



# Ocean and Coastal Acidification Monitoring

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## Summary

From November 8, 2016 to August 23, 2017, we monitored hourly water CO<sub>2</sub> partial pressure ( $p\text{CO}_2$ ) and pH (on the total pH scale) using Sunburst® SAMI-CO2 and SATlantic® SeaFET pH sensors, respectively, at ~1 m depth in the Aransas Ship Channel, Texas. The objective was to examine the estuarine acidification issue as a result of freshwater inflow from rivers.

Unfortunately, a post Hurricane Harvey accident destroyed the research pier of the University of Texas Marine Science Institute, where the two sensors were located. Therefore, the monitoring work had to be cut short. Nevertheless, during the approximately 10-month monitoring period, significant temporal variations of both  $p\text{CO}_2$  and pH were observed with a range of 251.2 – 619.7  $\mu\text{atm}$  and 7.789 – 8.451, respectively. Higher  $p\text{CO}_2$  and lower pH were observed during summer and lower  $p\text{CO}_2$  and high pH were observed during winter. Diel variability was higher during the summer months for  $p\text{CO}_2$  and during the winter months for pH. Salinity and temperature both exerted controls on the variations of  $p\text{CO}_2$  and pH at different extents, indicating sensitivity of the estuarine water carbonate system to changes in both hydrological condition and temperature. Carbonate alkalinity (C-Alk) was calculated based on  $p\text{CO}_2$  and pH data and was generally higher in winter months and lower in summer months. C-Alk also showed an inverse relationship with salinity. Carbonate saturation state with respect to aragonite ( $\Omega_{\text{Ar}}$ , the mineral for larval stage oysters) had a mean of 4.50, but it did drop to undersaturation (minimum 0.91) for a short period of time. Nevertheless,  $\Omega_{\text{Ar}}$  was greater than 1 for 99.8% of the time, and greater than 2 for 95.9% of time, indicating overall optimal but occasional sub-optimal condition in the Aransas Ship Channel, which serves as a conduit for the Mission-Aransas Estuary and the Gulf coast.

## **Acknowledgements**

We would like to thank the Ocean and Coastal Acidification Program at the U.S. Environmental Protection Agency and the Coastal Bend Bays and Estuaries Program for supporting this project. University of Texas Marine Science Institute (UTMSI) graciously provided the deployment platform on their research pier for us to carry out the monitoring work. Bill Adams at UTMSI helped with designing and mounting the monitoring structure on the research pier. Mission-Aransas Estuarine Research Reserve (MANERR) provided their monitoring data (salinity and temperature) for cross validation with ours.

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## Introduction

Ocean acidification (OA), widely known as caused by the invasion of atmospheric CO<sub>2</sub> into the surface ocean, has become a global concern because OA leads to decreases in both carbonate saturation state and pH (i.e., an increase in water proton level) in surface oceans (Doney et al., 2009; Feely et al., 2004). Seawater carbonate chemistry changes have been shown to affect calcifying organisms by depressing their calcification rates (Kleypas et al., 1999). Lower biological calcification rates not only lead to the reduced production of the calcifying organisms (Langdon et al., 2000; Waldbusser et al., 2014), but also cause a deterioration of habitats that these organisms maintain and thrive in, such as oyster reefs and coral reefs (Andersson, 2015; Shaw et al., 2012).

There have been many studies on effects of OA in open and tropical oceans, however studies on coastal ocean acidification have only recently started. In coastal oceans, multiple processes that lead to CO<sub>2</sub> buildup in seawater have been attributed to the acidification, including not only atmospheric CO<sub>2</sub> intrusion, but CO<sub>2</sub> from respiration within the water column due to settling of nutrient-enhanced surface primary production (Cai et al., 2011; Wallace et al., 2014). As the uptake of atmospheric CO<sub>2</sub> continues in coastal waters, it is expected that acidified coastal ocean could further acidify the estuaries, the continuum between rivers and the ocean. However, current studies have mostly focused on theoretical explorations of this “carry-over” effect based on modeling exercises (Hu and Cai, 2013; Miller et al., 2009), and few studies have been able to detect long-term carbonate chemistry changes in the field. This is mostly due to the large variations in estuarine carbonate chemistry that can be changed by a myriad of processes, including but not limited to primary production, respiration, calcification, and carbonate dissolution, all of which can occur either in pelagic or benthic settings.

A recent study published in the journal *Environmental Science and Technology* (Hu et al., 2015) revealed a broad decline in both pH and alkalinity (i.e., acidification) in many estuaries in the State of Texas (northwestern Gulf of Mexico). This study was based on a long-term dataset collected by the Texas Commission on Environmental Quality. Among these estuaries, the ones in the south Texas, which are subject to semi-arid climate influences, experience the greatest decline in both alkalinity and pH, including the Mission-Aransas Estuary that consists of Aransas, Copano, and Mesquite bays. Hu et al. hypothesized the reason for the change is that the long-term decrease in freshwater inflow, which is rich in alkalinity, causes declining alkalinity and pH in the receiving estuarine waters.

To study the acidification phenomenon in estuarine settings in south Texas, this project examined high temporal changes in both pH and partial pressure of CO<sub>2</sub> ( $p\text{CO}_2$ ) using two sensors, i.e., a SATlantic<sup>®</sup> SeaFET pH sensor and a Sunburst<sup>®</sup> Submersible Autonomous Moored Instrument for CO<sub>2</sub> (SAMI-CO<sub>2</sub>). These sensors are capable of taking measurements for extended period of time (projected to be years) with user-defined measurement frequency. The sensors were deployed at the research pier of the University of Texas Marine Science Institute (UTMSI), which is located in the Port Aransas Ship Channel, which connects estuarine water with that in the northwestern Gulf of Mexico.

This work complements ongoing field data collection (biweekly to monthly) at five System-Wide Monitoring Program (SWMP) sites, including the UTMSI research pier, located within the Mission Aransas National Estuarine Research Reserve (MANERR). The OA monitoring includes collection of a suite of water carbonate chemistry data (high precision pH, total dissolved inorganic carbon, and total titration alkalinity) and auxiliary data (dissolved oxygen, chlorophyll, and salinity). The high temporal resolution data from the sensors allowed us to examine both the short-term (daily to monthly) variations and long-term (interannual) changes in water carbonate system in the Port Aransas Ship Channel under the influence of freshwater inflow variation and ocean acidification effects.

