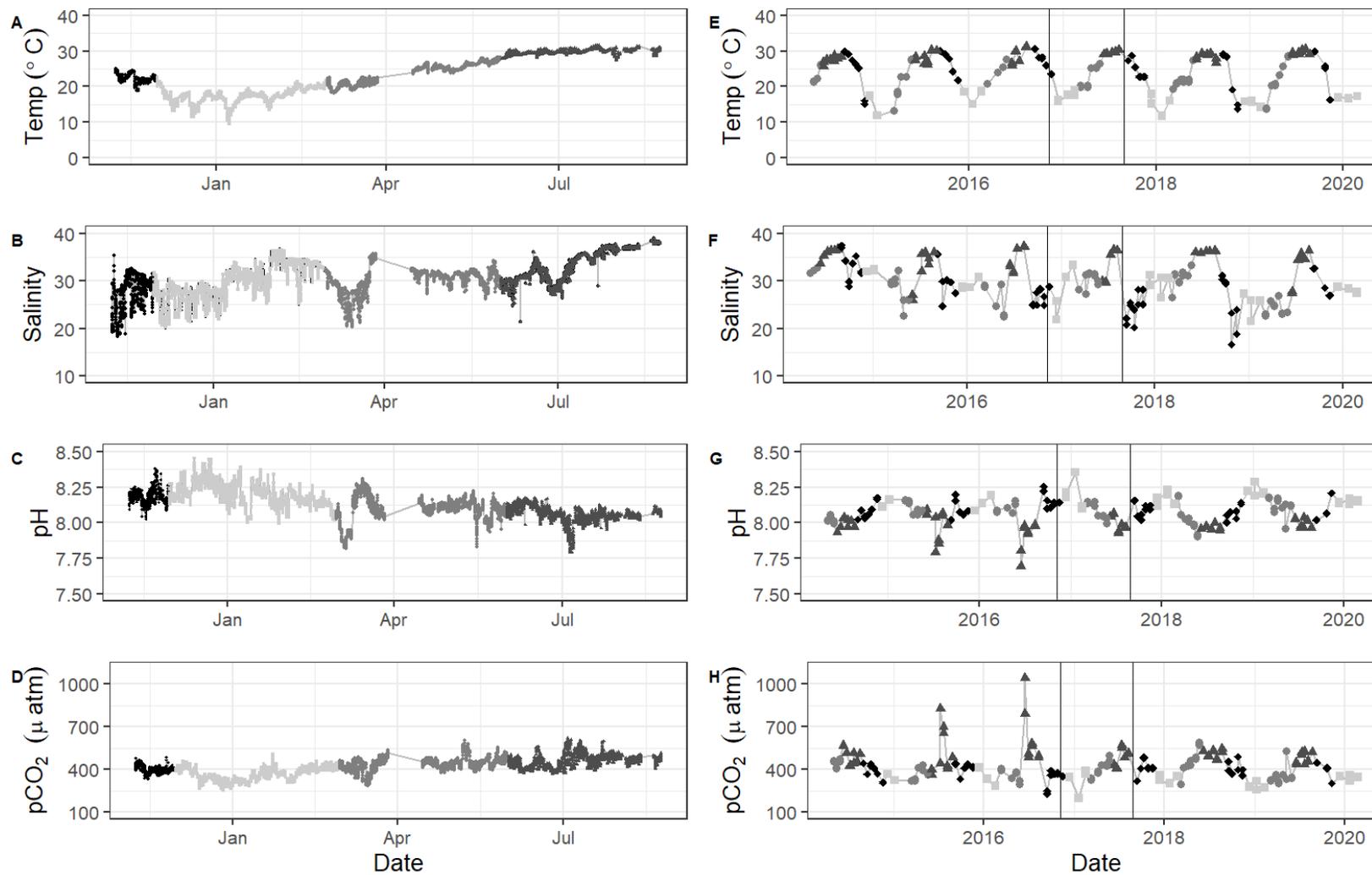**Biogeosciences**

Supplement of

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

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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.

