Variations in Tide Pool Carbonate Chemistry and Temperature

Rosaleen E. Gilmore[1], Roberta Challener[2], Rebecca Guenther[3], Laura Newcomb[4], Karen Rickards[5]

Ocean Acidification Course
Summer 2010

[1] Department of Atmospheric and Oceanic Sciences, University of California Los Angeles, Los Angeles, CA 90024
[2] Department of Biology, University of Alabama at Birmingham, Birmingham, AL 35294
[3] Department of Botany, University of British Columbia, Vancouver, BC V6T 1Z4
[4] Department of Biology, University of Washington, Seattle, WA 98195
[5] Department of Integrative Biology, University of Guelph, Guelph, ON N1G 2W1

Contact Information:
Rosaleen Gilmore
Department of Atmospheric and Oceanic Sciences
University of California, Los Angeles
405 Hilgard Avenue
Los Angeles, CA 90024
rgilmore@atmos.ucla.edu

Tide pools are known to have extreme variations in both their temperature and carbonate chemistry while they are isolated from the surrounding waters. These extreme environments provide an interesting view into how organisms are able to cope with large variations in temperature, pH and total carbon. The knowledge of how organisms cope with high temperature and low pH conditions will be beneficial when contemplating how organisms will deal with the conditions that are expected to come from global warming and ocean acidification in the not-too-distant future. In this study we observe several physical and chemical characteristics of two tide pools, comparing them to each other as well as to the waters surrounding them. We then manipulate one of the tide pools (by adding photosynthesizing organisms on one day and respiring organisms on the next day) in order to observe the biological impact on the carbon chemistry of a tide pool.

KEYWORDS: tide pools, intertidal, ocean acidification, temperature, *Ulva spp.*, *Mytilus Trossolus*

Studies on tide pools in the past have mainly been concerned with classifying the types of organism that inhabit them (Ambler and Chapman 1950, Altieri et al 2009, Romanuk and Kolasa 2002). This type of information can be important because these organisms are able to survive the extreme variations in their environment when the tide pool is isolated from the surrounding waters. Other studies have looked into the physical changes that these organisms go through during an intertidal cycle; mostly looking at temperature and salinity, as well as occasionally pH and Dissolved Oxygen (Truchot and Duhamel-Jouve 1980, Goss-Custard et al 1979, Morris and Taylor 1983, Huggett and Griffiths 1986). While these studies can provide some background on both the physical and the biological variations that have been observed in tide pools, most of them are several decades old, and the ones that do look at the chemistry of the pools have questionable techniques for their analysis of the carbonate chemistry. This study has two parts; the first observes the changes in two tide pools throughout the time that they are isolated from the surrounding waters, and the second observes changes in the chemistry of one pool, that has had specific organisms added to it, in comparison to the other pool. We propose that tide pools undergo vast changes in both temperature and carbon

composition whenever they are isolated from their surrounding waters, and that the addition of either photosynthesizing or respiring organisms will decrease or increase, respectively, the amount of carbon that is present in the pool.

METHODS

Study Site

Two rock tidal pools with similar tidal heights and relatively similar biota were selected in July of 2011 at Dead Man's Cove on San Juan Island, WA (figure 1). Using a meter stick, volume was based on rough estimates of surface area and average depth. Tidal height was determined by using stadia rods and a hand level and was the main factor used to select the pools in order to control for variation during an intertidal cycle as much as possible. With respect to tidal height, we looked for pools in the *Fucus* zone; thus the pools would be exposed for a large portion of the low tide and potentially increase the chance of detecting extreme variation. Abundance of macroalgal fauna was determined as percent cover by species and estimates of animal abundance were obtained by using the semi-quantitative scale: present/absent (none/1), few (< 10), abundant (< 50), and many (50+) (table 1).

Quantifying Chemical composition over a tidal cycle

Samples (500 ml) for carbonate chemistry were obtained from each pool at four time points during the intertidal cycle: immediately after isolation from sound waters (time zero), 2 hours after isolation, 4 hours after isolation, and right before the sound waters were beginning to re-enter into the pools. A sample of water from the Haro Strait (located about 100 meters from the tide pools within the cove, and at a depth of

approximately 0.04 meters) was also taken at the beginning and end of the intertidal cycle in order to characterize the extent of physical and chemical fluctuations tidal pool biota likely experience relative to the Strait. Samples were collected using a modified version (a rubber stopper with and air hole and tygon tubing running from the top of the stopper to the bottom of a Schott Duran borosilicate glass bottle) of the dissolved oxygen collecting device described in Daniel and Boyden (1975) in order to minimize gas exchange and perturbation of the chemistry. Samples were poisoned with mercuric chloride at the time of collection and stored according to the protocols described by Dickson et al. (2007) until analysis. At time zero, and every hour thereafter, temperature, salinity, and Dissolved Oxygen (D.O.) were measured at the surface of each tide pool and in the Strait using a temperature probe, and D.O. probe which also provided salinity measurements. On day two D.O. was not measured due to the unavailability of the instrument. A TidBit Temperature Data Logger (OnSet) was also placed at the bottom of each tide pool at time zero and removed after the last sample was taken each day.

DIC and total alkalinity were measured using a Licor infra –red analyzer and Agilent automatic titrator (model 34970). pH was measured using an Ocean Optics spectrophotometer with 10 cm pathlength optical cells following the methods of Dickson et al. (2007). As preliminary measurements of tide pool pH exhibited high pH values, we utilized two different dyes to measure pH. M-cresol purple can provide an accurate pH over the range of 7.4 to 8.2 (Dickson et al. 2007) while thymol blue has been reported to provide more accurate pH measurements for pH values higher than 8.0 (Zhang and Byrne 1996).

We mixed an 8×10^{-1} mol dm^{-3} solution of thymol blue in 10% ethanol, and 90% water under heat. To aid the dye in dissolution, we then added 600µL of NaOH while heating the dye. We calculated the pH of each sample on the spectrophotometer according to the procedure outlined by Zhang and Byrne (1996).

To check the accuracy of the measured pH values, we calculated pH at 25˚C in CO2Calc using the constants for Lueker et al. (2000), Dickson (1990b), and Wanninkhof (1992). These calculated values were closest to the *m*-cresol purple values. However, as *m*-cresol purple is not reported to be accurate above a pH of 8.2, we used the CO2Calc pH values in our analysis after they were corrected for sample temperature and reported on the total hydrogen ion scale (mol kg^{-1} SW). Values for these various pH measurements can be found in table 6 and figures 6 and 7. The plot of pH values produced by both dyes and CO2Calc that was used to compare the validity of each of these measurements can be found in figure 12.

Certified reference materials (Andrew Dickson, Scripps Institute of Oceanography) were used to calibrate and verify accuracy of the machines.

