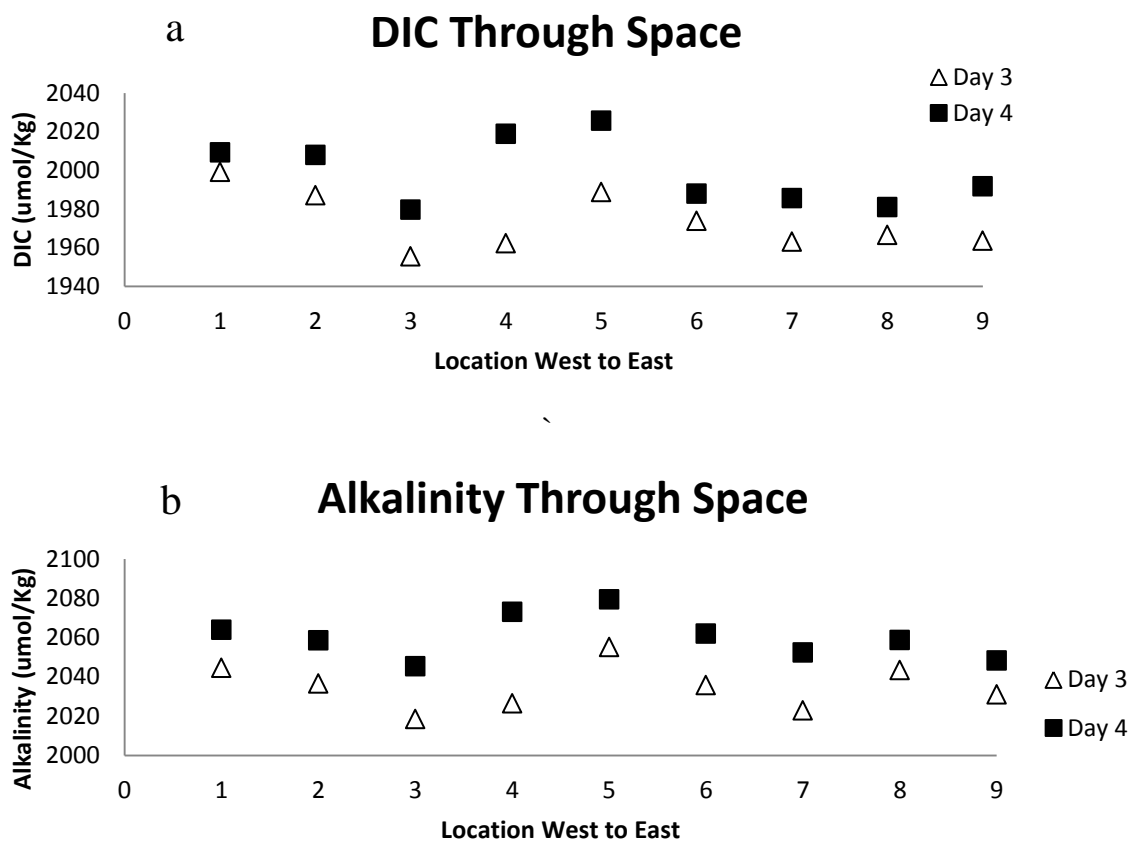


Figure 3a,b. Measured DIC and TA across all sites for days 3 and 4. (n=1 per site per day). (a) DIC (b) Total Alkalinity