Parameter		Continuous Monitoring	Discrete Sampling	
	Time Period	Nov. 8 2016 – Aug 23, 2017	Nov. 8 2016 – Aug 23, 2017	May 2, 2014- Feb. 25, 2020
Temperature (°C)	**Annual**	23.1 ± 5.3	23.5 ± 5.0	24.1 ± 5.3
	Winter	17.3 ± 2.1	17.3 ± 1.1	16.2 ± 2.0
	Spring	23.8 ± 2.8	23.4 ± 2.9	22.6 ± 3.7
	Summer	29.7 ± 0.8	29.6 ± 0.5	28.7 ± 1.4
	Fall	22.5 ± 2.1	23.6 ± 0.1	25.5 ± 4.5
Salinity	**Annual**	30.8 ± 3.7	30.4 ± 3.5	30.1 ± 4.4
	Winter	30.0 ± 3.7	29.3 ± 4.6	28.9 ± 2.9
	Spring	30.2 ± 2.6	30.0 ± 1.7	28.7 ± 3.4
	Summer	33.3 ± 3.2	33.6 ± 3.2	34.6 ± 2.8
	Fall	27.6 ± 3.7	28.8 ± 0.1	28.4 ± 4.5
pH	**Annual**	8.12 ± 0.10	8.092 ± 0.078	8.079 ± 0.092
	Winter	8.19 ± 0.08	8.157 ± 0.041	8.162 ± 0.065
	Spring	8.09 ± 0.09	8.078 ± 0.056	8.077 ± 0.066
	Summer	8.05 ± 0.06	7.999 ± 0.051	7.975 ± 0.046
	Fall	8.18 ± 0.05	8.136 ± 0.001	8.100 ± 0.071
pCO_2 (µatm)	**Annual**	416 ± 60	400 ± 71	406 ± 100
	Winter	365 ± 44	349 ± 31	331 ± 39
	Spring	436 ± 45	413 ± 54	396 ± 67
	Summer	463 ± 48	480 ± 59	511 ± 108
	Fall	400 ± 25	357 ± 2	386 ± 62
CO_2 Flux (mmol m^{-2} d^{-1})	**Annual**	**0.2 ± 23.7** [0.1, -87.6]	**-1.5 ± 9.2** [-2.6, -4.5]	**-0.8 ± 18.7** [-0.7, 5.3]
	Winter	**-16.9 ± 29.2** [-14.6, -444.0]	**-9.9 ± 5.2** [-8.3, -16.2]	**-13.0 ± 13.5** [-10.6, -25.6]
	Spring	**7.6 ± 15.0** [6.5, 109.0]	**1.0 ± 7.1** [1.0, 3.3]	**-6.5 ± 12.2** [-5.5, -18.0]
	Summer	**10.8 ± 13.3** [9.1, 28.9]	**10.5 ± 7.8** [8.6, 16.3]	**18.3 ± 19.6** [15.3, 65.5]
	Fall	**-0.9 ± 7.7** [-0.7, -44.0]	**-7.5** [-6.2, -11.4]	**-2.3 ± 13.7** [-1.9, -0.9]

19 Table S2. Tests examining differences in mean carbonate system parameters between seasons and between types of sampling. Statistic
20 p-values are listed, with significant results based on α=0.05 bolded, and the F statistic is in parentheses. Comparisons with
21 significantly different means in post-hoc analyses are listed as unequal beneath the one-way ANOVA results (All≠ indicates that every
22 individual comparison between levels had significantly different means. W = winter, Sp = spring, Su = summer, F = fall; C =
23 continuous sensor data, D = discrete sample data over the entire discrete monitoring period, D_C = Discrete sample data during only the
24 period of continuous monitoring).