Tide pool Manipulations

In order to better understand the relative contributions of photosynthesizing and respiring organisms, we added organisms to one of the tide pools on Day 2 and Day 3. On Day 1, both tide pools were sampled without addition of any biota. On Day 2, 1.04 m^2 of *Ulva spp*. collected from tanks at Friday Harbor labs and the area surrounding the pools were added at time zero to the Treatment tide pool and removed after the last sample was taken. Mussels used for Day 3 were collected from the dock at Argyle Creek six days prior to the start of the experiment. *Mytilus trossolus* were brought back to

Friday Harbor labs where all encrusting biota were removed. Buoyant weight was determined 24 hours prior to the addition to the pools by suspending mussles in seawater from a bottom-loading balance (Davies 1989). The mussels were maintained in a seawater table until addition. On Day 3, 278.1 g (buoyant weight) of *M. trossulus* were added throughout the small tide pool at time zero and then removed after the last sampling point.

RESULTS AND DISCUSSION

Temperature Changes

The temperature in each tide pool varied greatly throughout the course of the day, changing by as much as 8°C over six hours in both tide pools on Day 1. The variation in temperature in the various sampling locations throughout the course of this experiment can be seen in figure 4 and tables 2, 3, 4, and 5. The temperature of the tide pool seems to depend greatly on the ambient weather of the surroundings, the volume of the pool, and the depth within the pool at which the temperature is being taken. Day 1 was the only sunny and warm day throughout this experiment (see Figure 3 for an estimate of the incoming radiation throughout the experiment); both Day 2 and Day 3 were overcast with occasional rain. The temperature of the ambient air on Day 1 was much higher than any of the other days, resulting in the increase seen in both tide pools, with the Reference and Treatment tide pools getting as warm as 16°C and 17°C respectively. The temperatures observed on Day 2 and Day 3 were all much lower than those seen on Day 1 due to the difference in the ambient air temperature. The starting temperatures of the pools are surprising similar between days; the Treatment pool was consistently at 10.05°C, and the

Reference pool was consistently at 10.30°C, when the first samples were taken after the pools were isolated. On Day 1, there is a gap in the data where the TidBit Temperature Logger (OnSet) was unavailable until later in the day. The Reference tide pool contained approximately four times as much volume as the Treatment tide pool; the Reference tide pool also consistently had a temperature of about 1°C less than that of the Treatment tide pool by the end of the isolation period. This indicates that the volume of the pool changes how well it is heated throughout an intertidal cycle. Variation between temperatures recorded by the TidBit and the Temperature probe can be attributed to temperature stratification within the pool since probe measurements were taken at the surface of the pool, whereas the TidBit remained at the bottom of the pool throughout the course of the experiment.

Changes in the pH

The pH of a tide pool that is isolated from the surrounding water over the course of several hours is expected to increase (becoming more basic) during daylight hours, and decrease (becoming more acidic) during the nighttime. This pattern is expected because photosynthesis occurs whenever there is light is at a high enough level and can swamp the respiration signal. Photosynthesis takes carbon dioxide out of the surrounding waters and fixes it; and since carbon dioxide is relatively acidic, this will increase the pH of the pool. Respiration, on the other hand, releases carbon dioxide and decreases the pH. The variation in pH in the tide pools followed what is predicted for daytime changes fairly well. There are obvious differences between the two tide pools and the strait water; for example, the pH of the Reference Tide pool is consistently lower than that of the Treatment pool, and the pH signal in the Strait water is much lower than that seen in the

tide pools, but there is still a consistent increase in pH throughout the day seen in the data.

Since photosynthesis is expected to raise the pH of a tide pool, and respiration is expected to lower the pH of a tide pool, we added a photosynthesizing organism (*Ulva spp.*) on Day 2, and a respiring organism (*M. Trossolus*) on Day 3 to try to see that signal in our Treatment tide pool. The results from these additions can be seen in Table 6 and Figures 6 and 7. Unfortunately, we have a limited dataset due to the limited amount of time available for these experiments and therefore cannot back up these conclusions with statistical evidence. However, the trend does seem to follow what is expected, showing higher observed pH on Day 2 when Ulva were added, and lower observed pH on Day 3 when *M. Trossolus* were added to the Treatment pool.

The pH was normalized between the Reference and Treatment tide pools on Day 1 compared to Day 2 and Day 3 as shown in Equation 1. The normalized pH on both Day 2 and Day 3 show a similar trend, starting above 1, dipping down below 1, and then raising up again (Figure 5). No conclusions can be drawn from this data at present without additional study and experimentation. The normalized Aragonite saturation state was also plotted, but seems to follow the normalized pH exactly throughout the intertidal cycle on both days.

Changes in the Total Carbon

The total Dissolved Inorganic Carbon (DIC) in tide pools is expected to decrease throughout an intertidal cycle due to photosynthetic organisms taking it up to produce sugars. This trend has been demonstrated in this dataset (Table 7 and Figures 8 and 9); there is an obvious decrease (on average, about 1000μmol/kg over the course of six

hours) in the total carbon in both of the tide pools on all of the days, as well as a much smaller decrease in the total carbon of the strait water. The data from Day 3 has a smaller decrease in DIC throughout the intertidal cycle in both the Reference and Treatment pools; however, the DIC in the Treatment pool is slightly higher than that in the Reference pool. One possible cause of this decrease in the rate of carbon uptake is the lack of sunlight on Day 3, which resulted in a decrease rate of photosynthesis, and therefore less carbon was taken up.

The normalized total carbon (Figure 5) values tell an interesting story. The total tarbon Concentration on Day 2, when *Ulva* were added to the Treatment pool, became consistently lower throughout the day, with a marked decrease later in the day when the light was more intense. This indicates that the increased photosynthesis of the *Ulva* increased the amount of carbon removed from the surroundings. The normalized DIC signal on Day 3, when respiring *M. Trossolus* were added to the Treatment pool, is slightly more confusing. The total carbon seems to decrease throughout the day, until the last sampling time-point when there is a sudden increase in the amount of carbon present in the Treatment pool. One possible explanation for this is that the mussels were under stress for the first several hours after they were introduced to the Treatment pool, and they did not open and start respiring until four or five hours after they were added to the pool. If this is the case, then there is a huge signal from respiration seen over a very short period of time at the very end of the intertidal cycle on Day 3. Further experimentation could help determine whether this is a real signal or just noise.

Changes in the Total Alkalinity

The total alkalinity consistently decreases throughout the intertidal cycle, changing by about 500μmol/kg on average (Table 8, Figures 10 and 11). The causes for this drastic decrease in alkalinity are very difficult to understand or explain. The alkalinity of the Treatment pool is consistently higher than that of the Reference pool. The difference between the two tide pools over the three days is inconclusive. The normalization of total alkalinity (Figure 5) only complicates the problem as it jumps by about ten units (indicating a change of a factor of ten in the pools) over the course of two hours. The normalization data is impossible to explain with the amount of information that has been gained in this study. Future work should look into the causes for these huge differences in total alkalinity.

