



## **Ocean and Coastal Acidification Monitoring**

Final Report

Project Number 2435

Date Submitted: March 18, 2026

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This project has been funded wholly or in part by the United States Environmental Protection Agency under assistance agreement 4T-02F49201-0 to the Coastal Bend Bays & Estuaries Program. The contents of this document do not necessarily reflect the views and policies of the Environmental Protection Agency or the CBBEP, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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## Summary

From November 6, 2024 to October 31, 2025, we monitored hourly water CO<sub>2</sub> partial pressure ( $p\text{CO}_2$ ) and pH (on total scale) using a ProOceanus® CO<sub>2</sub> sensor and primarily a SAMI-pH sensor, 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. This project represents a continuation of a previously CBBEP-funded project in November 2016 to August 2017, which was disrupted by Hurricane Harvey on August 23 2017. During the 12-month monitoring period, significant temporal variations of both  $p\text{CO}_2$  and pH were observed with a range of 244.3 – 784.8  $\mu\text{atm}$  and 7.793 – 8.350, respectively. Higher  $p\text{CO}_2$  ( $534.7 \pm 72.3 \mu\text{atm}$ ) and lower pH ( $7.955 \pm 0.056$ ) were observed during summer and lower  $p\text{CO}_2$  ( $359.7 \pm 40.5$ ) and high pH ( $8.117 \pm 0.045$ ) 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.

## **Acknowledgements**

We would like to thank the Coastal Bend Bays and Estuaries Program for supporting this project. Aneena P. Raju, Rosemarijn van der Lint and Quynh Hoang helped with field sampling and lab analyses. Mission-Aransas Estuarine Research Reserve (MANERR) provided their monitoring data (salinity and temperature) for cross validation with ours.

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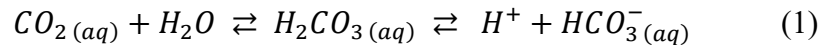
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## Background

Coastal and estuarine acidification can be affected by both ocean acidification and processes on a local scale including changes in hydrological state and metabolic processes. When the atmospheric carbon dioxide (CO<sub>2</sub>) level is greater than that in the surface ocean, a gradient is formed and more CO<sub>2</sub> is dissolved into ocean water, according to Henry's law of solubility (Doney et al., 2009). The influx of CO<sub>2</sub> leads to a decrease in pH and lower the carbonate saturation state (Feely et al., 2004). This process best described as a buffer or a shift in the carbonate system, see Eq. 1. When excess carbon dioxide dissolves into seawater, the excess amount that cannot be stored in the gas state will react with water to form carbonic acid. Carbonic acid is very unstable in the water as it only exists in small quantities. Therefore, carbonic acid will dissociate further into a proton and bicarbonate. The free proton will bind with water to form a hydronium ion. Meanwhile, bicarbonate will further break down in the water column forming a carbonate ion and another proton, see Eq. 2.

It is important to note that these reactions are always in a stable state, it is only when there is an excess of carbon dioxide does the system shift to form other species and decrease the pH.



This process of ocean acidification affects organisms as it creates an environment that is less favorable to the formation of shells and coral skeletons. This can be measured via the carbonate saturation state  $\Omega$ , see eq. 3 (Doney et al., 2009; Feely et al., 2004; Mucci, 1983; Zeebe et al., 2001).

$$\Omega = [Ca^{2+}][CO_3^{2-}]/K_{sp} \quad (3)$$

Acidified ocean waters have been shown to negatively affect calcifiers in the marine system, for example reef-building corals and oysters as well as pelagic species such as pteropods have shown to have reduced calcification when the carbonate saturation state decreases (Bednaršek et al., 2023; Langdon, 2000; Waldbusser et al., 2014a).

## Purpose of Monitoring

Although the process of ocean acidification has been well documented, ocean acidification in coastal and estuarine systems remains understudied (Council, 2010). However, these systems remain an important area of study due to the fact that they represent one of the barriers between human activities and the marine systems, and at the same time, provide essential ecosystem services to the coastal population.

Moreover, due to the fact that estuaries being a mix of freshwater inflow and semi enclose coastal area, they are inherently highly dynamic (Potter et al., 2010). Estuaries can exhibit large

fluctuations in temperature, salinity, and biological productivity on daily and annual timescales (Bianchi, 2007; Waldbusser et al., 2014b). Specifically, freshwater inflow can produce changes that alter the alkalinity and buffering capacity of natural water in estuary systems and provide a very informative and unique zone for research (Carstensen et al., 2019; Hu et al., 2013)

In the northwest Gulf of Mexico lies the Mission-Aransas National Estuarine Research Reserve, which comprises Aransas, Copano, and Mesquite bays. This region in particular is a priority for study as long-term data sets have revealed steady declines in both alkalinity and pH across the South Texas estuaries (Hu et al., 2015). In fact, some of the strongest trends are in the Mission Aransas system (Hu et al., 2015). This system also contains very strong daily and seasonal variability in temperature, salinity, and productivity (Evans et al., 2012). Therefore, continuous monitoring in the Mission Aransas system is necessary to discover mechanisms behind these changes that infrequent sampling cannot reveal.

## **Goals**

This project is a continuation of a previously CBBEP funded project that monitored pCO<sub>2</sub> and pH at Aransas Ship Channel between November 8, 2016 and August 23, 2017. This earlier effort was interrupted by the immediate threat of Hurricane Harvey and the subsequent destruction of the UTMSI research pier in August 2017. With the newly constructed pier in 2023, redeployment of this monitoring setup was desired.

The monitoring effort in Port Aransas Ship Channel seeks to investigate how acidification develops in this semi-arid estuary and adjacent coastal waters. The project aims to identify the chemical and physical drivers of acidification and establish a long-term site for monitoring coastal acidification. Hourly measurements are collected using an in-situ setup with a Sunburst SAMIpH and a ProOceanus CO<sub>2</sub> sensor, capturing both pH and the pCO<sub>2</sub>.

## **Methods**

### *Monitoring Location*

The monitoring effort to observe the acidification in Mission-Aransas Estuary and adjacent coastal waters was performed at the research pier of The University of Texas Marine Science Institute (UTMSI). The institute is an off-campus research facility under the University of Texas at Austin that is located in Port Aransas, Texas, and houses the Department of Marine Science. The research pier is a 300 ft long pier that is connected to a 1200 square ft lab on the mainland. The pier contains a 150 sq ft instrument room at the end of the pier that overlooks the Port Aransas Ship Channel. Beneath the instrument room is a small observation deck that houses multiple instruments for marine science research. The research pier is located at 27°50'17"N, 97°3'1"W and provides direct access to the Port Aransas ship channel for continuous measurements.

Complementary data was collected from a research station at the ship channel ran by the Mission Aransas National Estuarine Research Reserve (MANERR). A YSI 6600 datasonde was used to collect salinity, temperature, dissolved oxygen, pH, and turbidity, although only salinity and temperature data will be used in this project. MANERR sonde was replaced every two weeks

during warm months and every month in winter for cleaning and recalibration following the YSI manual.

The Port Aransas Ship channel is the main inlet for seawater to enter from the Gulf of Mexico to the connected bay system created by Mustang Island and San Jose Island. The ship channel primarily feeds into the Corpus Christi, Aransas, and Redfish Bays. From there secondary bays, such as the Nueces, Copano, Carlos, and Mesquite Bays, receive water through tidal exchange from the primary bays.

### *Monitoring Design*

The primary objective of this study was to examine the temporal changes in both pH (on total scale) and the partial pressure of pCO<sub>2</sub> in the Port Aransas Ship Channel. Measurements were collected in hourly intervals through two different sensor configurations. Data from the sensors was obtained weekly.

#### Ex situ measurements

The first set of measurements were collected inside of a 150-Qt Coleman cooler that housed two sensors (pH and pCO<sub>2</sub>). To minimize biofouling and algal growth, seawater from the Port Aransas Ship Channel was pumped into the cooler through a 1" copper intake pipe. This pipe would later be replaced with a ½" copper pipe after the original pipe was damaged. To ensure proper circulation of fresh ship channel water, the water flow into the cooler was initiated 20 minutes before each reading was taken, which was set on whole hours.

Inside the cooler, pH was measured using a SAMI-pH sensor from Sunburst Sensors. This sensor also had its own temperature sensor. pCO<sub>2</sub> was measured using a pro-Oceanus CO<sub>2</sub> sensor. Data from the SAMI-pH was processed using the MATLAB script provided by the vendor (Sunburst), and pCO<sub>2</sub> data was extracted from the ProOceanus via the ProOceanus software. Due to premature failure of the SAMI-pH sensor, data from a YSI EXO1 sonde equipped with a pH sensor was used starting on August 12, 2025 until October 16, 2025 when the SAMI-pH was returned from the vendor. The YSI sonde collected pH in the NBS scale. The YSI sonde was calibrated with two pH buffers weekly (pH 9 and 11) in the lab and redeployed after each calibration. The conversion between the pH value from the YSI is on NBS scale (pHNBS). To convert the pH value to the total scale (pHT) that the SAMIpH sensor collects, an equation in Millero (2001) was used.

$$pHT = pH_{NBS} + \log_{10}f_H$$

in which  $f_H$  is apparent total proton activity coefficient and defined as:

$$f_H = 1.2948 - 0.002036 \times T + (0.0004607 - 0.000001475 \times T) \times S^2$$

here T is absolute temperature and S is salinity, both are measured by the YSI.

#### In situ measurements

Temperature and salinity measurements were taken from a YSI 600OMS V2 sonde that was placed directly into the ship channel at 1-m depth from the UTMSI research pier. This sonde was later switched to a YSI EXO 1 model on August 12, 2025, due to the original YSI sensor failure,

which also took pH measurement on the NBS scale during the period of SAMI-pH sensor (see above).

#### In situ water samples

In addition to sensor measurements, weekly water samples were collected from both the ship channel and inside the cooler on the whole hour. At the time of water sample collection, temperature and salinity measurements were also taken. Following the standard operating protocol described in Dickson et al. (2007), water samples of the ship channel were collected using a Van Dorn water sampler and then transferred into a borosilicate sample bottle. Samples from the cooler were taken with sample bottles directly. After both samples were collected, 100  $\mu\text{L}$  of saturated  $\text{HgCl}_2$  was injected into the sample, and the bottles were capped with Apiezon grease-lubricated stoppers, which were secured using a rubber band and hose clamp. The bottles were inverted a few times to homogenize the reagent to arrest biological activities. The samples were used to measure dissolved inorganic carbon (DIC), pH, salinity, and total alkalinity (TA).

#### *Discrete Sampling and Laboratory Analyses*

##### Carbonate chemistry parameters

The weekly samples were stored in a fridge at  $4^\circ\text{C}$ . They were then processed within a month to measure DIC, pH, TA, and salinity. DIC was analyzed using a LI-5300A DIC analyzer (LiCor). The analyses followed the standard procedures of dissolved inorganic carbon extraction and  $\text{CO}_2$  detection described in Dickson et al. (2007). First a known volume of the sample is taken by the DIC analyzer and is mixed with acid, this step converts all DIC species into  $\text{CO}_2$  gas. The  $\text{CO}_2$  gas flows into the LI-COR gas analyzer where the concentration is determined via infrared detection.