## Methods

### *Monitoring Location*

This monitoring work was done on the lower deck of UTMSI's research pier, which was located at 27°50'17"N, 97°3'1"W and allowed direct access to *in situ* seawater at the Port Aransas Ship Channel (i.e., Aransas Pass tidal inlet), which connects the Gulf coastal water with the Aransas, Corpus Christi, and Redfish bays. As secondary bays to Corpus Christi and Aransas bays, Nueces and Copano bays receive freshwater input from Nueces River and Mission/Aransas rivers, respectively. Mesquite Bay also receives freshwater from Guadalupe/San Antonio rivers during high flow seasons. The 300 ft. pier had a 1200 sq. ft. lab at its base and a 150 sq. ft. instrument room on the end. The terminus of the pier and instrument room housed a weather station, tide gauge, current meter, and sensors for water temperature and salinity. Gauges and sensors were all located at ~5 m underwater. The Mission Aransas National Estuarine Research Reserve (MANERR) maintained the salinity and temperature sensors, and data are being recorded every 15 minutes.

### *Monitoring Design*

This project was designed to collect pH and  $p\text{CO}_2$  data using two *in situ* sensors and incorporated temperature and salinity data collected by a YSI® 600OMS V2 sonde. The pH data were collected using a SATlantic® SeaFET pH sensor (on the total pH scale) and  $p\text{CO}_2$  were collected using a Sunburst® SAMI-CO<sub>2</sub>. The pH and  $p\text{CO}_2$  sensors also collected temperature as temperature was used in the internal computations of these two instruments. Data collected by the sensors (pH,  $p\text{CO}_2$ , salinity, and temperature) were saved in the onboard data loggers for periodic download during our biweekly or monthly trips to the UTMSI pier.

Ideally, *in situ* sensors should be deployed under the sea surface. However, to reduce the cost of maintenance mostly related to biofouling (for example sending down divers every two weeks in warmer months or every one month during winter), the sensors measured both pH and  $p\text{CO}_2$  from an *ex situ* position but using *in situ* seawater pumped from ~1 m below the sea surface. A 100-Qt cooler was used to house the SAMI-CO<sub>2</sub> and SeaFET sensors. The cooler's bottom spigot was connected to a FLOJET diaphragm water pump (Model # 02130032A, 1.8 gal/min flow rate), which pumped water through a ½" copper pipe from ~1 m water depth at 20 minutes before each whole hour, when sensor readings were recorded. The copper pipe was housed inside a 2" PVC pipe, which was secured to the handrail of the deck using a wooden frame. A 1" hole was drilled at the opposite side of the spigot ~5" below the cooler rim across from the bottom water inlet to allow water outflow, which was directed back to the sea surface through plastic tubing. The YSI sonde was deployed inside a parallel 2" PVC pipe at ~1 m below the sea surface, along with the water inlet pipe (see Figure 1 for the monitoring set up).

Both sensors worked continuously for a 10-month period until Hurricane Harvey disrupted the deployment on August 23, 2017.

### *Sensor Maintenance*

All three sensors were serviced regularly by CCL personnel (Table 1). At each time the SAMI-CO<sub>2</sub> and SeaFET sensors were taken out of the cooler, and the cooler was cleaned to remove

sediment. Data from the prior deployment period were then downloaded to a laptop computer before placing the sensors back into the cooler. Initially, the YSI sensor was cleaned as best we could for biofouling at each visit. After about three months deployment (when temperature began to rise and biofouling was increasing), we noted substantial drift in the salinity signal, so on February 10, 2017 we began swapping out the YSI and replacing it with another pre-calibrated YSI during service trips.

Table 1. Maintenance record for the deployed sensors.

Date of Maintenance	Duties Performed					Notes: Pump Failure
	Cooler and Sensors Cleaned	Sensor Data Download	YSI swapped	Discrete Water Samples Collected	Pump Replaced	
11-08-2016	-	-	-	X	-	-
11-15-2016	X	X	-	X	-	-
11-29-2016	X	X	-	X	-	-
12-13-2016	X	-	-	-	-	X
12-14-2016	X	X	-	-	X	-
12-25-2016	X	-	-	-	-	-
1-13-2017	X	X	-	X	-	-
1-25-2017	X	-	-	-	-	-
2-3-2017	X	X	-	X	-	-
2-10-2017	X	-	X	X	-	-
2-24-2017	X	-	X	X	-	-
3-9-2017	X	X	X	X	-	-
3-24-2017	X	X	X	X	-	-
4-6-2017	X	X	X	X	-	X
4-14-2017	X	X	X	-	X	-
4-28-2017	X	X	X	X	-	-
5-12-2017	X	X	X	X	-	-
5-24-2017	X	X	X	X	-	-
6-9-2017	X	X	X	X	-	-
6-22-2017	X	X	X	X	-	-
7-7-2017	X	X	X	X	-	-
7-20-2017	X	X	X	X	-	-
8-4-2017	X	X	X	X	-	-
8-18-2017	X	-	X	-	-	X
8-19-2017	-	-	-	-	X	-

### *Discrete Water Sampling*

Duplicate water samples at both the pump inlet depth using a Van Dorn sampling bottle and inside the cooler were taken right after the last whole hour measurements before sensor cleaning or retrieval. Water temperature and salinity were collected using a handheld YSI data sonde at

the pump inlet depth and inside the cooler. Water sample collection followed standard protocol for ocean carbonate chemistry studies (Dickson et al., 2007). 250 ml ground glass borosilicate bottles were used and overflow of at least one bottle volume was ensured. After sample collection, 100  $\mu$ L saturated mercury chloride ( $\text{HgCl}_2$ ) was injected into the sampling bottle to arrest biological activity, and Apiezon  $\text{\textcircled{R}}$  grease was applied to the bottle stopper, which was then secured to the bottle using a rubber band and a nylon hose clamp.

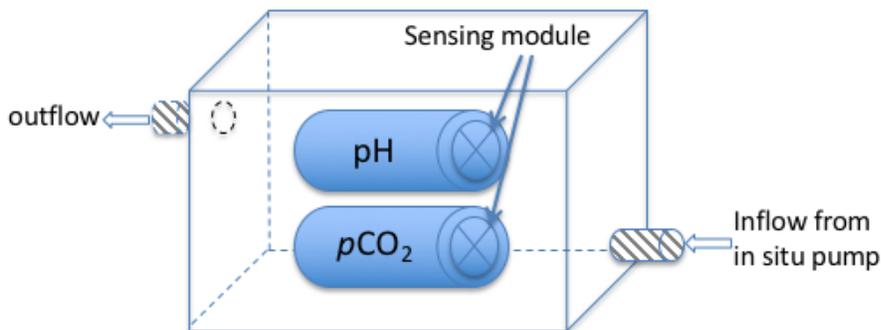


Figure 1. Monitoring setup on the lower deck of UTMSI's research pier.