CONCLUSIONS

The temperature and carbonate chemistry in the two tide pools studied here vary drastically over the course of their isolation from the surrounding sound water. The temperature of the pools seems to depend on the ambient weather of the surroundings, the volume of the pool, and the depth within the pool at which the temperature is being taken. The carbonate chemistry is dependent on the biology present in the pool and the amount of light available for the photosynthesizing organisms in the pool. The changes in pH and total carbon observed followed the expected trend with pH increasing and DIC decreasing throughout the intertidal cycle. There were big changes in total alkalinity that cannot be explained based on the information gained by this experiment. This experiment was extremely limited by the amount of time available, as well as by our

ability to find pools of similar size, tidal height, and biological composition. Future studies should try to expand on what we have performed here by attempting to gain enough statistical power to be able to go beyond a descriptive exploration of the changes observed in tide pool chemistry throughout the course of intertidal isolation.

ACKNOWLEDGEMENTS

We would like to thank Moose O'Donnell and Terrie Klinger for their time and guidance in the design of this study. Much thanks to Andrew Dickson for imparting his extensive knowledge of carbonate chemistry to us, and Emily Carrington for allowing us to use her lab for sample analysis. We would also like to thank Robin Elahi and Emma Timmins-Schiffman for their support and help making R behave itself and produce pretty plots. Deepest thanks to Florence Harrison and Aradhna Tripati (UCLA) for providing funding for me to participate in this course, and Friday Harbor Labs for putting this course on.

REFERENCES

Altieri A.H., Trussell G.C., Ewanchuk P.J., Bernatchez G., and Bracken M.E.S. (2009) Consumers control diversity and functioning of a natural marine ecosystem. *PLoS ONE* **4(4)**:e5291. Doi:10.1371/journal.pone.0005291

Ambler M.P. and Chapman V.J. (1950) A quantitative study of some factors affecting tide pools. *The Royal Society of New Zealand* **78(4)**, 394-409.

Daniel M. J. and Boyden C. R. (1975) Diurnal variations in physic-chemical conditions within intertidal rockpools. *Fld Stud.* **4**, 161-176.

Dickson A.G., Sabine C.L. and Christian J.R. (Eds.) (2007) Guide to Best Practices for Ocean CO_2 Measurements. PICES Special Publication 3, 191pp.

Goss-Custard S., Jones J., Kitching J.A. and Norton T.A. (1979) Tide pools of Carrigathorna and Barloge Creek. *Philosophical Transactions of the Royal Society of London*. Section B, Biological Sciences **287(1016)**, 1-44.

Huggett J. and Griffiths C.L. (1986) Some relationships between elevation, physic-chemical variables and biota of intertidal rock pools. *Mar. Ecol. Prog. Ser.* **29**, 189-197.

Morris S. and Taylor A.C. (1983) Diurnal and seasonal variations in physic-chemical conditions within intertidal rock pools. *Estuarine, Coastal and Shelf Science* **17**, 339-355.

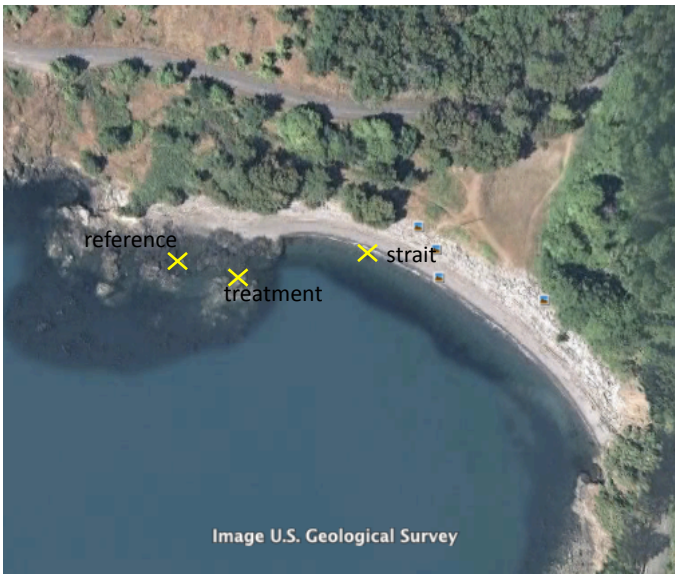
Romanuk T.N. and Kolasa J. (2002) Environmental variability alters the relationship between richness and variability of community abundances in aquatic rock pool microcosms. *EcoScience* **9(1)**, 55-62.

Truchot J.P. and Duhamel-Jouve A. (1980) Oxygen and carbon dioxide in the marine intertidal environment: Diurnal and tidal changes in rockpools. *Respirin Physiology* **39**, 241-254.

Zhang H. and Byrne R.H. (1996) Spectrophotometric pH measurements of surface seawater at in-situ conditions: absorbance and protonation behavior of thymol blue. *Marine Chemistry* **52**, 17-25.

FIGURES AND TABLES

Location, Tide and Light Conditions:
N 48˚30.837
W123˚08.763



7/12/11 12:36 AM PDT **7.34 Feet**
7/12/11 8:23 AM PDT -1.89 Feet
7/12/11 4:43 PM PDT **7.08 Feet**
7/12/11 8:34 PM PDT 6.40 Feet
7/13/11 1:30 AM PDT **7.16 Feet**
7/13/11 9:09 AM PDT -2.12 Feet
7/13/11 5:23 PM PDT **7.40 Feet**
7/13/11 9:36 PM PDT 6.27 Feet
7/14/11 2:24 AM PDT **6.97 Feet**
7/14/11 9:53 AM PDT -2.13 Feet
7/14/11 6:01 PM PDT **7.53 Feet**
7/14/11 10:30 PM PDT 5.97 Feet

Figure 1: **left:** The location of the Reference Tide pool, Treatment Tide pool, and Haro Strait Sampling points in Dead Man's Cove on San Juan Island in Washington (USGS). **Right:** predicted tidal heights throughout the study (Mr. Tides)

