Supplement of

Temporal variability and driving factors of the carbonate system in the Aransas Ship Channel, TX, USA: a time series study

Melissa R. McCutcheon et al.

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Fig S1. Time series data from continuous monitoring (A-D, Nov 8, 2016 to Aug 3, 2017) and discrete sample analysis (E-H, May 2, 2014- Feb. 25, 2020) at the Aransas Ship Channel. Gray scale (and shape) in the datapoints represents divisions between the four seasons. Vertical lines in (E-H) denote the period of continuous monitoring.
Table S1. Mean and standard deviation of annual and seasonal parameters from continuous monitoring and discrete sampling. CO\(_2\) fluxes and their standard deviations were calculated using the Jiang et al. (2008) wind speed parameterization for gas transfer velocity (in bold). Additional flux values reported in brackets use Ho et al. (2006) and Raymond and Cole (2001) parameterizations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Continuous Monitoring</th>
<th>Discrete Sampling</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature (°C)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annual</td>
<td>23.1 ± 5.3</td>
<td>23.5 ± 5.0</td>
</tr>
<tr>
<td>Winter</td>
<td>17.3 ± 2.1</td>
<td>17.3 ± 1.1</td>
</tr>
<tr>
<td>Spring</td>
<td>23.8 ± 2.8</td>
<td>23.4 ± 2.9</td>
</tr>
<tr>
<td>Summer</td>
<td>29.7 ± 0.8</td>
<td>29.6 ± 0.5</td>
</tr>
<tr>
<td>Fall</td>
<td>22.5 ± 2.1</td>
<td>23.6 ± 0.1</td>
</tr>
<tr>
<td><strong>Salinity</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annual</td>
<td>30.8 ± 3.7</td>
<td>30.4 ± 3.5</td>
</tr>
<tr>
<td>Winter</td>
<td>30.0 ± 3.7</td>
<td>29.3 ± 4.6</td>
</tr>
<tr>
<td>Spring</td>
<td>30.2 ± 2.6</td>
<td>30.0 ± 1.7</td>
</tr>
<tr>
<td>Summer</td>
<td>33.3 ± 3.2</td>
<td>33.6 ± 3.2</td>
</tr>
<tr>
<td>Fall</td>
<td>27.6 ± 3.7</td>
<td>28.8 ± 0.1</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annual</td>
<td>8.12 ± 0.10</td>
<td>8.092 ± 0.078</td>
</tr>
<tr>
<td>Winter</td>
<td>8.19 ± 0.08</td>
<td>8.157 ± 0.041</td>
</tr>
<tr>
<td>Spring</td>
<td>8.09 ± 0.09</td>
<td>8.078 ± 0.056</td>
</tr>
<tr>
<td>Summer</td>
<td>8.05 ± 0.06</td>
<td>7.999 ± 0.051</td>
</tr>
<tr>
<td>Fall</td>
<td>8.18 ± 0.05</td>
<td>8.136 ± 0.001</td>
</tr>
<tr>
<td><strong>pCO(_2)(µatm)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annual</td>
<td>416 ± 60</td>
<td>400 ± 71</td>
</tr>
<tr>
<td>Winter</td>
<td>365 ± 44</td>
<td>349 ± 31</td>
</tr>
<tr>
<td>Spring</td>
<td>436 ± 45</td>
<td>413 ± 54</td>
</tr>
<tr>
<td>Summer</td>
<td>463 ± 48</td>
<td>480 ± 59</td>
</tr>
<tr>
<td>Fall</td>
<td>400 ± 25</td>
<td>357 ± 2</td>
</tr>
<tr>
<td><strong>CO(_2) Flux (mmol m(^{-2}) d(^{-1}))</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annual</td>
<td>0.2 ± 23.7</td>
<td>-1.5 ± 9.2</td>
</tr>
<tr>
<td>Winter</td>
<td>-16.9 ± 29.2</td>
<td>-9.9 ± 5.2</td>
</tr>
<tr>
<td>Spring</td>
<td>7.6 ± 15.0</td>
<td>10.0 ± 7.1</td>
</tr>
<tr>
<td>Summer</td>
<td>10.8 ± 13.3</td>
<td>10.5 ± 7.8</td>
</tr>
<tr>
<td>Fall</td>
<td>-0.9 ± 7.7</td>
<td>-7.5</td>
</tr>
</tbody>
</table>