Parameter	Two-way ANOVA			One-way ANOVA and post-hoc multiple comparison results for differences between types of sampling				One-way ANOVA and post-hoc multiple comparison results for difference between seasons		
	Interaction	Season	Sampling type	winter	spring	summer	fall	Continuous	Discrete (Continuous Period)	Discrete (Entire Period)
Temp (°C)	**<0.0001** (15.8)	**<0.0001** (12369.7)	0.7346 (0.3)	0.0710 (2.6)	0.1052 (2.3)	**<0.0001** (19.6)	**<0.0001** (61.4)	**<0.0001** (12559)	**<0.0001** (22.8)	**<0.0001** (58.2)
						D≠C	D≠C	All≠	W≠Su; W≠Sp; W≠F; Su≠Sp; Su≠F	All≠
Salinity	**0.0141** (2.7)	**<0.0001** (598.7)	0.6509 (0.4)	0.1716 (1.8)	**0.0013** (6.7)	0.1921 (1.7)	0.7007 (0.4)	**<0.0001** (580.0)	0.2516 (1.6)	**<0.0001** (17.5)
					D≠C			W≠Su; W≠F; Su≠Sp; Su≠F; Sp≠F		W≠Su; Su≠Sp; Su≠F
pH	**0.0013** (3.7)	**<0.0001** (1412.3)	**<0.0001** (24.0)	0.4026 (0.9)	0.9238 (0.1)	**<0.0001** (24.1	**<0.0001** (33.2)	**<0.0001** (1381.2)	**0.0152** (5.7)	**<0.0001** (35.3)
						D≠C C≠D_C	D≠C	All≠	W≠Su	W≠Su; W≠Sp; W≠F; Su≠Sp; Su≠F
*p*CO$_2$ (µatm)	**<0.0001** (10.4)	**<0.0001** (1747.3)	**0.0147** (4.2)	**0.0018** (6.4)	**<0.0001** (17.4)	**0.0002** (8.4)	0.0398 (3.2)	**<0.0001** (1737.6)	**0.0407** (4.0)	**<0.0001** (8.4)
				D≠C	D≠C	D≠C	**All=**	All≠	W≠Su	W≠Su; W≠Sp; W≠F; Su≠Sp; Su≠F
CO$_2$ Flux (mmol m^{-2} d^{-1})	**0.0144** (2.6)	**<0.0001** (738.1)	0.6739 (0.4)	0.9140 (0.1)	**<0.0001** (11.8)	**0.0214** (3.9)	0.5849 (0.5)	**<0.0001** (725.9)	**0.0299** (4.5)	**<0.0001** (19.2)
					D≠C	D≠C		All≠	W≠Su	W≠Su; W≠F; Su≠Sp; Su≠F

4

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 α=0.05 are bolded. Reported fluxes use the Jiang et al. (2008) gas transfer velocity parameterization.

Parameter	Time Period	Daytime Mean	Nighttime Mean	Day versus Night p-value	Mean Diel Range	Minimum Diel Range	Maximum Diel Range
Temperature (°C)	**Full Sampling Period**	23.0 ± 5.3	23.2 ± 5.4		1.3 ± 0.8	0.30	3.93
	Winter	17.2 ± 2.1	17.4 ± 2.1	0.2055	1.5 ± 0.8	0.3	3.8
	Spring	23.7 ± 2.7	23.8 ± 2.9	0.5579	1.2 ± 0.6	0.3	3.0
	Summer	29.6 ± 0.7	29.9 ± 0.8	**<0.0001**	1.0 ± 0.6	0.3	3.8
	Fall	22.0 ± 1.19	23.0 ± 1.0	**<0.0001**	1.8 ± 0.9	0.8	3.9
Salinity	**Full Sampling Period**	30.5 ± 4.1	31.0 ± 3.3		3.4 ± 2.7	0.250	15.870
	Winter	29.6 ± 4.2	30.4 ± 3.1	**0.0051**	3.8 ± 2.2	0.25	9.48
	Spring	30.1 ± 2.6	30.2 ± 2.6	0.5604	2.5 ± 2	0.4	8.17
	Summer	33.4 ± 3.2	33.1 ± 3.3	0.0550	2.0 ± 1.7	0.3	9.73
	Fall	25.9 ± 3.9	29.0 ± 3.2	**<0.0001**	7.7 ± 3.6	1.2	15.87
pH	**Full Sampling Period**	8.12 ± 0.10	8.13 ± 0.09		0.09 ± 0.05	0.02	0.28
	Winter	8.18 ± 0.08	8.20 ± 0.07	**0.0108**	0.10 ± 0.05	0.02	0.28
	Spring	8.09 ± 0.09	8.10 ± 0.08	0.3286	0.08 ± 0.03	0.03	0.18
	Summer	8.04 ± 0.06	8.07 ± 0.05	**<0.0001**	0.08 ± 0.04	0.03	0.19
	Fall	8.20 ± 0.05	8.17 ± 0.05	**0.0038**	0.12 ± 0.04	0.03	0.20
pCO_2 (µatm)	**Full Sampling Period**	417 ± 54	416 ± 65		58 ± 33	12.6	211.3
	Winter	374 ± 44	358 ± 43	**<0.0001**	43 ± 21	12.6	121.1
	Spring	438 ± 42	437 ± 48	0.7237	61 ± 31	20.5	152.8
	Summer	452 ± 44	471 ± 51	**0.0003**	74 ± 42	23.6	211.3
	Fall	406 ± 24	399 ± 27	0.0545	56 ± 18	22	92.2
CO_2 Flux (mmol m^{-2} d^{-1})	**Full Sampling Period**	0.0 ± 6.3	-1.3 ± 5.9		34.1 ± 29.0	2.7	189.0
	Winter	-14.9 ± 8.4	-19.1 ± 7.7	0.0676	46.6 ± 38.9	2.7	189.0
	Spring	7.6 ± 5.2	7.0 ± 5.2	0.6680	27.5 ± 18.5	4.9	115.0
	Summer	9.4 ± 5.6	11.7 ± 5.2	0.1167	32.3 ± 22.9	4.5	111.0
	Fall	0.1 ± 3.8	-0.3 ± 3.5	0.7449	17.0 ± 10.2	3.9	40.1