Kanaka Bay, San Juan Island, Haro Strait, Washington

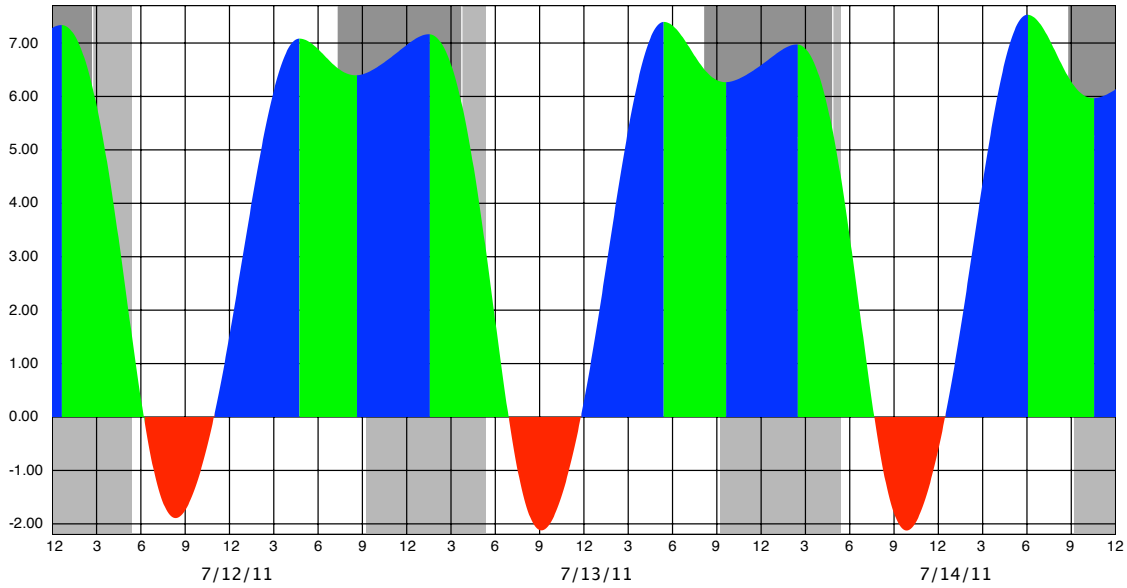


Figure 2: Tide chart for the three sampling days; Day 1 is 7/12/2011, Day 2 is 7/13/2011, and Day 3 is 7/14/2011 (Mr. Tides)

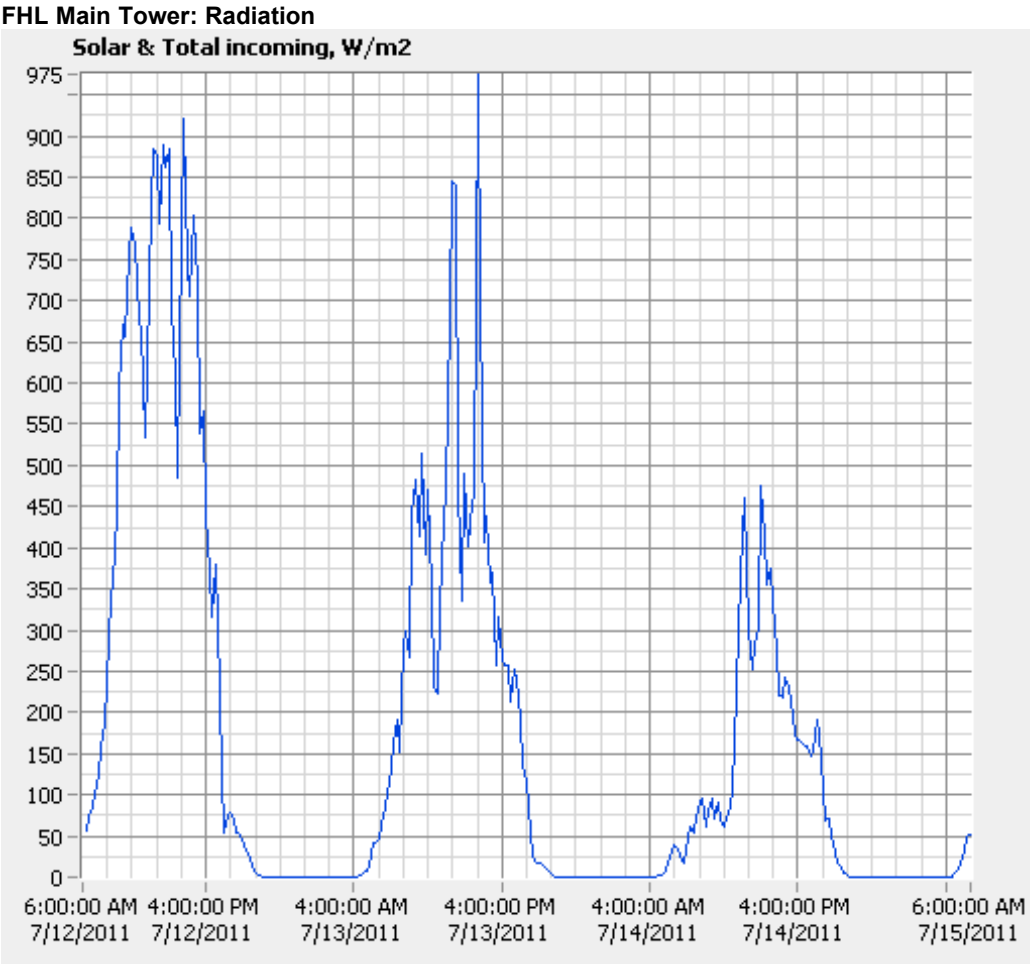


Figure 3: Incoming Solar Radiation at the Friday Harbor Laboratories Weather Station (located 10.9 km from our sampling location) over the three days of sampling (Carrington Weather Station).

General Characteristics of the Pools and the Strait Waters:

Tide pool	Present	Few	Many	Abundant
Manipulated		Chitin, thatch barnacles, amphipods, top snail, *Littorina sitkana*, *Nucella*		Medium and large hermit crabs, two species of limpets
Un-manipulated	blood worms, bake Katie chitin	*Hemigraspsus nudus*	*Littorina sikana*, small hermit crabs (*Pagarus* spp), *Spirorbidae* spp., limpets, *Littorina* complex	Sculpins, *Nucella*

Tide pool	Species	Percent Cover
Manipulated	Crustose coralline	40%
	Corallina vancouveriensis and *Bossiella plumosa.*	35%
	Ulva sp.	15%
	Polysiphonia sp.	<1%
	Porphyra sp.	<1%
	Fucus distichus i.	<1%
	Saccharina sessilis	<1%
	Hallosaccion glandiforme	<1%
	Microcladia coulteri	<1%
	Odonthalia floccosa	<1%
Un-manipulated	Crustose coralline	10%
	Corallina vancouveriensis and *Bossiella plumosa*	55%
	Fucus distichus. (loose)	5%
	Odonthalia floccosa	30%
	Prionitis lanceolata	<5%
	Leathesia marina	<5%
	Soranthera ulvoidea	<1%

Table 1: Species composition in both of the tide pools determined the day before the start of the study.