Table S2. Tests examining differences in mean carbonate system parameters between seasons and between types of sampling. Statistic p-values are listed, with significant results based on $\alpha=0.05$ bolded, and the F statistic is in parentheses. Comparisons with significantly different means in post-hoc analyses are listed as unequal beneath the one-way ANOVA results (All≠ indicates that every individual comparison between levels had significantly different means. W = winter, Sp = spring, Su = summer, F = fall; C = continuous sensor data, D = discrete sample data over the entire discrete monitoring period, DC = Discrete sample data during only the period of continuous monitoring).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Two-way ANOVA</th>
<th>One-way ANOVA and post-hoc multiple comparison results for differences between types of sampling</th>
<th>One-way ANOVA and post-hoc multiple comparison results for difference between seasons</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Interaction</td>
<td>Season</td>
<td>Sampling type</td>
</tr>
<tr>
<td>Temp (°C)</td>
<td>&lt;0.0001 (15.8)</td>
<td>&lt;0.0001 (12369.7)</td>
<td>0.7346 (0.3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salinity</td>
<td>0.0141 (2.7)</td>
<td>&lt;0.0001 (598.7)</td>
<td>0.6509 (0.4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>0.0013 (3.7)</td>
<td>&lt;0.0001 (1412.3)</td>
<td>&lt;0.0001 (24.0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pCO2 (µatm)</td>
<td>&lt;0.0001 (10.4)</td>
<td>&lt;0.0001 (1747.3)</td>
<td>0.0147 (4.2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO2 Flux (mmol m−2 d−1)</td>
<td>0.0144 (2.6)</td>
<td>&lt;0.0001 (738.1)</td>
<td>0.6739 (0.4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table S3. Diel variability in system parameters from continuous sensor data. Reported p-values are from a paired-\(t\) test; all significant results based on \(\alpha=0.05\) are bolded. Reported fluxes use the Jiang et al. (2008) gas transfer velocity parameterization.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Time Period</th>
<th>Daytime Mean</th>
<th>Nighttime Mean</th>
<th>Day versus Night p-value</th>
<th>Mean Diel Range</th>
<th>Minimum Diel Range</th>
<th>Maximum Diel Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>Full Sampling Period</td>
<td>23.0 ± 5.3</td>
<td>23.2 ± 5.4</td>
<td>1.3 ± 0.8</td>
<td>0.30</td>
<td>3.93</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>17.2 ± 2.1</td>
<td>17.4 ± 2.1</td>
<td>0.2055</td>
<td>1.5 ± 0.8</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spring</td>
<td>23.7 ± 2.7</td>
<td>23.8 ± 2.9</td>
<td>0.5579</td>
<td>1.2 ± 0.6</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>29.6 ± 0.7</td>
<td>29.9 ± 0.8</td>
<td>&lt;0.0001</td>
<td>1.0 ± 0.6</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fall</td>
<td>22.0 ± 1.19</td>
<td>23.0 ± 1.0</td>
<td>&lt;0.0001</td>
<td>1.8 ± 0.9</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>Salinity</td>
<td>Full Sampling Period</td>
<td>30.5 ± 4.1</td>
<td>31.0 ± 3.3</td>
<td>3.4 ± 2.7</td>
<td>0.250</td>
<td>15.870</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>29.6 ± 4.2</td>