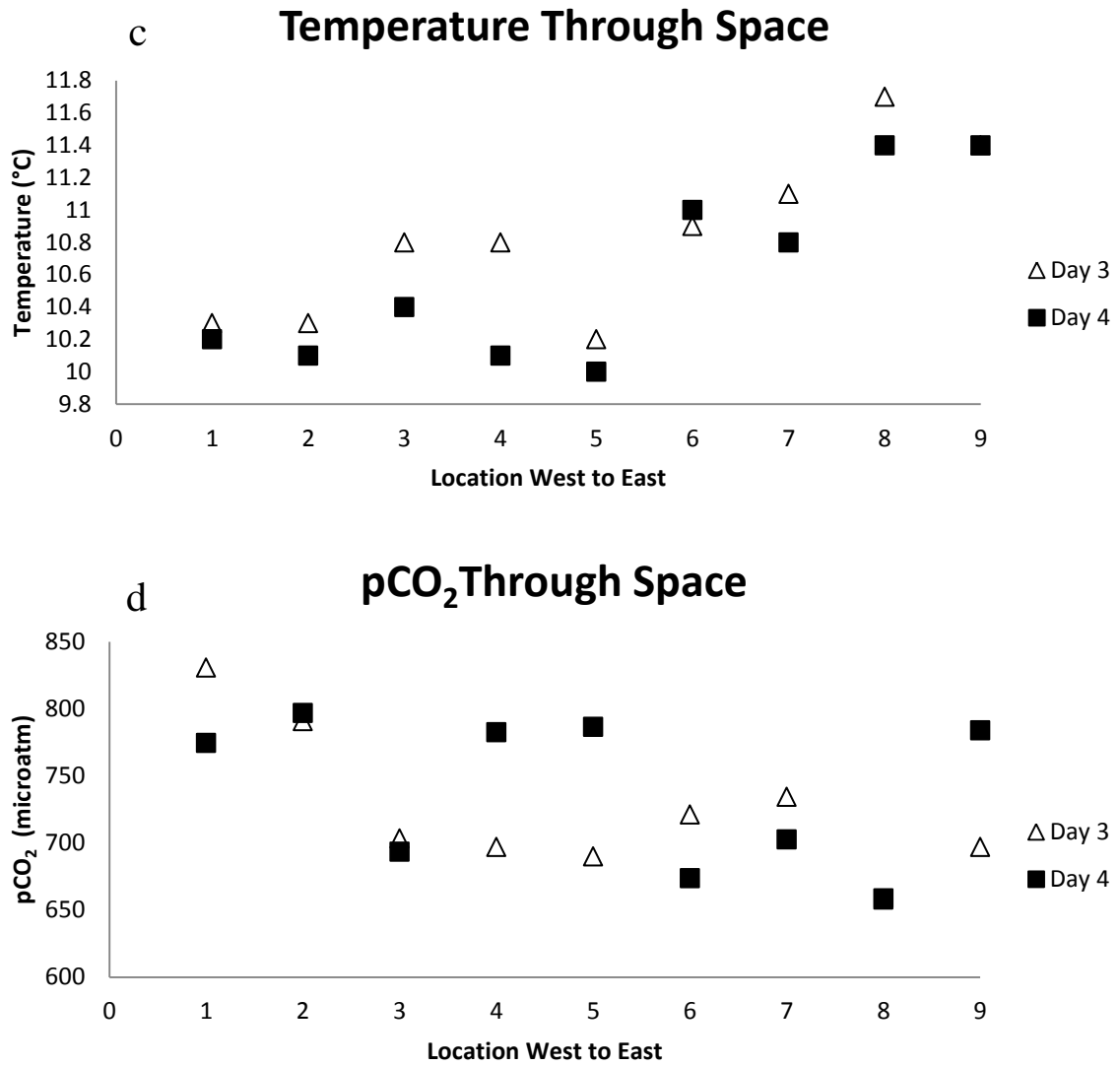


Figure 3c,d. Measured temperature and calculated pCO₂ across all sites for days 3 and 4. (c) Temperature (d) pCO₂

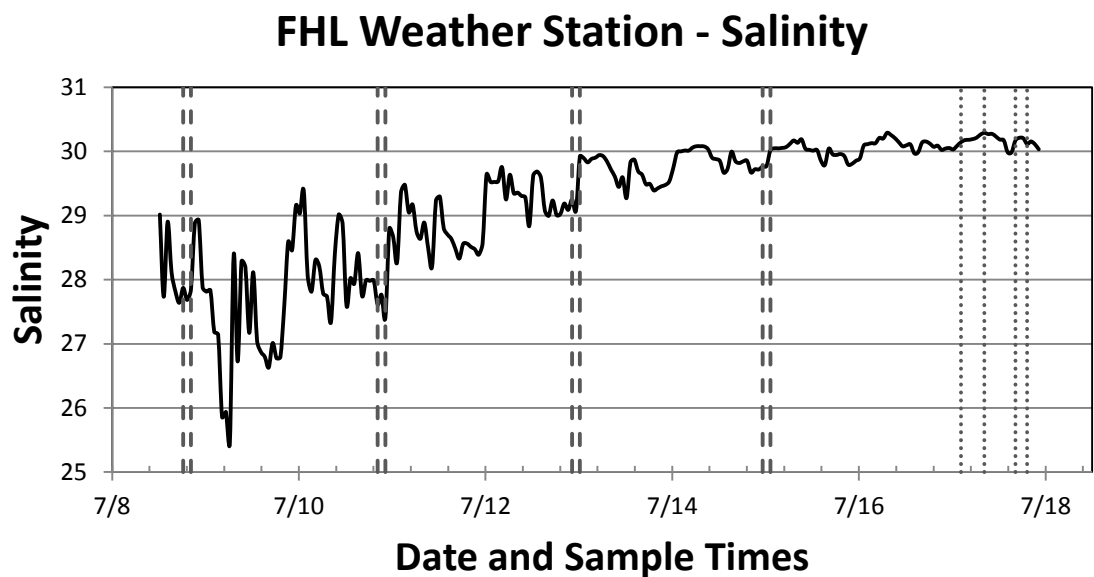


Figure 4. Salinity data from the weather station at the Friday Harbor Laboratories, Washington. Salinity sensor located at ~ 3 meters depth. Dashed lines indicate range of times when water samples were collected from the San Juan Archipelago (sites 1-9). Single dotted lines indicate times when water samples were collected from Friday Harbor Channel during one tidal cycle, July 17-18, 2011. See Figure 9 & 10 below.