Tide pool	Day	Time	Minimum Temp (°C)	Time	Maximum Temp (°C)
Reference	1	06:38	10.30	12:17	15.99
	2	06:49	10.30	13:21	15.20
	3	07:13	10.30	13:50	11.98
Treatment	1	09:49	13.22	11:49	17.02
	2	07:04	10.05	12:34	13.79
	3	07:19	10.05	13:04	12.93

Table 2: Temperature maximum and minimums recorded by the TidBit Temperature Logger

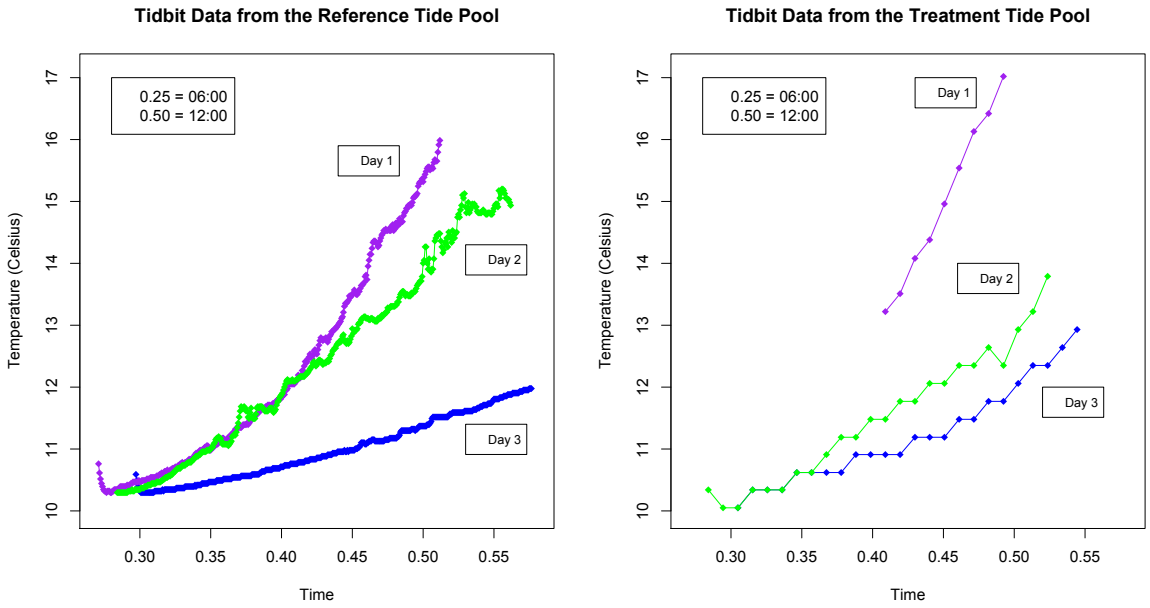


Figure 4: The variation in temperatures in the Reference pool (**left**) and Treatment pool (**right**) as recorded by the TidBit Temperature Loggers.

Day	Time	Temp (°C)	Salinity (ppt)	D.O. (mg/L)	D.O. (%)
1	06:13	10.25	30.1	4.80	43.2%
1	07:26	10.80	30.2	6.01	54.5%
1	08:25	11.322	30.0	10.31	95.7%
1	09:31	12.300	30.4	16.39	256.6%
1	10:36	14.855	30.5	21.30	224.4%
1	11:08	15.543	31.3	-	>200%
1	11:29	18.686	31.5	-	>200%
1	12:16	17.960	31.3	-	>200%
2	06:38	10.201	-	-	-
2	08:41	11.390	-	-	-
2	10:44	13.732	-	-	-
2	13.29	18.122	-	-	-
3	07:08	10.395	30.4	6.99	63.4%
3	08:01	10.54	30.9	7.41	67.2%
3	09:00	-	30.8	9.57	87.2%
3	09:56	-	30.8	11.97	110.1%
3	11:05	-	30.7	15.17	140.8%
3	11:59	-	30.7	19.03	178.7%
3	13:15	-	30.5	-	>200%
3	13:50	-	30.6	-	>200%

Table 3: Variations in temperature, salinity and dissolved oxygen in the Reference tide pool over the course of the study as determined by probe measurements.

Day	Time	Temp (°C)	Salinity (ppt)	D.O. (mg/L)	D.O. (%)
1	06:16	10.10	30.8	4.80	42.8%
1	07:30	10.63	30.5	6.84	61.6%
1	08:27	10.98	30.3	13.66	125.9%
1	09:37	12.752	30.4	21.38	203.0%
1	10:42	15.026	30.6	-	>200%
1	11:17	17.658	31.5	-	>200%
1	11:31	17.956	31.5	-	>200%
1	11:56	18.506	30.8	-	>200%
2	06:45	10.149	-	-	-
2	08:47	11.238	-	-	-
2	10:46	13.707	-	-	-
2	12:45	17.412	-	-	-
3	07:12	10.27	30.8	8.60	77.6%
3	08:02	10.53	31.0	9.41	85.2%
3	09:10	-	31.0	12.24	111.3%
3	10:02	-	31.0	14.67	134.2%
3	11:13	-	30.9	21.09	196.3%
3	12:03	-	30.7	-	>200%
3	13:01	-	30.8	-	>200%

Table 4: Variations in temperature, salinity and dissolved oxygen in the Treatment tide pool over the course of the study as determined by probe measurements.

Day	Time	Temp (°C)	Salinity (ppt)	D.O. (mg/L)	D.O. (%)
1	06:22	10.17	30.4	6.91	61.5%
1	07:34	10.03	30.4	8.76	78.1%
1	08:35	10.26	30.7	10.5	95.2%
1	09:39	11.110	29.8	10.35	94.6%
1	10:49	12.640	30.4	11.46	114.5%
1	11:35	11.469	31.0	9.29	86.6%
1	12:20	12.246	31.1	8.45	84.8%
2	06:59	10.130	-	-	-
2	08:55	10.628	-	-	-
2	10.55	10.690	-	-	-
2	12:57	11.273	-	-	-
3	07:22	10.25	30.8	8.65	77.4%
3	08:06	10.21	30.5	8.09	72.4%
3	09:16	11.0	29.2	10.26	92.9%
3	10:04	10.3	31.3	9.89	88.2%
3	11:17	10.7	31.3	10.23	91.8%
3	12:08	11.3	30.6	10.67	97.5%
3	13:20	11.1	30.9	8.02	72.6%
3	13:38	11.3	30.8	8.06	73.4%

Table 5: Variations in temperature, salinity and dissolved oxygen in the Haro Strait over the course of the study as determined by probe measurements.