<td>30.4 ± 3.1</td>
<td>0.0051</td>
<td>3.8 ± 2.2</td>
<td>2.5 ± 2</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>Spring</td>
<td>30.1 ± 2.6</td>
<td>30.2 ± 2.6</td>
<td>0.5604</td>
<td>2.5 ± 2</td>
<td>0.4</td>
<td>8.17</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>33.4 ± 3.2</td>
<td>33.1 ± 3.3</td>
<td>0.0550</td>
<td>2.0 ± 1.7</td>
<td>0.3</td>
<td>9.73</td>
</tr>
<tr>
<td></td>
<td>Fall</td>
<td>25.9 ± 3.9</td>
<td>29.0 ± 3.2</td>
<td>&lt;0.0001</td>
<td>7.7 ± 3.6</td>
<td>1.2</td>
<td>15.87</td>
</tr>
<tr>
<td>pH</td>
<td>Full Sampling Period</td>
<td>8.12 ± 0.10</td>
<td>8.13 ± 0.09</td>
<td>0.09 ± 0.05</td>
<td>0.02</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>8.18 ± 0.08</td>
<td>8.20 ± 0.07</td>
<td>0.0108</td>
<td>0.10 ± 0.05</td>
<td>0.02</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>Spring</td>
<td>8.09 ± 0.09</td>
<td>8.10 ± 0.08</td>
<td>0.3286</td>
<td>0.08 ± 0.03</td>
<td>0.03</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>8.04 ± 0.06</td>
<td>8.07 ± 0.05</td>
<td>&lt;0.0001</td>
<td>0.08 ± 0.04</td>
<td>0.03</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>Fall</td>
<td>8.20 ± 0.05</td>
<td>8.17 ± 0.05</td>
<td>&lt;0.0001</td>
<td>0.12 ± 0.04</td>
<td>0.03</td>
<td>0.20</td>
</tr>
<tr>
<td>(p)CO(_2) (µatm)</td>
<td>Full Sampling Period</td>
<td>417 ± 54</td>
<td>416 ± 65</td>
<td>58 ± 33</td>
<td>12.6</td>
<td>211.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>374 ± 44</td>
<td>358 ± 43</td>
<td>&lt;0.0001</td>
<td>43 ± 21</td>
<td>12.6</td>
<td>121.1</td>
</tr>
<tr>
<td></td>
<td>Spring</td>
<td>438 ± 42</td>
<td>437 ± 48</td>
<td>0.7237</td>
<td>61 ± 31</td>
<td>20.5</td>
<td>152.8</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>452 ± 44</td>
<td>471 ± 51</td>
<td>0.0003</td>
<td>74 ± 42</td>
<td>23.6</td>
<td>211.3</td>
</tr>
<tr>
<td></td>
<td>Fall</td>
<td>406 ± 24</td>
<td>399 ± 27</td>
<td>0.0545</td>
<td>56 ± 18</td>
<td>22</td>
<td>92.2</td>
</tr>
<tr>
<td>CO(_2) Flux (mmol m(^{-2}) d(^{-1}))</td>
<td>Full Sampling Period</td>
<td>0.0 ± 6.3</td>
<td>-1.3 ± 5.9</td>
<td>34.1 ± 29.0</td>
<td>2.7</td>
<td>189.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>-14.9 ± 8.4</td>
<td>-19.1 ± 7.7</td>
<td>0.0676</td>
<td>46.6 ± 38.9</td>
<td>2.7</td>
<td>189.0</td>
</tr>
<tr>
<td></td>
<td>Spring</td>
<td>7.6 ± 5.2</td>
<td>7.0 ± 5.2</td>
<td>0.6680</td>
<td>27.5 ± 18.5</td>
<td>4.9</td>
<td>115.0</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>9.4 ± 5.6</td>
<td>11.7 ± 5.2</td>
<td>0.1167</td>
<td>32.3 ± 22.9</td>
<td>4.5</td>
<td>111.0</td>
</tr>
<tr>
<td></td>
<td>Fall</td>
<td>0.1 ± 3.8</td>
<td>-0.3 ± 3.5</td>
<td>0.7449</td>
<td>17.0 ± 10.2</td>
<td>3.9</td>
<td>40.1</td>
</tr>
</tbody>
</table>
Table S4. Thermal versus non-thermal control on $pCO_2$ over different time scales using both continuous sensor data (C) and discrete sample data (D). If more than one segment of time is being considered (n>1), $\Delta pCO_2$ values are the mean ± standard deviation of all segments. T/B range is the minimum and maximum T/B, and the number out of n with T/B>1 is recorded.