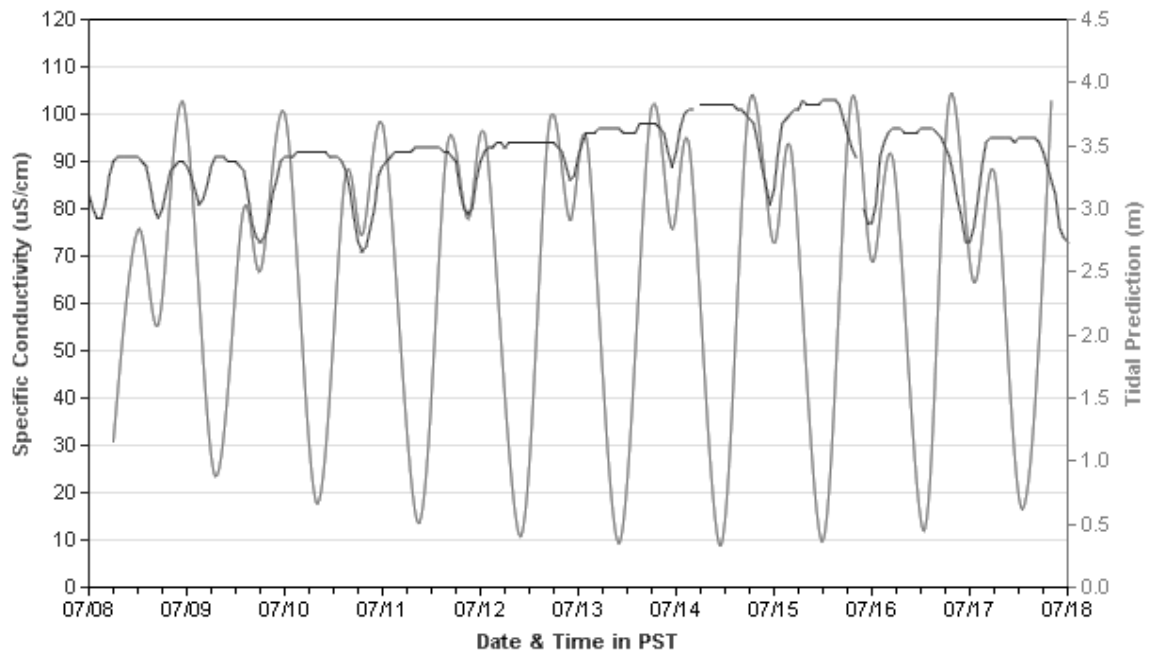


Figure 5. Specific conductivity ($\mu\text{S}/\text{cm}$) and tidal prediction (meters) at the Fraser River buoy from July 8 to July 18, 2011. Neap tide – July 7, Spring tide – July 14.

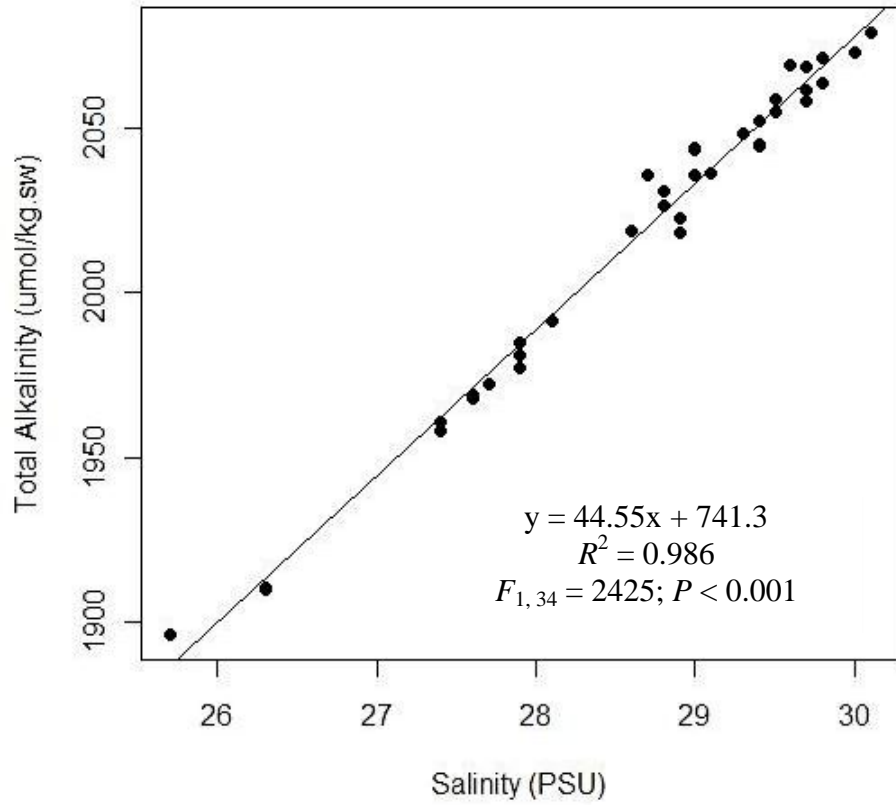


Figure 6. Measured Salinity and Total Alkalinity ($\mu\text{mol kg}^{-1}$ seawater). Discrete water samples collected and analyzed from all sites July 9- July 15, 2011.