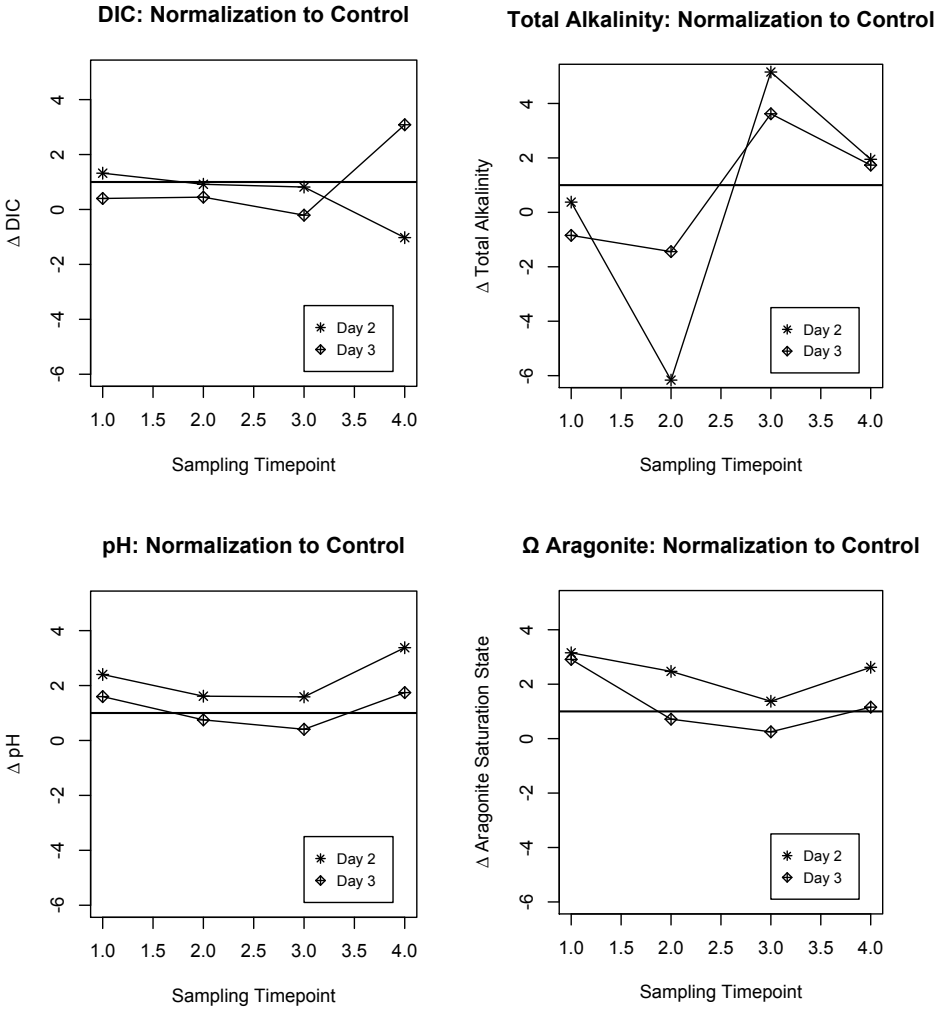


Figure 5: Normalization of total carbon, total alkalinity, pH and Aragonite saturation state for Day 2 and Day 3 according to Equation 1.

Equation 1: an example of how the normalized values were calculated

$$Normalized\ pH\ (Day\ 2) = \frac{(pH\ in\ Treatment\ pool - pH\ in\ Reference\ pool)Day2}{(pH\ in\ Treatment\ pool - pH\ in\ Reference\ pool)Day\ 1}$$

Tide pool	Day	Time	Minimum pH	Time	Maximum pH
Reference	1	06:13	7.361	12:16	8.602
	2	06:38	7.439	13:30	8.692
	3	07:00	7.605	13:50	8.340
Treatment	1	06:16	7.443	12:08	8.676
	2	06:45	7.636	12:45	8.942
	3	07:12	7.736	13:01	8.469

Table 6: pH maximum and minimums calculated in CO2Calc from DIC, AT, Temperature and Salinity data.

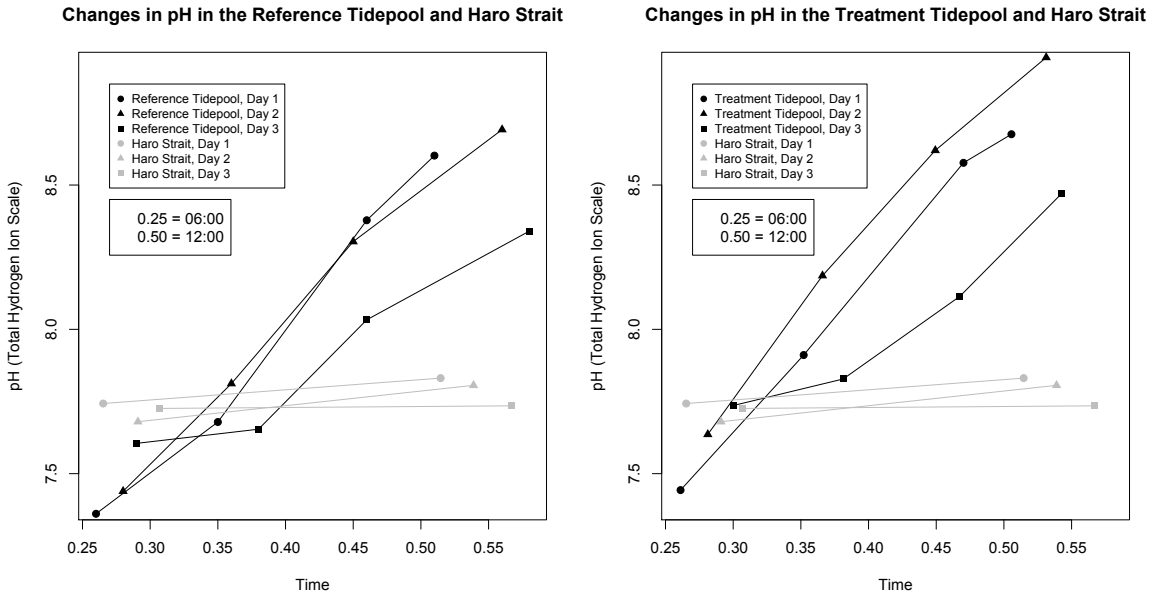


Figure 6: Changes observed in pH (total hydrogen ion scale) in the Reference tide pool (**left**), Treatment tide pool (**right**), and Haro Strait (superimposed in both for reference levels) over the three days of the experiment.

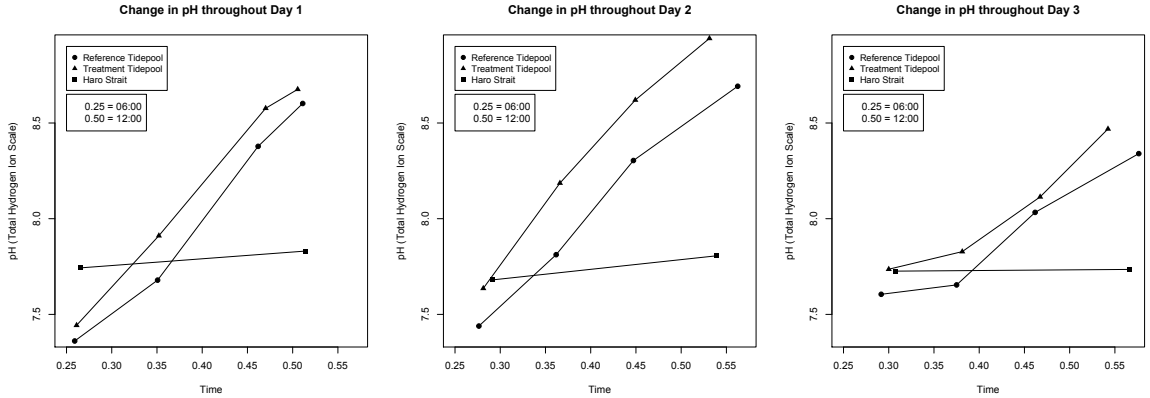


Figure 7: Changes observed in pH (total hydrogen ion scale) on Day 1 (**left**), Day 2 (**middle**), and Day 3 (**right**) in the two tide pools and Haro Strait water.