<table>
<thead>
<tr>
<th>Time Period / Scale</th>
<th>Sampling type</th>
<th>n</th>
<th>$\Delta pCO_2$, t (µatm)</th>
<th>$\Delta pCO_2$, nt (µatm)</th>
<th>T/B</th>
<th>Number out of n with T/B &gt;1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full Monitoring Period (May 2, 2014- Feb. 25, 2020)</td>
<td>D</td>
<td>1</td>
<td>301.9</td>
<td>537.8</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td>Annual</td>
<td>D</td>
<td>5</td>
<td>259.3 ± 16.0</td>
<td>333.3 ± 120.0</td>
<td>0.50 – 1.16</td>
<td>1/5</td>
</tr>
<tr>
<td>Continuous Monitoring Period (Nov 2016 – August 2017)</td>
<td>C</td>
<td>1</td>
<td>355.0</td>
<td>360.7</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>1</td>
<td>236.3</td>
<td>229.9</td>
<td>1.03</td>
<td></td>
</tr>
<tr>
<td>Winter</td>
<td>C</td>
<td>1</td>
<td>168.2</td>
<td>328.4</td>
<td>0.51</td>
<td>1/6</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>6</td>
<td>42.2 ± 23.4</td>
<td>101.7 ± 78.7</td>
<td>0.20 – 4.90</td>
<td>1/6</td>
</tr>
<tr>
<td>Spring</td>
<td>C</td>
<td>1</td>
<td>171.4</td>
<td>246.9</td>
<td>0.69</td>
<td>2/6</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>6</td>
<td>142.3 ± 53.7</td>
<td>147.8 ± 67.3</td>
<td>0.59 – 2.42</td>
<td>2/6</td>
</tr>
<tr>
<td>Summer</td>
<td>C</td>
<td>1</td>
<td>100.2</td>
<td>179.9</td>
<td>0.56</td>
<td>0/6</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>6</td>
<td>46.9 ± 26.6</td>
<td>176.9 ± 108.3</td>
<td>0.21 – 0.35</td>
<td>0/6</td>
</tr>
<tr>
<td>Fall</td>
<td>C</td>
<td>1</td>
<td>105.9</td>
<td>181.6</td>
<td>0.58</td>
<td>2/6</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>6</td>
<td>179.8 ± 59.5</td>
<td>176.6 ± 78.1</td>
<td>0.59 – 3.06</td>
<td>2/6</td>
</tr>
<tr>
<td>Daily</td>
<td>C</td>
<td>178</td>
<td>21.8 ± 11.8</td>
<td>63.8 ± 30.3</td>
<td>0.05 – 1.68</td>
<td>11/178</td>
</tr>
</tbody>
</table>
Table S5. Pearson correlation coefficients between carbonate system parameters and other environmental parameters for both continuous sensor data and discrete sample data. Parameter pairs with a significant correlation based on α=0.05 have a correlation coefficient reported. Asterisks are used to indicate the level of significance of the correlation, * p<0.05, ** p<0.01, *** p<0.0001. The correlation coefficient is listed as 0 if the relationship was not significant. N/A is listed when the analysis was omitted because the environmental parameter did not have observations corresponding to the date and time of at least half of our discrete sample measurements (45 observations).