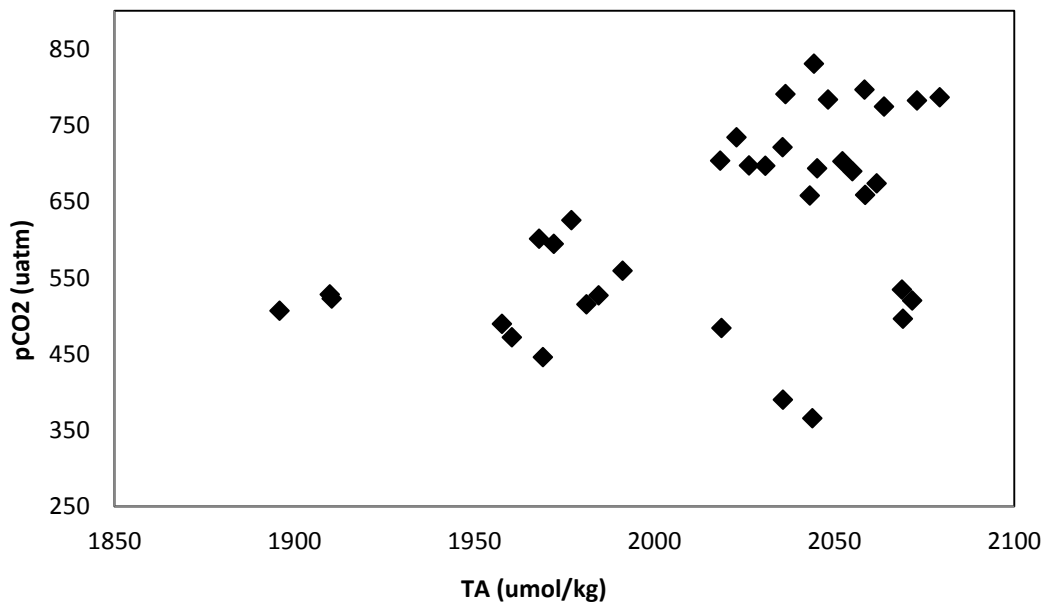


Figure 7. Measured total alkalinity ($\mu\text{mol kg}^{-1}$ seawater) and pCO_2 (μatm) for all sites and days.

pCO₂ and pH of Friday Harbor over One Tidal Cycle

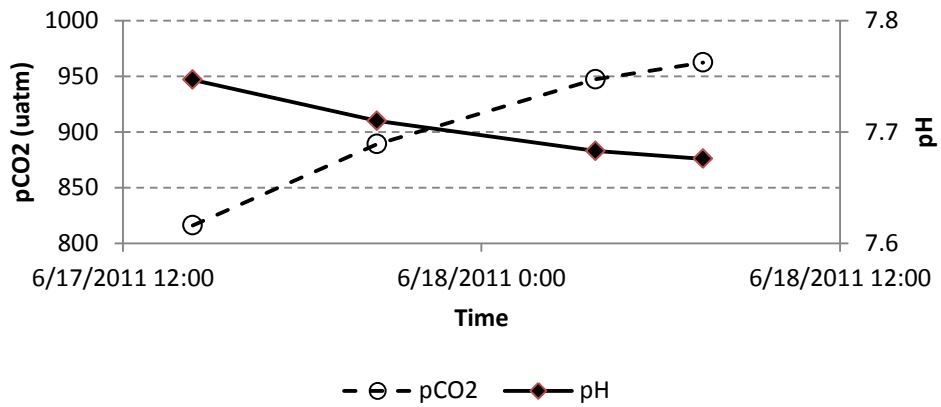


Figure 8. Calculated pCO₂ (µatm) and pH at 10 meters depth over one tidal cycle. See Table 2 for exact GPS coordinates and times of sampling.