#### *Discrete Sample Analysis*

TA was measured using open-cell Gran titration at  $22 \pm 0.1^\circ\text{C}$  using a water-jacketed circulation system. DIC was measured by injecting 0.5 ml sample with a high-precision Kloehn syringe pump into 1 ml 10%  $\text{H}_3\text{PO}_4$  (balanced by 0.5 M NaCl). The product  $\text{CO}_2$  gas through sample acidification was then stripped using high-purity nitrogen gas and carried into an infrared gas detector. Both TA and DIC analyses had a precision of 0.1%. Certified Reference Material was used to ensure the accuracy of the analyses (Dickson et al., 2003). For samples with salinity  $>20$ , pH was measured using a spectrophotometric method at  $25 \pm 0.1^\circ\text{C}$  (Carter et al., 2013) and the Douglas and Byrne (2017) equation. A calibrated Orion Ross glass pH electrode was used to measure pH when salinity  $<20$  at  $25 \pm 0.1^\circ\text{C}$ . All pH values obtained using the potentiometric method were converted to total scale at *in situ* temperature (Millero, 2001). Salinity of the discrete samples was measured using a benchtop salinometer calibrated by MilliQ water and known salinity CRM.

#### *Statistical Methods for Sensor Data Processing*

Salinity, temperature, pH, and  $p\text{CO}_2$  data from sensors were used to calculate other carbonate parameters in the Excel program CO2Sys (Pierrot et al., 2006). Carbonate alkalinity was also calculated using pH and  $p\text{CO}_2$  as input variables. The linear relationship between salinity and calcium was determined using data collected from The Mission-Aransas Estuary (Copano and Aransas bays and the Aransas Ship Channel) between 2016 and 2017 (Eq. 1). This relationship was used as a correction factor for the saturation state of aragonite ( $\Omega_{\text{Ar}}$ ) value that was calculated in CO2Sys to take into consideration that calcium is not zero at zero salinity (Eq. 2).

$$Ca = 0.2672 \times Sal + 0.6225 \quad (1)$$

$$\Omega_{corr} = \frac{\Omega_{CO2Sys}}{\frac{Sal_{ocean}}{Ca_{ocean}} \times \frac{Ca_{sample}}{Sal_{sample}}} \quad (2)$$

The diel range was calculated for each day as the maximum minus the minimum measurement for a parameter. Differences between daytime and nighttime  $pCO_2$  and pH were investigated using paired t-tests to compare the averages on given dates. Daytime was defined as 16:00-22:00 UTC (10:00 – 16:00 CST) and nighttime was defined as 03:00-09:00 UTC (21:00 – 03:00 CST).

River flow data were obtained from the USGS at <https://maps.waterdata.usgs.gov/mapper/index.html?state=tx>. River discharge rates over the period of 11-08-2016 – 08-23-2017 from the Aransas, Nueces and Guadalupe (after merging with the San Antonio River) rivers were obtained from the stations closest to the bay (Skidmore, TX, Calallen, TX, and Tivoli, TX). Correlations between river discharge and measured parameters were examined.

## Results and Discussion

### *Internal Consistency*

The cooler design was demonstrated to be an appropriate *ex situ* representation of the in-situ conditions (Table 2). The average difference in pH between the ship channel and the cooler was about  $-0.005 \pm 0.023$ . The average difference in  $p\text{CO}_2$  between the ship channel and the cooler was about  $-0.95 \pm 26.23$ —a standard deviation within 6.3% of the calculated  $p\text{CO}_2$ .

The agreement between the continuous monitoring of the sensors and the measured/calculated parameters in the lab was fair, with pH and  $p\text{CO}_2$  having standard deviations of  $\sim 0.1$  pH units and 9.7% ( $\sim 45 \mu\text{atm}$ ) of their measured values, respectively (Table 3). In the case of  $p\text{CO}_2$ , much of the variability in  $p\text{CO}_2$  can be accounted for by one outlier—removing the  $p\text{CO}_2$  datum from July 7, 2017. Doing so would decrease this value to the standard deviation from within 9.7% to within 6% (or  $\sim 27 \mu\text{atm}$ ) (Figure 2). There was no significant difference (t-test  $p > 0.05$ ) between the sensor pH or  $p\text{CO}_2$  with the lab measured pH or calculated  $p\text{CO}_2$ , respectively, since the differences fluctuated around zero (Figure 2). This indicates that the use of calculated  $p\text{CO}_2$  from DIC and pH can be appropriate for carbonate chemistry studies in these estuarine waters. Of the tested carbonic acid dissociation constants, it appears that those reported in Millero (2006) or Millero (2002) provided the best fit for the speciation calculations (Table 2).

Table 2. Average and standard deviation of the difference between in situ bottle samples and the *ex situ* sensor location.  $p\text{CO}_2$  is calculated using pH and DIC measurements and pH was converted from lab measured to *in situ* given different sets of equilibrium constants.

<b><i>In situ</i> Bottle Sample – Cooler Bottle Sample</b>						
	Millero 2010	Hanson 1973, refit by Dickson	Millero 2006	Mehrback 1973, refit by Dickson	Lueker 2000	Millero 2002
$p\text{CO}_2$	$-5.95 \pm 25.30$	$-12.22 \pm 25.65$	$-5.16 \pm 25.25$	$-2.34 \pm 25.01$	$-2.33 \pm 25.02$	$-0.95 \pm 26.23$
pH	$-0.005 \pm 0.023$	$-0.005 \pm 0.023$	$-0.005 \pm 0.023$	$-0.005 \pm 0.023$	$-0.005 \pm 0.023$	$-0.005 \pm 0.023$

Table 3. Average and standard deviation of the difference between sensor measurements and calculated *in situ*  $p\text{CO}_2$  and pH from discrete bottle samples given different sets of equilibrium constants.

<b>Sensor – Cooler Bottle Sample</b>						
	Millero 2010	Hanson 1973, refit by Dickson	Millero 2006	Mehrback 1973, refit by Dickson	Lueker 2000	Millero 2002
$p\text{CO}_2$	$-12.51 \pm 42.98$	$-18.77 \pm 44.17$	$-11.71 \pm 42.79$	$-8.90 \pm 42.86$	$-8.89 \pm 43.26$	$-7.51 \pm 40.19$

pH	$-0.048 \pm 0.092$	$-0.048 \pm 0.093$	$-0.047 \pm 0.092$	$-0.048 \pm 0.092$	$-0.048 \pm 0.092$	$-0.049 \pm 0.094$
<b>Sensor – <i>In situ</i> Bottle Sample</b>						
$p\text{CO}_2$	$-6.56 \pm 34.13$	$-12.78 \pm 35.38$	$-5.78 \pm 33.9$	$-3.01 \pm 34.28$	$-3.09 \pm 34.76$	$-1.83 \pm 30.99$
pH	$-0.054 \pm 0.101$	$-0.055 \pm 0.101$				

Despite that the sensor pH data were not statistically different from the discrete bottle data from either the cooler or directly from the sea surface, we corrected sensor pH using the offset between the pH recorded by the SeaFet and the measured pH value from the discrete cooler samples collected during the entire sensor deployment period. This approach forced the mean difference between the sensor values and discrete water values (both from the cooler) to be zero, as recommend by the best practice method used in the literature (Bresnahan et al., 2012). All pH values were adjusted by adding 0.048 (Table 3). There was not a similar correction done for the  $p\text{CO}_2$  data since the SAMI-CO2 should not experience any drift due to its dependence on spectrophotometric measurements.