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>pCO₂</th>
<th>pCO₂, nonthermal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Continuous</td>
<td>Discrete</td>
<td>Continuous</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>-0.55 ***</td>
<td>-0.59 ***</td>
<td>0.75 ***</td>
</tr>
<tr>
<td>Salinity</td>
<td>-0.47 ***</td>
<td>-0.74 ***</td>
<td>0.53 ***</td>
</tr>
<tr>
<td>Wind Speed (m s⁻¹)</td>
<td>-0.04 **</td>
<td>N/A</td>
<td>0.15 ***</td>
</tr>
<tr>
<td>Dissolved Oxygen (mg L⁻¹)</td>
<td>0.55 ***</td>
<td>0</td>
<td>-0.81 ***</td>
</tr>
<tr>
<td>Tide Level (m)</td>
<td>0</td>
<td>0</td>
<td>-0.15 ***</td>
</tr>
<tr>
<td>Turbidity</td>
<td>-0.08 ***</td>
<td>N/A</td>
<td>-0.14 ***</td>
</tr>
<tr>
<td>Fluor. Chlorophyll</td>
<td>0.12 ***</td>
<td>N/A</td>
<td>-0.22 ***</td>
</tr>
</tbody>
</table>
**Sensor deployment details**

Ideally, *in-situ* sensors should be deployed under the sea surface. However, to reduce the maintenance cost and effort for sensors deployed in warm water that experiences intense biofouling, the sensors were set up to measure pH and $p\text{CO}_2$ from an *ex situ* position using *in situ* seawater. Water was pumped from ~1 m below the sea surface into the bottom spigot of a 100-Qt cooler that housed the SAMI-CO2 and SeaFET sensors. To allow water outflow, a 1” hole was drilled at the opposite side of the spigot near the top of the cooler rim, allowing water to flow back to the sea surface. The pump was programmed to turn on 20 minutes before each hour, pumping more than enough water to fully flush the cooler, and sensors recorded measurements on the hour. The YSI sonde was deployed directly into ASC inside a 2” PVC pipe at ~1 m below the sea surface.

Hourly data (single hourly measurements, measured on the hour) collected by all sensors (pH, $p\text{CO}_2$, salinity, and temperature) were saved in the onboard data loggers and downloaded during service trips. Sensor failures or pump failures occurred for short periods of time throughout the deployment. Measurements were recorded on 262 individual days, with 176 of those days having the full set of 24 (hourly) measurements. Service trips to the field site were conducted every two weeks to service all sensors and clean the cooler. Additionally, duplicate, discrete water samples were collected on the hour during service trips for quality assurance of sensor data and to check that surface water and cooler chemistries aligned (referred to throughout as quality assurance or QA samples).

The sensor deployment was shorter than intended because the pier was destroyed in the aftermath of Hurricane Harvey in 2017.
**Removal of suspicious sensor 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, which would result in the cooler not appropriately representing the *in-situ* environment (Figure S2). Pump failure resulted in notable increases in $pCO_2$ and decreases in pH due to the buildup of respirational products (Fig. S2). Sensor data during known periods of pump failure were omitted from analysis (Fig. S2). Other suspect data based on the multiple data correlation comparisons were also removed as they were assumed to represent sensor malfunction (Fig. S3).

![Figure S2. All recorded $pCO_2$ and pH data. Data points flagged for removal prior to analysis are shown in red.](image-url)
Figure S3. Relationships between sensor-measured carbonate system parameters and temperature and salinity. Data points flagged for removal are shown in red.

**Sensor data correction and direct agreement of measurement methods**

Discrete, QA samples were collected during each sensor maintenance trip from both the channel near the pump inlet and from the cooler that housed the sensors. The same laboratory methods used for discrete sample analysis (Section 2.3) also apply for these discrete, QA samples. These samples were only used for comparison to sensor values and correction of sensor values; they were not included in the discrete sample analyses. Water temperature and salinity were also measured in both locations using a handheld YSI data sonde.

The offset between the sensor and laboratory pH was used to establish a correction to sensor pH. The mean difference between the SeaFET pH measurements and the QA samples
(continuous – discrete) was 0.05 ± 0.08. Since there was not a clear pattern over time in the difference between sensor and laboratory-measured pH (Fig. S4), the average offset was used for a correction to all sensor data.