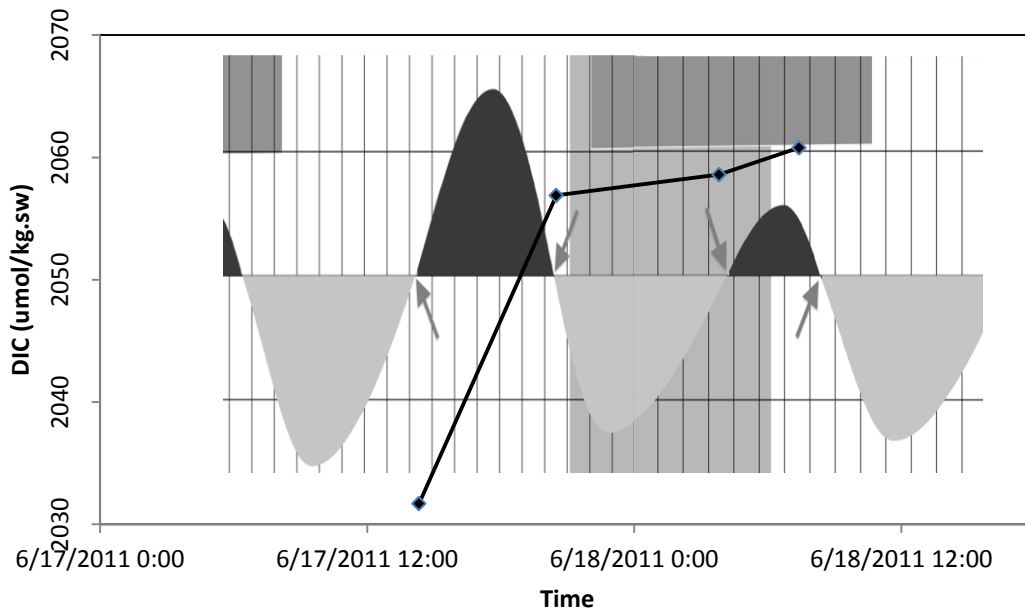


Figure 9. Discrete DIC values superimposed onto current velocity projection. Current velocity projection from the Turn Rock current buoy on July 17 and July 18, 2011. Arrows indicate approximate time of collection at slack tides. Y-axis units are in knots. Source: Mr. Tides.

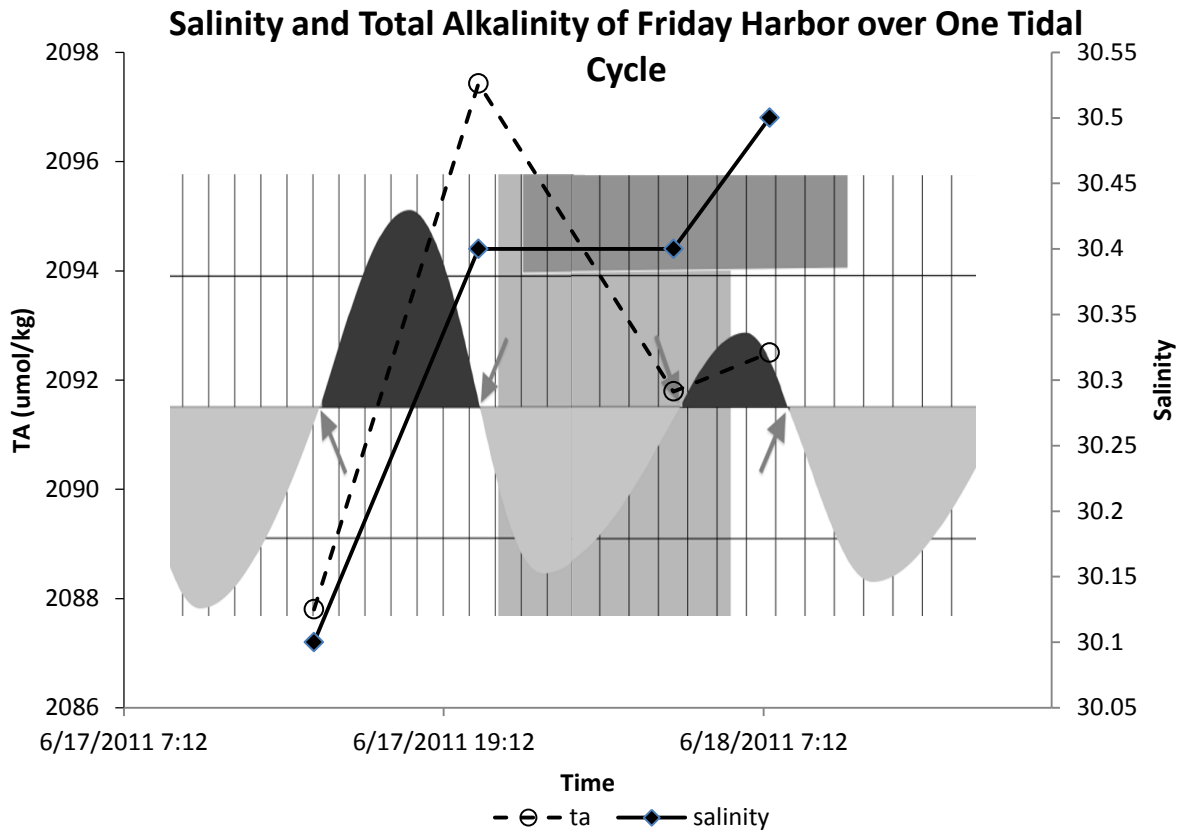


Figure 10. Discrete salinity and TA values superimposed onto current velocity projection. Current velocity projection from the Turn Rock current buoy on July 17 and July 18, 2011. Arrows indicate approximate time of collection at slack tides. Y-axis units are in knots. Source: Mr. Tides.