28 Table S4. Thermal versus non-thermal control on pCO_2 over different time scales using both continuous sensor data (C) and discrete
29 sample data (D). If more than one segment of time is being considered (n>1), ΔpCO_2 values are the mean ± standard deviation of all
30 segments, T/B range is the minimum and maximum T/B, and the number out of n with T/B>1 is recorded.

Time Period / Scale	Sampling type	n	$\Delta pCO_{2,t}$ (µatm)	$\Delta pCO_{2,nt}$ (µatm)	T/B	Number out of n with T/B >1
Full Monitoring Period (May 2, 2014- Feb. 25, 2020)	D	1	301.9	537.8	0.56	
Annual	D	5	259.3 ± 16.0	333.3 ± 120.0	0.50 – 1.16	1/5
Continuous Monitoring Period (Nov 2016 – August 2017)	C	1	355.0	360.7	0.98	
	D	1	236.3	229.9	1.03	
Winter	C	1	168.2	328.4	0.51	
	D	6	42.2 ± 23.4	101.7 ± 78.7	0.20 – 4.90	1/6
Spring	C	1	171.4	246.9	0.69	
	D	6	142.3 ± 53.7	147.8 ± 67.3	0.59 – 2.42	2/6
Summer	C	1	100.2	179.9	0.56	
	D	6	46.9 ± 26.6	176.9 ± 108.3	0.21 – 0.35	0/6
Fall	C	1	105.9	181.6	0.58	
	D	6	179.8 ± 59.5	176.6 ± 78.1	0.59 – 3.06	2/6
Daily	C	178	21.8 ± 11.8	63.8 ± 30.3	0.05 – 1.68	11/178

31
32

33   Table S5. Pearson correlation coefficients between carbonate system parameters and other environmental parameters for both
34   continuous sensor data and discrete sample data. Parameter pairs with a significant correlation based on α=0.05 have a correlation
35   coefficient reported. Asterisks are used to indicate the level of significance of the correlation, * p<0.05, ** p<0.01, *** p<0.0001. The
36   correlation coefficient is listed as 0 if the relationship was not significant. N/A is listed when the analysis was omitted because the
37   environmental parameter did not have observations corresponding to the date and time of at least half of our discrete sample
38   measurements (45 observations).

	pH		pCO_2		pCO_2, nonthermal	
	Continuous	**Discrete**	**Continuous**	**Discrete**	**Continuous**	**Discrete**
Temperature (°C)	-0.55 ***	-0.59 ***	0.75 ***	0.53 ***	-0.73 ***	-0.45 ***
Salinity	-0.47 ***	-0.74 ***	0.53 ***	0.69 ***	-0.28 ***	0.35 **
Wind Speed (m s^{-1})	-0.04 **	N/A	0.15 ***	N/A	0	N/A
Dissolved Oxygen (mg L^{-1})	0.55 ***	0	-0.81 ***	0	0.45 ***	0
Tide Level (m)	0	0	-0.15 ***	0	-0.15 ***	-0.55 **
Turbidity	-0.08 ***	N/A	-0.14 ***	N/A	-0.28 ***	N/A
Fluor. Chlorophyll	0.12 ***	N/A	-0.22 ***	N/A	0.34 ***	N/A

39

40   *Sensor deployment details*

41   Ideally, *in-situ* sensors should be deployed under the sea surface. However, to reduce the

42   maintenance cost and effort for sensors deployed in warm water that experiences intense