The pH of the samples was analyzed using an Agilent 8453. By measuring the absorbance of purified m-cresol purple indicator at 434 nm and 578 nm. Using a 10 cm glass tube the absorbance ratio of  $R = R_{578} / R_{434}$  was obtained, and the pH was calculated using the equation of Liu et al. (2011). The pH values obtained are in total hydrogen scale. All measurements were performed as  $25^\circ\text{C}$  and salinity from lab analysis was included directly into the pH calculation.

TA was measured using a LI-5800A (LiCor) alkalinity titrator. The instrument uses an open cell HCl titration while continuously measuring the pH using an electrode. After titration the titrator software applied a Gran-function analysis to determine the endpoint, following Dickson et al. (2007) (2007).

For both DIC and TA analyses, certified reference materials (CRMs) were used to ensure the data quality (Dickson et al., 2003).

Salinity of the discrete samples were measured via a benchtop conductivity probe calibrated with a commercial conductivity standard (RICCA chemical company). The probe measures the electrical conductivity of the sample, which is then converted to salinity. Measurements were taken twice and to ensure accuracy were corrected using the conductivity standard. All measurements were taken at  $22^\circ\text{C}$ .

### Temperature

Temperature data were assembled from multiple sources including the YSI 600OMS V2 (later changed to the YSI EXO 1), the MANERR temperature record, and the temperature output from the SAMI-pH sensor. Our YSI sensors served as our primary temperature record. When gaps occurred, they were filled with the MANERR data, as the dataset closely resembled our own measurements. If both our primary temperature sensor and the MANERR temperatures were unlivable, the SAMi -pH temperature data was used. In addition to any outages, periods of rapid drift were conservatively removed before gap filling.

### Salinity

Salinity values for the monitoring were obtained from the MANERR YSI sonde, after correcting for the difference (usually less than 0.3) between the lab measured salinity and the sonde data at the time of taking water samples.

### Speciation calculations

Lab measured pH was obtained at 25°C and was converted to in pH at situ temperature using the CO2SYS program (Pierrot et al., 2006) and measured DIC as the second input parameter. In situ pCO<sub>2</sub> was also obtained in the same calculation. The speciation calculations were performed using the following constants: K<sub>1</sub> and K<sub>2</sub> from Millero (2010), the bisulfate dissociation constant from Dickson (1990), the boric acid constant from Dickson & Riley (1979), and total boron concentration from Uppstrom (1974).

### *Data Processing and Corrections*

Throughout the monitoring period (11/1/2024-10/31/2025), multiple equipment failures (both the water pump and individual sensors, Table 1) have occurred. Extensive steps were taken to remove sensor data during these occurrences and make necessary corrections using discrete water sample data (Figure 1).

Table 1. A list of events including sensor malfunction and pump failure

Est. Outage Data (UTC)	Reason	Instrument Affected	Date Restored (UTC)
11/7/24 12:00	Sensor Malfunction	ProOceanus (pCO <sub>2</sub> )	11/8/24 21:00
11/11/24 13:00	Sensor Malfunction	SAMI-pH	11/24/24 16:00
11/22/24 23:00	Sensor Malfunction	ProOceanus (pCO <sub>2</sub> )	12/5/24 23:00
1/26/25 20:00	Pump Outage	ProOceanus (pCO <sub>2</sub> ) SAMI-pH	1/31/25 18:00
3/4/25 22:00	Sensor Malfunction	ProOceanus (pCO <sub>2</sub> )	3/17/25 16:00
3/28/25 21:00	Sensor Malfunction	ProOceanus (pCO <sub>2</sub> )	3/29/25 16:00
3/30/25 0:00	Sensor Malfunction	ProOceanus (pCO <sub>2</sub> )	3/30/25 23:00
3/31/25 18:00	Sensor Malfunction	ProOceanus (pCO <sub>2</sub> )	4/1/25 16:00
5/22/25 21:00	Sensor Malfunction	SAMI - pH	5/23/25 19:00
5/31/25 18:00	Pump Outage	ProOceanus (pCO <sub>2</sub> ) SAMI-pH	6/4/25 18:00
6/18/25 20:00	Sensor Malfunction	ProOceanus (pCO <sub>2</sub> )	6/19/25 21:00

6/26/25 9:00	Pump Outage	ProOceanus (pCO <sub>2</sub> ) SAMI-pH	7/10/25 20:00
7/18/25 17:00	Pump Outage	ProOceanus (pCO <sub>2</sub> ) SAMI-pH	7/24/25 21:00
7/18/25 17:00	Sensor Malfunction	SAMI-pH replaced w/YSI EXO 1	8/13/25 1:00
9/2/25 15:00	Sensor Malfunction	YSI EXO 1	9/9/25 19:00
9/15/2025 0:00	Pump Outage	ProOceanus (pCO <sub>2</sub> ) SAMI-pH	9/17/2025 5:00
10/2/25 21:00	Sensor Malfunction	YSI EXO 1	10/3/25 19:00
10/7/25 20:00	Sensor Malfunction	ProOceanus (pCO <sub>2</sub> )	10/23/25 22:00
10/30/25 22:00	Sensor Malfunction	ProOceanus (pCO <sub>2</sub> )	11/1/25 0:00

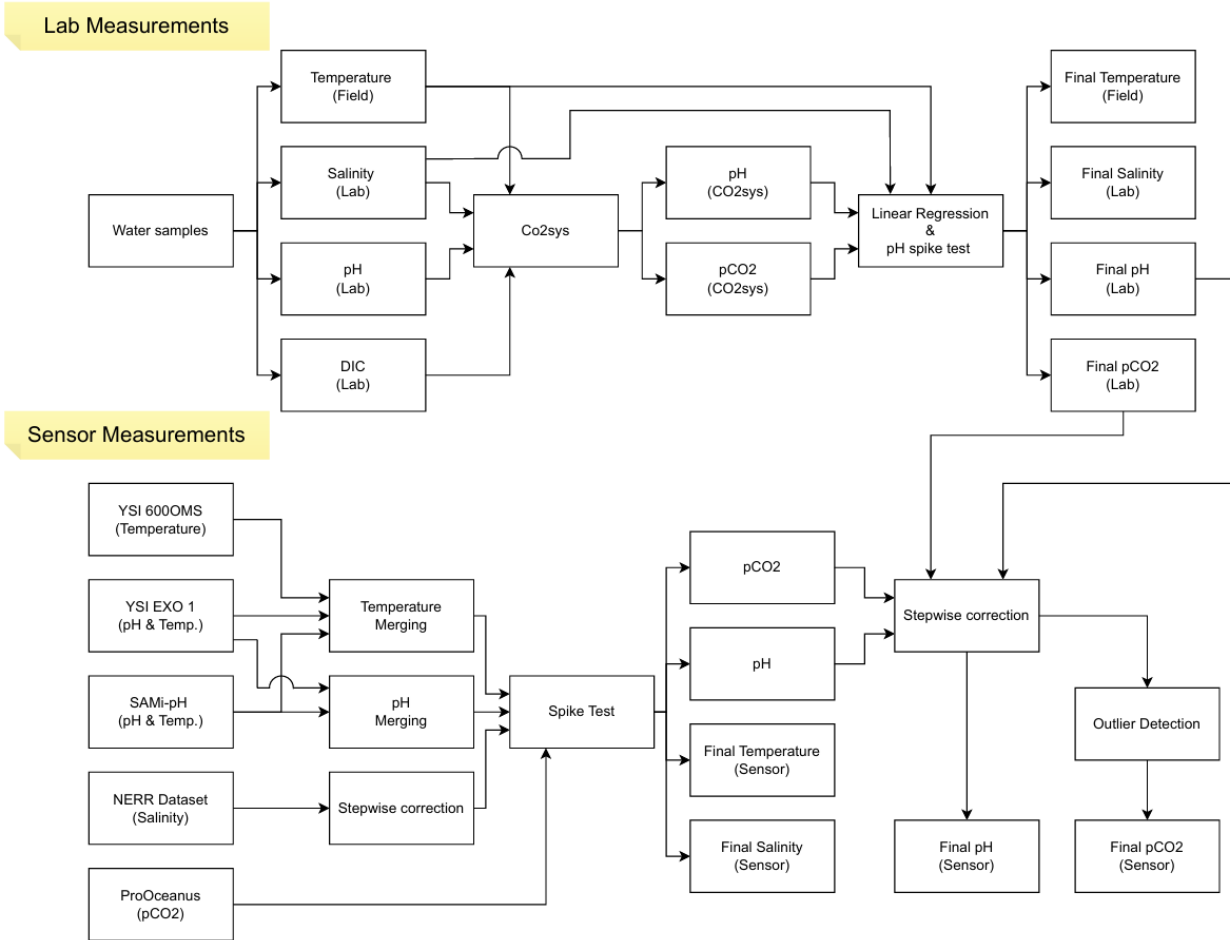


Figure 1. Data quality control workflow for samples collected using discrete and sensor measurements.

The flowchart summarizes the full QC process applied to salinity, temperature, pH, pCO<sub>2</sub>, and all discrete water sample analyses. Steps include but not limited to using CO2SYS to correct for in

situ conditions of pH and pCO<sub>2</sub>, linear regressions, spike tests, step wise corrections, as detailed below.

### Removal of extreme values

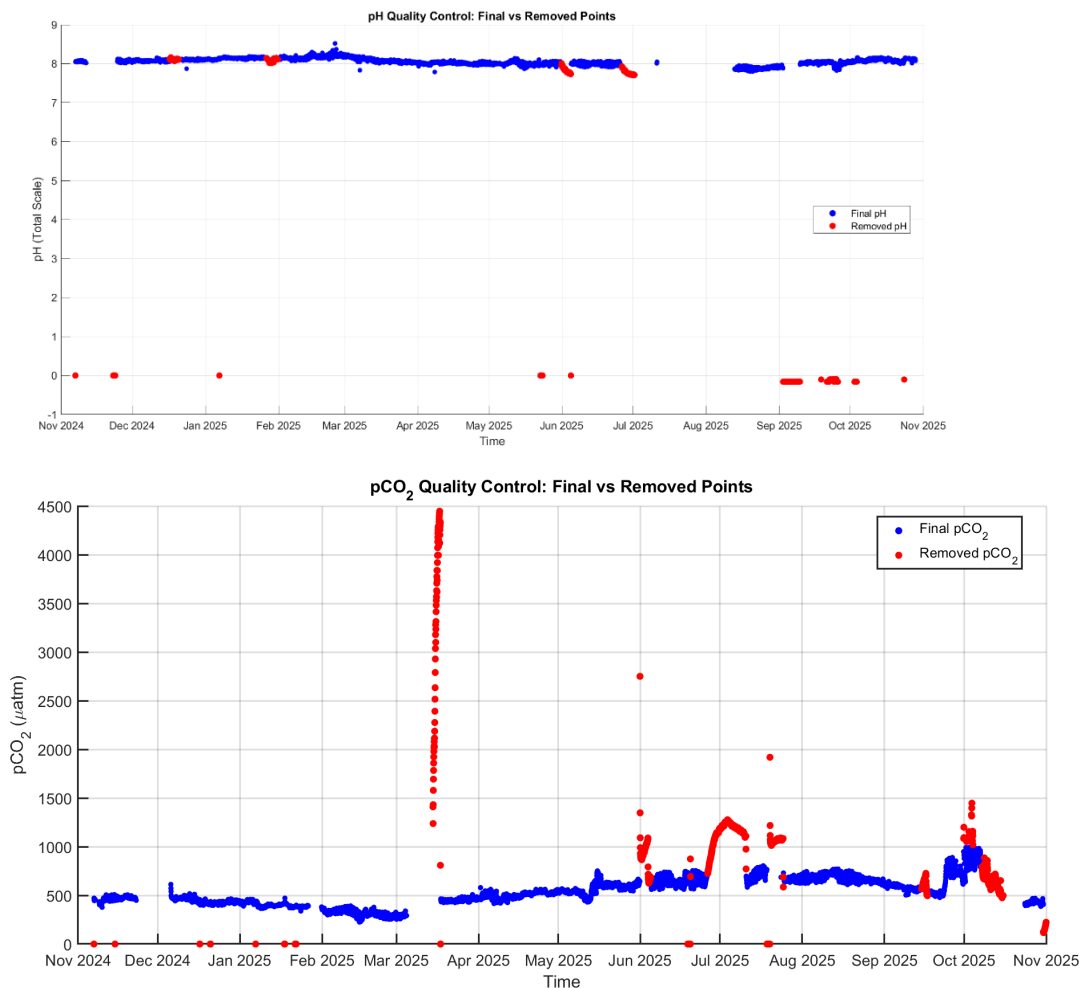


Figure 2. Sensor outage data points for pCO<sub>2</sub> and pH over the deployment period. These plots highlight the data points removed from the SAMI-pH and ProOceanus sensors due to power outages, pump failures, and sensor malfunctions.