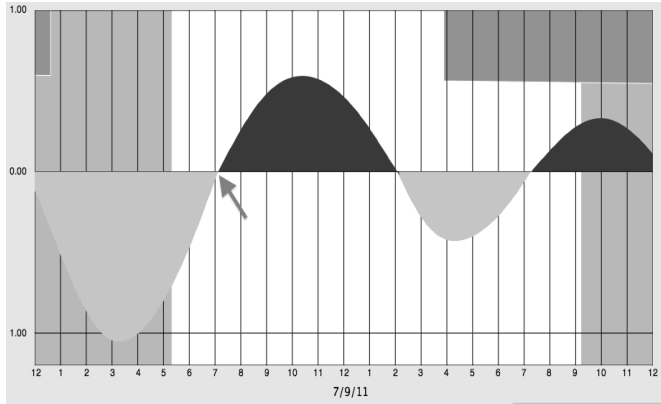


Figure 11a. Current velocity projection from the Harney Channel current buoy on July 9, 2011. Arrow indicates time of collection at low slack. Y-axis units are in knots. Source: Mr. Tides 3.

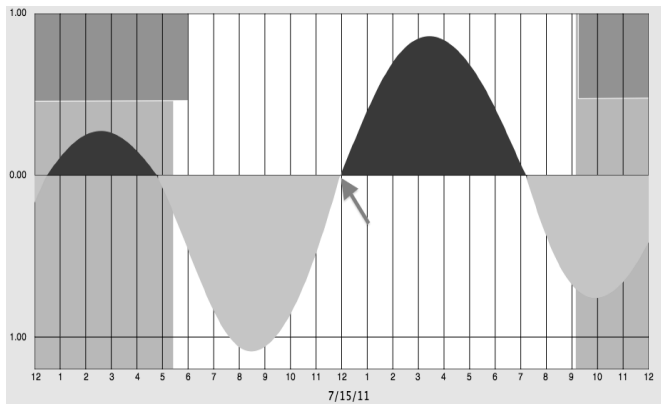


Figure 11b. Current velocity projection from the Harney Channel current buoy on July 15, 2011. Arrow indicates time of collection at low slack. Y-axis units are in knots. Source: Mr. Tides 3.

Figure 11c. Current velocity projection from the Spring Passage current buoy on July 9, 2011. Arrow indicates time of collection at low slack. Y-axis units are in knots. Source: Mr. Tides 3.

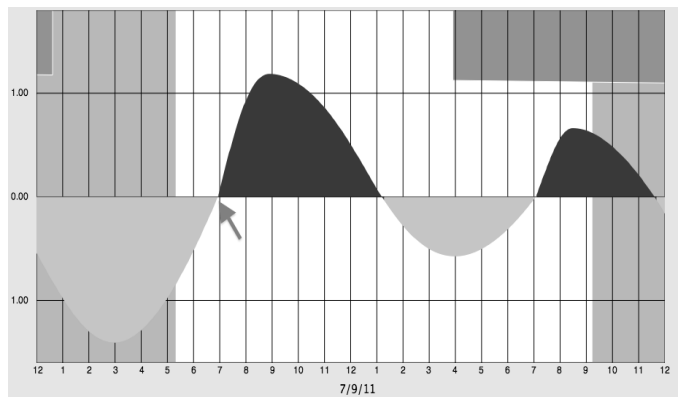
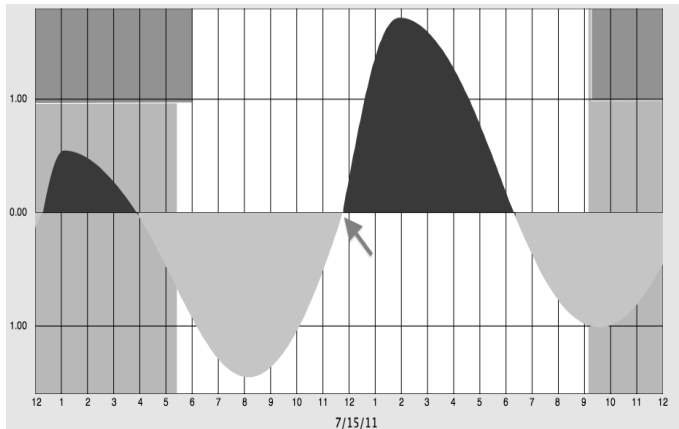


Figure 11d. Current velocity projection from the Spring Passage current buoy on July 15, 2011. Arrow indicates time of collection at low slack. Y-axis units are in knots. Source: Mr. Tides 3.