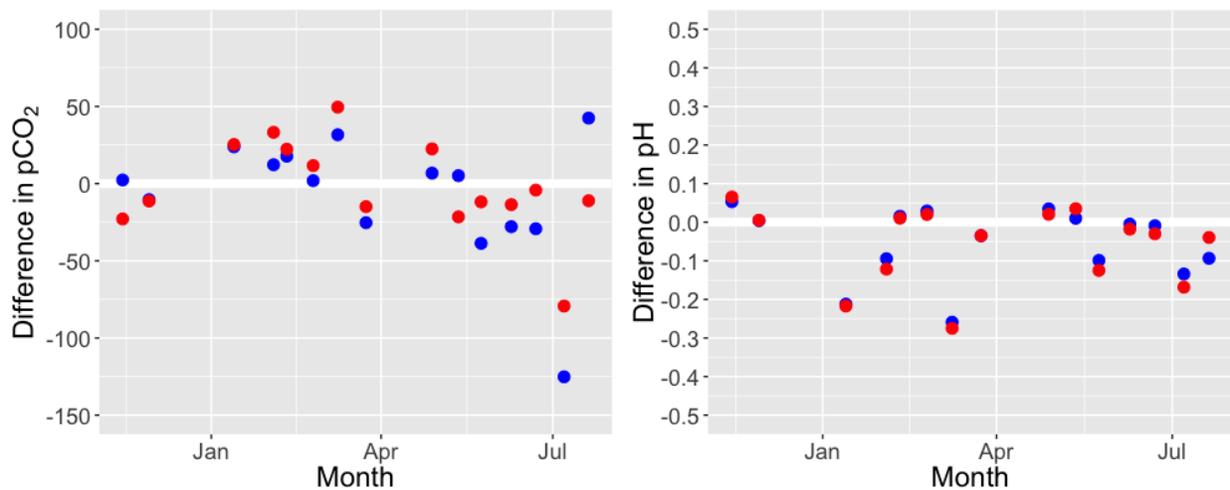


Figure 2. Differences in  $p\text{CO}_2$  and pH between *in situ* sensors and lab-analyzed bottle samples from the cooler (blue) and the ship channel (red)

### *Salinity Correction*

For quality assurance, our YSI sonde data were compared with the YSI sonde deployed by the MANERR at the same location but at  $\sim 6$  m depth (Figure 3). In all cases of issues with our YSI sonde, including deployment issues, skewed measurements due to substantial biofouling, or substantial outliers, salinity and temperature corrections were made.

To incorporate any measurement differences associated with sensor depth in the water column into the salinity corrections, the average difference between the MANERR YSI and our YSI at surface water during periods of proper functioning was used as a correction to the MANERR

data. The period between 02-24-2017 and 05-15-2017, was set as the reference for “good” YSI data (Figure 3). During this period, the average difference between NERR and YSI salinity and temperature data was 0.3411 and 0.07 °C (less on the surface), respectively. Time periods of salinity correction include 01-06-2017 – 02-24-2017 (drift associated with biofouling and deployment issue with tide lowering beneath sensor), 08-04-2017 – 08-04-2017 (drained YSI sonde batteries), 08-04-2017 – 08-23-2017 (YSI sonde lost due to the aftermath of Hurricane Harvey), and periodic obvious outliers with large differences between our YSI data sonde and the MANERR data (Figure 4) possibly due to large ripples caused by passage of vessels that exposed our YSI sonde to air when a measurement was due to be taken.

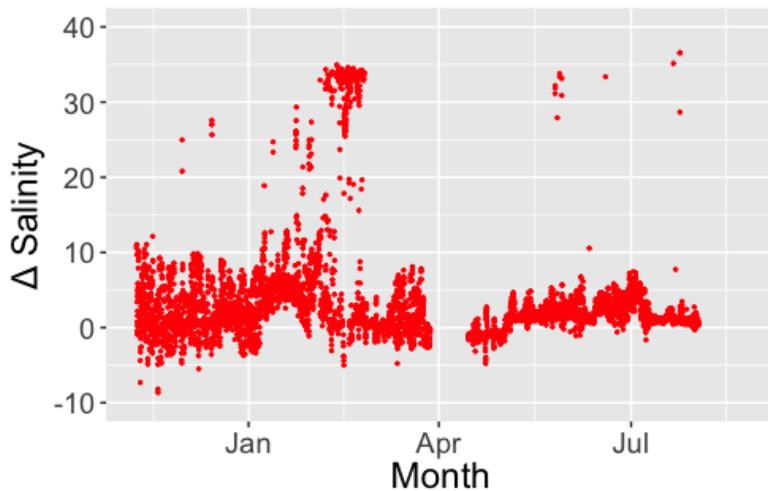


Figure 3. Difference in salinity between YSI deployed at ~6 m depth by the Mission-Aransas National Estuarine Research Reserve and our YSI deployed ~1 m depth.

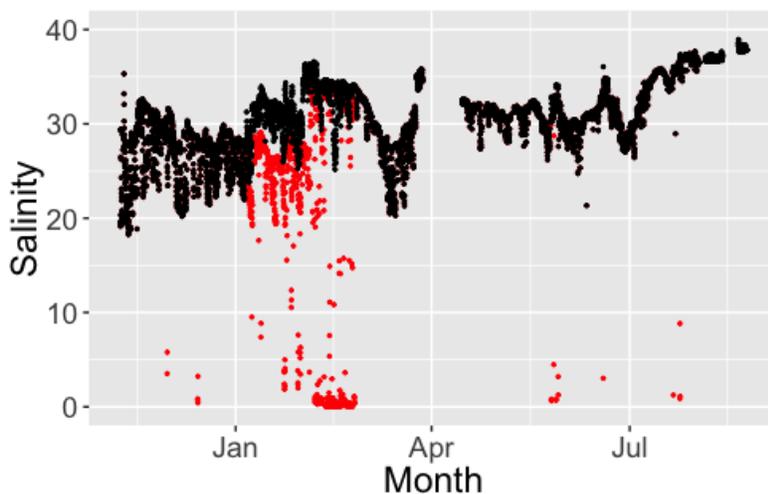


Figure 4. Salinity profiles of the deployed YSI data sonde (red) and the corrected salinity as used for all analyses (black).