During the deployment period, multiple system failures occurred with both the SAMi-pH and ProOceanus CO<sub>2</sub> sensors. To consolidate the data into an easy-to-read table we labeled the outages as two separate categories, “Pump outage” and “Sensor Malfunction”. Extreme and impossible values for both sensors were removed and labelled as sensor malfunction. The ProOceanus had values ranging from over 4500 to 0, these values were removed (Figure 2). The values that were below zero from the SAMi-pH and the YSI EXO 1, were removed from the data and labelled accordingly. Power outages that extended longer than what our backup power was equipped for, were labeled as during pump failures the loss of power prevented water from replenishing the cooler. Other causes for outages included barnacle growth as the internal pump (ProOceanus), water intrusion (YSI), non-scheduled recalibrations (YSI), low dye volumes

(mCP), and sporadic system errors were also labeled accordingly depending on the system affected.

### Outlier detection and removal

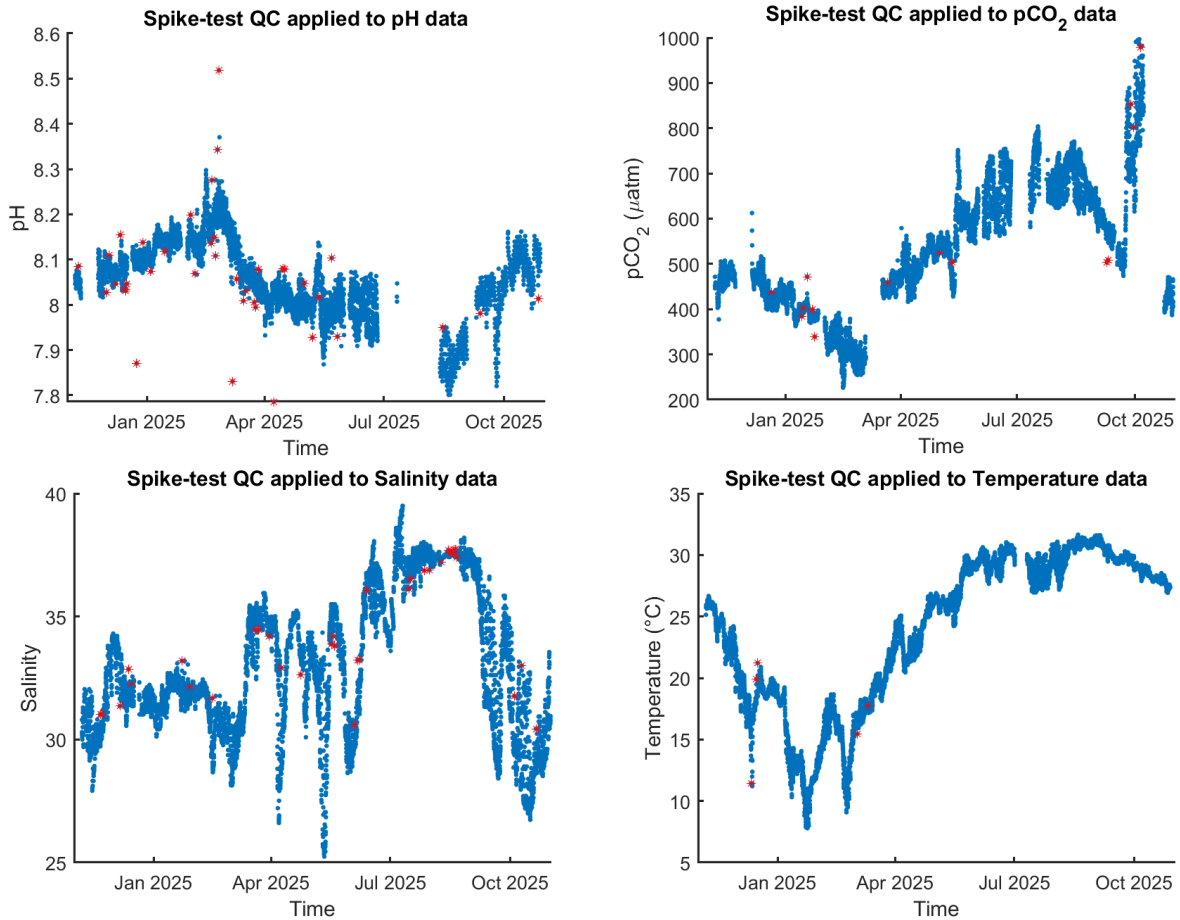


Figure 3. Spike-test detection on raw sensor data (Salinity, temperature, pH, and pCO<sub>2</sub>). Flagged points using a 30-point window spike test. Points falling outside  $\pm 3\sigma$  of the window were highlighted and removed as likely sensor spikes or single point failures.

To identify questionable sample points in salinity, temperature, pH, and pCO<sub>2</sub>, we applied a spike test to detect individual points that did not follow the general trend of the data (Figure 3). The Port Aransas Ship Channel follows a 25-hour tidal cycle. This leads to a range of values that resemble a predictable wave-like pattern each day. Therefore, to ensure the spike test accounts for the range of values in a 25-hour wave period a 30-point moving window was used to calculate the standard deviation. Within this window if the difference of any point and the average of its neighbors is greater than three times the calculated standard deviation the point is flagged. The flagged points are then observed manually and any value that clearly did not align with the general pattern was given a QC flag of “4” (suspected data) and removed from the subsequent analysis.

For the pH and pCO<sub>2</sub> datasets, data points were removed using the spike test. In which the points of either side are averaged and if the difference between the average and the point of interest is greater than 3 times the standard deviation the point is flagged. Each point flagged by the test is manually inspected and removed if the point clearly deviates from the surrounding points, appears isolated, or as an extreme outlier.

### Comparison of Van Dorn and Cooler samples

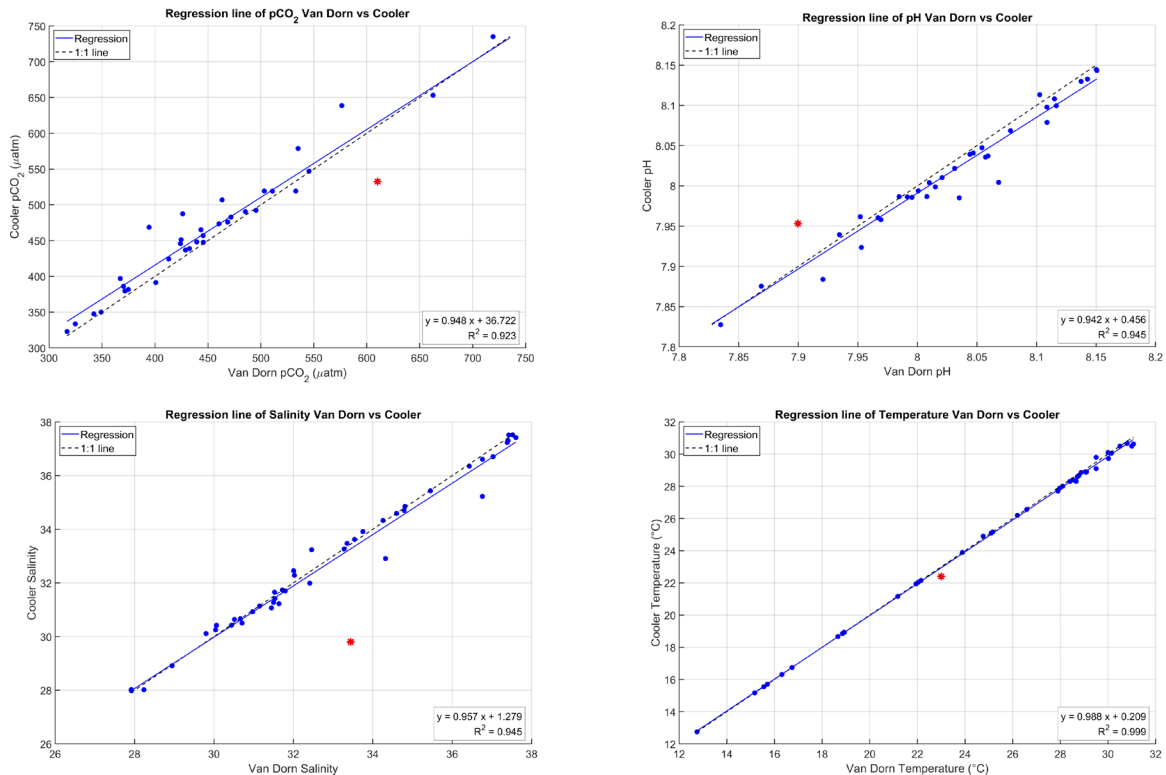


Figure 4. Linear Regression of Van Dorn versus cooler samples. The linear relationships for the pCO<sub>2</sub>, pH, salinity, and temperature were evaluated to determine whether the cooler was accurately representing the water from the ship channel. Residuals were calculated and used to identify cooler artifacts. Data points found were removed from the data set.

To determine whether the cooler water intake system represented the estuarine water from the ship channel, paired water samples were collected from both inside the cooler and the in-situ water via a Van Dorn sampler (hereafter defined as in-situ sample). The samples served as an internal control to ensure the water in the cooler was representative of in situ ship channel water (Fig. 4).

Three samples pH values that were below 7.8 were flagged as extreme values and were removed from the dataset. Despite the fact that care was taken with sample collection and preservation, these low pH values indicated that respiration was likely not completely stopped. In addition,

periods when there was no water flowing into the cooler due to a pump outage and discrete water sample data points that did not have a pair were excluded from the cooler data set.