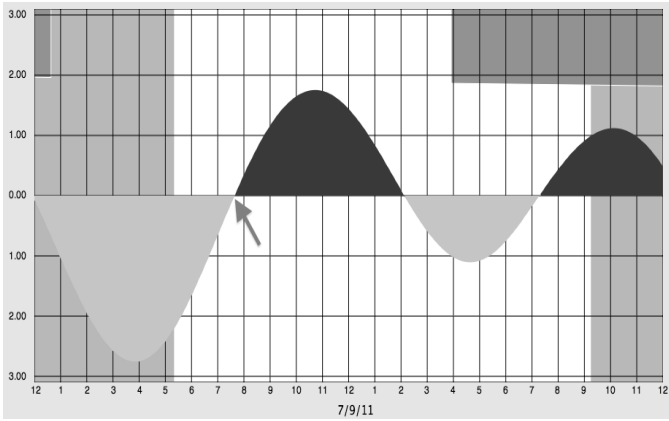


Figure 11e. Current velocity projection from the Kellett Bluff current buoy on July 9, 2011. Arrow indicates time of collection at low slack. Y-axis units are in knots. Source: Mr. Tides 3.

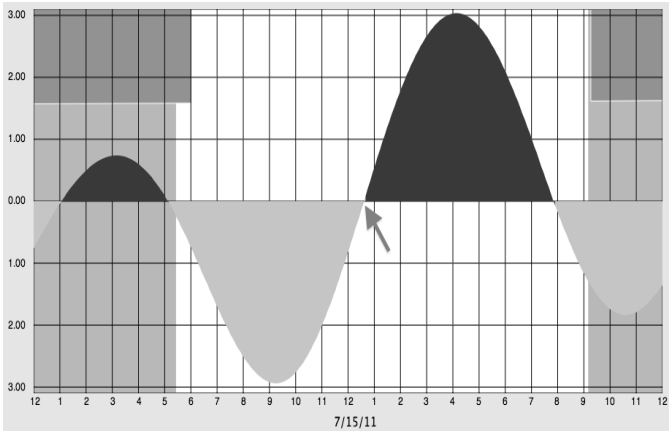


Figure 11f. Current velocity projection from the Kellett Bluff current buoy on July 15, 2011. Arrow indicates time of collection at low slack. Y-axis units are in knots. Source: Mr. Tides 3.

Bottle ID	Site ID #	Date	North coordinates	West coordinates	Collection time	Low slack at nearest current buoy
E001	9	07/09/11	48° 40.080	122° 53.900	6:55 AM	7:07 AM (HC)
E002	9	07/09/11	48° 40.020	122° 53.776	7:07 AM	7:07 AM (HC)
E003	9	07/09/11	48° 39.930	122° 53.755	7:15 AM	7:07 AM (HC)
SJ001	4	07/09/11	48° 35.043	123° 02.158	7:12 AM	6:56 AM (SP)
SJ002	4	07/09/11	48° 34.961	123° 02.247	7:00 AM	6:56 AM (SP)
SJ003	4	07/09/11	48° 35.003	123° 02.490	6:45 AM	6:56 AM (SP)
W001	1	07/09/11	48° 35.164	123° 12.791	8:12 AM	7:40 AM (KB)
W002	1	07/09/11	48° 35.049	123° 12.759	8:04 AM	7:40 AM (KB)
W003	1	07/09/11	48° 34.939	123° 12.732	7:55 AM	7:40 AM (KB)
E004	9	07/11/11	48° 40.220	122° 53.857	8:50 AM	8:57 AM (HC)
E005	9	07/11/11	48° 40.560	122° 53.824	9:06 AM	8:57 AM (HC)
E006	9	07/11/11	48° 39.890	122° 53.789	9:20 AM	8:57 AM (HC)
W004	1	07/11/11	48° 35.166	123° 12.658	9:32 AM	9:28 AM (KB)
W005	1	07/11/11	48° 35.022	123° 12.665	9:25 AM	9:28 AM (KB)
W006	1	07/11/11	48° 34.951	123° 12.640	9:16 AM	9:28 AM (KB)
SJ 004	4	07/11/11	48° 35.186	123° 02.303	8:44 AM	8:46 AM (SP)
SJ 005	4	07/11/11	48° 35.004	123° 02.231	8:36 AM	8:46 AM (SP)
SJ 006	4	07/11/11	48° 34.917	123° 02.183	8:29 AM	8:46 AM (SP)
EW 007	9	07/13/11	48° 40.014	122° 53.795	10:07 AM	10:34 AM (HC)
EW 008	8	07/13/11	48° 38.485	122° 52.752	10:23 AM	10:34 AM (HC)
EW 009	7	07/13/11	48° 36.479	122° 51.341	10:40 AM	10:34 AM (HC)
EW 010	6	07/13/11	48° 34.179	122° 34.064	10:57 AM	10:34 AM (HC)
EW 011	5	07/13/11	48° 32.819	122° 59.277	11:22 AM	11:37 AM (TR)
EW 012	4	07/13/11	48° 35.053	123° 02.314	10:16 AM	10:23 AM (SP)
EW 013	3	07/13/11	48° 37.055	123° 04.447	10:41 AM	10:23 AM (SP)
EW 014	2	07/13/11	48° 37.960	123° 09.473	11:00 AM	11:09 AM (KB)
EW 015	1	07/13/11	48° 35.158	123° 12.494	11:20 AM	11:09 AM (KB)
EW 016	9	07/15/11	48° 40.037	122° 53.764	12:10 PM	11:56 AM (HC)
EW 017	8	07/15/11	48° 38.529	122° 52.760	12:25 PM	11:56 AM (HC)
EW 018	7	07/15/11	48° 36.171	122° 51.495	12:36 PM	11:56 AM (HC)
EW 019	6	07/15/11	48° 34.263	122° 54.031	12:50 PM	11:56 AM (HC)
EW 020	5	07/15/11	48° 32.777	122° 59.362	N/A	1:01 PM (TR)
EW 021	4	07/15/11	48° 35.048	123° 02.170	11:28 AM	11:45 AM (SP)
EW 022	3	07/15/11	48° 36.963	123° 04.384	11:50 AM	11:45 AM (SP)
EW 023	2	07/15/11	48° 37.990	123° 09.618	12:10 PM	12:37 PM (KB)
EW 024	1	07/15/11	48° 35.013	123° 12.458	12:28 PM	12:37 PM (KB)