*Removal of Suspicious pCO<sub>2</sub> and pH Data*

While the *ex situ* position of the cooler was beneficial for easy maintenance of the deployed sensors, there was an issue of periodic pump failure due to a manufacture flaw that was later discovered (Table 1, Table 4), which would result in the cooler not appropriately representing the *in situ* environment (Figure 5). Pump failure resulted in notable increases in  $p\text{CO}_2$  and decreases in pH due to the buildup of respirational products inside the cooler. During such instances of pump failure, the sensor data was flagged as suspicious data prior to analysis. Additional instances of suspicious sensor data due to assumed sensor malfunction were also flagged based on the multiple data correlation comparisons (Figure 6).  $p\text{CO}_2$  data was flagged as suspicious during 05-07-2017 – 05-08-2018 and 08-22-2017 – 08-23-2017, while only single outliers where flagged in the pH dataset.

Table 4. Record of pump failure

Date pump issue was discovered	Suspected date of pump failure	Date of pump replacement
12-12-2016	12-12-2016	12-13-2016
04-06-2017	03-28-2017	04-14-2017
08-18-2017	08-12-2017	08-19-2017

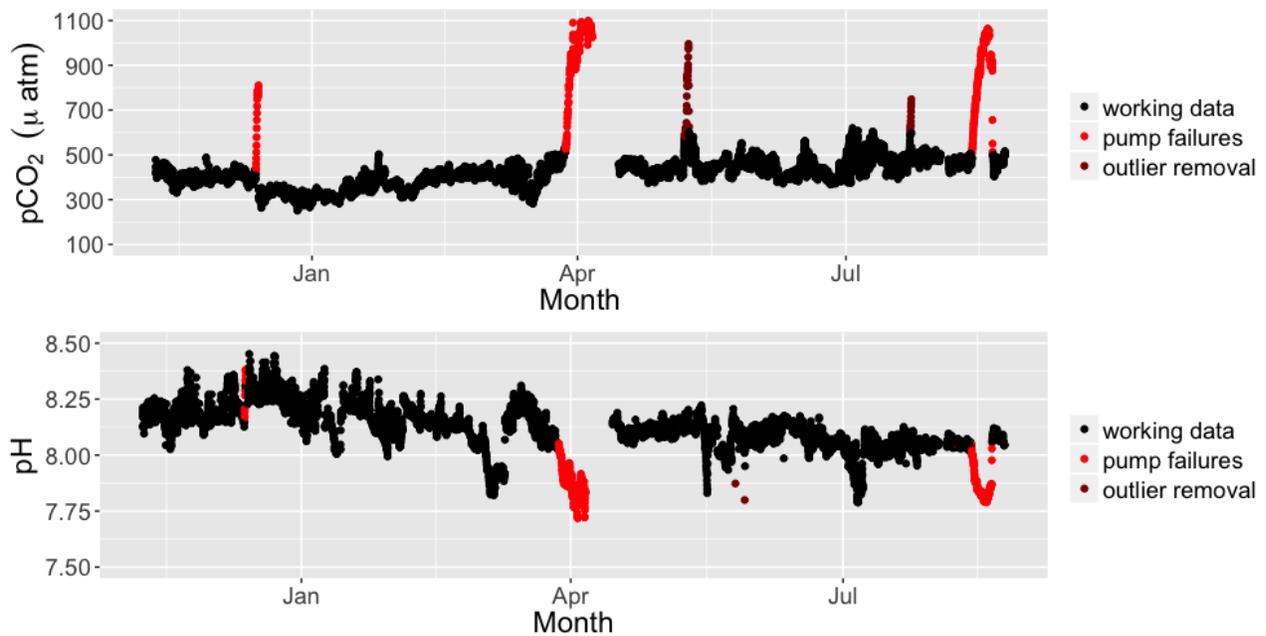


Figure 5. All recorded  $p\text{CO}_2$  and pH data. Data points flagged for removal prior to analysis are shown in red.