Temperature, salinity, pH, and pCO<sub>2</sub> of the cooler and in-situ samples were compared via a linear regression, and residuals were calculated for each variable. Any residual that held a value greater than three times the standard deviation from the regression line was classified as non-representative of the ship channel. Given the cooler is more prone to artifacts such as incomplete mixing and flow interruptions, the flagged data points were assumed to be from the cooler system and removed from the cooler data set for any future analysis. Additionally, any cooler data point that did not have a corresponding in-situ sample was removed from the dataset.

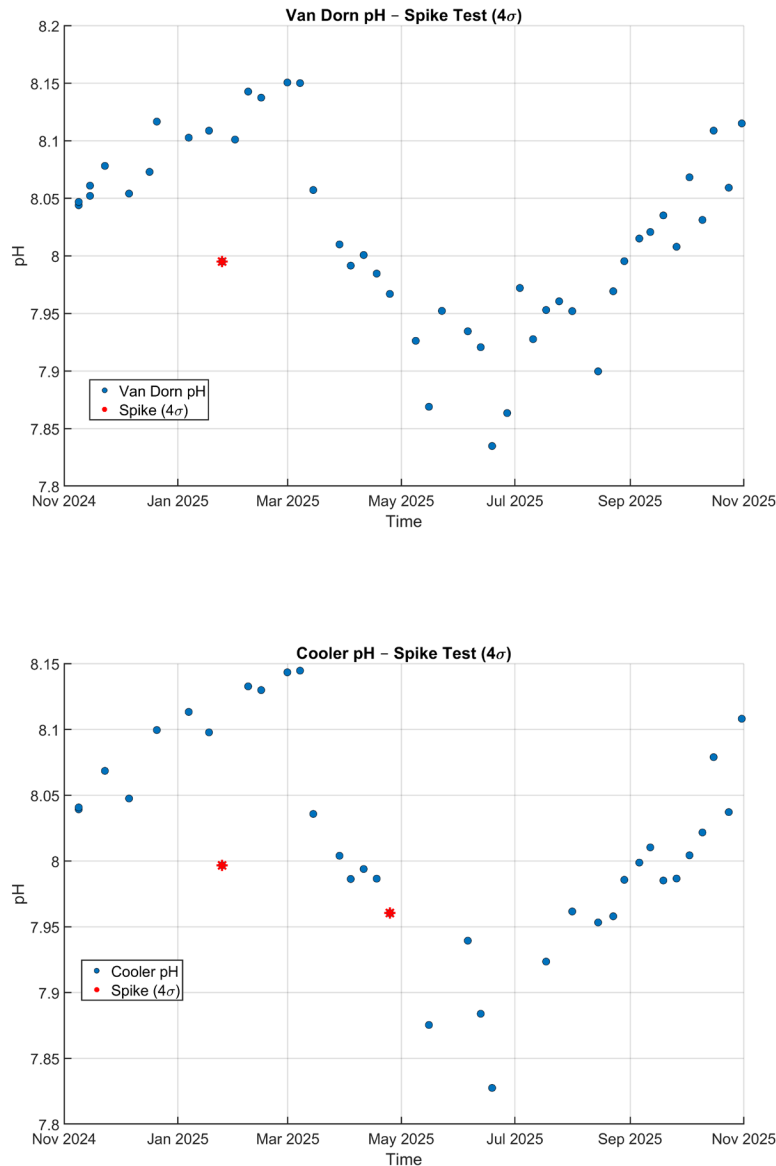


Figure 5 Spike test for in-situ and cooler pH data. Given the low population size and high variability throughout the year, the spike test for the pH samples was done using a 4σ threshold.

These points represented samples affected by excess respiration, contamination, or sampling error.

In order to confirm the samples used for calculation were free from any lingering microbial activities, the spike test was applied to the pH of the in-situ and cooler samples (Figure 5). Due to the variability of the pH across the year the standard deviation was multiplied by four. The data points flagged were removed from both the pCO<sub>2</sub> and pH data sets as the low pH values would have been caused by respiration.

Drift and agreement (difference between the sensor vs cooler)

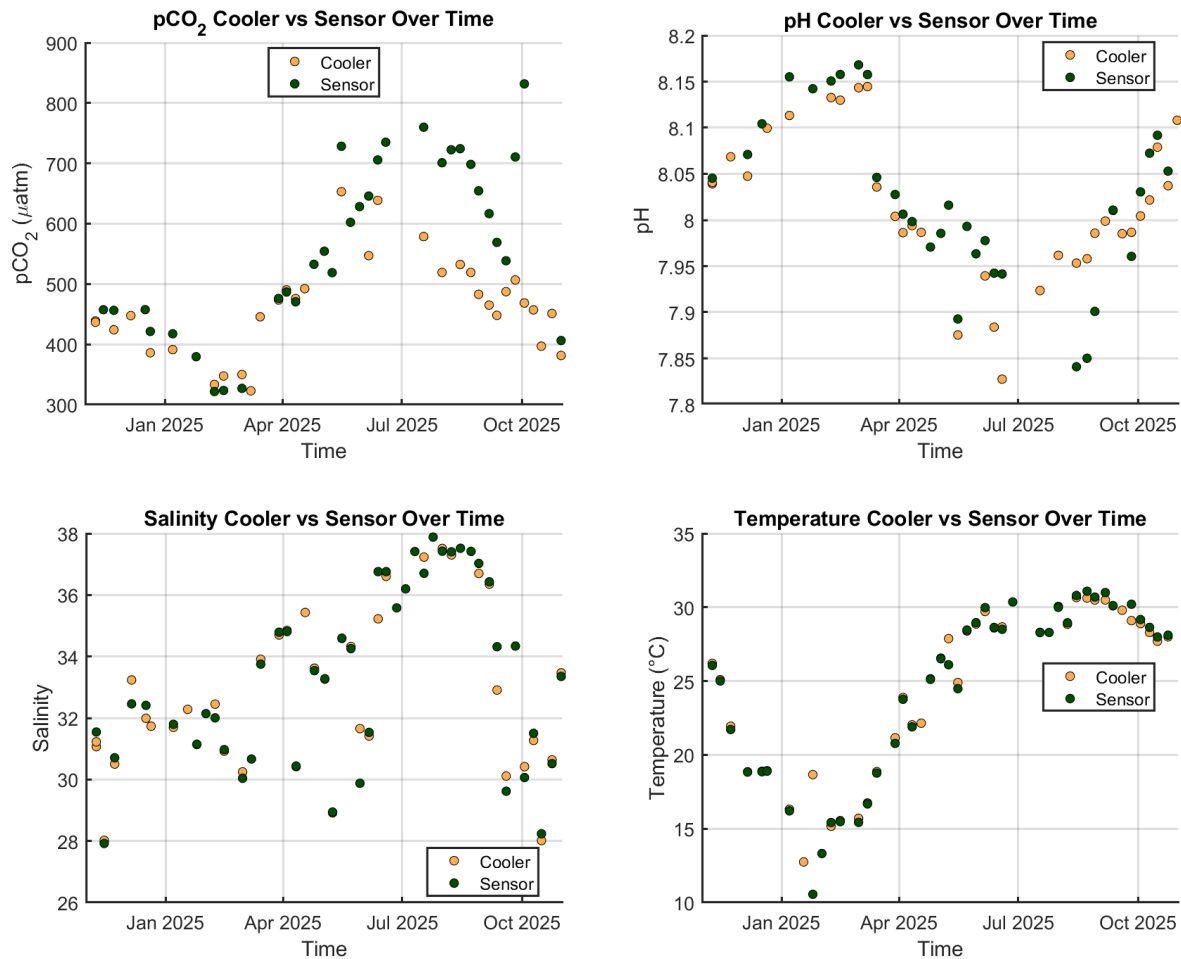


Figure 6 Comparison of sensor and cooler data. Temporal alignment of the cooler and ship channel measurements was used to check the precision between the cooler and the sensor measurements to determine if a general offset need to be applied to the entire data or if a more isolated correction was needed.

Sensor drift was evaluated by comparing the sensor measurements to the corresponding samples taken from the cooler. A time series plot of the cooler samples overlaid with the measurements

from the sensor was used to locate any consistent patterns that could resemble drift in the sensors (Figure 6).

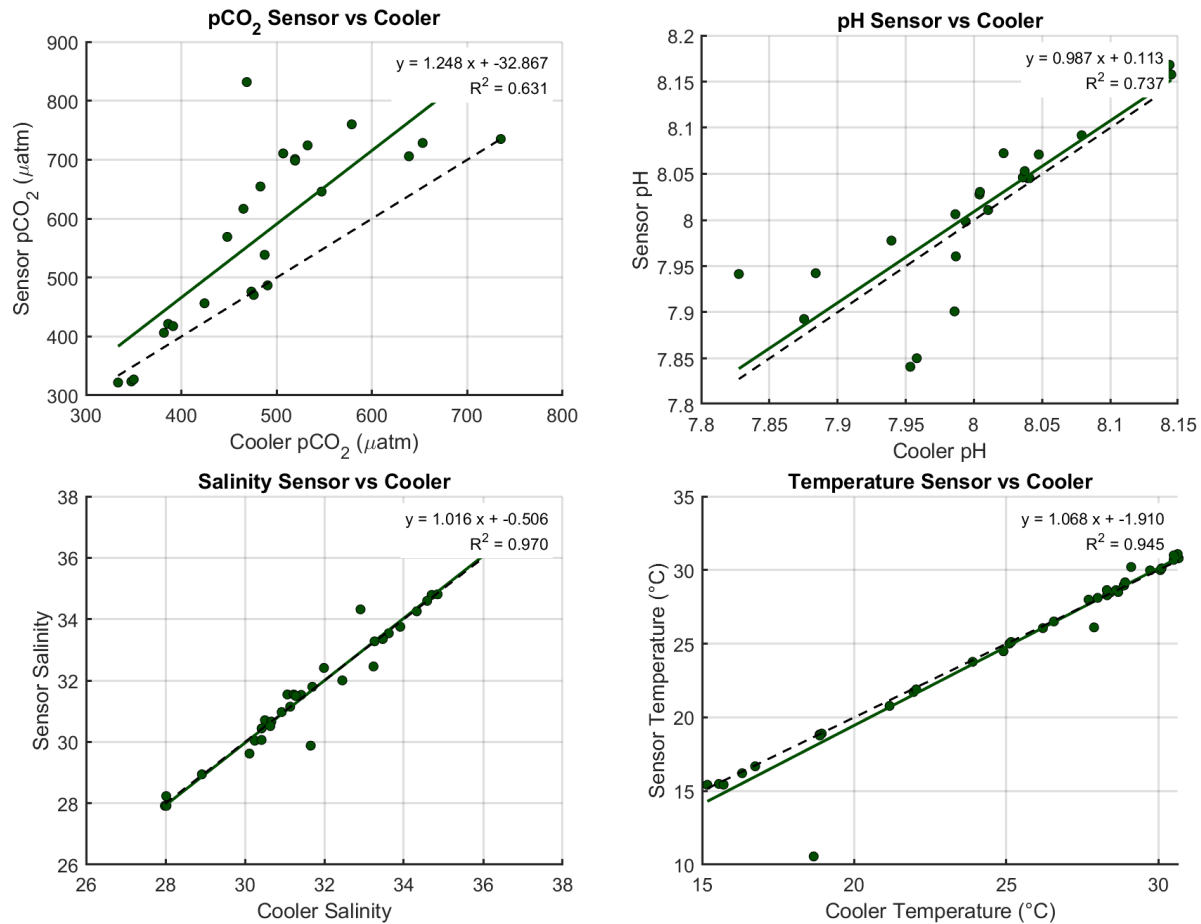


Figure 7 Linear regression of sensor values versus the cooler samples. To quantify any constant offset a linear regression was applied to the cooler values and corresponding time of the sensor values. The slope, intercept, R<sup>2</sup> were calculated to determine agreement.