Table 1. List of sample stations, description of the location, associated GPS coordinates and time of collection. Low slack times 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 Turn Rock buoy
TC001	FHL Weather Station	07/17/11	48° 32.664	123° 00.347	2:20 PM	2:17 PM (Low)
TC002	FHL Weather Station	07/17/11	N/A	N/A	8:30 PM	8:25 PM (High)
TC003	FHL Weather Station	07/18/11	48° 32.672	123° 00.446	3:49 AM	3:44 AM (Low)
TC004	FHL Weather Station	07/18/11	48° 32.665	123° 00.454	7:25 AM	7:24 AM (High)

Table 2. Collection location (GPS coordinates), date and time of collection, and time of slack tide at Turn Rock. Source: Mr. Tides 3.

		Measured Parameters			
Date	Site ID	Salinity	Temperature (°C)	TA ($\mu\text{mol/kg.sw}$)	DIC ($\mu\text{mol/kg.sw}$)
7/9/2011	West (#1)	27.7 ± 0.2	10.6 ± 0.1	1972.4 ± 4.5	1900.8 ± 6.2
	SJC (#4)	26.1 ± 0.4	10.9 ± 0.1	1905.4 ± 8.2	1824.7 ± 9.1
	East (#9)	29.7 ± 0.1	10.8 ± 0.1	2069.9 ± 1.6	1963.9 ± 4.6
7/11/2011	West	27.5 ± 0.1	11.1 ± 0.1	1962.4 ± 5.9	1859.9 ± 0.9
	SJC	28.0 ± 0.1	10.8 ± 0.1	1985.7 ± 5.1	1896.4 ± 9.3
	East	28.8 ± 0.2	13.0 ± 0.7	2032.8 ± 12.9	1890.7 ± 12.7
7/13/2011	West	29.4	10.3	2044.4	1999.2
	SJC	28.8	10.8	2026.4	1962.3
	East	28.8	11.4	2030.9	1963.7
7/15/2011	West	29.8	10.2	2063.9	2009.2
	SJC	30.0	10.1	2073.1	2018.9
	East	29.3	11.4	2048.3	1991.8
		Calculated parameters based on TA/DIC			
Date	Site ID	pH	pCO ₂ (μatm)	$\Omega_{\text{aragonite}}$	Ω_{calcite}
7/9/2011	West (#1)	7.9 ± 0.01	607 ± 16.4	1.02	1.63
	SJC (#4)	7.9 ± 0.01	519 ± 11.0	1.08	1.08
	East (#9)	7.9 ± 0.02	517 ± 19.2	1.32	2.10
7/11/2011	West	8.0 ± 0.02	469 ± 21.9	1.27	2.04
	SJC	7.9 ± 0.02	533 ± 22.7	1.16	1.86
	East	8.0 ± 0.06	413 ± 62.5	2.64	1.66
7/13/2011	West	7.7	830	0.84	1.34
	SJC	7.8	697	0.97	1.55
	East	7.8	697	1.00	1.60
7/15/2011	West	7.8	774	0.91	1.45
	SJC	7.8	782	0.91	1.45
	East	7.8	784	0.93	1.48

Table 3. Mean (\pm s.d.) carbonate system parameters of the San Juan Archipelago, Washington. CO2Calc (Robbins et al. 2010) batch processing was used to calculate pH, pCO₂, $\Omega_{\text{aragonite}}$, Ω_{calcite} . CO₂ constants from Lueker et al. 2000, KSO₄ constants from Dickson, Total pH scale, Air-sea Flux from Wanninkhof. TA, total alkalinity; DIC, dissolved inorganic; Ω , saturation state.