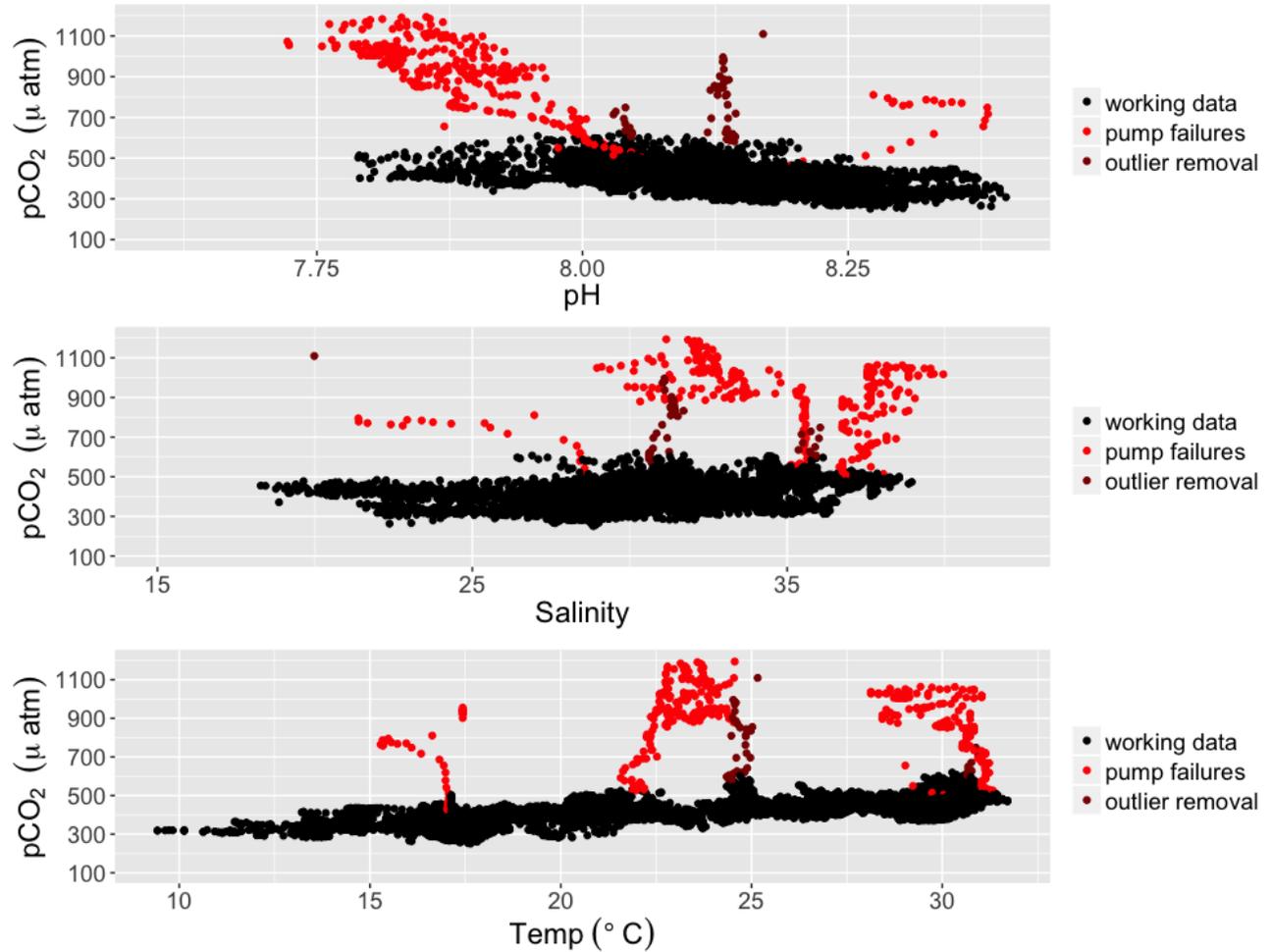


Figure 6. Relationships between sensor-measured carbonate system parameters and temperature and salinity. Data points flagged for removal are shown in red.

#### *Temporal Variations of Carbonate Parameters*

Temperature varied over the deployment period between 9.43°C and 31.71°C, with a mean of  $23.14 \pm 5.34$ °C. Salinity varied between 18.28 and 38.96, with a mean of  $30.81 \pm 3.69$ . The average *in situ* pCO<sub>2</sub> during the deployment period was  $416.3 \pm 59.9$  µatm, with a minimum of 251.2 µatm and a maximum of 619.7 µatm. The average *in situ* pH during the deployment period was  $8.123 \pm 0.095$  with a minimum of 7.789 and a maximum of 8.451. There is an apparent seasonal trend with higher pH (and lower pCO<sub>2</sub>) in the winter months and vice versa for the summer months (Figure 7).

There was substantial diel variability in both pCO<sub>2</sub> and pH, with average daily ranges of 59.3 µatm and 0.092, respectively. The minimum and maximum diel ranges were 12.6 µatm and 211.3 µatm, respectively for pCO<sub>2</sub> and 0.016 and 0.283, respectively for pH. Diel variability was intensified during the summer months for pCO<sub>2</sub> and intensified during the winter months for pH (Figure 8). This diel variability does not reveal any significant difference in daytime versus nighttime pCO<sub>2</sub> (paired t-test, p=0.65), but it does reveal that daytime pH is significantly lower

than nighttime pH by an average of 0.007 ( $p=0.004$ ). This suggests that there may be stronger physical controls than biological controls on the carbonate system in the studied area since the minima and maxima did not align as would be expected for metabolic activities, i.e., primary production dominates during daytime and increases pH, while respiration dominates at nighttime and reduces pH.

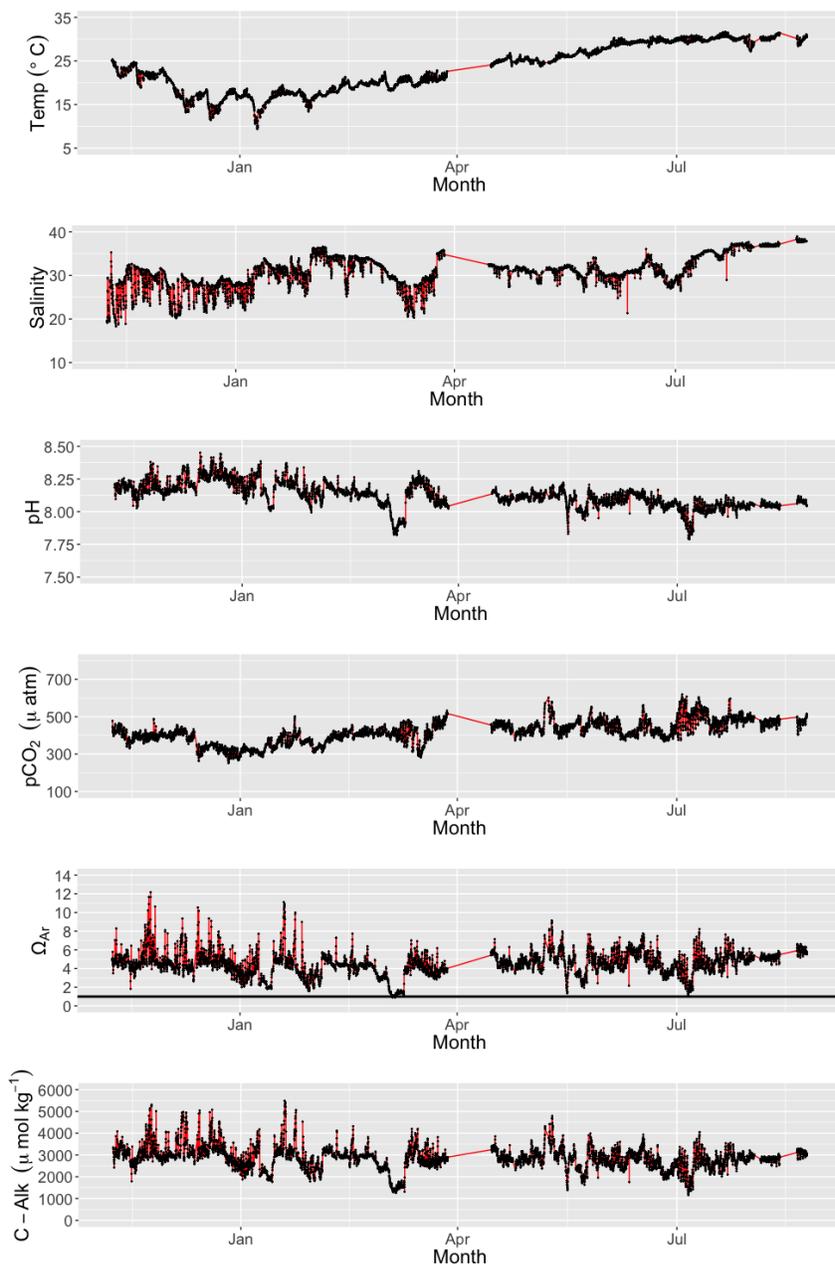


Figure 7. Temperature, salinity, pH, and  $p\text{CO}_2$  data along with calculated saturation state of aragonite and carbonate alkalinity during the deployment period. The black data points represent hourly measurements. Gaps between points occur when there was outliers due to various reasons (see Figure 6 and text for details).