A linear regression and R<sup>2</sup> were used to determine any systemic changes in the sensor as well as the value of an average systemic drift (Figure 7). Given the fact that the cooler water represented the ship channel, any consistent variation was interpreted as potential sensor drift, whereas isolated events were attributed to minor artifacts during measurement. Sensor performance was evaluated by comparing the devices measurements directly to the corresponding in-situ sample measurements taken at the same time. Sensor accuracy was assessed using an ordinary least square linear regression between the in-situ samples and the sensor values. This quantifies agreement using the regression slope, intercept, and coefficient of determination (R<sup>2</sup>).

Data validation (Bias, RSME, MAE)

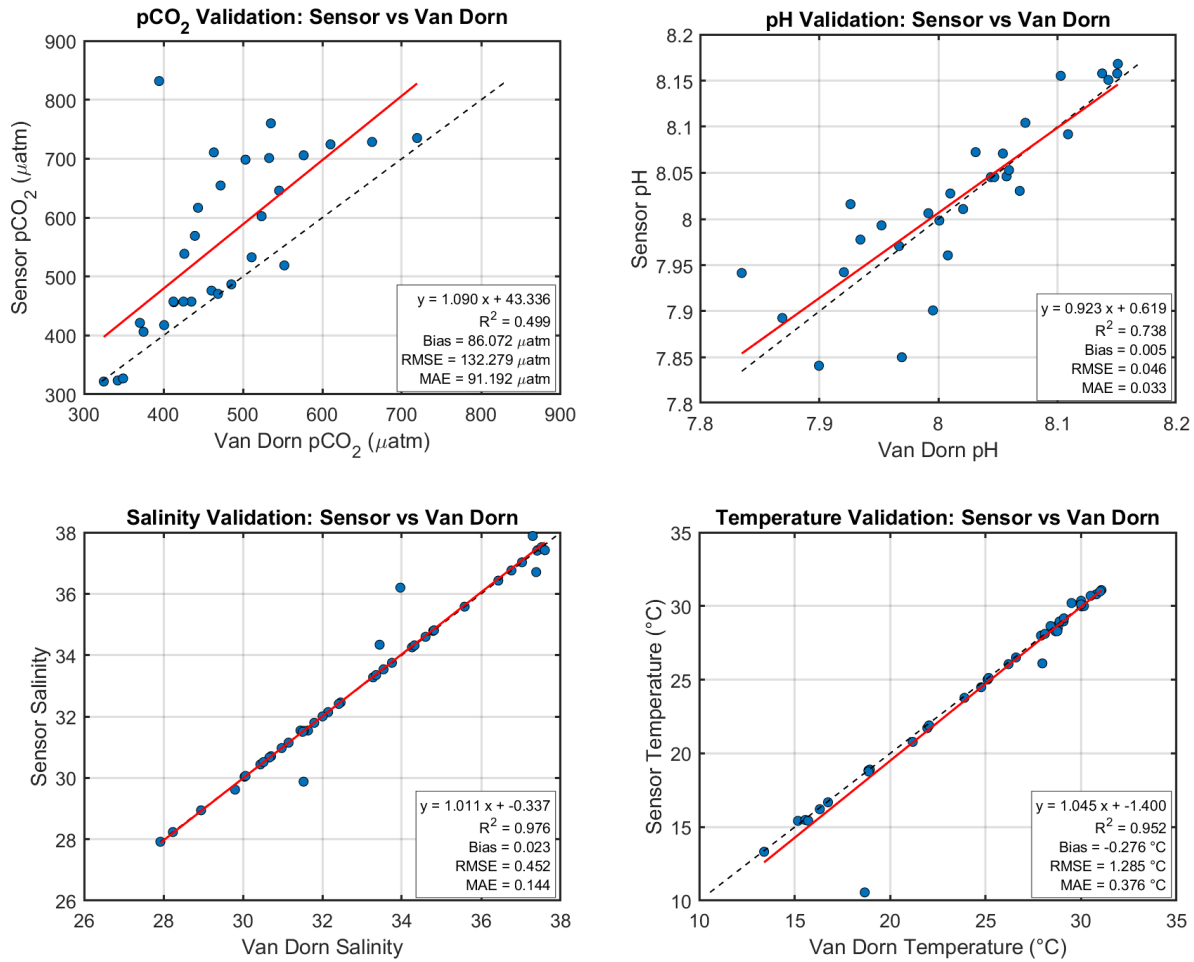


Figure 8 Bias, RMSE, and MAE for sensor performance evaluations using in-situ water data. The accuracy of the sensor measurements was assessed using the water samples taken directly from the ship channel. The over systemic error (bias), error magnitude (RMSE), and average disagreement (MAE) were calculated for pCO<sub>2</sub>, pH, salinity, and temperature.

Sensor accuracy was assessed by comparing the sensor measurements to the corresponding in-situ samples using an ordinary least square regression. Using this we were able to evaluate the agreement between the reference and the sensor, determine the average offset, and overall agreement. To quantify the systematic error, the root mean square error (RMSE), mean absolute error (MAE), and bias were calculated.

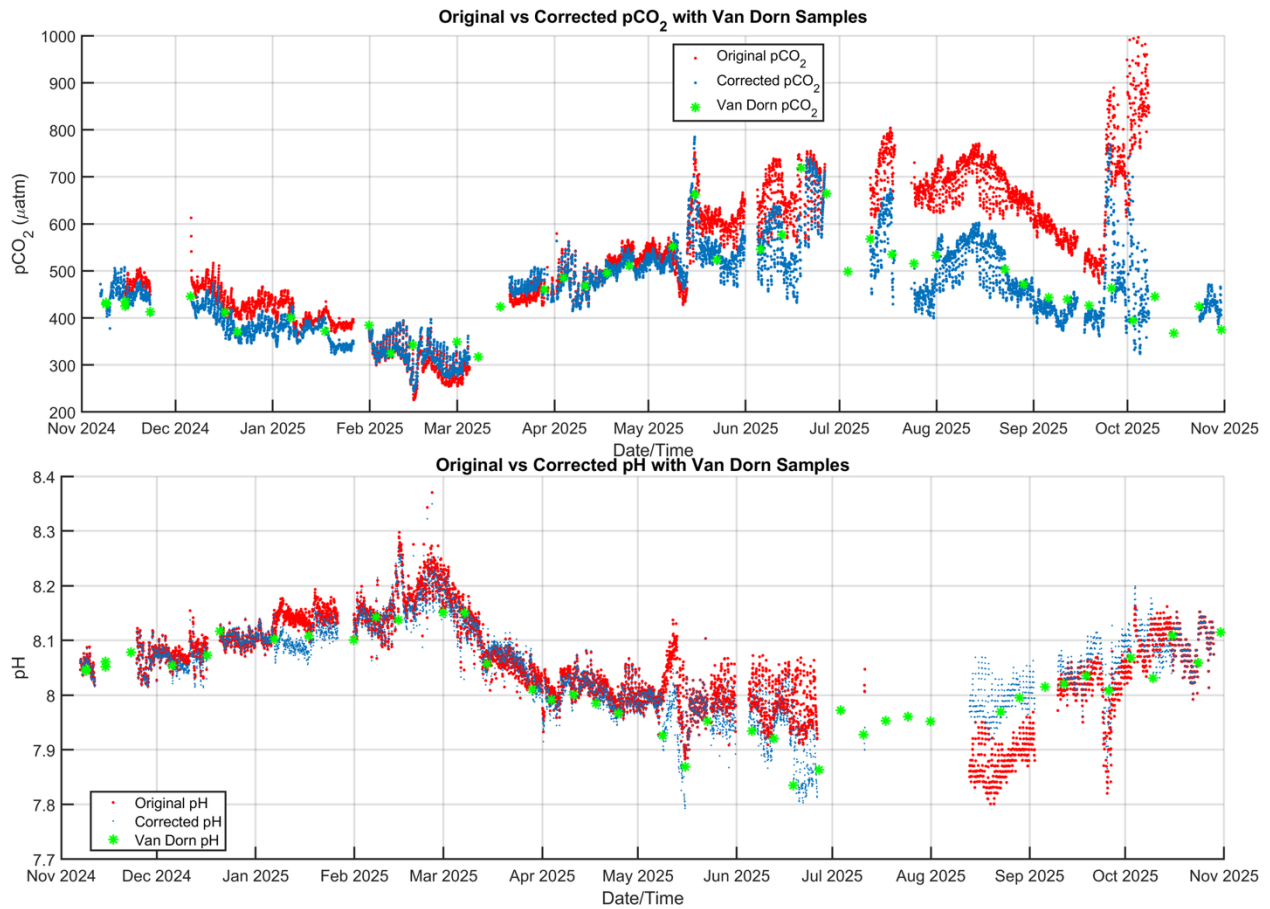


Figure 9 Original and correct pH and pCO<sub>2</sub> sensor data with water samples overlaid. To demonstrate the stepwise correction using the in-situ samples.

The original data points for the pH and the pCO<sub>2</sub> were plotted with both sets of water sample data overlaid (Figure 9), and the pH and pCO<sub>2</sub> sensors a stepwise, piecewise-constant correction was applied using the in-situ samples. In which the difference between the in-situ sample and the corresponding sensor value (Van Dorn - Sensor) was added to the data until the next verified in-situ data point. Although most areas were corrected via a stepwise correction, a small section from August 13<sup>th</sup> – August 22<sup>nd</sup> in the pH was corrected using the August 22<sup>nd</sup> point, as there was not an available sensor pH point to use for correction.