The difference between the sensor $pCO_2$ and calculated $pCO_2$ was -18 ± 44 (Fig. S4, Table S6). This difference was not used for a correction since there is error associated with the calculation of $pCO_2$ from discrete samples and the spectrophotometric measurements of the SAMI-CO2 should not experience drift. We used several different constants to calculate $pCO_2$ to check the offset between measurements from sensors and laboratory-analyzed bottle samples; all were similar in mean and standard deviation, but the offset could be slightly reduced using Millero (2002) constants. Mean offsets and their associated standard deviations were larger when comparing sensor data to samples taken during our long-term discrete monitoring effort compared to the directly associated QA samples (Table S6). This is not surprising given that the
discrete sample collection did not occur at the exact time of the sensor measurement or the exact location of the cooler pump inlet.

Given that the analytical accuracy of the SeaFET instrument is 0.05 pH units (Table S6), the average offset between sensor and laboratory values of quality control samples demonstrates fair agreement (Table S6). Given that calculated uncertainty associated with calculated discrete $pCO_2$ was 7 ± 2, we did not see great agreement between SAMICO2 $pCO_2$ and laboratory-calculated $pCO_2$ for QA samples. Greater sensor-laboratory agreement has been achieved for open ocean settings, but this larger standard deviation is likely a result of the temporal variability in the more complex estuarine environment where these instruments have been much less widely deployed to date.

Table S6. Mean ± standard deviation of the difference between discrete and continuous values. Reported pH differences are after the sensor pH correction.

<table>
<thead>
<tr>
<th>Difference between sampling methods</th>
<th>Sensor – QA samples * (n=12)</th>
<th>Sensor – discrete samples ** (n=13)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity</td>
<td>-0.16 ± 1.44</td>
<td>0.50 ± 1.69</td>
</tr>
<tr>
<td>pH</td>
<td>0.00 ± 0.08</td>
<td>0.01 ± 0.12</td>
</tr>
<tr>
<td>$pCO_2$ (µatm)</td>
<td>-18 ± 44</td>
<td>25 ± 63</td>
</tr>
</tbody>
</table>

* Difference between sensor measurements and laboratory measurement of QA bottle samples taken at exact time of sensor measurement and directly from the sensor cooler

** Difference between sensor measurements and laboratory measurement of discrete samples for our 5+ year monitoring. These discrete samples were taken from a nearby station (within 100 m), and they were not taken directly on the hour, so sampling time was rounded to the nearest hour to pair with sensor data.

Quantified uncertainties associated with parameters

Propagated error associated with calculated carbonate system parameters was calculated using the seacarb package in R (Gattuso et al., 2021) using analytical errors associated with the
measurements of the input pair, *in-situ* temperature and salinity, total boron, and the key
dissociation constants (Table S7). Error associated with calculated parameters from discrete
bottle samples was relatively small and likely a result of uncertainties in constants (Orr et al.,
2018), but error associated with parameters calculated from sensor data was relatively large
(Table S7). This large error is likely a result of both the relatively low analytical precision
associated with the pH sensor and the poor mathematical combination of variables for speciation
calculations. This high error is the reason that we decided to omit the discussion of any other
calculated carbonate system parameters from the manuscript. The high error suggests that it will
be important that autonomous sensors that can measure alternative parameters and allow for
lower propagated error are developed and broadly used to gain a full understanding of carbonate
chemistry on high-frequency timescales.

Table S7. Analytical error for directly measured parameters and propagated error for calculated
parameters (mean ± standard deviation).