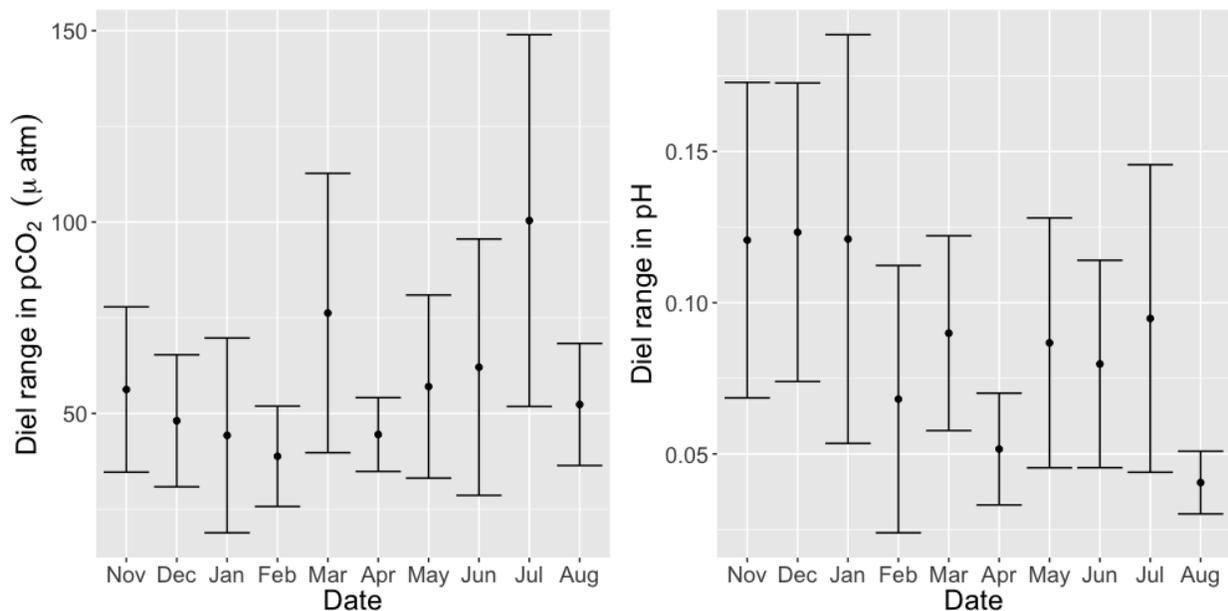


Figure 8. Monthly averaged diel ranges of  $p\text{CO}_2$  and pH. Error bars represent the mean  $\pm$  the standard deviation of the diel range for each month.

### Controlling Factors

Significant correlations were found between both pH and  $p\text{CO}_2$  with both salinity and temperature (Table 5, Figure 9). In the case of both parameters there was a stronger correlation with temperature than that with salinity. C-Alk and  $\Omega_{\text{Ar}}$  also had significant correlations with both temperature and salinity, but the correlations were much weaker.

Table 5. Pearson's Correlation Tests for carbonate system relationships with salinity and temperature.

		p-value	Correlation coefficient	95% CI
pCO <sub>2</sub>	Sal	<0.001	0.379	0.358 – 0.401
	Temp	<0.001	0.719	0.706 – 0.730
pH	Sal	<0.001	-0.464	-0.484 – (-0.444)
	Temp	<0.001	-0.603	-0.619 – (-0.587)
C-Alk	Sal	<0.001	-0.163	-0.188 – (-0.139)
	Temp	<0.001	-0.165	-0.189 – (-0.140)
$\Omega_{\text{Ar}}$	Sal	<0.001	0.086	0.061 – 0.111
	Temp	<0.001	0.202	0.178 – 0.226