## Post correction outlier removal

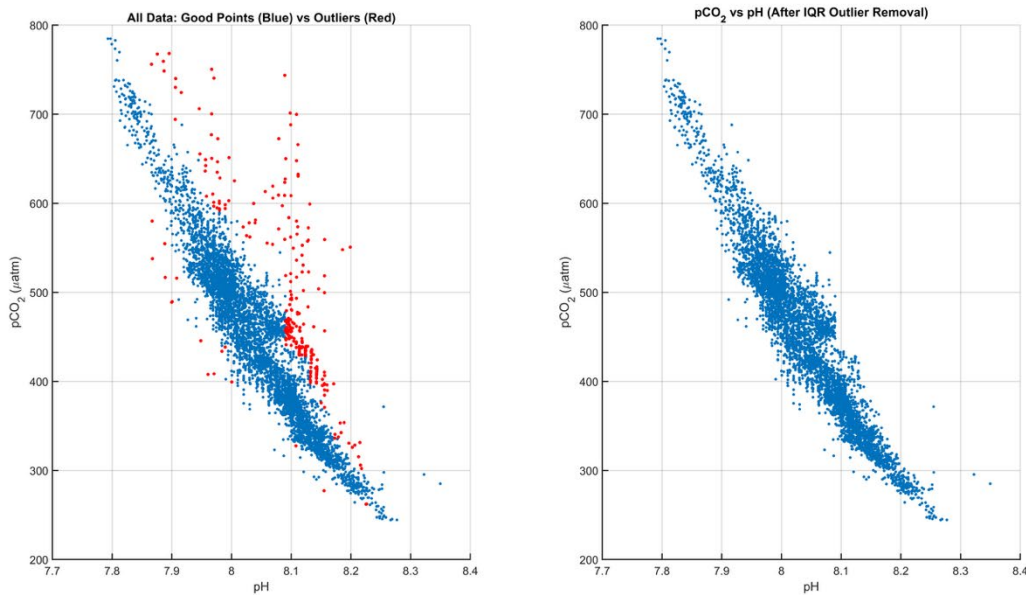
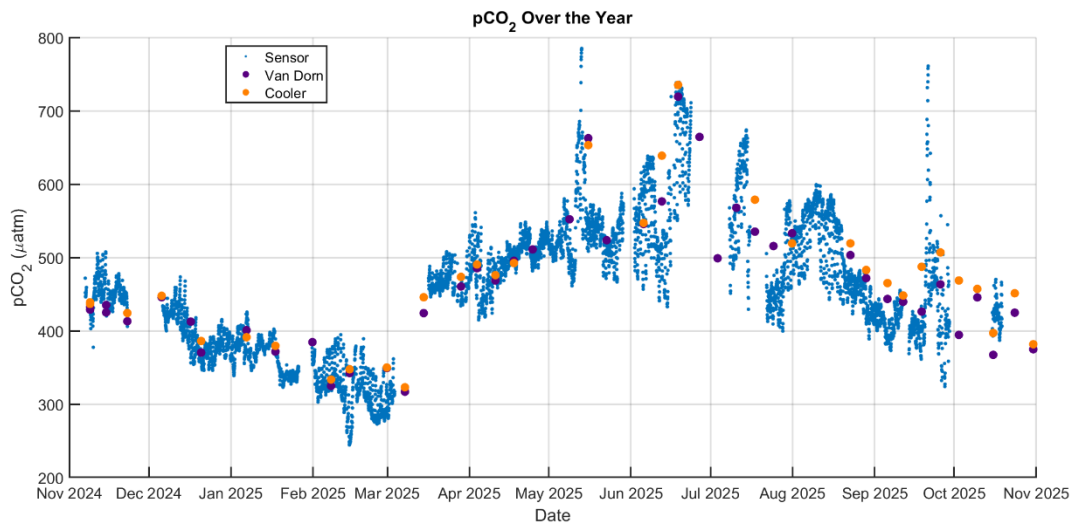
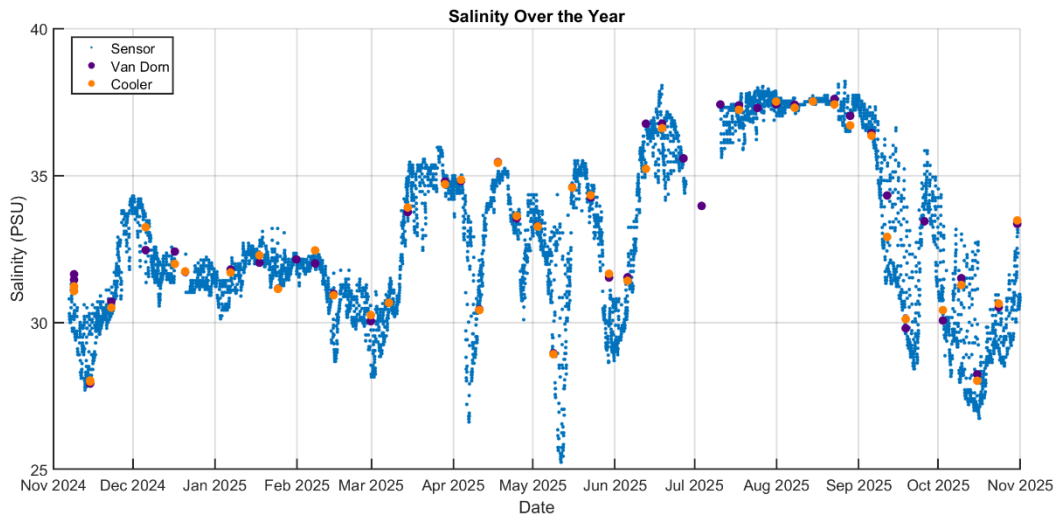
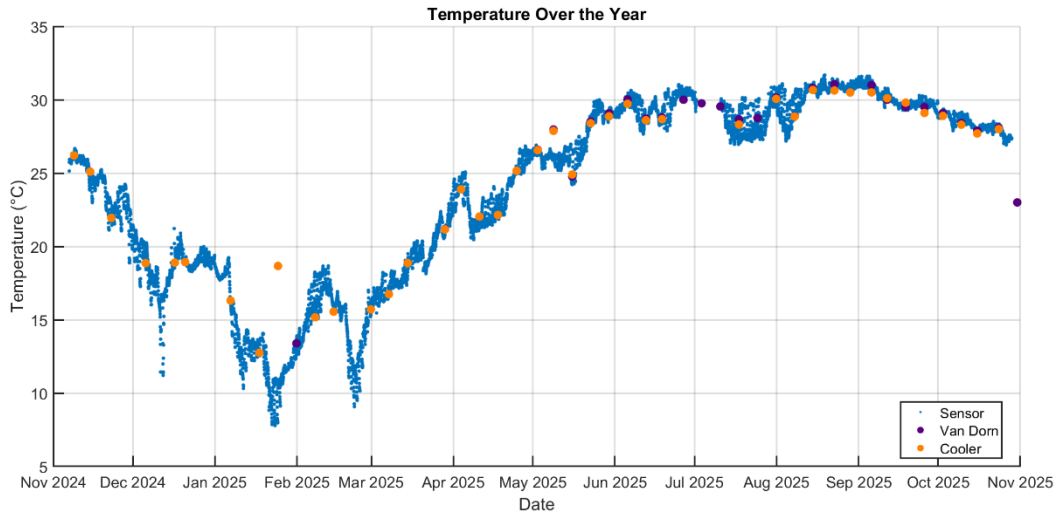


Figure 10 Post correction outlier screening for pCO<sub>2</sub> using corrected pH. The pCO<sub>2</sub> data was further corrected using binned pH-binned IQR filtering. Points outside the set threshold ( $1.5 \cdot \text{IQR}$ ) were flagged and removed.

After correction of the pH and pCO<sub>2</sub> datasets, additional outliers in the pCO<sub>2</sub> measurements were found using an interquartile range (IQR) filter using the pH as the reference variable. Both datasets were collected in a narrow range of salinity hence they are expected to follow a tight inverse relationship. The pH dataset was treated as the reference for this step, as the ProOceanus sensor contained a membrane that was susceptible to accumulation of sediments and organic matter. Whereas the pH sensor used an optical window for absorbance measurements internally hence is not subject to this influence. To filter out outliers in the pCO<sub>2</sub> dataset pH was divided into 0.2 pH unit bins. Within each bin the 25<sup>th</sup> percentile (Q1), 75<sup>th</sup> percentile (Q3), and interquartile range (IQR) were calculated. Outliers were determined to be one outside the  $Q1 - 1.5 \cdot \text{IQR}$  and  $Q3 + 1.5 \cdot \text{IQR}$ . Outliers were flagged and removed from the pCO<sub>2</sub> dataset.



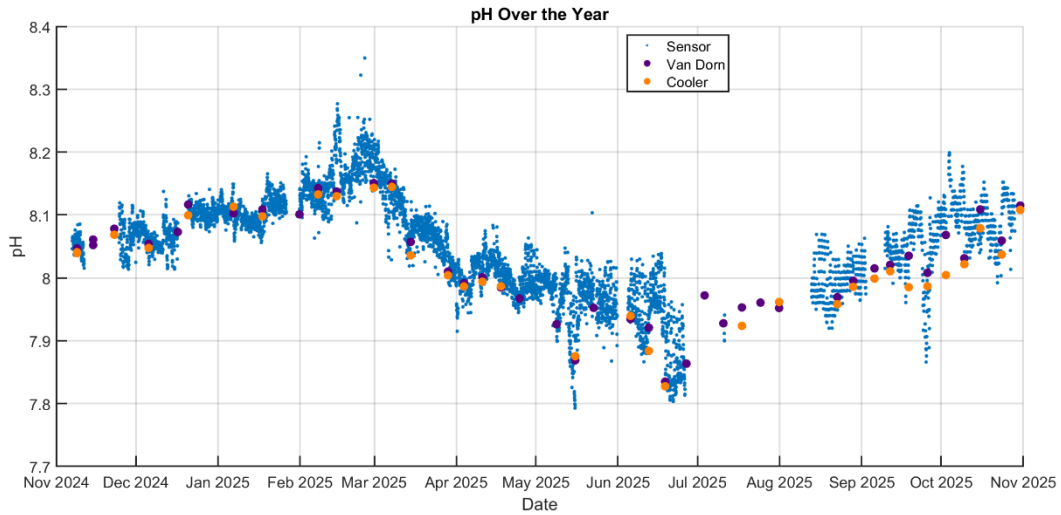
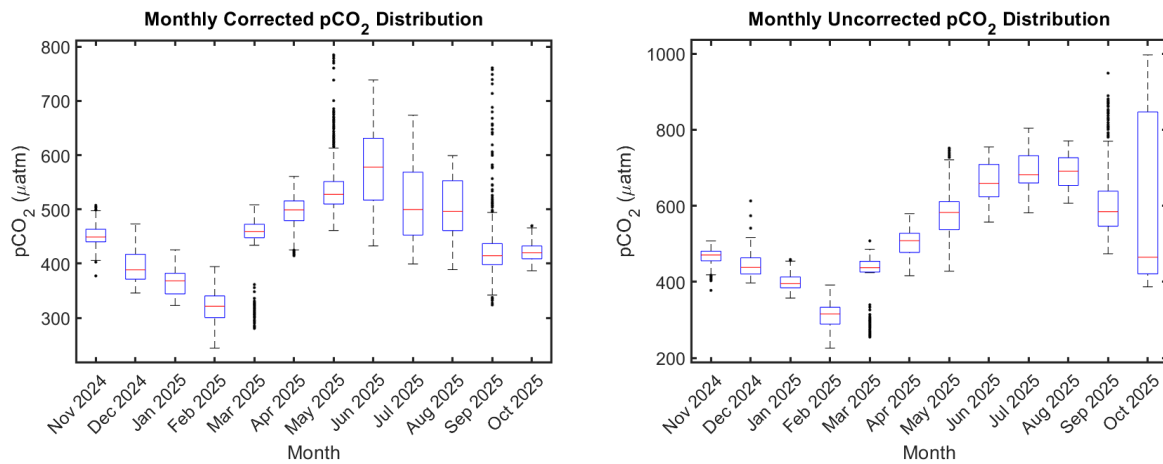


Figure 11 Final sensor salinity, temperature, pH, and pCO<sub>2</sub> data overlaid with the weekly lab-based results using in-situ samples.