Tide pool	Day	Time	Min. DIC (μmol/kg)	Time	Max. DIC (μmol/kg)
Reference	1	12:16	1216.10	06:13	2171.46
	2	13:30	1099.41	06:38	2121.32
	3	13:50	1414.52	07:00	2046.31
Treatment	1	12:08	1237.01	06:16	2125.43
	2	12:45	1077.95	06:45	2060.52
	3	13:01	1479.05	07:12	2027.87

Table 7: Total carbon maximum and minimums, determined as described in the methods.

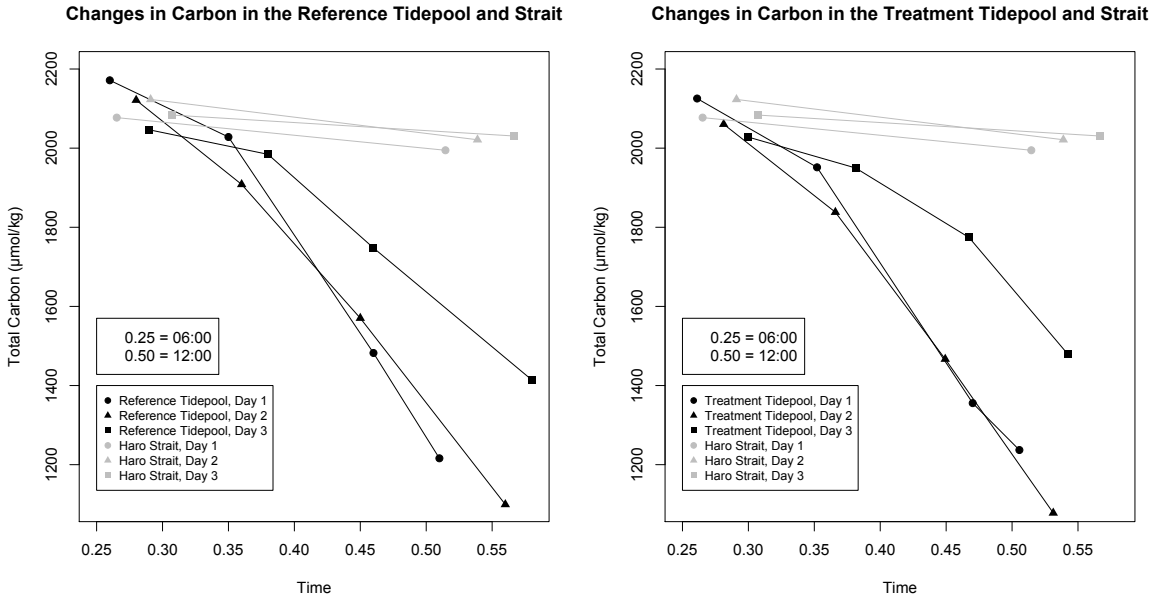


Figure 8: Changes observed in total carbon (μmol/kg) in the Reference tide pool (**left**), Treatment tide pool (**right**), and Haro Strait (superimposed in both for reference levels) over the three days of the experiment.

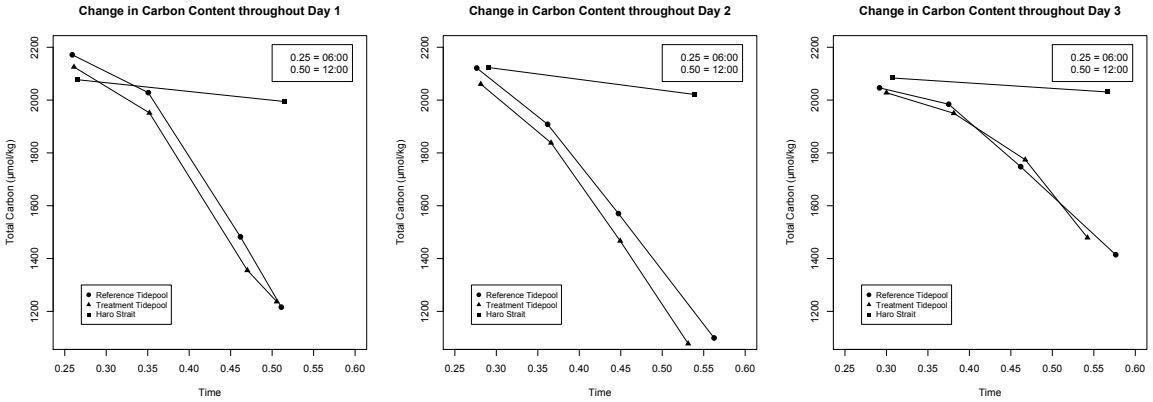


Figure 9: Changes observed in total carbon (μmol/kg) on Day 1 (**left**), Day 2 (**middle**), and Day 3 (**right**) in the two tide pools and Haro Strait water.

Tide pool	Day	Time	Minimum TA (μmol/kg)	Time	Maximum TA (μmol/kg)
Reference	1	12:16	1669.9	06:13	2116.5
	2	13:30	1577.7	06:38	2089.5
	3	13:50	1691.8	07:00	2061.3
Treatment	1	12:08	1753.3	06:16	2096.0
	2	12:45	1740.2	06:45	2081.8
	3	13:01	1836.4	07:12	2078.7

Table 8: total alkalinity maximum and minimums, determined as described in the methods.