<table>
<thead>
<tr>
<th>Error (Analytical or Propagated)</th>
<th>Discrete Sampling (n = 104)</th>
<th>Continuous Monitoring (n = 6088)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Salinity</td>
<td>0.01</td>
<td>0.1</td>
</tr>
<tr>
<td>pH</td>
<td>0.0004</td>
<td>0.05</td>
</tr>
<tr>
<td>( pCO_2 ) (µatm)</td>
<td>7 ± 2</td>
<td>1.0</td>
</tr>
<tr>
<td>DIC (µmol kg(^{-1}))</td>
<td>2.5</td>
<td>327.4 ± 63.2</td>
</tr>
<tr>
<td>TA (µmol kg(^{-1}))</td>
<td>7.4 ± 0.9</td>
<td>400.7 ± 81.0</td>
</tr>
<tr>
<td>( \Omega_{Ar} )</td>
<td>0.19 ± 0.03</td>
<td>1.08 ± 0.31</td>
</tr>
</tbody>
</table>

Additional information on CO\(_2\) flux calculations and windspeed data

The majority of atmospheric xCO\(_2\) data that were used in CO\(_2\) flux calculations were
retrieved from NOAA’s flask sampling network from Key Biscayne, FL,
However, Key Biscayne data were not yet available for January 2019 – February 2020, so global average values were used for these 16 months. We justified this substitution of global average values because the monthly means between Key Biscayne and global \(\text{xCO}_2\) over the initial 56 months of our discrete sampling only differed by \(1.2 \pm 1.5 \mu\text{atm}\) (i.e. \(0.3\% \pm 0.4\%\)). While atmospheric \(\text{xCO}_2\) values at our exact location would have been preferable, they were unavailable, and our calculations include the assumption that the Florida and global values are not significantly different from atmospheric \(\text{xCO}_2\) at ASC. We believe this is warranted, given the relatively homogenous levels of atmospheric CO\(_2\), with the most variation occurring between hemispheres.

The \(\text{xCO}_2\) values that were incorporated into calculations were monthly averages. We believe that this method is justified for flux calculations (even for pairing with the hourly continuous data), as the one example of frequent (i.e., every three hour) sampling of atmospheric \(\text{xCO}_2\) in the Gulf of Mexico (off Louisiana coast) shows very little diel or even monthly fluctuation in atmospheric \(\text{xCO}_2\) ([https://www.pmel.noaa.gov/co2/story/Coastal+LA](https://www.pmel.noaa.gov/co2/story/Coastal+LA)). While variability in atmospheric CO\(_2\) on diel and weekly timescales is often small at a single site, especially small variability on short time scales likely occurs in the nwGOM due to predominantly southeast winds, blowing from offshore. As a result, diel fluctuations in atmospheric \(\text{xCO}_2\) that could be present due to biological cycles of terrestrial plants or anthropogenic influence are likely negligible at ASC.

NOAA/TCOON’s Port Aransas (<2 km inshore from monitoring location) and Aransas Pass (<2 km offshore from monitoring location) stations did not begin recording windspeed data.
until Aug 5, 2016. Therefore, flux calculations for our discrete monitoring data spanning from May 2, 2014 to Aug 5, 2016 used windspeed data from the Nueces Bay Station (~40 km from our monitoring location). During the continuous monitoring period (Nov 8, 2015 – Aug 3, 2017), about 55 days (<20% of observations) lacked windspeed data from Port Aransas or Aransas Pass stations and used data from Nueces Bay station. Following the continuous monitoring period (Aug 23, 2017 – Feb 25, 2020), only about nine days of wind data had to be retrieved from the Nueces Bay station. For those days during the 5+ year monitoring period that data were available at both the Port Aransas Station and the Nueces Bay station, the Nueces Bay Station did have higher windspeeds by an average of ~2.33 m/s, which could result in overestimation of the magnitude of CO₂ fluxes. Given this station windspeed offset (along with the many other factors that complicate the calculation of fluxes through windspeed parameterization), the actual values of CO₂ flux should not be taken at face value. Missing data at the Port Aransas and Aransas Pass stations generally spanned full days (not individual hours of missing data), so both calculations of CO₂ flux with the continuous data and the discrete data would be pulling from the same station on the same day, which validates the comparison of methods as flux calculated by both sampling methods would receive the same bias.