After the previous steps of outlier removal and correction, the final data series were shown in Figure 11, and a comparison between pre- and post-correction are shown in Figure 12.

A comparison between sensor data (before and after corrections)



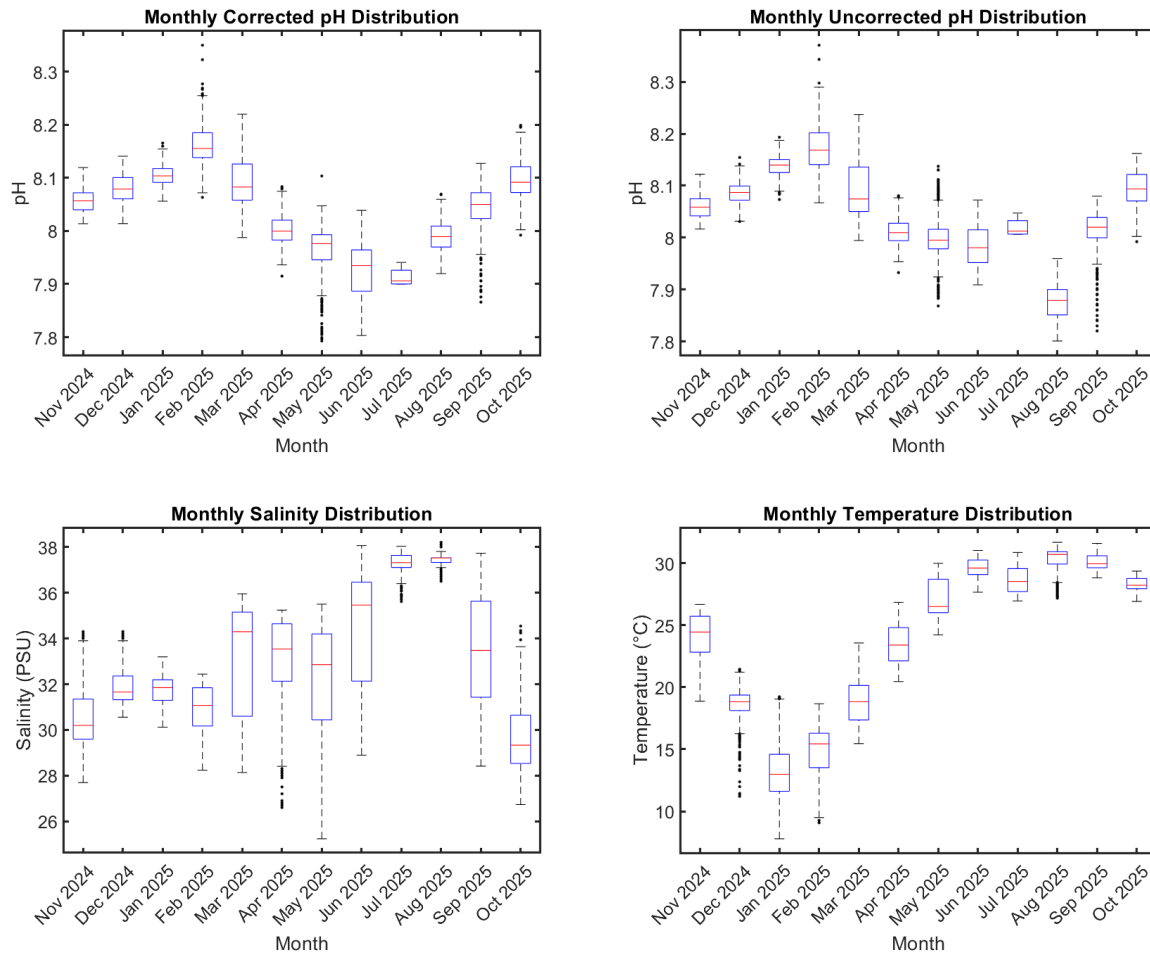


Figure 12 Monthly box plots for temperature, salinity pH, and pCO<sub>2</sub> data.

## Results and Discussion

### *Data quality control considerations*

Hourly measurements of the Port Aransas ship channel were collected from November 6, 2024 through October 31, 2025. This was accomplished via a flow-through system that received fresh estuarine water into the cooler every hour via a diaphragm pump. This flow-through system was used to for taking both pH and pCO<sub>2</sub> measurements using chemical sensors. Even though we used YSI to take hourly salinity data at the ship channel directly, after careful evaluating using in-situ water data, we chose supplemental salinity data from the MANERR and used this dataset, after correction, to calculate pH. During the deployment, multiple outages occurred due to pump failures, power outages, biofouling, and sensor malfunctions. This resulted in several periods in which sensor data became unreliable or unavailable.

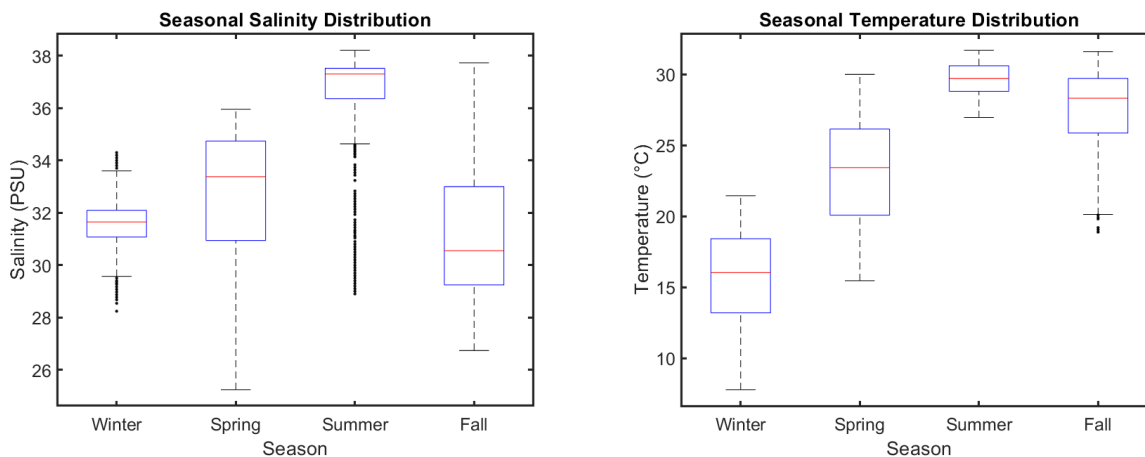
The quality control included measuring against water samples taken weekly from both the ship channel and the cooler. A spike test was used for the sensor data to remove any point spikes that may have been caused by potentially erroneous reading. For the water samples a linear

regression was used to determine if measurements in the cooler represented the ship channel condition. Points removed from this test were assumed to be caused by artifacts in the cooler and were removed from the cooler dataset. In total four points were removed from the total dataset. In order to determine if any of the water samples had residual microbial respiration that may have altered water chemistry, a separate spike test was applied to the pH as it was directly measured. As a result, three samples were discarded for analysis after this test.

In the overall sensor data, in the salinity data six data points were removed, 296 points were removed for temperature, 2097 points were removed for pH, and 1688 were removed for pCO<sub>2</sub>. Of the lab measurements 16 cooler samples for pH and pCO<sub>2</sub>, 5 pH and pCO<sub>2</sub> samples, and 5 cooler salinity samples were removed for analysis due to pump outages in the cooler, extreme values, and internal quality controls.

The sensors accuracy was evaluated by comparing the sensor values directly to those taken by the Van Dorn sampler. An ordinary least squares regression, bias, root mean square error, and mean absolute error were applied to the comparison on the sensor and in-situ sample data. The metrics showed that the SAMI-pH, salinity, and temperature data generally maintained a low bias and high agreement with the discrete measurements. However, the SAMI-pH had a relatively higher intercept on the least square regression line, indicating possible misalignment in the sensor data. On the other hand, the ProOceanus sensor exhibited larger inconsistencies that required correction. This was most likely due to the membrane of the ProOceanus sensor accumulating organic matter or sediments during deployment. These comparisons suggested that correcting for the pH and pCO<sub>2</sub> measurements were necessary.

Both pH and pCO<sub>2</sub> datasets were corrected using a stepwise piece wise constant approach. This correction however was not applied to the first two days of the data from the pH sensor, nor to the first two weeks of data from the pCO<sub>2</sub> sensor. Additionally, although a forward correction was applied, a short section of the pH data between August 13<sup>th</sup> and August 22<sup>nd</sup>, 2025 required correction backwards using the August 22<sup>nd</sup> sample. This correction was performed as there was no other nearby data to perform a correction. This lack of data was a due to the SAMI-pH being replaced by the YSI EXO 1. This replacement was driven by an excessive biofouling at the optical window during prolonged deployment, and low reagent volume hence the SAMI-pH sensor had to be sent back to the vendor for refurbishment.



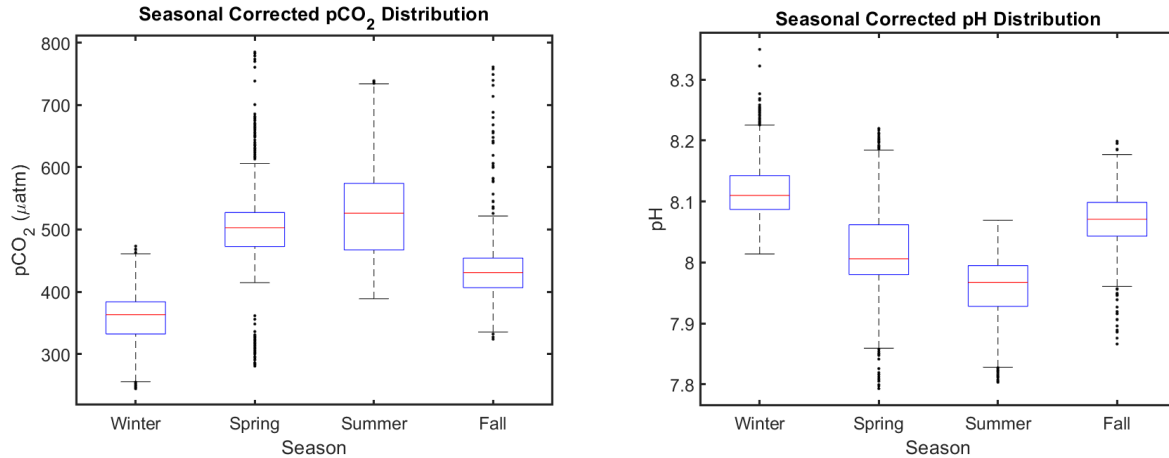


Figure 13 Box plots of seasonal variations of monitored temperature, salinity, pH and pCO<sub>2</sub>.

Table 2 Summary statistics of seasonal data collected during the deployment period (11/6/2024-10/31/2025).