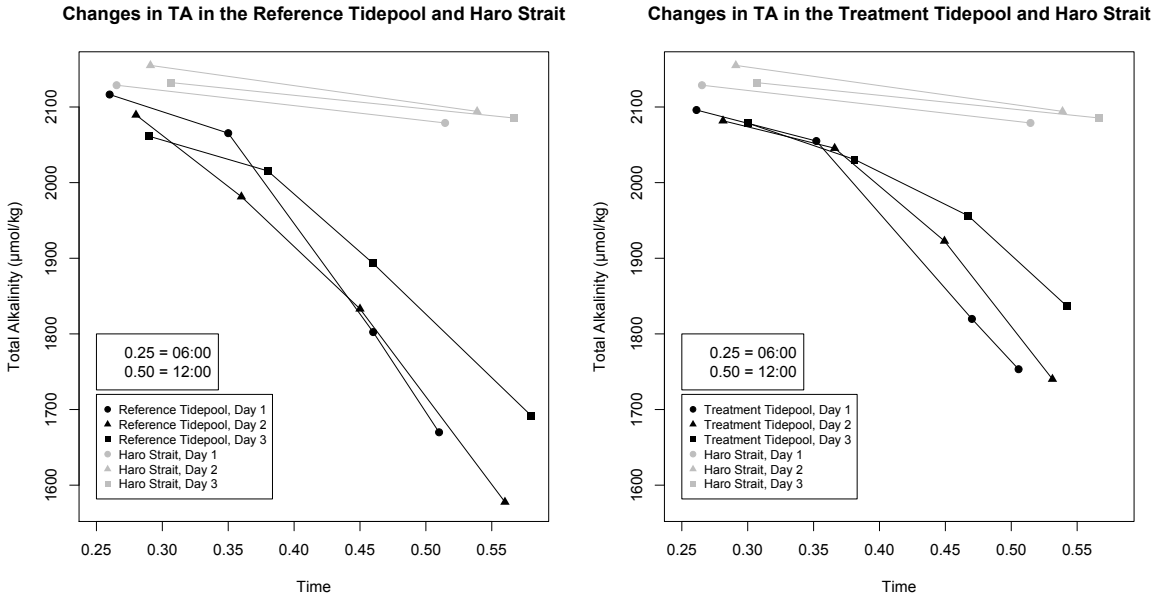


Figure 10: Changes observed in total alkalinity (μmol/kg) in the Reference tide pool (**left**), Treatment tide pool (**right**), and Haro Strait (superimposed in both for reference levels) over the three days of the experiment.

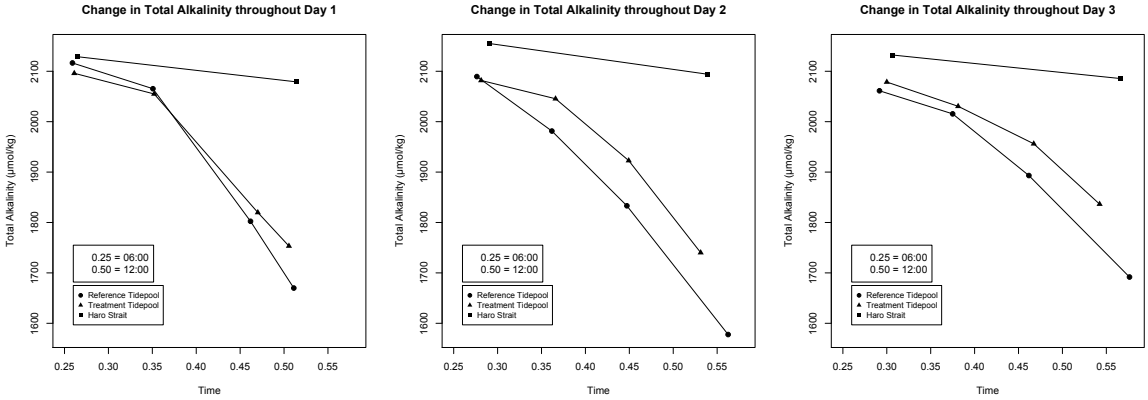


Figure 11: Changes observed in total alkalinity (μmol/kg) on Day 1 (**left**), Day 2 (**middle**), and Day 3 (**right**) in the two tide pools and Haro Strait water.

Tide pool	Day	Time	Minimum Ω_{ARAG}	Time	Maximum Ω_{ARAG}
Reference	1	06:13	0.392	12:16	4.388
	2	06:38	0.458	13:30	4.575
	3	07:00	0.662	13:50	2.729
Treatment	1	06:16	0.470	12:08	5.127
	2	06:45	0.704	12:45	6.511
	3	07:12	0.889	13:01	3.584

Table 9: Aragonite saturation state maximum and minimums calculated in CO2Calc from DIC, AT, Temperature and Salinity data.

Tide pool	Day	Time	Minimum $\Omega_{CALCITE}$	Time	Maximum $\Omega_{CALCITE}$
Reference	1	06:13	0.623	12:16	6.840
	2	06:38	0.729	13:30	7.154
	3	07:00	1.054	13:50	4.294
Treatment	1	06:16	0.745	12:08	7.994
	2	06:45	1.118	12:45	10.20
	3	07:12	1.409	13:01	5.646

Table 10: Calcite saturation state maximum and minimums calculated in CO2Calc from DIC, AT, Temperature and Salinity data.

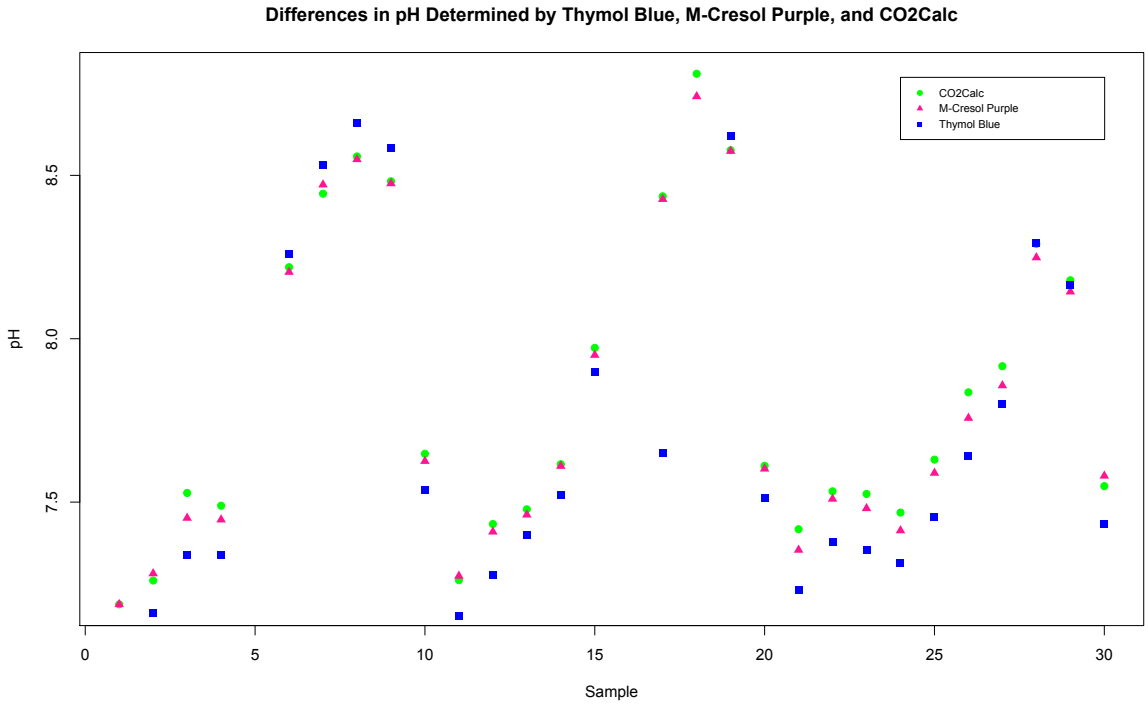


Figure 12: the pH (total hydrogen ion scale) measured or calculated for each sample at 25°C: calculated in CO2Calc (**green circles**), determined using m-cresol purple dye and spectrophotometry (**pink triangles**), and determined using thymol blue dye and spectrophotometry (**blue diamonds**). The pH values from CO2Calc were calculated using total carbon, total alkalinity, temperature, and salinity.