43   biofouling, the sensors were set up to measure pH and pCO_2 from an *ex situ* position using *in situ*

44   seawater. Water was pumped from ~1 m below the sea surface into the bottom spigot of a 100-Qt

45   cooler that housed the SAMI-CO2 and SeaFET sensors. To allow water outflow, a 1" hole was

46   drilled at the opposite side of the spigot near the top of the cooler rim, allowing water to flow

47   back to the sea surface. The pump was programmed to turn on 20 minutes before each hour,

48   pumping more than enough water to fully flush the cooler, and sensors recorded measurements

49   on the hour. The YSI sonde was deployed directly into ASC inside a 2" PVC pipe at ~1 m below

50   the sea surface.

51   Hourly data (single hourly measurements, measured on the hour) collected by all sensors

52   (pH, pCO_2, salinity, and temperature) were saved in the onboard data loggers and downloaded

53   during service trips. Sensor failures or pump failures occurred for short periods of time

54   throughout the deployment. Measurements were recorded on 262 individual days, with 176 of

55   those days having the full set of 24 (hourly) measurements. Service trips to the field site were

56   conducted every two weeks to service all sensors and clean the cooler. Additionally, duplicate,

57   discrete water samples were collected on the hour during service trips for quality assurance of

58   sensor data and to check that surface water and cooler chemistries aligned (referred to throughout

59   as quality assurance or QA samples).

60   The sensor deployment was shorter than intended because the pier was destroyed in the

61   aftermath of Hurricane Harvey in 2017.

62

63   *Removal of suspicious sensor data*

64   While the *ex-situ* position of the cooler was beneficial for easy maintenance of the

65   deployed sensors, there was an issue of periodic pump failure due to a manufacture flaw that was

66   later discovered, which would result in the cooler not appropriately representing the *in-situ*

67   environment (Figure S2). Pump failure resulted in notable increases in $p\mathrm{CO_2}$ and decreases in

68   pH due to the buildup of respirational products (Fig. S2). Sensor data during known periods of

69   pump failure were omitted from analysis (Fig. S2). Other suspect data based on the multiple data

70   correlation comparisons were also removed as they were assumed to represent sensor

71   malfunction (Fig. S3).

72

73
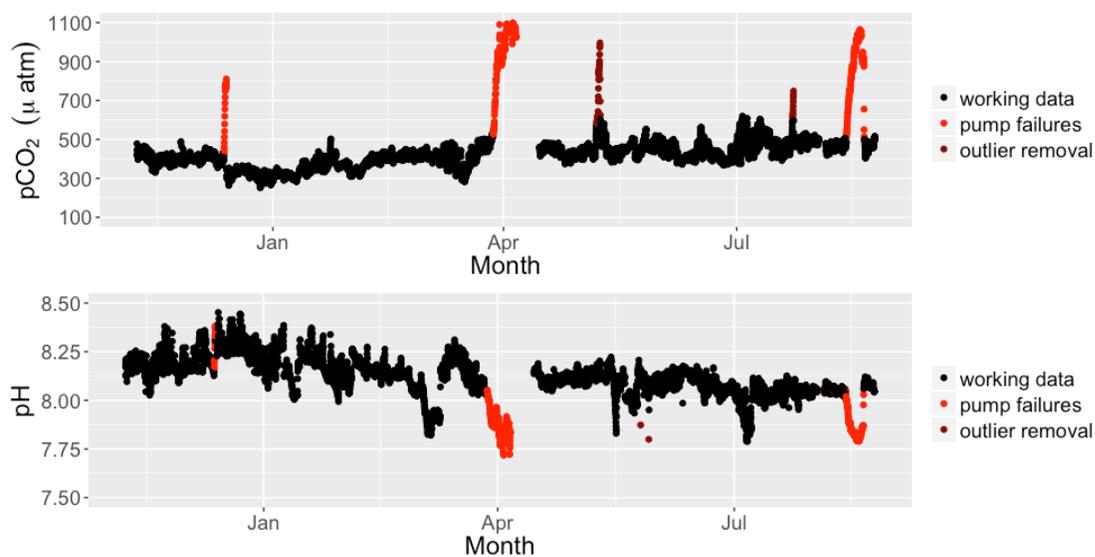
74   Figure S2. All recorded $p\mathrm{CO_2}$ and pH data. Data points flagged for removal prior to analysis are
75   shown in red.