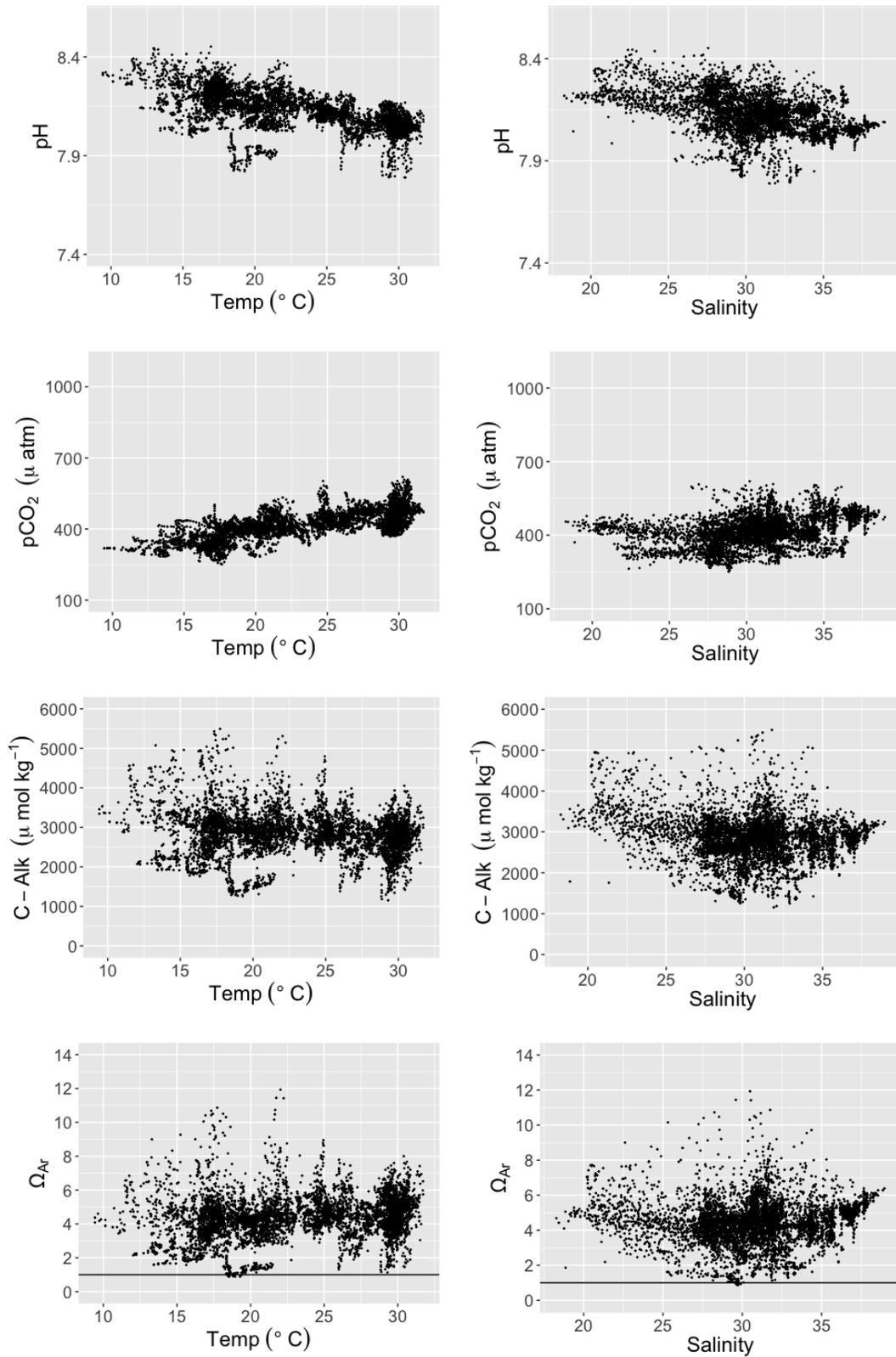


Figure 9. Relationships between sensor-measured and calculated carbonate system parameters (pH,  $p\text{CO}_2$  carbonate alkalinity, and  $\Omega_{\text{ar}}$ ) and temperature and salinity.

There was a significant relationship between the salinity at the ship channel and riverine discharge from the Aransas River (in the Mission-Aransas estuary) and the Guadalupe/San Antonio rivers (in the Guadalupe estuary to the North), and the Nueces River (in the Nueces estuary), indicating possible influence of riverine inflows on salinity in the ship channel. This relationship was not very strong, especially for the Aransas and Nueces rivers. For the relationship with the Aransas River discharge, one measurement of high riverine discharge with corresponding depressed salinity seems to drive this relationship (Figure 10a). For the relationship with the discharge from Guadalupe/San Antonio rivers, the relationship seems to be most prominent in the lowest river discharge measurements when elevated salinity was observed (Figure 10b). In this case, we argue that correlation does not necessarily mean causation, and it is likely that the salinity is driven by local runoff and precipitation rather than riverine freshwater inflow, which likely did not reach this exterior location in the estuary since there were no substantial rains during the deployment period.

Table 6. Pearson’s Correlation Tests for carbonate system relationships with local river discharge

River	p-value	Correlation coefficient	95% CI
Aransas	0.004	-0.172	-0.284 – (-0.055)
Guadalupe	<0.001	-0.426	-0.518 – (-0.324)
Nueces	0.003	-0.179	-0.291 – (-0.063)

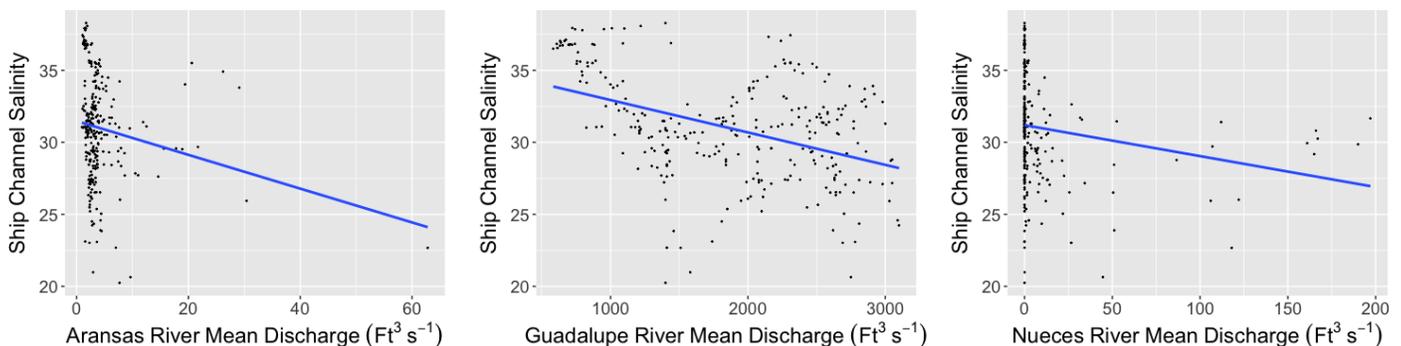


Figure 10. Relationship between the salinity in the Aransas Ship Channel and the river discharge from the three closest systems.

### *Recommendations and Future Work*

We encountered two problems with the OA monitoring effort during the sensor deployment.

1. There have been three instances of pump failure
2. Hurricane disruption caused project being on-hold

Regarding the pump failure issue, the first pump lasted a little over a month (Table 4), the second pump lasted about 3.5 months. After the second failure, we discovered a flaw in the pump design, which was the rubber gasket that was supposed to seal between the pump head and pump body leaked overtime. Therefore, we applied silicone glue around the gasket on the third pump.

Despite this remedy, the third pump only lasted slightly longer (about 4 months, Table 4). If the ship channel monitoring resumes in the future, we will start rotating a new pump every four months to. The cost of a pump is modest (\$170 as of April 2017) and should not be a burden to acquire on a regular basis.

Since the post-hurricane accident destroyed the research pier, rebuilding the pier has been in discussion but it is unlikely that a new one will be ready soon (1-2 years from now). In an effort to maintain the data coverage, regular biweekly to monthly sampling for water carbonate chemistry characterization has been remaining in place using the MANERR's SWMP opportunities. Discrete water chemistry data, in conjunction with the river inflow record, will still allow us to make inference on the hydrological control on estuarine acidification during the period of no high resolution monitoring. In addition, we recently identified a private pier location in the south bank of Corpus Christi Bay that may be suitable for *in situ* monitoring. A discussion with CBBEP may be warranted to determine whether a change of monitoring location is desired.

## Conclusions

The average  $p\text{CO}_2$  and pH at the Aransas Ship Channel during the deployment period for this ocean acidification study were  $416.3 \pm 59.9 \mu\text{atm}$  and  $8.123 \pm 0.095$ , respectively. At this location, surface water experienced seasonal trends in carbonate system parameters. The elevated pH and depressed  $p\text{CO}_2$  in the summer, and vice versa in the winter, is likely controlled by both salinity and temperature depending on the conditions as well as seasonal shifts in biological metabolism. This area also experienced substantial diel variability that was likely caused more by the physical processes than the biological activities. For the majority of the sampling period, the temperature had a stronger control on carbonate system parameters than the salinity, but there was still a significant linear relationship between local river discharge and the ship channel salinity. The carbonate chemistry, as it was measured at the Aransas Ship Channel, appears suitable for proliferation of oysters given its high carbonate saturation state for aragonite ( $\Omega_{\text{AR}}$ ). It is important to remember that the interior portions of primary bays and especially secondary bays may likely be more heavily influenced by the variability in freshwater inflow, which may exert stronger control on estuarine carbonate chemistry and acidification. Some areas in both the Copano and Aransas Bay have been important oyster production ground, thus continued studies on carbonate chemistry are warranted.

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