Seasonal Summary: Temperature (°C)						
Season	N	Median	Q1	Q3	Min	Max
Winter	2160	16.03	13.195	18.42	7.79	21.45
Spring	2208	23.43	20.075	26.145	15.46	29.99
Summer	1990	29.7	28.8	30.6	26.96	31.682
Fall	1914	28.316	25.86	29.701	18.88	31.6
Seasonal Summary: Salinity						
Season	N	Median	Q1	Q3	Min	Max
Winter	2065	31.649	31.073	32.095	28.24	34.3
Spring	2207	33.378	30.941	34.739	25.245	35.952
Summer	1897	37.3	36.36	37.52	28.9	38.202
Fall	2039	30.553	29.243	33	26.736	37.727
Seasonal Summary: Corrected pH						
Season	N	Median	Q1	Q3	Min	Max
Winter	1943	8.11	8.087	8.1425	8.014	8.3497
Spring	2176	8.0061	7.98	8.0618	7.7929	8.2199
Summer	975	7.9674	7.928	7.9949	7.8033	8.0693
Fall	1421	8.0709	8.0432	8.0986	7.8661	8.1989
Seasonal Summary: Corrected pCO <sub>2</sub>						
Season	N	Median	Q1	Q3	Min	Max
Winter	1898	363.18	332.33	383.88	244.35	473.34
Spring	1767	502.91	472.7	527.22	280.64	784.83
Summer	1656	526.23	467.18	574.14	388.91	738.72
Fall	1039	430.89	406.59	454.11	323.98	760.93

Table 3. Seasonal means of temperature, salinity, pH and pCO<sub>2</sub> (mean ± standard deviation)

Season	Temp (°C)	Salinity	pH	pCO <sub>2</sub> (µatm)
Fall	27.70±2.67	31.21±2.62	8.070±0.043	445.6±63.9
Winter	15.68±3.07	31.58±0.97	8.117±0.045	359.7±40.5
Spring	23.15±3.75	32.76±2.33	8.020±0.065	496.7±62.7
Summer	29.61±1.11	36.35±2.10	7.955±0.056	534.7±72.3

### *Seasonality and Controlling Factors of pH and pCO<sub>2</sub>*

The season patterns of (winter, spring, summer, and fall) were plotted in Figure 13, and the samples size, median, 25<sup>th</sup> percentile (Q1), 75<sup>th</sup> percentile (Q3), minimum, and maximum were summarized in summary Table 2.

Season were broken up into four categories to look at the general trends of the estuary, Winter (December, January, February), Spring (March, April, May), Summer (June, July, August), and Fall (September, October, November). Due to the schedule of the monitoring record the fall category includes the initial month of November 2024, and September and October of 2025. The season grouping is intended to reflect general environmental seasonality in the Port Aransas Ship channel, allowing for comparison of conditions across seasonal periods.

Overall, the temperature showed a strong and predictable seasonal cycle, with a clear pattern of warming going from winter into spring and summer. The winter temperatures marked the lowest temperature for the ship channel with the seasons with the median being 16.03°C and a range of 7.79 to 21.45°C. The spring temperature was a transition period with a median of 23.43°C. Summer was the hottest period with a slightly increased median of 29.70 C and maximum of 31.68°C. The Fall remained relatively warm with a median of 28.32°C.

The salinity exhibited no apparent seasonal patterns throughout the year, mostly likely driven by sporadic freshwater influence and evaporation. In winter, fall and spring salinity has a median between 29 and 32, however ranged vary by season. The winter season had a median of 31.65 with a range between 28.2 to 34.3. Spring appeared to have some more freshwater input and as the salinity range increased to between 25.3 to 36.0, and a median value of 33.4. Summer appears to mark the start of evaporation dominance, as the median shifts to above typical Gulf salinity of 36 to a median of 37. The range also shifts to between 28.9 to 38.2. In the fall season, although having a maximum value of 37.7, has a median of 30.6 which may indicate freshwater mixing.

The corrected pH showed a clear seasonal pattern, with higher values during the colder months and lower values during the warmer periods. This seasonal pattern is consistent with typical estuarine carbonate dynamic, as in colder temperatures respiration is reduced, and lower temperature leads to slightly elevated pH. Conversely, warmer temperature leads to depressed pH.

pCO<sub>2</sub> data showed an inverse relationship with pH in the ship channel. pCO<sub>2</sub> values were lower in the winter with higher values in the summer. The rise in pCO<sub>2</sub> from the winter season into the

spring and eventually summer, illustrates the temperature dependence of pCO<sub>2</sub>. This inverse relationship between pH and pCO<sub>2</sub> aligns with previously observed season cycles of estuaries driven by temperature, biological activity, and air-sea exchange.

A multilinear regression was taken to analyze how pH and pCO<sub>2</sub> would vary as functions and salinity and temperature. It is clear that both temperature and salinity control pH and pCO<sub>2</sub> variations. pH decreases with increasing temperature and salinity, and pCO<sub>2</sub> increases with increasing temperature and salinity.

Estimated Coefficients (pH model):

	Estimate	SE	t	p
(Intercept)	8.4989	0.0097044	875.77	0
Temperature	-0.0073982	0.00012914	-57.287	0
Salinity	-0.0086902	0.00032171	-27.012	<<0

Estimated Coefficients:

	Estimate	SE	t	p
(Intercept)	-57.952	11.123	-5.2099	<<0
Temperature	8.7002	0.14803	58.774	0
Salinity	9.4481	0.36875	25.622	<<0

Comparison with the 2016-2017 monitoring effort

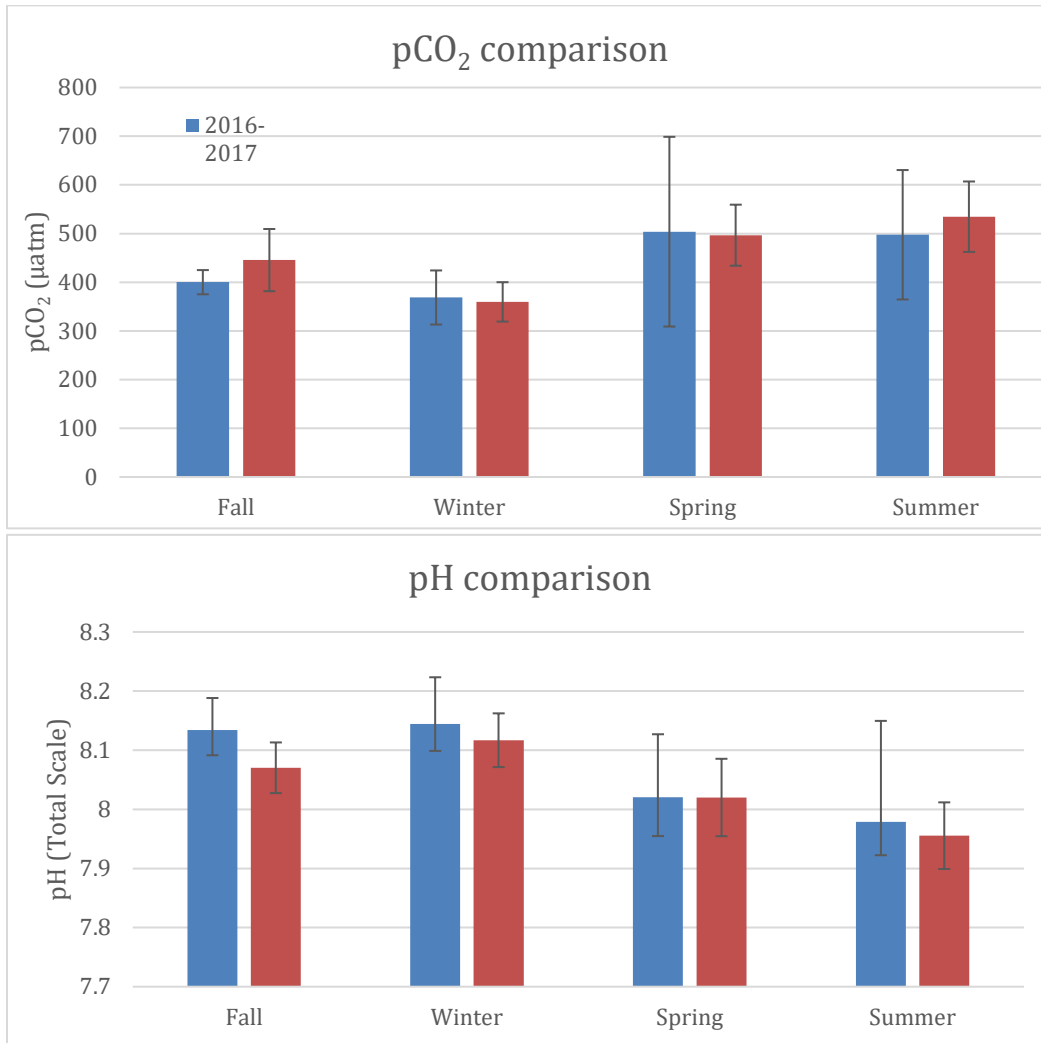


Figure 14. Comparison of pCO<sub>2</sub> and pH grouped by season between this project and that collected in 2016-2017.

At this coastal site, a seven-year span, i.e., from August 2017 when the prior project was halted till the initiation of this project, is not expected to produce significant differences in both pCO<sub>2</sub> and pH, given the large dynamic ranges of both parameters and variable physical and chemical conditions. Nevertheless, it is worth comparing these two sets of observations (Figure 14), bearing in mind that the 2016-2017 project did not have a complete annual dataset, e.g., because there was no data from September and October that would have been a part of the fall dataset. While both fall and summer pCO<sub>2</sub> appeared to be higher in 2024-2025 project year by 37-45 µatm, and pH values in the 2024-2025 project year were consistently lower than those in 2016-2017 (-0.0002 ~ -0.0064 pH units), none of these comparisons were statistically significant. Therefore, sustained monitoring is needed to reveal both longer term trends and short-term variabilities caused by stronger yet local events, for example freshwater pulses and associated water column production and respiration.

## **Conclusions**

The average pCO<sub>2</sub> and pH at the Aransas Ship Channel during the deployment period (November 2024-October 2025) for ocean acidification study were  $456.5 \pm 90.7 \mu\text{atm}$  and  $8.050 \pm 0.077$ , respectively. At this location, surface water experienced seasonal trends in carbonate system parameters, with elevated pH and depressed pCO<sub>2</sub> in the summer and vice versa in the winter, controlled by both salinity and temperature as well as hopefully seasonal shifts in biological metabolism. For the majority of the sampling period, the temperature had a stronger control on carbonate system parameters than the salinity. 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.

## **Future Directions**

Future monitoring efforts would benefit from specialized improvements to the sampling infrastructure to continue operation under unforeseen circumstances. In this project, we have encountered multiple pump failures and sensor failures, which have put strains on accomplishing the monitoring work on time.

The most troublesome issue in this project was pump performance, as multiple pump failures occurred throughout this monitoring effort. Future pump systems should be more robust, ideally with minimal moving parts that encounter sediments or a filtration system to reduce sediment exposure to the pump system, which can potentially degrade the pump suction power and weaken the flow over time. To reduce the chances of pump burnout, a one-way valve can be added to the plumbing system to prevent the water on the suction side from falling down to the sea level, this has made it difficult for the pump to draw up water especially if the pump was weakened. Additionally, maintaining at least two identical back up pumps would reduce downtime and improve data continuity.

The SAMI-pH sensor was not functional due to optical window fouling, which had to be repaired by the manufacturer. This has led to the usage of an alternative pH monitoring using a YSI sonde. It is suspected that stagnant water inside the cooler, despite the fact that it is renewed on hourly basis, has encouraged the growth of biofouling organisms. Together with the pump issues above we have encountered, a continuous flow through system using a more powerful pump is warranted.

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