76
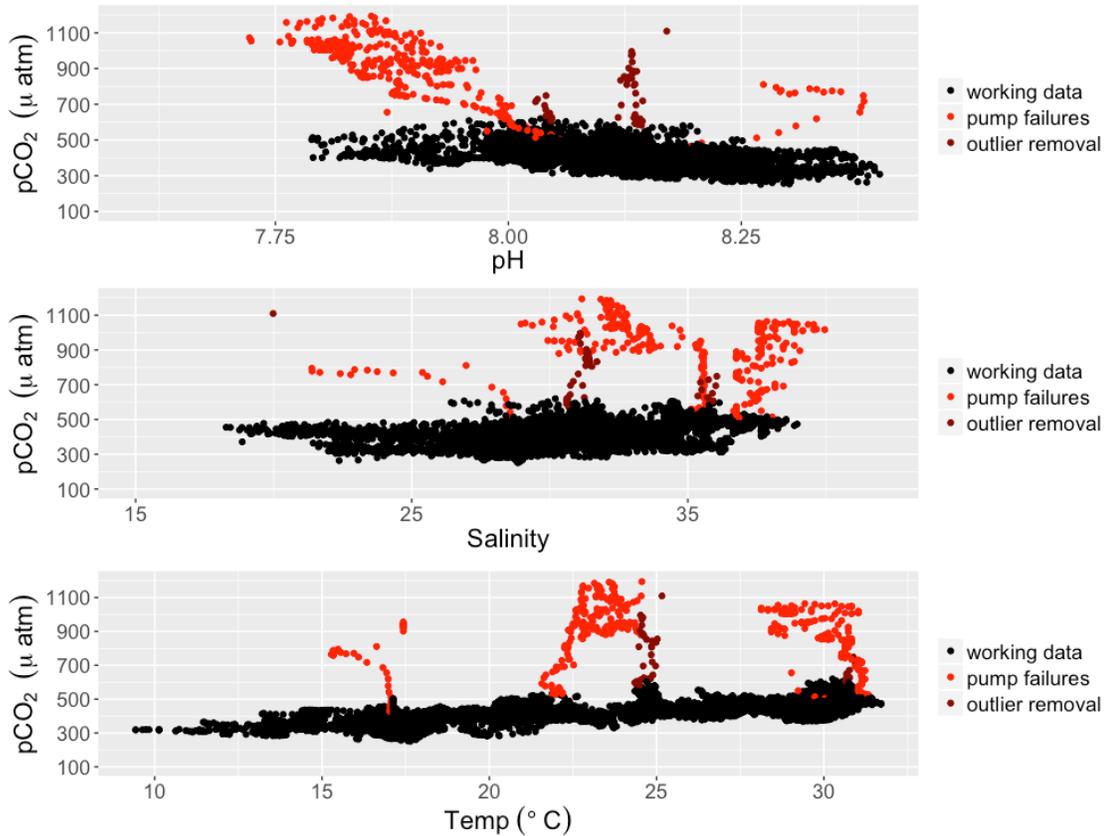
Figure S3. Relationships between sensor-measured carbonate system parameters and temperature and salinity. Data points flagged for removal are shown in red.

79

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

89   (continuous – discrete) was 0.05 ± 0.08. Since there was not a clear pattern over time in the

90   difference between sensor and laboratory-measured pH (Fig. S4), the average offset was used for

91   a correction to all sensor data.

92
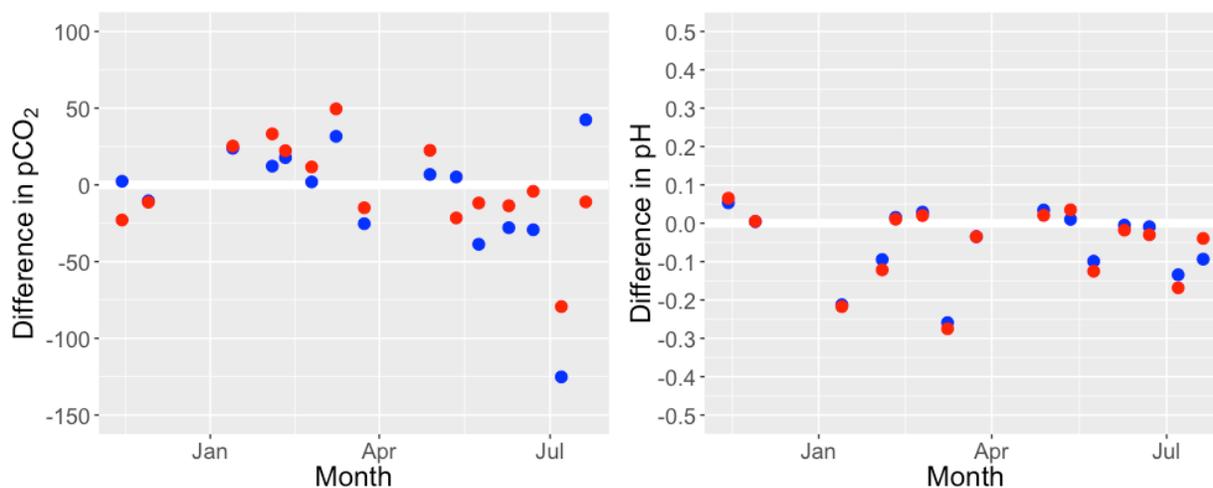
93

94   Figure S4. Differences in pCO_2 and pH between *in situ* sensors and lab-analyzed bottle samples
95   from the cooler (blue) and the ship channel (red)
96

97   The difference between the sensor pCO_2 and calculated pCO_2 was -18 ± 44 (Fig. S4,

98   Table S6). This difference was not used for a correction since there is error associated with the

99   calculation of pCO_2 from discrete samples and the spectrophotometric measurements of the

100   SAMI-CO2 should not experience drift. We used several different constants to calculate pCO_2 to

101   check the offset between measurements from sensors and laboratory-analyzed bottle samples; all

102   were similar in mean and standard deviation, but the offset could be slightly reduced using

103   Millero (2002) constants. Mean offsets and their associated standard deviations were larger when

104   comparing sensor data to samples taken during our long-term discrete monitoring effort

105   compared to the directly associated QA samples (Table S6). This is not surprising given that the

106   discrete sample collection did not occur at the exact time of the sensor measurement or the exact

107   location of the cooler pump inlet.

108   Given that the analytical accuracy of the SeaFET instrument is 0.05 pH units (Table S6),

109   the average offset between sensor and laboratory values of quality control samples demonstrates

110   fair agreement (Table S6). Given that calculated uncertainty associated with calculated discrete

111   pCO_2 was 7 ± 2, we did not see great agreement between SAMICO2 pCO_2 and laboratory-

112   calculated pCO_2 for QA samples. Greater sensor-laboratory agreement has been achieved for

113   open ocean settings, but this larger standard deviation is likely a result of the temporal variability

114   in the more complex estuarine environment where these instruments have been much less widely

115   deployed to date.

116

117   Table S6. Mean $\pm$ standard deviation of the difference between discrete and continuous values.
118   Reported pH differences are after the sensor pH correction.

	Difference between sampling methods	
	Sensor – QA samples * (n=12)	Sensor – discrete samples ** (n=13)
Salinity	-0.16 ± 1.44	0.50 ± 1.69
pH	0.00 ± 0.08	0.01 ± 0.12
pCO_2 (µatm)	-18 ± 44	25 ± 63

119   * Difference between sensor measurements and laboratory measurement of QA bottle samples taken at exact time of sensor measurement and
120   directly from the sensor cooler
121   ** Difference between sensor measurements and laboratory measurement of discrete samples for our 5+ year monitoring. These discrete samples
122   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
123   to pair with sensor data.
124

125   *Quantified uncertainties associated with parameters*

126   Propagated error associated with calculated carbonate system parameters was calculated

127   using the *seacarb* package in R (Gattuso et al., 2021) using analytical errors associated with the

128   measurements of the input pair, *in-situ* temperature and salinity, total boron, and the key

129   dissociation constants (Table S7). Error associated with calculated parameters from discrete

130   bottle samples was relatively small and likely a result of uncertainties in constants (Orr et al.,

131   2018), but error associated with parameters calculated from sensor data was relatively large

132   (Table S7). This large error is likely a result of both the relatively low analytical precision

133   associated with the pH sensor and the poor mathematical combination of variables for speciation

134   calculations. This high error is the reason that we decided to omit the discussion of any other

135   calculated carbonate system parameters from the manuscript. The high error suggests that it will

136   be important that autonomous sensors that can measure alternative parameters and allow for

137   lower propagated error are developed and broadly used to gain a full understanding of carbonate

138   chemistry on high-frequency timescales.

139

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

	Error (Analytical or Propagated)	
	Discrete Sampling (n = 104)	**Continuous Monitoring (n = 6088)**
Temperature (°C)	0.1	0.1
Salinity	0.01	0.1
pH	0.0004	0.05
pCO_2 (µatm)	7 ± 2	1.0
DIC (µmol kg^{-1})	2.5	327.4 ± 63.2
TA (µmol kg^{-1})	7.4 ± 0.9	400.7 ± 81.0
Ω_{Ar}	0.19 ± 0.03	1.08 ± 0.31

142

143

144   *Additional information on CO_2 flux calculations and windspeed data*

145   The majority of atmospheric xCO_2 data that were used in CO_2 flux calculations were

146   retrieved from NOAA's flask sampling network from Key Biscayne, FL,

147 (https://www.esrl.noaa.gov/gmd/dv/data/index.php?site=KEY&parameter_name=Carbon%2BDi

148 oxide). However, Key Biscayne data were not yet available for January 2019 – February 2020,

149 so global average values were used for these 16 months

150 (ftp://aftp.cmdl.noaa.gov/products/trends/co2/co2_mm_mlo.txt). We justified this substitution of

151 global average values because the monthly means between Key Biscayne and global xCO_2 over

152 the initial 56 months of our discrete sampling only differed by 1.2 ± 1.5 µatm (i.e. $0.3\% \pm 0.4\%$).

153 While atmospheric xCO_2 values at our exact location would have been preferable, they were

154 unavailable, and our calculations include the assumption that the Florida and global values are

155 not significantly different from atmospheric xCO_2 at ASC. We believe this is warranted, given

156 the relatively homogenous levels of atmospheric CO_2, with the most variation occurring between

157 hemispheres.

158 The xCO_2 values that were incorporated into calculations were monthly averages. We

159 believe that this method is justified for flux calculations (even for pairing with the hourly

160 continuous data), as the one example of frequent (i.e., every three hour) sampling of atmospheric

161 xCO_2 in the Gulf of Mexico (off Louisiana coast) shows very little diel or even monthly

162 fluctuation in atmospheric xCO_2 (https://www.pmel.noaa.gov/co2/story/Coastal+LA). While

163 variability in atmospheric CO_2 on diel and weekly timescales is often small at a single site,

164 especially small variability on short time scales likely occurs in the nwGOM due to

165 predominantly southeast winds, blowing from offshore. As a result, diel fluctuations in

166 atmospheric xCO_2 that could be present due to biological cycles of terrestrial plants or

167 anthropogenic influence are likely negligible at ASC.

168 NOAA/TCOON's Port Aransas (<2 km inshore from monitoring location) and Aransas

169 Pass (<2 km offshore from monitoring location) stations did not begin recording windspeed data

170   until Aug 5, 2016. Therefore, flux calculations for our discrete monitoring data spanning from

171   May 2, 2014 to Aug 5, 2016 used windspeed data from the Nueces Bay Station (~40 km from

172   our monitoring location). During the continuous monitoring period (Nov 8, 2015 – Aug 3, 2017),

173   about 55 days (<20% of observations) lacked windspeed data from Port Aransas or Aransas Pass

174   stations and used data from Nueces Bay station. Following the continuous monitoring period

175   (Aug 23, 2017 – Feb 25, 2020), only about nine days of wind data had to be retrieved from the

176   Nueces Bay station.

177   For those days during the 5+ year monitoring period that data were available at both the

178   Port Aransas Station and the Nueces Bay station, the Nueces Bay Station did have higher

179   windspeeds by an average of ~2.33 m/s, which could result in overestimation of the magnitude

180   of CO_2 fluxes. Given this station windspeed offset (along with the many other factors that

181   complicate the calculation of fluxes through windspeed parameterization), the actual values of

182   CO_2 flux should not be taken at face value. Missing data at the Port Aransas and Aransas Pass

183   stations generally spanned full days (not individual hours of missing data), so both calculations

184   of CO_2 flux with the continuous data and the discrete data would be pulling from the same

185   station on the same day, which validates the comparison of methods as flux calculated by both

186   sampling methods would receive the same bias.